STRAIN-INDUCED MAGNETO-TRANSPORT

PROPERTIES OF MANGANITE THIN FILMS

A Thesis in

Physics

by

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ABSTRACT

This dissertation consists of three parts. The first part focuses on the studies of the low-field magnetoresistance (LFMR) properties of strained manganite thin films, namely, La_{0.67}A_{0.33}MnO_3 thin films (A=Ca, Sr, Ba) and Pr_{1-x}Sr_xMnO_3 thin films (x=0.2, 0.25, 0.33 and 0.4). In the second part, we discuss the studies of the high field magnetoresistance anisotropy properties of the strained thin films. The observed large anisotropic magnetoresistance cannot be explained by the existing theories. In the last part, we presented some preliminary data on the manganite nanostructures.

Chapter 1 briefly overviews the studies of the colossal magnetoresistance in the manganite materials, and the low-field magnetoresistance in manganite thin films. It also gives an overview of the theories involved in this dissertation, which covered the conventional theories and recently proposed theory on the domain wall resistance in ferromagnetic materials, and the theories on the magnetoresistance anisotropy.

Chapter 2 describes the experimental methods to prepare the high quality manganite thin films, i.e., the pulse-laser deposition technique, and the characterization of the structural, electrical and magnetic properties of the films using X-ray diffraction (XRD), atomic force microscopy (AFM) and other measurements.

Chapter 3 focuses on the low-field magnetoresistance properties of the strained La_{0.67}A_{0.33}MnO_3 and Pr_{1-x}Sr_xMnO_3 thin films. First, strain-induced large low-field magnetoresistance (LFMR) has been systematically studied in La_{0.67}Ca_{0.33}MnO_3 (LCMO), La_{0.67}Sr_{0.33}MnO_3 (LSMO) and La_{0.67}Ba_{0.33}MnO_3 (LBMO) thin (50-200 Å) films grown on different substrates, such as LaAlO_3(001) (LAO), NdGaO_3(110) (NGO) and
SrTiO$_3$ (001) (STO). Due to the lattice mismatch between the films and the substrates ranging from -2.6% to +1%, compressive and tensile strains were imposed to the films grown on LAO and STO substrates, respectively. Large LFMR was observed in LCMO and LSMO thin films on LaAlO$_3$ substrates, and positive magnetoresistance was observed in most of the films grown on SrTiO$_3$ substrates. The large LFMR is strongly dependent on the film thickness, temperature and the composition of the manganites.

Second, strain-induced large LFMR has been systematically studied in Pr$_{1-x}$Sr$_x$MnO$_3$ \((x=0.2, 0.25, 0.33, 0.4)\) ultrathin films (45-300 Å) grown on LAO and STO substrates. The films are under compressive (grown on LAO substrates) or tensile (grown on STO substrates) strain imposed by the lattice mismatch with the substrates. Large LFMR was observed in all compressive-strained Pr$_{1-x}$Sr$_x$MnO$_3$ films when the magnetic field is applied perpendicular to the film plane, but the LFMR ratio is larger for the films with lower carrier concentration \((x)\). Large LFMR was identified as domain wall resistance in the compressive strained LCMO, LSMO and Pr$_{1-x}$Sr$_x$MnO$_3$ thin films. The effect will be discussed based on strain-induced magnetic anisotropy and unconventional domain walls.

Chapter 4 is devoted to the high field anisotropic magneto-transport properties of strained manganite thin films. A systematic study of the out-of-plane (magneto-crystalline) anisotropic magnetoresistance (AMR) has been conducted for the differently strained Pr$_{1-x}$Sr$_x$MnO$_3$ \((x=0.2, 0.25, 0.33, 0.4)\) ultrathin films (40-300 Å). The compressive- and tensile- strained ultrathin Pr$_{1-x}$Sr$_x$MnO$_3$ films show anomalously large out-of-plane AMR, but with opposite signs. In contrast, the almost strain free Pr$_{1-x}$Sr$_x$MnO$_3$/NGO films with the same thickness show much lower out-of-plane AMR. As
the thickness increases, the AMR of all the films becomes small. In addition, the field dependence of the out-of-plane AMR shows a crossover at the metal-insulator transition temperatures for all three types of the films. The in-plane AMR of the films are smaller regardless of the film thickness and the substrate. Out-of-plane AMR on strained La$_{0.67}$A$_{0.33}$MnO$_3$ thin films was also presented, and the large out-of-plane AMR was observed in tensile strained films in this series. The anomalous AMR results in the strained Pr$_{1-x}$Sr$_x$MnO$_3$ thin film are explained in terms of the orbit ordering and spin-orbit coupling. It is originated from the energy band splitting of the manganese e$_g$ level and the differential occupation probability of the d$_{x^2-y^2}$ and the d$_{3z^2-r^2}$ orbital due to the static Jahn-Teller distortion. However, the large AMR, indicating an enhanced spin-orbital coupling due to strain, have not been discussed in the current theories.

In chapter 5 we presented some preliminary data on the manganite nanostructures. We found that, while the manganite nanostructure maintains all the LFMR and DWR properties as in the un-patterned manganite thin films, it shows the nonlinear $I$-$V$ characteristics below and well above $T_c$. And the $I$-$V$ curves were fitted very well with the Simmons tunneling model, which indicates that tunneling is a dominant factor in the transport property.

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Chapter 1
Introduction

1.1 Overview in Manganite Materials

1.1.1 Background

Transition-metal oxides exhibit a wide range of exotic and still incompletely-understood structural, magnetic and electronic properties, and have been studied for a long time. Their properties cannot be simply explained by the one-electron band theory that usually works well for the most other solids, and this demonstrates the importance of strong electron-electron and electron-lattice correlations.

The magnetoresistance (MR) means the resistance change induced by an external magnetic field, and it is observed almost in all metals and semiconductors. In 1993, it has been recognized that some 3-d transition-metal oxides, mixed-valent manganite perovskites, possess large room-temperature magnetoresistance associated with a paramagnetic-ferromagnetic phase transition[1-3]. The resistivity change observed was so large (as shown in Figure 1-1) that it could not be compared with any other forms of magnetoresistance in metallic systems. It was therefore dubbed “colossal” magnetoresistance (CMR).

Magnetoresistance is important in many technological applications, such as magnetic data storage, and magnetic sensors. Whether the manganite perovskites will
become technologically useful is still far from clear. But the discovery of colossal magnetoresistance has launched a new scientific race mainly aimed at understanding and improving their magnetoresistance properties, and at examining other related classes of transition-metal oxides (such as spinels, pyrochlores and magnetites) which display similar behavior and may have more technologically attractive properties. On the other hand, manganites are opening up vast and exciting possibilities for basic condensed-matter physics. The delicate interplay between different sources of energy, such as the kinetic and electro-static energies of the mobile carriers and their coupling to the lattice, and strong coupling between spin, charge, and lattice degrees of freedom, leads to a wide range of striking physical phenomena. These interactions can be tuned by simply

Figure 1-1: Resistivity as the function of temperature of a La$_{2/3}$Ba$_{1/3}$MnO$_3$ thin film at 0 and 5 T. The top panel is as-deposited film and the bottom panel is after annealing. (Reproduced from reference [2].)
modifying the chemical composition. These materials provide a unique opportunity to study the physics of complex systems in which electrons, spins and phonons are strongly coupled, and in particular, to elucidate the interplay between local structural deformations and macroscopic transport, magnetic and optical properties.

The focus of this thesis is dedicated to the studies of magneto-transport properties of manganite thin films. Therefore, it is important to introduce the basic properties and research results of previous studies on those materials.

1.1.2 Lattice and Electronic Features

The magnetoresistance of manganites has been known to exist since 1950[4, 5]. The manganites that show colossal magnetoresistance form a simple perovskite crystal structure (as shown in Figure 1-2), derived from the general formula T_{1-x}D_xMnO_3, where T is a trivalent lanthanide cation (such as La, Pr, Nd), and D is a divalent alkaline-earth cation (such as Ca, Sr, Ba). For the end members of this series, LaMnO_3 and CaMnO_3, the ground state is antiferromagnetic (AF). The undoped lanthanum manganite compound corresponds to the following ionic composition La^{3+}Mn^{3+}O_3. The neutral Mn atom electronic configuration is 3d^54s^2, which means that the Mn^{3+} has 4 d-electrons which will be responsible for its electronic properties. If the La atom is substituted by Ca, the Ca^{2+}Mn^{4+}O_3 compound will be obtained where the Mn valence is +4. Thus, the Mn ion in the CaMnO_3 has 3 d-electrons. For a partial substitution, La_{1-x}Ca_xMnO_3 (0<x<1), Mn ions are mixed-valent, and average number of d-electrons at the Mn-site is 4-x. Although both LaMnO_3 and CaMnO_3 are antiferromagnetic insulators, the intermediate compound
La$_{1-x}$Ca$_x$MnO$_3$ exhibits strong magnetism over a broad range of carrier concentrations and temperatures which will be discussed in more detail below.

![Figure 1-2: Schematic crystal structure of the manganite perovskite. (Reproduced from reference [6].)](image)

The Mn$^{3+}$ ion has four electrons in its outermost $3d$ energy level. The $3d$ orbitals on the Mn-site placed in such an octahedral coordination are subject to the partial lifting of degeneracy by the crystal field, as shown in Figure 1-3. In the cubic lattice environment, the five-fold degenerate $3d$-orbitals of an isolated atom or ion are split into a manifold of three lower energy levels ($d_{xy}$, $d_{yz}$ and $d_{zx}$), usually referred to as “$t_{2g}$” once mixing with the surrounding oxygens is included, and two higher energy states ($d_{x^2-y^2}$ and $d_{3z^2-r^2}$) are called “$e_g$”. The valence of Mn-ions is either four (Mn$^{3+}$) or three (Mn$^{4+}$), and their relative fraction is controlled through chemical doping. The large Hund’s coupling dictates that spin of all electrons should point in the same direction to minimize the electrostatic repulsions. Therefore, $t_{2g}$ levels contain three electrons forming a spin $3/2$ state, while the $e_g$ either contains one electron or none. In the Mn$^{3+}$-based
compounds, the Mn site shows the electronic configuration of $t_{2g}^3 e_{g}^1$ (a spin 2 state). The single electron at $e_g$ level is unstable, and the system reduces its energy by splitting the doublet state into another two hyperfine energy levels. This well-known phenomenon is called the Jahn-Teller effect. The $e_g$ electrons can be itinerant and hence play the role of conduction electrons, when electron vacancies or holes are created in the $e_g$ orbital states of the crystal. The hole-doping procedure corresponds to creation of mobile Mn$^{4+}$ species on the Mn site. By contrast, the $t_{2g}$ electrons, less hybridized with O 2$p$ states and stabilized by the crystal field splitting, are viewed as always localized by the strong correlation effect and forming the local spin $S=3/2$ even in the metallic state.

![Diagram](image)

Figure 1-3: Field splitting of five-fold degenerate atomic 3$d$ levels into lower $t_{2g}$ (triply degenerate) and higher $e_g$ (doubly degenerate) levels. Jahn-Teller distortion of MnO$_6$ octahedron further lifts each degeneracy as shown in the figure. (Reproduced from reference [6].)

The hopping electrons are shared with the oxygen ions, forming an energy band that extends throughout the solid. The motion of charge carriers through this energy band...
is largely controlled by the width of the band, which is determined by the overlapping of the manganese and oxygen orbitals. Change in the bond length will affect the overlapping between the orbitals and therefore the conductivity of the materials. For a given bond length between the manganese and oxygen ions, the overlap is largest when the Mn-O-Mn bond angle ($\theta$) is 180°. If the lanthanum is replaced by a smaller ion, the bond angle becomes smaller and hence the overlap between the orbitals.

Perovskite-based structures sometimes show lattice distortion as modifications from the cubic structure. One of the possible origins in the lattice distortion is the deformation of the MnO$_6$ octahedron arising from the Jahn-Teller effect that is inherent to the high-spin ($S=2$) Mn$^{3+}$ with double degeneracy of the $e_g$ orbital. Another lattice deformation comes from the connection pattern of the MnO$_6$ octahedra in the perovskite structures, forming the rhombohedral and orthorhombic lattices, as shown in Figure 1-3. Such a lattice distortion of the perovskite in the form of ABO$_3$ (here A=$T_{1-x}D_x$ and B=Mn) is governed by the so-called tolerance factor $f$ [7], which is defined as:

$$f = (r_B + r_O) / (r_A + r_O).$$  \[1.1\]

Here, $r_i$ ($i=$A, B or O) represents the (averaged) ionic size of each element. The bond angle distortion decreases the effective $d$-electron hopping interaction or the one-electron bandwidth $W$, since the effective $d$ electron transfer interaction between the neighboring B-site is governed by the supertransfer process via O 2p state. Thus, $W$ for the $e_g$ electrons is approximately proportional to $\cos^2\theta$. 


1.1.3 Phase Diagram of La$_{1-x}$Ca$_x$MnO$_3$

As discussed earlier, the undoped lanthanum manganite LaMnO$_3$ is an insulator. The electrical properties of the materials can be modified by substituting a divalent alkaline element into lanthanum sites, i.e., La$_{1-x}$A$_x$MnO$_3$ where A could be Ca, Sr, Ba, etc. This doping changes some of the Mn ions from Mn$^{3+}$ to Mn$^{4+}$, and creates holes in the singlet energy state. The electrons can then hop between Mn$^{3+}$ and Mn$^{4+}$ states and the material becomes metallic. A phase diagram in the doping (x) and temperature (T) plane for one representative material, La$_{1-x}$Ca$_x$MnO$_3$, is shown in Figure 1-4.

![Figure 1-4: Phase diagram of La$_{1-x}$Ca$_x$MnO$_3$ showing magnetic and structural phase boundaries. The horizontal axis shows the value of x in the formula. Phase include charge-ordered (CO), antiferromagnet (AF), canted antiferromagnet (CAF), ferromagnetic metal (FM), ferromagnetic insulator (FI). The unlabled region of the phase diagram has neither magnetic nor charge order. (Reproduced from reference [8]).](image)

The stoichiometric samples of La$_{1-x}$Ca$_x$MnO$_3$ reveal well-resolved physical anomalies at the commensurate concentrations of x = N/8 with N = 1, 3, 4, 5, 7. These
findings provide critical insights into understanding the physics of doped manganite materials. The Curie temperature \((T_c)\) is maximized at \(x = 3/8\) according to Cheong and Hwang[8], contrary to the widely believed optimal doping level of \(x = 0.3\) for ferromagnetism. Cheong and Hwang also remarked that in the large-bandwidth compound \(\text{La}_{1-x}\text{Sr}_x\text{MnO}_3\), the Curie temperature is also maximized at \(x = 3/8\) doping level, implying that this phenomenon is universal.

In this thesis, most samples under study show the metal-insulator transition and reach ferromagnetic state at low temperatures. This corresponds to the doping range of \(0.2 < x < 0.5\) in the \(\text{La}_{1-x}\text{Ca}_x\text{MnO}_3\) system, where CMR effect has been observed. CMR occurs as a result of a rapid shift of the temperature for the sharp drop of resistance to higher temperatures in the presence of a magnetic field. The magnetoresistance at \(T \sim T_c\) can be very large as shown in Figure 1-5. The large magnetoresistance is not surprising: ferromagnetic transitions are in general very sensitive to applied magnetic fields. In the manganite materials, the ferromagnetic transition is also a “metal-insulator” transition, so that it is natural to expect the resistivity to be strongly dependent on the magnetic field in the vicinity of the transition.

1.1.4 Structural Changes and Chemical Pressure Effect

In the phase diagram of \(\text{La}_{1-x}\text{Ca}_x\text{MnO}_3\) as shown in Figure 1-4, \(x\) variation represents variation of Mn 3d site density, in turn, hole concentration and band filling are varied. Alternatively, the average size of A cation, \(<r_A>\), in the ABO3 formula can be varied. This will alter the lattice constant and thus the one-electron bandwidth.
al have systematically studied the evolution of $T_c$ in the compounds $\text{La}_{0.7-x}\text{Pr}_x\text{Ca}_{0.3}\text{MnO}_3$ and $\text{La}_{0.7-y}\text{Y}_y\text{Ca}_{0.3}\text{MnO}_3$ while keeping the Ca concentration fixed[10]. In the top panel of Figure 1-6, $\log \rho(T)$ is shown at magnetic field $B = 0$ and 5 Tesla for $\text{La}_{0.7-x}\text{Pr}_x\text{Ca}_{0.3}\text{MnO}_3$ (at $x = 0, 0.175, 0.35, 0.525, 0.6, 0.7$) and $\text{La}_{0.7-y}\text{Y}_y\text{Ca}_{0.3}\text{MnO}_3$ (at $y = 0.35, 0.5$). Since the ionic radius of La is greater than that of Pr, which is in turn greater than that of Y, $<r_A>$ monotonically decreases in this series of samples while the carrier concentration remains fixed. Decreasing $<r_A>$ causes a decrease of $T_c$ and an increase in the magnitude of the drop of the resistivity $\rho$ at $T_c$. Note that for $x = 0.7$, $\rho$ exhibits an insulating behavior to the lowest temperatures in $B = 0$, while in 5 Tesla there is a field induced transition to
metallic behavior, giving rise to an enormous MR. For $y = 0.35$ and 0.5, $\rho$ is always insulating both in 0 and 5 Tesla, although for $y = 0.35$ there is a feature at $\sim 60$ K in 5 Tesla which seems consistent with the systematic trend in $\rho_{ST}$ with decreasing $\langle r_4 \rangle$. The bottom panel of Figure 1-6 demonstrates the MR specified as $\log((\rho_{0T}-\rho_{ST})/\rho_{ST})$ for the data taken while cooling. The temperature for the maximum MR correlates well with the peak in $\rho_{0T}$ (shown with arrows). With the reduction of $\langle r_4 \rangle$, $T_c$ decreases monotonically and the magnitude of the maximum MR increases exponentially.

---

**Figure 1-6**: Top panel: $\log \rho(T)$ in $B = 0$ and 5 Tesla magnetic field for a series of samples of $\text{La}_{0.7-x}\text{Pr}_{x}\text{Ca}_{0.3}\text{MnO}_3$, for $x = 0$, 0.175, 0.35, 0.525, 0.6, 0.7, and $\text{La}_{0.7-y}\text{Y}_y\text{Ca}_{0.3}\text{MnO}_3$ for $y = 0.35$, 0.5. Bottom panel: MR (cooling data) for $x=0$, 0.175, 0.35, 0.525, 0.6, 0.7 specified as $\log(\rho_{0T}-\rho_{ST})/\rho_{ST}$, with the maximum in $\rho_{0T}$ indicated by arrows. (Reproduced from reference [10].)
A geometrical quantity called “tolerance factor” has been previously defined in Eq. 1.1. This factor $f$ is a simple characterization of the size mismatch that occurs when the A-site ions are too small to fill the space in the BO$_6$ octahedra. For manganite, tolerance factor can also be derived as $f = d_{\text{A-O}}/(\sqrt{2} d_{\text{Mn-O}})$. Here $d_{\text{A-O}}$ is the distance between the A site, where the trivalent or divalent non-Mn ions are located, to the nearest oxygen. Remember that the A ion is at the center of a cube with Mn in the vertices and O in between the Mn’s. $d_{\text{Mn-O}}$ is the Mn-O shortest distance. Since for an undistorted cube with straight Mn-O-Mn link, $d_{\text{A-O}} = \sqrt{2}$ and $d_{\text{Mn-O}} = 1$ in units of the Mn-O distance, $f = 1$ in this perfect system. However, sometimes the A ions are too small to fill the space in the cube centers and for this reason the oxygens tend to move toward that center,
reducing $d_{A-O}$. In general $d_{Mn-O}$ also changes at the same time. Therefore, $f < 1$ as the A radius is reduced, and the Mn-O-Mn angle $\theta$ becomes smaller than 180°. The hopping amplitude for carriers to move from Mn to Mn naturally decreases as $\theta$ becomes smaller than 180°. Consequently, as $f$ decreases, the tendencies to charge localization increase due to the reduction in the mobility of carriers. Figure 1-7 summarizes the evolution of $T_c$ with chemical pressure for a series of samples in which the average ionic radius of the A-site $\langle r_A \rangle$ is systematically varied, while keeping the Mn$^{3+}$/Mn$^{4+}$ ratio fixed at 7/3. With changing (chemical) pressure, $T_c$ can be significantly reduced, charge localization tendency increases, and eventually charge ordering is realized. The MR increases exponentially with decreasing $T_c$, leading to CMR for low $T_c$ manganites.

1.1.5 Charge- and Orbital-Ordering in Manganite

As shown in Figure 1-4, upon doping, the manganites exhibit a wide variety of ordered states, including ferromagnetic and charge-ordered (CO) phases. In those compounds, there exist orbital degrees of freedom of the $e_g$ electrons in Mn$^{3+}$ ions, and orbital ordering can lower the electronic energy through the Jahn-Teller mechanism. Therefore, charge- and orbital-ordering effects are particularly pronounced in mixed-valent manganites.

The pattern of charge- and orbital-order in the CO states of Figure 1-4 is not trivial and still under discussion. Some of the arrangements that have been identified are those shown in Figure 1-8. At $x = 0$, the A-type spin state is orbitally ordered as it appears in Figure 1-8(a). Shown in Figure 1-8(b) is the related charge- and orbital-
ordering scheme for $x = 0.5$, where there are the same amount of Mn$^{4+}$ ions and Mn$^{3+}$ ions, and the famous charge-exchange (CE) type\cite{11} arrangement is formed. In La$_{1/3}$Ca$_{2/3}$MnO$_3$, there are twice as many Mn$^{4+}(3d^3)$ ions as the Mn$^{3+}(3d^4)$ ions, and the ordering of the diagonal rows of Mn$^{4+}$ and Mn$^{3+}$ ions plus the orientational ordering of the $d_{z^2}$ orbitals in Mn$^{3+}$ gives rise to the stripe pattern shown in Figure 1-8(c).

Many other manganites present CE-type CO-phases at $x = 0.5$ as well. A sketch of the complex orbital, charge, and spin order is shown in Figure 1-9. While the spins are purely antiferromagnetic, the charge and orbital ordering occurs in alternate $b$-$c$ planes, giving rise to charge-stack order. This state can be easily destroyed by a magnetic field in

\begin{figure}[h]
    \centering
    \includegraphics[width=\textwidth]{figure1-8.png}
    \caption{The charge and orbital ordering configurations in the orthorhombic basal plane for $x = 0$, 1/2 and 2/3 of La$_{1-x}$Ca$_x$MnO$_3$. Open circles are Mn$^{4+}$ and the lobes show the orbital ordering of the $e_g$ electrons of Mn$^{3+}$. (Reproduced from reference [8]).}
\end{figure}
a first-order transition[12]. The effect of magnetic fields on several manganites is shown in Figure 1-10.

Figure 1-9: Spin, charge, and orbital ordering pattern of CE antiferromagnetic type observed for most of the $x=1/2$ manganites. The $e_g$-orbital ordering on Mn$^{3+}$ sites is also shown. The Mn$^{4+}$ sites are indicated by closed circles. (Reproduced from reference [13]).

Investigations on charge-ordering have established the intimate connection of the lattice distortion to CO. It is the lattice distortion associated with orbital ordering that appears to localize the charge and initiate charge-ordering. Eventually, the Coulomb interaction wins over the kinetic energy of the electrons to form long range CO state. The scale of the energy involved with CO as measured by the charge-ordering gap is around 0.5-1 eV. This is similar to the unscreened bare nearest neighbor Coulomb repulsion. This is also close to the approximate energy required to create $\sim 1\%$ orthorhombic distortion. It is likely that both the energy scales along with magnetic exchange decide the energy scale of the charge-ordering gap.
1.1.6 Double-Exchange Theory

Soon after Jonker and Van Santen [4, 5] discovered the strong correlation between ferromagnetism and metallic conductivity in doped manganites, Zener[14] offered an explanation that remains the core of the understanding of magnetic oxides. He noted that, the two configurations $\psi_1$: Mn$^{3+}$O$^{2-}$Mn$^{4+}$ and $\psi_2$: Mn$^{4+}$O$^{2-}$Mn$^{3+}$ in doped manganese oxides are degenerate and connected by the so-called double-exchange matrix element. This matrix element arises via the transfer of an electron from Mn$^{3+}$ to the central O$^{2-}$ simultaneous with transfer from O$^{2-}$ to Mn$^{4+}$. This process can be
schematically written[15] as $\text{Mn}^{3+}_{1\uparrow,1\uparrow,3\downarrow} \text{O}^{2-}_{2\uparrow,3\downarrow} \text{Mn}^{4+} \rightarrow \text{Mn}^{4+}_{1\uparrow,3\downarrow} \text{O}^{2-}_{1\uparrow,3\downarrow} \text{Mn}^{3+}_{2\uparrow}$ where 1, 2, and 3 label electrons that belong either to the oxygen between manganese, or to the $e_g$-level of the Mn ions. In this process there are two simultaneous motions (thus the name double exchange) involving electron 2 moving from the oxygen to the right Mn ion, and electron 1 from the left Mn ion to the oxygen (see Figure 1-11(a)).

Figure 1-11: (a) Sketch of the Double Exchange mechanism which involves two Mn ions and one O ion. (b) The mobility of $e_g$ electrons improves if the localized spins are polarized. (c) Spin-canted state which appears as the interpolation between FM and AF states in some mean-field approximations. (Reproduced from reference [16]).

Zener points out that the degeneracy of $\psi_1$ and $\psi_2$, a consequence of the two valencies of the Mn ions, make this process fundamentally different from conventional superexchange. Because of strong Hund’s coupling, the transfer-matrix element has finite
value only when the core spins of the Mn ions are aligned ferromagnetically, again distinguished from superexchange which favors antiferromagnetism. As usual, the coupling of degenerate states lifts the degeneracy, and the system resonates between $\psi_1$ and $\psi_2$ if the core spins are parallel, leading to a ferromagnetic, conducting ground state.

Anderson and Hasegawa[17] revisited Zener’s argument, treating the core spin of each Mn ion classically, but the mobile electron quantum mechanically. It involves a second-order process in which the two states described above go from one to the other using an intermediate state $\text{Mn}^{3+}_{1\uparrow}\text{O}_{3\downarrow}\text{Mn}^{3+}_{2\uparrow}$. In this context the effective hopping for the electron to move from one Mn site to the next is proportional to the square of the hopping involving the $p$-oxygen and $d$-manganese orbitals. In addition, if the localized spins are considered classical and with an angle $\theta$ between nearest-neighbor ones, the effective hopping becomes proportional to $\cos(\theta/2)$. The energy is lower when the itinerant electron’s spin is parallel to the total spin of the Mn cores. If $\theta = 0$ the hopping is the largest, while if $\theta = \pi$, corresponding to an antiferromagnetic background, then the hopping cancels. The quantum version of this process has been described by Kubo and Ohata[18].

The physics of the CMR in the manganites is obviously more complex. Many important factors other than the above simple double-exchange scenario, such as electron-lattice interaction, antiferromagnetic superexchange interaction between the $t_{2g}$ local spins, intersite exchange interaction between the $e_g$ orbitals, intrasite and intersite Coulomb repulsion interactions among the $e_g$ electrons, and etc., are necessary to interpret important experimental results. These interactions compete with the
ferromagnetic double-exchange interaction, producing complex but intriguing electronic phases as well as the gigantic response of the system to an external field, such as CMR or the field-induced insulator-metal transition.

Among the above interactions other than the double-exchange interaction, the important electron-lattice interaction stems from the Jahn-Teller type coupling of the conduction $e_g$ electrons with oxygen displacement. The Jahn-Teller type lattice distortion lifts the orbital degeneracy and lowers the electronic energy as shown in Figure 1-3. A large Jahn-Teller effect occurring in the Mn$^{3+}$ ions produces a strong electron-phonon coupling that persists even at densities where a ferromagnetic ground state is observed. In fact, in the undoped limit $x = 0$, and even at finite but small $x$, it is known that a robust static structural distortion is present in the manganites[19, 20]. It is natural to imagine the existence of small lattice polarons in the paramagnetic phase above $T_c$, and it was believed that these polarons lead to the insulating behavior of this regime.

The double-exchange and the Jahn-Teller model provide a mechanism for strong coupling between the electronic, magnetic, and lattice degrees of freedom. This unusual interaction results in many anomalous physical properties which have not been fully investigated and understood. This also implies that any changes in spin, charge, or lattice degrees of freedom will remarkably affect the physical properties of the manganites.

1.1.7 Phase Separation in Manganites

In certain manganite, a spectacularly diverse range of exotic electronic and magnetic phases can coexist at different locations within a single crystal. This striking
behavior arises in manganites because their magnetic, electronic, and crystal structures interact strongly with one another. For example, a ferromagnetic metal can coexist with an insulator in which the electrons and their spins adopt intricate patterns.

An early suggestion that two-phase separation might govern the colossal magnetoresistive regime was made by Gor’kov[21]. Monte Carlo simulations of the double-exchange model with Jahn-Teller coupling also suggested phase segregation of ferromagnetic metal from antiferromagnetic insulator regimes. Among the most important experimental results that have convincingly shown the presence of intrinsic mixed-phase tendencies in manganites are those reported by Uehara et al[22] in their study of La$_{5/8-y}$Pr$_y$Ca$_{3/8}$MnO$_3$ using transport, magnetic, and electron microscopy techniques. They demonstrated phase separation in this particular manganite that has been known previously to exhibit both charge-ordered insulator (COI) and ferromagnetic metal (FMM) phases. They identified submicron COI patches using dark-field transmission electron microscopy (TEM), as shown in Figure 1-12. The two phases looked different under the microscope because charge order confers a new periodicity on the crystal lattice.

Renner et al combined scanning tunneling microscope (STM) spectroscopy with atomic resolution STM imaging to study the Bi$_{1-x}$Ca$_x$MnO$_3$ single crystal samples[23]. They found two distinct and separated phases: surface regions that have a periodic superstructure--believed to be due to charge ordering--have a semiconducting gap, whereas regions that lack charge ordering are metallic. As shown in Figure 1-13, Renner et al showed the data to connect the different tunneling spectra to distinct phases at the atomic scale. The atomically sharp boundary separates an insulating charge-ordered
phase from a weakly conducting charge-disordered phase. In the charge-ordered phase, the I-V curve displays insulating behavior, whereas the charge-disordered phase shows an ohmic, metallic regime near zero voltage.

Figure 1-12: Dark-field images for La$_{5/8-y}$Pr$_y$Ca$_{3/8}$MnO$_3$ obtained by using a super-lattice peak caused by CO. Panel a shows the coexistence of charge-ordered (insulating) and charge-ordered (FM metallic) domains at 20 K for $y = 0.375$. The charge-disordered domain (dark area) is highlighted with dotted lines for clarity. The curved dark lines present in CO regions are antiphase boundaries, frequently observed in dark-field images for the commensurate CO states of La$_{0.5}$Ca$_{0.5}$MnO$_3$. Panels b and c, obtained from the same area for $y = 0.4$ at 17 K and 120 K, respectively, show the development of nanoscale charge-disordered domains at $T > T_c$. The curved lines in a, b, c signify the presence of antiphase boundaries of the domains. (Reproduced from reference [22]).
Figure 1-13: Topographic and spectroscopic atomic scale signatures of phase separation into metallic and insulating regions in the paramagnetic phase of Bi$_{0.24}$Ca$_{0.76}$MnO$_3$ at 299 K. 

- **a**, 3.5x3.5 nm$^2$ STM image of a grain boundary (yellow line) between an insulating $\sqrt{2}a_0 \times \sqrt{2}a_0$ charge-ordered region (upper right) and a more metallic homogeneous cubic region (lower left).
- **b**, Intensity profile extracted along the orange line in **a**. Note the larger amplitude modulation in the ordered region owing to charge ordering.
- **c**, Charge-ordered regions with the $\sqrt{2}a_0 \times \sqrt{2}a_0$ lattice (purple) yield insulating $dl/dV(V)$ characteristics, while the disordered cubic regions (green) are characterized by more metallic $dl/dV(V)$ characteristics (numerical derivatives normalized to the metallic junction resistance $R=V/I$ at 0.7 V). The low-bias part of the corresponding $I(V)$ data are shown in the inset. The spectra were taken at the yellow crosses on the 3.7x2.9 nm$^2$ STM images (white squares, cubic unit cell). (Reproduced from reference [23]).
Recently, Loudon et al used electron diffraction and dark-field imaging to study the La$_{0.5}$Ca$_{0.5}$MnO$_3$ polycrystalline manganite[24], as shown in Figure 1-14. Grain 1 is ferromagnetic, where grain 3 is in a charge-ordered phase that possesses no net magnetic moment. Such phase coexistence is expected. However, grain 2 is surprising. When viewed in dark-field (b), mesoscopically textured bright regions of strong charge-order appear that coincide with the fully ferromagnetic domains seen in (a). This observation represents the discovery of a new and unexpected phase: Charge-order and ferromagnetism were previously thought to be mutually exclusive.

Figure 1-14: Coexistence of ferromagnetism and charge order. Three grains (labeled 1, 2, and 3) are present in the image. The grain boundary is indicated by the white dots. a. A color image of the magnetic structure derived from available holography data overlaid on a Fresnel image. The color wheel indicates the direction of the local magnetization (marked with arrows). The apparent texture within each domain is likely to be an artefact of the Fresnel filtering process used to reconstruct the phase of the exist wavefunction. b, A dark-field image on the same scale from grain 2, taken using the (1/2, 0, 2) charge-ordered reflection. (Reproduced from reference [24]).
Most recently, Murakami et al use the electron microscopy to study the magnetic microstructure and development of ferromagnetic domains in the mixed-phase state of La$_{1-x}$Sr$_x$MnO$_3$ (x=0.54, 0.56) ceramic samples[25]. Figure 1-15 shows the temperature dependence of the magnetic microstructure in the mixed-phase state of La$_{0.44}$Sr$_{0.56}$MnO$_3$ sample. It is seen that, in the absence of a magnetic field, the magnetic flux is closed within the FM region at every stage of the AFM to FM transformation, resulting in a negligible magnetic interaction between well-separated FM islands without applied
magnetic field. But these islands are believed to interact with each other when a magnetic field is applied. Figure 1-15 (i) shows that the magnetization is uniform over the FM region, but that it abruptly diminishes at the interface with the AFM phase. The authors also speculate that, the spacing of the white lines is almost unchanged through the transformation, that is, the FM island has strong magnetization from the beginning of its formation in the AFM phase. They proposed that the delicate nature of the magnetic microstructure in the mixed-phase state of hole-doped manganites is responsible for the CMR effect, in which significant conduction paths form between the ferromagnetic domains upon application of a magnetic field.

1.2 Manganite Thin Films

1.2.1 Background

Besides the discovery of the large room-temperature magnetoresistance, the renewed interest in manganite perovskites has been propelled by another reason: the ability to synthesize high quality thin film as well as single crystal forms of complex perovskite oxide materials. The emergence of epitaxial metal oxide films has been one of the most attractive subjects for the condensed matter community in the last decade, which was primarily stimulated by the discovery of high-temperature superconductors (HTSC) and more recently by the discovery of CMR effect in the manganite perovskites.

The synthesis of the first high-temperature superconducting oxide thin films more than 16 years ago generated great interest in the thin-film community. This resulted in the
development of various techniques such as sputtering, molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD), but most popular technique is probably the pulsed-laser deposition (PLD)[26]. This latter method is used extensively to synthesize cuprate and HTSCs, which are now routinely made in laboratories, and it has been easily and rapidly adapted for manganites. The manganite oxides are highly sensitive to the strain effect, and this offers the possibility of studying its influence upon various properties such as insulator-metal transition temperature ($T_{IM}$), Curie temperature ($T_c$), structure and microstructure/morphology.

This section will present a brief review of the experimental work done on the manganite thin films in the past few years. Since it is the interest of this thesis to study the strain-induced magneto-transport properties of manganite thin films, this brief review will focus on the transport and magnetic properties. In particular, strain effect on the physical properties of the manganite thin films will be given more attention.

### 1.2.2 Grain Boundary (GB) Effect

Grain boundaries (GB) strongly affect the properties of manganite thin films. Low-field magnetoresistance (LFMR) has been reported and attributed to the spin-dependent scattering of polarized electrons at GB[27]. Since large LFMR is highly desirable for practical applications, much effort has been taken to enhance this property by artificially creating an interface between two elements.
The simplest way to create a natural GB is to grow the film on polycrystalline substrates[28]. Most of this work was done by IBM[28, 29] on La-Ca-Mn-O (LCMO) and La-Sr-Mn-O (LSMO) films. The resistivity-temperature curve of such films depends on the grain size, as shown in Figure 1-16: resistivity in zero field decreases when the grain size increases, but the peak temperature of approximately 230 K is almost independent of the grain size[28]. Gu et al show that the low-field magnetoresistance at low temperature has a dramatic dependence on the nature of the in-plane GB[30]. The reduction of zero-field low-temperature resistivity might be explained by the spin-polarized tunneling across half-metallic grains. Another possibility for obtaining
polycrystalline samples is to decrease the deposition temperature. The resulting GB results from a lower crystalline quality of the film[31].

Figure 1-17: (a) Resistance (left axis) and magnetoresistance ratio $\Delta R/R_0$ at 1 T (right axis) of a (100) grain boundary mechanically induced in a LCMO film. The LCMO film has a thickness of about 15 nm. (b) Resistance (left axis) and magnetoresistance ratio $\Delta R/R_0$ at 1 T (right axis) of an epitaxial LCMO film on LaAlO$_3$. The film has a thickness of about 15 nm. (Reproduced from reference [32]).

Another method has been used to create artificial GB by mechanically induced growth disorder[32]. A single crystal LaAlO$_3$ substrate is deformed prior to film deposition by scratching with a commercially available diamond needle along (100) and (110) directions, respectively. La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO) films are then deposited using pulsed laser deposition technique. Imaging of the scratched substrate with optical
microscopy and atomic force microscopy indicates a deformed region with a width of about 50 nm and a depth of about 500 nm. The resistance-temperature curve of such films is shown in Figure 1-17. The disordered LCMO film has a much higher resistance indicating that mainly the disordered region contributes to the resistance. The magnetoresistance of the epitaxial film peaks near the metal–insulator transition, whereas the mechanically induced grain boundary shows a magnetoresistance in an applied field of 1 T that is nearly independent of temperature between 4.2 K and the Curie temperature $T_c=230$ K. Since the magnetoresistance maximum observed here strongly depends on the direction of the applied field and on the grain boundary direction, Srititiwarawong et al.[32] argue that the magnetoresistance of the disordered structure is partially due to spin-polarized tunneling.

Bicrystal substrates with a single GB have also been utilized to study the transport across a GB. LCMO and LSMO thin films were deposited on bicrystalline SrTiO$_3$ substrates having a specific misorientation angle[33, 34]. To measure the properties of the GB only, the film was patterned into a Wheatstone bridge. The GB resistance and its magnetic field dependence are strongly dependent on the misorientation angle[34] (see Figure 1-18). It is seen that the MR increases with increase of the misorientation angle of the bicrystal[34]. The change of the resistance is 3% under a 2 mT magnetic field at 300 K for La$_{0.7}$Ca$_{0.3}$MnO$_3$. At 77 K, a large bridge resistance (27%) is observed during magnetic field sweeps between ±200 mT over a temperature range down to 77 K. Steenbeck et al used La$_{0.8}$Sr$_{0.2}$MnO$_3$ films grown on SrTiO$_3$ bicrystals with a misorientation angle of 36.8°[35] or 24°[36]. They found that the GB magnetoresistance occurs at low temperature, separate from the intrinsic MR near $T_c$, and that the sign of the
MR at the GB depends on the domain structure and $H$ [35]. Moreover, current-voltage measurements show that the field dependence might not be related to the tunneling[37].

1.2.3 Strain Effect

The influence of substrate strain is the main factor distinguishing manganite thin films from bulk ceramic samples. This is due to the fact that Mn $e_g$ electrons, which determine most of the physical properties, are coupled to the lattice of freedom through the Jahn-Teller trivalent manganese. Thus, strains affect the properties of the manganite

![Figure 1-18: Normalized GB MR as a function of the applied field for different bicrystal angles measured at room temperature. The insets show the (a) low-field and (b) high-field dependences for the 24° device. The applied magnetic field is in the plane and perpendicular to the GB. (Reproduced from reference [34]).](image)
thin films. Consequently, to obtain and improve the desired properties, one needs to correctly understand the effects of the strains on the manganite thin films.

Jin et al have studied the effect of various substrates as well as film thickness on MR[38]. They find that the strain effect, expressed through the MR ratio, is most pronounced for epitaxial films. They speculate that stress is most effectively propagated through the film thickness in the absence of grain boundaries. Many other groups have investigated the strain effects by growing various films on different substrates[39-43]. The physical properties of these materials depend on the overlap between the manganese \( d \) orbitals and oxygen \( p \) orbitals, which are closely related to the Mn-O-Mn bond angle and the Mn-O distance. As the unit cell of the thin film is modified with respect to that of the bulk material, the Mn-O distances and Mn-O-Mn angles are altered, inducing variations in the electronic properties.

Both in-plane and out-of-plane lattice parameters are often modified by strain effects when different substrates are used. Figure 1-19 shows an example for 300 Å thin films of \( \text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \) (PSMO) grown on \( \text{LaAlO}_3 \) (LAO), \( \text{SrTiO}_3 \) (STO) and \( \text{NdGaO}_3 \) (NGO) substrates[39]. The 002 peaks of the PSMO/LAO and PSMO/STO films are at 46.2° and 47.8°, corresponding to an out-of-plane parameter of 3.93 Å and 3.81 Å, respectively. Comparing to the lattice parameter of 3.87 Å found in the bulk PSMO, this indicate that the films are under tensile strain on STO and under compressive strain on LAO due to the lattice mismatch between the film and the substrate at the room temperature. The diffraction peak of the PSMO/NGO film is almost indistinguishable from the substrate peak due to the small lattice mismatch. The strain also influences the bond lengths and bond angles. Miniotas et al[44] have evaluated the Mn-O and Mn-Mn
distances in La$_{1-x}$Ca$_x$MnO$_3$ films grown by MBE. The Mn-O bond length was found to be fixed at 1.975 Å, independent of the substrate type, while the Mn-Mn distance (and subsequently the Mn-O-Mn bond angle) were calculated to be 3.93 Å for the film on STO and 3.84 Å for the film on LAO.

The influence of the film thickness is primarily seen in the lattice parameter changes of the films. The evolutions of the three-dimensional strain states and crystallographic domain structures were studied on epitaxial La$_{0.8}$Ca$_{0.2}$MnO$_3$ as a function of lattice mismatch with two types of (001) substrate, SrTiO$_3$ and LaAlO$_3$[45, 46]. It was shown by normal and grazing-incidence x-ray diffraction techniques that the unit-cell volume is not conserved and varies with the substrate as well as the film thickness (see Figure 1-20).

Figure 1-19: XRD patterns of three 30 nm thick PSMO films grown on LAO, NGO, and STO substrates, respectively. The arrows indicate the PSMO 002 peaks. (Reproduced from reference [39]).
It is found that for a tensile strained film, the out-of-plane and in-plane parameters growing gradually increase and decrease, respectively, as a function of the film thickness[47]. For example, for Nd$_{2/3}$Sr$_{1/3}$MnO$_3$ film grown on SrTiO$_3$ substrate, the out-of-plane parameter increases from 3.8 Å for a 200 Å thick film to 3.86 Å for a 1000 Å film, which is close to the bulk value[48]. In the case of compressively strained films such as in La$_{0.7}$Sr$_{0.3}$MnO$_3$ on (100)-oriented LaAlO$_3$ substrate[49]: the out-of-plane parameter decreases from 3.94 Å for a 300 Å thick film to 3.9 Å for a 4500 Å thick film, while at the same time the in-plane parameter changes from 3.82 Å to 3.88 Å. Shown in Figure 1-21 is the $c$-axis lattice parameter as a function of the film thickness for compressive-, tensile- and almost non-strained PSMO films. It clearly indicates that the crystal lattice of the PSMO film in the out-of-plane direction is expanded for the
compressive-strain films and contracted for the tensile-strain films. The strain is gradually relieved with increasing film thickness when the thickness is larger than 200 Å and the out-of-plane lattice parameter value gradually approaches that of the bulk PSMO crystal (3.867 Å).

Ultrathin films (<30 nm) of PSMO on LAO have been studied using transmission electron microscopy (TEM) by MacLaren et al [50]. It was found that the films are highly uniform and defect-free, and that they are coherently strained to the smaller lattice parameter of the substrate, resulting in a tetragonal expansion perpendicular to the film plane and a change of crystal structure from the ordered orthorhombic of bulk materials to a simple tetragonal perovskite.

Strain effect on the magnetic properties has also been investigated. Using magnetic force microscopy (MFM), Kwon et al [51] showed on La_{0.7}Sr_{0.3}MnO_{3} film a
“feather-like” pattern, indicating an in-plane magnetization on (100)-oriented SrTiO$_3$ substrate, while on (100)-oriented LaAlO$_3$ substrate, a “maze-like” pattern corresponding to a perpendicular magnetization anisotropy is seen, as shown in Figure 1-22. A study of this kind was reproduced and extended by Desfeux et al using other substrates[52].

![Image](image.png)

Figure 1-22: AFM (left) and MFM (right) images of LSMO/LAO (top) and LSMO/STO (bottom) samples. The images are taken at zero field and room temperature. (Reproduced from reference [51]).

O’Donnell et al have studied strain-induced magnetic anisotropy in fully strained epitaxial La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO) films on (100) SrTiO$_3$ (STO) substrates[53]. A tensile strain of 0.8% is introduced by the lattice mismatch. The magnetic anisotropy in LCMO/STO system has been shown to be uniaxial with the easy plane being the film plane. The anisotropy energy is dominated by strain-induced anisotropy from the lattice mismatch between film and substrate: the intrinsic magnetocrystalline anisotropy of the
bulk cubic system is negligible. Wu et al[54] investigated the dependence of the magnetic anisotropy in both compressive and tensile strained films of Pr$_{0.67}$Sr$_{0.33}$MnO$_3$ (PSMO). They find that compressive strain induced by growth on LaAlO$_3$ (LAO) substrates results in a spontaneous out-of-plane magnetization, while tensile strain (grown on SrTiO$_3$) results in in-plane magnetization (see Figure 1-23).

The phase diagram of La$_{0.67}$Sr$_{0.33}$MnO$_3$ was plotted for different substrates by Tsui et al[55]. A strong dependence of the anisotropy and Curie temperature on the lattice strain is observed. The effect of uniaxial strain was studied theoretically by Ahn and Millis[56]. The Curie temperature $T_c$ for Pr$_{0.67}$Sr$_{0.33}$MnO$_3$ (PSMO) films with different types of strain was also studied by Wang et al[39] to verify the theoretical.

Figure 1-23: The magnetization loops of (a) PSMO/STO and (b) PSMO/LAO for magnetic field parallel to the film plane and perpendicular to the film plane, indicating a spontaneous out-of-plane magnetization in PSMO/LAO films, and in-plane magnetization for PSMO/STO films. (Reproduced from reference [54]).
prediction about the significance of Jahn-Teller distortion (uniaxial distortion) on $T_c$ in manganites. They found that the $T_c$ of the tensile-strained film is always the lowest and that of non-strain film the highest among films with the same thickness. These results were quantitatively in agreement with the theoretical prediction.

Another important physical property of strained manganite thin films is the low-field magnetoresistance (LFMR). The strain effects on the LFMR were first studied for the polycrystalline La$_{0.67}$Sr$_{0.33}$MnO$_3$ thin films[28, 29], and it was shown that the LFMR is dominated by the grain boundaries in this case. Wang et al studied the strain effects extensively on the LFMR for Pr$_{0.67}$Sr$_{0.33}$MnO$_3$ (PSMO) epitaxial thin films[57-59]. They discovered that films with compressive strains (grown on LaAlO$_3$) show a large LFMR[58] when the field is applied perpendicularly to the substrate plane (see Figure 1-24), while they exhibit a small positive MR when the films are under tensile strains.

Figure 1-24: Normalized $R(H)$ curves of a 7.5-nm-thick PSMO/LAO film measured with the magnetic field parallel ($H_\parallel$) and perpendicular ($H_\perp$) to the film plane, respectively. Arrows indicate the scanning sequence of the magnetic field. (Reproduced from reference [59]).
Almost no LFMR is observed when the film is strain free (grown on NdGaO$_3$). Wang et al reported the largest LFMR ever reported in FM thin films. He proposed that the large LFMR is due to strain-induced magnetic anisotropy and spin-dependent scattering at domain boundaries.

Magnetic anisotropy was investigated by Eckstein et al for the fully strained La$_{0.7}$Ca$_{0.3}$MnO$_3$ thin films made by molecular beam epitaxy[60, 61]. They measured the anisotropic magnetoresistance (AMR) by rotating the magnetic field in the film plane and measuring the resistance as a function of the angle between the field and the \{100\} axis of the film (in-plane AMR), as shown in Figure 1-25. Their results showed that the behavior of the AMR is very different from that found in conventional metallic alloys. Its magnitude is peaked near the Curie temperature $T_c$ and becomes small at low
temperature. In the very low-temperature metallic regime, the observed small AMR amplitude has been shown to be consistent in magnitude with that predicted by conventional metallic theory. The much larger magnitude near $T_c$, as well as the change in symmetry between low and high temperature, strongly argues for a qualitatively different mechanism for AMR in the hopping regime such as the orbital deformation suggested in their studies.

Figure 1-26: The $[R(\theta)-R_{||}] / R_{||}$ vs $\theta$ curves for a 50 Å thick PSMO/LAO film (top) and a 150 Å thick PSMO/STO film (bottom) measured at different temperatures. (Reproduced from reference [62]).
Li et al.[62] studied the AMR for different types of strained Pr$_{0.67}$Sr$_{0.33}$MnO$_3$ (PSMO) thin films. In their studies, the AMR was measured at a given magnetic field and temperature, by rotating the sample around the axis parallel to the current direction so that the angle between the substrate normal and the magnetic field was changed (out-of-plane AMR). The magnetic field is always applied perpendicular to the applying current in their out-of-plane AMR measurements. The results showed that both compressive-strained (grown on LaAlO$_3$) and tensile-strained (grown on SrTiO$_3$) PSMO ultrathin films (50–150 Å) exhibit unusually large AMR, but with opposite signs. Figure 1-26 shows the AMR curves of a 50 Å thick PSMO/LAO film and a 150 Å thick PSMO/STO film measured at different temperatures. The AMR ratios are much larger than that observed by Eckstein et al. In contrast, the almost strain free PSMO films show much smaller AMR over all the temperature and field ranges. They speculate that the atomic orbital ordering caused by the strain-induced static Jahn-Teller distortion and the spin-orbit coupling may play crucial roles in the AMR properties.

1.3 Low-field Magnetoresistance (LFMR)

1.3.1 Background

In the practical application aspect, two main issues remain. One is the low-field magnetoresistance (LFMR) magnitude, and the other one is the room temperature operation. Since LFMR in the manganite thin films is an important part of this thesis, we
will briefly discuss some of the approaches to achieve the large LFMR. Many approaches have been studied to achieve large LFMR, such as grain boundary (GB) effect, giant magnetoresistance (GMR) effect, tunneling magnetoresistance (TMR) effect, magnetoresistance of magnetic nanocontact or ballistic magnetoresistance (BMR), and strain effect. GB effect has been discussed in the section 1.2.2, and the strain effect will be discussed in detail in the Chapter 3. This section will give a brief review of the GMR, TMR and magnetic nanocontact.

1.3.2 Giant Magnetoresistance (GMR)

The giant magnetoresistance (GMR) effect was discovered by Baibich et al[63] in Fe/Cr multilayers in 1988. Baibich et al found that when the thickness of the non-magnetic Cr layers is decreased below 20 Å, the Fe layers are coupled antiferromagnetically. With an applied magnetic field, the magnetization of the Fe layers gets progressively more aligned and the resistance of the multiplayer structure decreases. GMR multilayers with 30 Fe/Cr layers showed changes of resistance of up to 50% at 4.2 K in a magnetic field of 2 Tesla (see Figure 1-27). This value is halved when measured at room temperature.

GMR effect occurs in materials consisting of thin alternating layers of ferromagnetic and non-magnetic metals, and the effect arises as a result of spin-dependent transport within the system. The resistivity of the system depends on the relative alignment (parallel or antiparallel) of the moments of the ferromagnetic layers. Layers with parallel magnetic moments have less scattering at the interfaces, longer mean
free paths and lower resistance. Layers with antiparallel magnetic moments have more scattering at the interfaces, shorter mean free paths and higher resistance.

There are two principal configurations for the GMR system: the current-in-plane (CIP) configuration where the current flows in the plane of the layers, and the current-perpendicular-to-plane (CPP) configuration where the current flows perpendicular to the plane of the layers. In the same magnetic multiplayer, CPP-GMR is usually found larger than CIP-GMR (by a factor of up to 10) and values of up to 115% for Co-Ni-Cu/Cu multilayer[64] and up to 108% in Fe/Cr multilayers[65] have been reported. CPP-GMR is also less sensitive than CIP-GMR to sample inhomogeneities. This makes CPP-based nanodevices attractive and competitive vs. CIP ones for sensor applications in ultrahigh

Figure 1-27: Magnetoresistance of Cr/Fe multilayers measured at 4.2 K. (Reproduced from reference [63]).
density magnetic storage[66, 67]. Furthermore, CPP configuration is easier to analyze theoretically.

In a theoretical study of GMR, Zhang and Levy[68] proposed that a larger effect could be measured if the current were driven perpendicular to the plane of the layers (CPP configuration). They observed that, due to the inhomogeneous nature of multiplayer structures, the application of a uniform electric field does not imply that the internal electronic field is uniform. If the electric field is applied parallel to the layers, the uniformity is maintained; if applied perpendicular to the layers, the field varies from layer to layer. In the CIP configuration, the conduction electrons are not scattered by all the layers and all the interfaces; instead, the electrons sample only from a region of size of the mean free path. While in the CPP configuration, the electrons are scattered by every interface and every layer. As a result, for either the case where spin-dependent scattering is included or interface scattering is assumed to be negligible, the CPP-GMR is higher because it samples all the layers and interfaces. Pratt et al[69] confirmed this prediction by comparing the GMR of Co/Ag multilayers in the standard CIP geometry. By placing additional Nb electrodes at the top and bottom of the multiplayer the authors were able to measure the CPP-GMR. The measured CPP-GMR of the samples with various Co and Ag thickness had values ranging from 10 to 50% at 4.2 K and 500 Gauss. The values measured under the same conditions in the CIP configuration are three to ten times smaller.

The simplest model for GMR is what is commonly referred as the resistor network theory of GMR. In this model, the resistance of a spin traveling through the ferromagnetic layer of opposite orientation (call it $R_{\uparrow \downarrow}$) and the resistance of the spin
traveling through a ferromagnetic layer of the same orientation \((R_{\uparrow\uparrow} \text{ or } R_{\downarrow\downarrow})\) must be known. Furthermore, the resistance of each of the spins traveling through the non-magnetic layers \((R_{\uparrow} \text{ or } R_{\downarrow})\) must be known. This is often referred as majority and minority channels. The resistance can then be calculated as a two independent channels of spin, operation in parallel, where the resistances used are based upon the orientation of the layers. In the ferromagnetic configuration where the magnetic moments of all the ferromagnetic layers are aligned in the same direction, the resistance is

\[
\frac{1}{R_f} = \left( \frac{1}{R_{\uparrow\uparrow} + R_{\uparrow} + R_{\uparrow\uparrow}} + \frac{1}{R_{\downarrow\downarrow} + R_{\downarrow} + R_{\downarrow\downarrow}} \right).
\]

In the antiferromagnetic configuration where the magnetic moments of the two neighboring ferromagnetic layers are aligned in the opposite directions, the resistance is

\[
\frac{1}{R_A} = \left( \frac{1}{R_{\downarrow\uparrow} + R_{\downarrow} + R_{\uparrow\uparrow}} + \frac{1}{R_{\downarrow\downarrow} + R_{\downarrow} + R_{\downarrow\downarrow}} \right) = \frac{2}{R_{\downarrow\downarrow} + R_{\downarrow} + R_{\downarrow\downarrow}},
\]

assuming that \(R_{\downarrow\downarrow}\) is larger than \(R_{\uparrow\uparrow}\) or \(R_{\downarrow\downarrow}\) and \(R_{\downarrow} = R_{\downarrow}\), this means that \(R_f << R_A\).

A theoretical treatment of the CPP-GMR based on thermodynamic considerations has been proposed by Johnson[70] for the case of a paramagnetic layer separating two ferromagnetic electrodes. This model not only accounts for spin dependent scattering, but also introduces the concept of spin accumulation, the build-up of magnetic moments (of spin), at the interfaces. It considers that slow spin diffusion or relaxation leads to a steady-state non-equilibrium magnetization around the interface. This magnetization acts as a bottleneck for spin transport across the interface, which in turn will hinder the flow of charge. As there is no net charge transfer across the layers in the CIP case, there is no spin accumulation and therefore CIP-GMR < CPP-GMR.
Valet and Fert[71] developed a CPP-GMR model that provides great insight into the problem. The Boltzmann equation is solved at zero temperature by introducing into the distribution function an isotropic term to account for spin accumulation. The equations for the interface coupled resistances per unit area in the parallel and antiparallel cases are

\[
R^{(P)} = 2\beta^2 \frac{\rho_N \rho_F}{\rho_F \coth(t_N / 2l_{SD}) + \rho_N \coth(t_F / 2l_{SD})} l_{SD},
\]

\[
R^{(AP)} = 2\beta^2 \frac{\rho_N \rho_F}{\rho_F \tanh(t_N / 2l_{SD}) + \rho_N \coth(t_F / 2l_{SD})} l_{SD}
\]

where \(\rho\) is a factor expressing the spin-dependent bulk scattering and the subscripts \(N\) and \(F\) refer to the normal metal and the ferromagnetic layers respectively, clearly show the dependence on the spin scattering length. And \(t_N\) and \(t_F\) are the thickness of the normal metal and the ferromagnetic layers respectively, \(l_{SD}\) the spin diffusion length. Even when a more complete analysis is performed by solving the Boltzmann equation with spin-dependent bulk and interface scattering[72, 73] and taking account of the two conduction channels (depending on the density of states) of 3\(d\) metals, the physics remains essentially the same as that shown in Eq. 1.4. This simple model describes the main features of magnetoresistive multilayers i.e.

(i) increase in MR with decreasing temperature,

(ii) increase in MR with decreasing layer thickness and

(iii) increase in MR with increasing number of layers.
1.3.3 Tunneling Magnetoresistance (TMR)

Another approach to optimizing low-field MR is the tunneling magnetoresistance (TMR) in the magnetic tunnel junctions. This phenomenon combines quantum tunneling with magnetoresistance. If a potential is applied between two conducting layers separated by a thin insulating film, an electrical current passes between the metal electrodes by quantum mechanical tunneling of the current carrier. The tunneling rate for carriers of particular energy is proportional to the product of the carrier densities of states at that energy on each side of the barrier. Also, the thinner the barrier and the lower the barrier height, the larger the current is. Spin tunneling is analogous to quantum tunneling, except that instead of metal electrodes, ferromagnetic electrodes are used. They exhibit (see Figure 1-28) large changes in tunnel resistance depending on the relative alignment of the magnetizations of the ferromagnetic electrodes. This effect is called tunneling magnetoresistance (TMR) and may be understood, at least simplistically, by Julliere’s model[75].

A simple expression for the tunneling magnetoconductance can be derived as follows[75]. Let $P$ and $P'$ denote the spin-polarization of the ferromagnetic electrodes. If the carrier spin is conserved during tunneling, the conductance is proportional to the sum of the products of the spin-polarized densities of states. One obtains in the parallel (↑↑) and antiparallel (↑↓) states

$$G_{↑↑} \propto (1 + P)(1 + P') + (1 - P)(1 - P') \quad 1.5$$

$$G_{↑↓} \propto (1 + P)(1 - P') + (1 - P)(1 + P'). \quad 1.6$$

This yields for the magnetoconductance and magnetoresistance (TMR), respectively
In the case of two identical ferromagnets, the magnetoresistance is always negative; it diverges for two half-metallic electrodes. In the general case, the magnetoresistance can be both positive and negative.

\[
\frac{\Delta G}{G} = \frac{G_{\uparrow\uparrow} - G_{\uparrow\downarrow}}{G_{\uparrow\uparrow}} = \frac{2PP'}{1 + PP'} \quad \text{(1.7)}
\]

\[
\frac{\Delta R}{R} = \frac{R_{\uparrow\downarrow} - R_{\uparrow\uparrow}}{R_{\uparrow\uparrow}} = \frac{2PP'}{1 - PP'} \quad \text{(1.8)}
\]

In the experiments\([76, 77]\), the tunneling electrons appear to be predominately from the near free-electron \(s-d\) hybridized bands rather than the more localized \(d\)-bands,

---

**Figure 1-28**: Experimental signature of spin tunneling; resistance of CoFe/Al\(_2\)O\(_3\)/Co tunneling junction plotted as a function of \(H\) in the film plane, at 295 K. Also shown is the variation of CoFe and Co resistance. The arrows indicate the direction of \(M\) in the two films. (Reproduced from reference [74]).

In the experiments\([76, 77]\), the tunneling electrons appear to be predominately from the near free-electron \(s-d\) hybridized bands rather than the more localized \(d\)-bands,
roughly consistent with band structure calculations and de Haas-van Alphen measurements for Fe, Ni and Co[78]. The overlap of these free-electron-like wave functions deep in the tunnel barrier govern the tunneling rate, and within a WKB approximation, they lead to a form for the spin polarization:

\[ P = \frac{k_{F\uparrow} - k_{F\downarrow}}{k_{F\uparrow} + k_{F\downarrow}}, \]

where \( k_{F\uparrow\downarrow} \) are the majority/minority Fermi wavevectors. This is consistent with \( P \) depending on the polarization of three-dimensional density of states of the free-electron-like bands for the bulk ferromagnet. The ferromagnetic exchange energy of the tunneling electron was assumed to convert to kinetic energy as the barrier is entered.

This early model does not predict any barrier width or height dependence of the tunneling magnetoresistance, in clear contradiction to the measured results[74, 79]. The necessity of modifying Julliere’s model was first realized by Slonczewski[80], who argued that because most practical barriers are relatively permeable, the wavefunction overlap within the barrier means that wavefunction matching must be considered across the entire device. Slonczewski calculated the tunneling conductance within a free electron model using Landauer-Büttiker formula. The exchange fields in the ferromagnetic electrodes were assumed to span an angle \( \Theta \). The transmission coefficient \( T(k_{//}) \) of an incoming electron of defined spin is calculated. \( k_{//} \) denotes the wavevector component parallel to the barrier. Assuming the absence of diffusing scattering in the barrier, the tunneling conductance is given by

\[ G = \frac{e^2}{(2\pi)^2\hbar} \int d^2k_{//} T(k_{//}). \]
Slonczewski evaluated Eq. 1.10 by integrating over $k_{/\parallel}$ and keeping only the leading term in $1/d$. The conductance is found to be of the form

$$G \propto \left[ 1 + P_{fb}^2 \cos \Theta \right]$$

1.11

with an effective polarization $P_{fb}$ depending on the band splitting. In the one-band case $P_{fb} = 1$ resulting in a complete spin-valve effect, in the two-band case

$$P_{fb} = \frac{(k_{\uparrow} - k_{\downarrow}) (k_{\uparrow} - k_{\downarrow})}{(k_{\uparrow} + k_{\downarrow}) (k_{\uparrow} + k_{\downarrow})} \equiv \frac{P}{A_{fb}}$$

1.12

with the wavevectors $k_{\uparrow}, k_{\downarrow}$ of the $\uparrow$ and $\downarrow$ electrons and the inverse of the decay length in the barrier $\kappa = \sqrt{2(U_0 - E_F)}$. $U_0$ denotes the barrier height and $E_F$ the Fermi energy. For free electrons, the first factor in Eq. 1.12 simply reduces to the standard definition of the spin-polarization $P = (n_{\uparrow} - n_{\downarrow})/(n_{\uparrow} + n_{\downarrow})$, where $n_{\uparrow}$ and $n_{\downarrow}$ are the densities of states at the Fermi level. The second factor $A_{fb}$, however, is related to interface properties and has the range $-1 < A_{fb} < 1$. It changes sign as a function of barrier height, indicating that the sign of the apparent spin-polarization can be modified by the appropriate choice of the barrier material. Slonczewski’s expression for $\Delta G/G$ is a good approximation for large barrier thickness and small barrier heights.

MacLaren et al[79] further calculated the tunneling conductance taking into account the band-structure of the iron electrodes. These results also confirm a considerable dependence of the tunneling magnetoresistance on the barrier height and a small variation with barrier thickness. Therefore, it has to be concluded that Julliere’s model fails to incorporate the relevant physics of spin-polarized tunneling. This model
yields TMR values in surprisingly good with experiment, if the spin-polarization is defined in an appropriated way.

The bias-dependence of the tunneling conductance is generally quite complicated. Since the carriers tunnel directly between the electrodes, a quadratic voltage dependence is expected at low bias according to the Simmons model for free electron tunneling[81]. Guinea[82] investigated the bias dependence due to the excitation of bulk and interface magnons. He found that, for a barrier of thickness $d$, bulk magnons with wavelengths larger than $d$ can be created with roughly equal probability. At zero temperature magnons are created at finite voltage bias yielding a conductance

$$G(V) \propto \begin{cases} (V/J)^{3/2} & : V << J(a^2/d^2) \\ (a/d)^3 & : V >> J(a^2/d^2). \end{cases}$$

$G(V)$ denotes the lattice parameter and $J$ the exchange constant.

The contribution to the bias dependence by interface antiferromagnons was found to be

$$G(V) \propto \begin{cases} (V/J_{AF})^2 & : V << J_{AF}(a/d) \\ (a/d)^2 & : V >> J_{AF}(a/d). \end{cases}$$

$J_{AF}$ denotes the interface exchange constant.

Magnetic tunnel junctions based on manganite electrodes were fabricated and investigated by many groups[83-94]. Kwon et al[95] investigated LSMO ramp-edge junctions. Heteroepitaxial magnetite tunneling junctions were investigated by Li et al[96] and van der Zaag et al[97]. A ‘mixed’ junction based on an LSMO and a magnetite electrode was studied by Ghosh et al[98]. This research was motivated by the large spin-
polarization of the manganites and of magnetite. Indeed, TMR values in excess of 100% at 4.2 K have been reported by Sun et al[87], Viret et al[89] and Obata et al[92].

Figure 1-29: A schematic view of an LSMO/STO/LSMO trilayer thin-film junction structure. (a) Left: top view of the device; right: three-dimensional illustration of the current-perpendicular pillar structure. (b) Side view of the structure, showing the over-etch steps which add additional magnetic coupling between the top and bottom ferromagnetic electrodes. (c) Schematic junction resistance as a function of sweeping magnetic field, showing the transitions from parallel to anti-parallel to parallel state of the magnetic moment alignments of the electrodes. (Reproduced from reference [88]).

A schematic view of an LSMO/STO/LSMO trilayer thin-film junction structure is shown in Figure 1-29. These structures show nonlinear conductance curves; the nonlinear conductance is often found to be quadratic in the bias voltage at low voltage, which is taken as an indication of tunneling as the main transport mechanism. However, more complex bias voltage dependences of the conductance have been reported that are not understood at present[88]. Figure 1-30 shows (a) the magnetization hysteresis of a single LSMO layer indicating the coercive field and (b), (c) the resistance hysteresis at 4.2 K of two LSMO/STO/LSMO tunneling junctions. Both junctions show typical TMR behavior: a resistance maximum for anti-parallel alignment of the electrode magnetizations and a
nearly field-independent resistance for parallel alignment. The resistance hysteresis of the larger tunneling junction in Figure 1-30 (b) is very similar to the corresponding curves of conventional ferromagnetic tunneling junctions. The smaller junction in Figure 1-30 (c) shows large noise, presumably due to complicated domain patterns in the ferromagnetic

Figure 1-30: Comparing the $R(H)$ curves of devices with magnetic hysteresis from a blank film. (a) Magnetic hysteresis loop of a blank film. (b) $R(H)$ loop of a low-resistance junction. The similar switching field as the blank film’s coercive field $H_c$. (c) High resistance junction. The lower switching field corresponds well to the blank film’s $H_c$, whereas the upper switching field is well above $H_c$, indicating an additional magnetic interaction present for magnetic states within the pillar. The insets in (b) and (c) show the geometry of the electrodes for the particular junctions and the relative field orientation in each case. (Reproduced from reference [88]).
electrodes. The magnetoresistance of the junction in (c) reaches about 200%, whereas the larger junction in (b) has a magnetoresistance of only 20%. Very large values of 870%[87] and 450%[89] have been reported at low temperatures. However, the junction characteristics are not reproducible.

Several groups have investigated the TMR ratio as a function of temperature. Lu et al[84] reported a strong decrease of the magnetoresistance with temperature in LSMO/STO/LSMO junctions; the TMR ratio is found to vanish above about 200 K, whereas the Curie temperature of the electrodes is much higher with $T_c = 347$ K. Obata et al[92] report TMR values extending up to the Curie temperature in LSMO/STO/LSMO junctions with very smooth interfaces and thin STO barriers with thickness of 1.6 nm, see

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**Figure 1-31:** Temperature dependence of maximum TMR ratios for $La_{0.8}Sr_{0.2}MnO_3/SrTiO_3/La_{0.8}Sr_{0.2}MnO_3$ junctions with different areas and SrTiO$_3$ thicknesses. (Reproduced from reference [92]).
Figure 1-31. Yin et al[93] obtained a similar result in LSMO/La$_{0.85}$Sr$_{0.15}$MnO$_3$/LSMO junctions. However, even in this case the TMR ratio decreases much faster with temperature than the bulk magnetization. This behavior might not be surprising, since the spin-polarization is controlled by the interfacial magnetization that shows a much stronger decay with temperature than the bulk magnetization. The strong temperature dependence, however, might to some extent still be of extrinsic origin related to non-stoichiometry of the interface region and interface roughness. For example, Sun et al[86] found indications of variable-range hopping in the junction resistance above about 130 K, whereas the TMR vanishes. This was interpreted as indicating a high defect density in the SrTiO$_3$ barrier leading to defect-state-mediated tunneling through the barrier at higher temperatures.

1.3.4 Magnetoresistance of Nanocontact

Magnetic nanocontacts have stirred a great deal of interest because of the high values of MR reported in low magnetic fields. The MR observed in the spin-polarized ferromagnets connected by nanoconstrictions often exceeds giant magnetoresistance (GMR) and tunneling magnetoresistance (TMR) effects at room temperature. Therefore, it has great potential for the application to the magnetoelectronic devices such as nonvolatile memory and high performance magnetic field sensors for information storage[99, 100].

García et al[101] reported the first transport measurements on magnetic nanocontacts on two Ni crystals, demonstrating that the conductance through the
nanocontact formed by two wires depends on the relative orientation of the magnetization of the wires. The experimental set-up is shown in Figure 1-32. The nanocontact was made by contacting the rounded tips of two Ni wires 2 mm in diameter and applying a voltage to the ends of the wires until a current was observed. The wires were tightly bound to a Teflon tube with resin to give rigidity to the structure. Two coils, one at the end of each wire, set the magnetization of each wire. The current through the nanocontact and the coils is monitored on two channels of an oscilloscope.

Figure 1-32: Experimental set-up for measuring magnetoresistance of nanocontacts. (Reproduced from reference [101]).

When no current is applied to coils, the current through the nanocontact is constant. When a square wave is applied to coil 2 (to alternate the magnetization of wire 2) and a constant current is applied to coil 1 (to fix the magnetization along the axis of the
wire), steps in the conductance of the nanocontact are observed which correspond to a switch of the relative orientation of the magnetization of the two wires (Figure 1-33). Magnetoconductance of 280% at room temperature and 20 Oe can be obtained. It was also observed that the magnetoresistance decreases as the contact size increases. In order to prove that this conductance has a magnetic origin, the same experiment was performed with Ni-Cu and Cu-Cu nanocontacts and no variation of conductance with magnetic field was observed.

Figure 1-33: (a) Conductance variation of Ni nanocontacts with applied magnetic field. (b) Magnetoresistance at room temperature of the Ni contacts. (Reproduced from reference [101]).
Despite differences in formulation, several theories\(^{[102-108]}\) suggest that the effect is due to spin scattering at the domain wall and is dependent of the ratio of the spin relaxation length with the domain wall width. In bulk materials where the domain wall width is much larger than the Fermi wavelength \(\lambda_F\), the electron spin can adiabatically accommodate the change in magnetization as it travels through the domain wall and therefore the measured magnetoresistance is small. However, in a nanocontact, the domain wall width is much smaller than the spin scattering length\(^{[107]}\) and the electron crosses the wall without changing its spin. Therefore, it will be scattered according to the density of states configuration on the other side of the domain wall. Since the domain wall width is a function of the junction area, the effect is consequently a function of the contact area as well. At the moment, a technique with which to accurately determine the area has not yet been developed, so experimental comparison with theory is based solely on the change of conductance (or resistance) as a function of the conductance (or resistance), namely magnetoconductance (or magnetoresistance).

The principal ingredient in all successful experiments is the formation of very small contact areas that join two ferromagnetic electrodes. The magnetoconductance decreases rapidly with the contact area and the magnetoconductance peak occurs for nanometer size contacts. In some cases, the contact is estimated to be a few atoms wide. Many materials have been chosen to make the nanocontacts, and very large magnetoconductance (or magnetoresistance) have been reported. García et al\(^{[101, 107, 109]}\) have reported up to 700% magnetoconductance in electrodeposited Ni-Ni nanocontacts of 30 nm in size. Recently, a magnetoconductance of more than 3000% was reported by Chopra and Hua using electrodeposition\(^{[110]}\). Apart from transition metals,
500% magnetoresistance has been reported for half-metallic magnetite Fe$_3$O$_4$ crystallites by Versluijs et al[111]. Chung et al[112] also reported 400% magnetoconductance in another half-metallic ferromagnets CrO$_2$-CrO$_2$ nanocontact. But in the half-metallic manganite nanocontact made of La$_{0.7}$Sr$_{0.3}$MnO$_3$, the magnetoresistance is only 45% at room temperature and 70 Oe[113].

1.4 Domain Wall Resistance

1.4.1 Domain, Domain Wall (DW) and Domain Wall Resistance (DWR)

Domains are uniformly magnetized regions that appear spontaneously within otherwise unstructured ferromagnetic (FM) materials. Domains form in FM materials to reduce the magnetic dipolar energy, at the cost of the ferromagnetic exchange and magnetic anisotropy energies[114]. In other words, alternating the direction of the magnetization with respect to a surface can minimize the energy in static magnetic fields surrounding a finite, magnetized material. Many types of domains are possible depending on what energy contribution is dominant and what the magnetic history is.

Three different energy terms dominate domain formation: magnetostatic, exchange and anisotropy. The effect of each of these can be illustrated using a large rectangular magnet magnetized along its easy axis[115], as shown in Figure 1-34(a). In this case, the exchange energy (the energy proportional to the angle between two spins) and anisotropy energy (the energy proportional to the orientation of the magnetization relative to the crystalline axes) are both zero. However, the magnetostatic energy (the
energy due to the field produced by the magnet) is maximized since the magnet acts like a single, giant dipole. In order to minimize the total energy, two parallel domains and two closure domains will form, as shown in Figure 1-34(b). This increases the anisotropy and exchange energies due to the transition regions between the domains, but significantly reduces the magnetostatic energy. The total energy can be further reduced by decreasing the size of the closure domains (the shaded region in Figure 1-34(c)) by forming three additional domains. This reduces the overall anisotropy energy (since fewer moments are aligned perpendicular to the easy direction) as well as the magnetostatic energy, but the exchange and anisotropy energies originating from the transition regions increase.
However, if the magnet is small enough, the anisotropy energy cost of the shaded areas shown in Figure 1-34(c) is less than the exchange and anisotropy energy cost to form the extra domain walls, hence Figure 1-34(b) would be the final domain configuration. In general the domain structure in zero field is determined by minimizing the sum of these energies, and will depend considerably on the size, shape, and type of magnetic materials.

Uniaxial magnetic materials are an interesting and simple example in which the magnetization is favored by anisotropy forces to lie along a particular axis (the easy axis), taken to be the $z$-axis. Sample surface perpendicular to this axis lead to a stripe domain pattern, in which the magnetization direction alternates along the $+z$ and $-z$ directions[116]. Figure 1-35 shows schematic illustrations of stripe domains. The domain configurations near sample boundaries are important to understand the transport properties of stripe domain materials. Magnetic configurations at the sample boundaries are determined by the ratio of the anisotropy to magnetostatic energy, denoted by $Q$. For
small Q (Q<<1), flux closure domains $M \perp z$ are favored to reduce the magnetostatic energy (Figure 1-35(a)), while for large Q (Q>>1), stripe domains which intersect the surface with $M // z$ are favored to reduce the magnetocrystalline energy (Figure 1-35(b)).

A domain wall (DW) is an interface region between domains with different magnetization directions. The length scale, domain wall width, over which the magnetization direction changes is determined by material parameters (the exchange and magnetic anisotropy energies) as well as the sample geometry. There are two simple types of domain walls that separates two domains of opposite magnetizations, Bloch wall, and Néel wall, as shown in Figure 1-36.

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Figure 1-36: Illustration of two simplest domain wall structures that separates two domains of opposite magnetizations: (a) Bloch wall, and (b) Néel wall. (Reproduced from reference [114]).
Early theoretical studies of the electronic properties of DWs were stimulated by magnetotransport experiments on single crystal Fe whiskers[102-118]. Starting from a multidomain state a small field was observed to erase the DWs and produce large changes in resistivity at low temperatures (a reduction of the resistivity by an order of magnitude at 4 K)[119]. The next two sections will briefly discuss the theories of domain wall resistance (DWR) for conventional ferromagnetic (FM) materials and manganite materials, respectively. The discussion will be focused on the stripe domain materials, which are ideal for DWR studies because of the large density of DWs.

1.4.2 DWR in Conventional Ferromagnetic Materials

The concept of domain wall (DW) scattering emerged in 1960s from the experimental work on Fe whiskers by Taylor et al[119] and the theoretical work by Cabrera and Falicov[102, 117] and Berger[118]. The first model of DW scattering proposed by Cabrera and Falicov considered the reflection of incoming electrons by the effective potential created by the rotating magnetization (and hence internal exchange field) within the domain wall[102]. They show that only when the domain wall width is comparable to the Fermi wavelength of the spin-polarized electrons, the domain wall scattering can become significant and result in large domain wall resistance.

The key ingredients in recent models of DW scattering are spin-dependent potentials and scattering rates, namely potentials and electron relaxation times that are different for majority (up) and minority (down) electrons in the ferromagnet. The basic idea is the following. In a uniformly magnetized ferromagnetic metal a large fraction of
the total current is carried by one spin channel, either the majority or minority spins. Due
to a small non-adiabaticity of the electron spin in traversing the wall, there is mixing of
spin channels within the DW[120]. This mixing partially eliminates the “short circuit”
provided by the lower resistivity spin channel and increases the resistivity of the DW
region. In a semiclassical Boltzmann calculation Levy and Zhang found that the MR for
current parallel to the DW (CIW-current in wall) is:

\[ R_{\text{CIW}} = \frac{\rho_{\text{CIW}} - \rho_0}{\rho_0} = \frac{5}{\xi} \left( \rho_0^\uparrow - \rho_0^\downarrow \right)^2 \rho_0^\uparrow \rho_0^\downarrow \]  \hspace{1cm} 1.15

here the parameter \( \xi = \hbar v_f/(J\delta) \) is a measure of the non-adiabaticity (\( \xi = 0 \) is an adiabatic
crossing), where \( J \) the internal exchange energy, \( v_f \) is the Fermi velocity, \( \delta \) is the DW
width, and \( \rho_0^\uparrow(\downarrow) \) is the resistivity of the spin up (down) channel. Physically, \( \xi \) is the ratio
of the precession time of an electron in the exchange field to the time the electron takes to
ballistically traverse the DW. Clearly, as the wall region is narrowed the DW-MR is
predicted to increase. Levy and Zhang further found that DWs cause larger MR when
aligned perpendicular to the current flow (CPW-current perpendicular to wall).

\[ R_{\text{CPW}} = \frac{\rho_{\text{CPW}} - \rho_0}{\rho_0} = \frac{5}{\xi} \left( \rho_0^\uparrow - \rho_0^\downarrow \right)^2 \left( 3 + \frac{10 \sqrt{\rho_0^\uparrow \rho_0^\downarrow}}{\rho_0^\uparrow + \rho_0^\downarrow} \right) \]  \hspace{1cm} 1.16

Since the intrinsic reflection is assumed to be small, spin accumulation effects are not
taken into account here. Similar results have also been obtained by Brataas et al, who
considered both ballistic and diffusive transport through a DW[121]. For typical
parameters for Co, \( k_f = 10 \text{ nm}^{-1} \) and \( J = 0.5 \text{ eV} \), and \( \rho_0^\uparrow / \rho_0^\downarrow = 5 \), \( \delta = 15 \text{ nm} \), one finds a
CPW-MR of 2\%. 
Some models also predict an intrinsic negative DW contribution to the resistivity, which means that DWs reduce the sample resistivity. Tatara and Fukuyama[122] and Lyanda-Geller et al[123] pointed out that DWs might contribute to de-coherence of electrons, thus leading to a resistivity decrease due to the suppression of weak localization effects. Weak localization is pronounced in low dimension disordered systems and arises due to quantum interference, which enhances electron backscattering and resistivity. Tatara and Fukuyama found that DWs destroy the electron coherence necessary for weak localization at low temperatures. As a consequence, in their model erasing DWs with a magnetic field restores weak localization and leads to an increase in resistivity.

A recent model by Gorkom et al[124] found out that a negative DWR can also arise from the reduced magnetization in a DW, if the ratio of the spin-dependent relaxation times is appropriate. The essential idea is that the effective exchange field within a DW is weakened due to the non-collinear spin alignment. As a result, within a two-band Stoner model of the ferromagnet, there will be a redistribution of charge among the majority and minority spin bands. The Drude resistivity of a single-domain ferromagnet is given within the two-band Stoner model by

$$\rho = \frac{m}{e^2} \frac{1}{n_\uparrow \tau_\uparrow + n_\downarrow \tau_\downarrow},$$

where \( n_\uparrow (n_\downarrow) \) denote the majority (minority) density of states and \( \tau_\uparrow (\tau_\downarrow) \) the relaxation time for majority (minority) electrons. A redistribution of the electrons in a DW with

\[ n_{\uparrow(\downarrow)} = n_{0\uparrow(\downarrow)} + \delta n_{\downarrow(\uparrow)}, \quad \delta n_\uparrow = -\delta n_\downarrow \]

modifies the resistivity according to
Depending on the relaxation times of the bands, this can produce a positive or negative DW contribution to the resistivity. Gorkom et al[124] found that the magnitude of this effect can be the same order as those treated by Levy and Zhang.

Despite the experimental and theoretical debate on the relation between DW-MR and DW width, it is generally accepted that a significant MR will only arise in a case of a narrow wall.

### 1.4.3 DWR in Manganites

Within the double-exchange model, the transfer integral \( t \cos(\theta/2) \) for the \( e_g \) electrons depends sensitively on the angle \( \theta \) between the core spins of the adjacent Mn\(^{3+}\) and Mn\(^{4+}\) sites. Therefore, it is expected that a narrow DW has a considerable influence on the conductance of the manganites. The scattering by DWs in double-exchange ferromagnets was treated by Zhang and Yang[125], Yamanaka and Nagaosa[126], and Brey[127]. Whereas Zhang and Yang calculated the temperature and field dependence of the resistivity due to the temperature and field dependence of the average domain size, Yamanaka and Nagaosa calculated the conductance of a single DW as a function of the DW width \( \delta \). They assumed a 180° Néel wall with a constant spin-rotation angle in the wall, \( \theta = \pi a/\delta \), where \( a \) denotes the lattice parameter. They numerically calculated the conductivity as a function of the energy \( \epsilon \) of the incident electron using Landauer’s
formula. In the case of a thick wall, a one-dimensional continuum model can be applied. An effective potential

\[
V(x) = \begin{cases} 
2t \left[ 1 - \cos \left( \frac{\pi a}{2\delta} \right) \right] & \text{in the wall} \\
0 & \text{elsewhere}
\end{cases}
\]

was used in the one-dimensional Schrödinger equation leading to a transmission coefficient

\[
G_s(\varepsilon) = \frac{1}{1 + \frac{V^2}{4\varepsilon(V-\varepsilon)} \sinh^2 \left( \frac{\delta}{a} \sqrt{\frac{V-\varepsilon}{t}} \right)}
\]

with \( \varepsilon = 2t[1-\cos(ka)] \). For large domain-wall thicknesses this can be approximated by

\[
G_s \sim \begin{cases} 
\left( \frac{\delta}{a} \right)^2 \frac{\varepsilon}{t} & \varepsilon < t \left[ \frac{a}{\delta} \right]^2 \\
1 & \varepsilon > t \left[ \frac{a}{\delta} \right]^2
\end{cases}
\]

Integrating over all wavevectors up to \( k_f \) yields

\[
\frac{\Delta G_{\text{wall}}}{G_0} = \frac{2}{5} \left( \frac{1}{k_f \delta} \right)^3
\]

which decays very strongly with the DW thickness \( \delta \).

Brey calculated the MR of a DW in the manganites numerically as a function of DW thickness taking into account the modulation of the hopping amplitude due to the spin canting inside the DW as well as the shift of the chemical potential of the Mn ion.
levels. He obtained a decreasing MR with increasing wall thickness; for a wall thickness of $10a < \delta < 30a$ he found a value MR = $(G_0 - G_{DW})/G_0 \sim 1-2\%$.

Experimentally, DWR in the manganites has been studied by Wolfman et al[128], Wang and Li[57], Mathur et al[129], Wu et al[130], Ziese et al[131] and Suzuki et al[49]. Mathur et al measured the resistivity of a patterned La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO) track. This track had narrow constrictions separating regions with wider linewidth (“bellies”); small permanent magnets were placed near every second belly. After magnetizing to saturation in an in-plane field, the magnetic field was slowly reversed; the unbiased “belly” regions are believed to reverse the magnetization at small negative fields, thus creating DWs near the constrictions. Mathur et al estimated the DWR, which is a value four orders of magnitude larger than the expected by the double-exchange model.

Wu et al and Suzuki et al investigated the MR of compressively strained La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) films on LaAlO$_3$ (LAO) substrate. These films have a perpendicular magnetic anisotropy leading to the formation of perpendicular magnetic domains on a scale of about 200 nm. If the MR is measured after sweeping an in-plane or out-of-plane field perpendicular to the current, the resistivity should return to the same value in zero field apart from DW scattering effects due to the different domain configurations. The measurement on a 80 nm LSMO film at 300 K yield a deviation of about 0.1% in two filed configurations, indicating a significantly smaller DWR than obtained by Mathur et al.

The MR of Pr$_{0.67}$Sr$_{0.33}$MnO$_3$ (PSMO) films grown under compressive strain on LAO substrates was investigated by Wang and Li, and Wolfman et al. In these samples a
large MR arises when the magnetic field is applied perpendicular to the film plane. It is known from magnetic anisotropy investigations that manganite films under compressive strain exhibit a perpendicular anisotropy[53, 54]. Since the observed MR is not correlated to specific crystallographic defects, the authors suggested that it arises from DW scattering at DWs separating out-of-plane domains.

1.5 Anisotropic Magnetoresistance (AMR)

1.5.1 Background

The electric field within a single domain ferromagnetic film with in-plane magnetization can be written as[132]

\[ E_x = j\rho_\perp + j(\rho_\parallel - \rho_\perp)\cos^2 \theta, \]

\[ E_y = j(\rho_\parallel - \rho_\perp)\sin \theta \cos \theta, \]

where the current density \(j\) is assumed to be uniformly distributed along the applied current direction, \(x\) and \(y\) are the longitudinal and transverse axes, and \(\theta\) is the angle between the magnetization and current density \(j\). \(\rho_\parallel\) and \(\rho_\perp\) are the resistivities for current orientation parallel and perpendicular to the magnetization. The anisotropic magnetoresistance phenomenon is described by Eq. 1.23, and the transverse resistance is expressed in Eq. 1.24.

An anomalous anisotropic magnetoresistance effect has been observed in ferromagnetic materials by Mott[133], and Smit[134]. This effect in transition metals is
expected to be due to spin-orbit interaction. In this case, the resistivity depends on the orientation of magnetization with respect to the direction of the electric current. The effect is often called the anisotropic magnetoresistance (AMR)[135].

Figure 1-37 presents the change of the resistivity of NiCo alloy versus the magnetic field. The longitudinal resistivity $\rho_l$ (or $\rho_{//}$) of the material magnetized parallel to the current direction is larger than the transverse resistivity $\rho_t$ (or $\rho_\perp$) of the material magnetized perpendicular to the current direction. The anisotropic magnetoresistance is often defined as[134]

$$AMR = \frac{\Delta \rho}{\rho_{av}} = \frac{\rho_l - \rho_t}{\frac{1}{3}\rho_l + \frac{2}{3}\rho_t}$$  \hspace{1cm} (1.25)

where $\rho_{av}$ is the average resistivity (resistivity of the demagnetized specimen).

Figure 1-37: The change of resistivity of NiCo alloy versus the external magnetic field. (Reproduced from reference [135]).
1.5.2 AMR in Ferromagnetic Metals

The microscopic origin of electrical transport in ferromagnetic metals was discussed in detail in many papers in the 1960s and 1970s. As a basis for these papers Smit’s results of investigations of magnetoresistance in ferromagnetics[134] have been used. Smit had explained the phenomenon of anisotropic magnetoresistivity using Mott’s two-current model of conduction in transition metals[133]. Jan[136] and McGuire and Potter[135] summarized the knowledge about the anisotropic magnetoresistance.

It is convenient to explain the anisotropy of magnetoresistance by taking into account the existence of spin-orbit coupling and the anisotropic scattering mechanism of \( s \) and \( d \) electrons[137-139]. Figure 1-38(b) shows the schematic \( d \) density of states for Fe-Ni or Fe-Ni-B alloy. This band structure is split into two different sub-bands representing the different orientations of the electron spins (with magnetic moments parallel or antiparallel to the total magnetization). When the \( 3d \) band is not fully filled, scattering of \( 4s \) electrons to the \( 3d \) band is probable. The current of \( 4s \) electrons with small effective mass \( m_s^* \) (comparable with free electron mass) is predominant. The \( 3d \) electrons with large effective mass \( m_d^* \) have low mobility (for iron \( m_d^* \approx 30 m_s^* \)). Due to magnetic ordering the \( 3d \) sub-bands are not equally filled. Therefore there is another probability of scattering from the \( 4s \uparrow \) state to the \( 3d \uparrow \) state than from the \( 4s \downarrow \) state to the \( 3d \downarrow \) state. For ferromagnetic Ni only scattering from the \( 4s \downarrow \) state to the \( 3d \downarrow \) state is probable, because the \( 3d \uparrow \) sub-band is below the Fermi level.

In Smit’s model it is assumed that the influence of the magnetic field and spin-orbit interaction cause mixing of \( d \uparrow \) and \( d \downarrow \) states. It can be demonstrated that this mixing
is anisotropic and the probability of \( s-d \) scattering is larger for electrons traveling parallel to the magnetization. Thus resistivity \( \rho_I \) is larger than \( \rho_t \), as shown in Figure 1-37.

**Figure 1-38:** (a) Schematic two-current conduction model for ferromagnetic transition-metal alloys with \( s \) and \( d \) scattering. For strong ferromagnetism \( \rho_{sd}=0 \). Usually \( \rho_{ss\uparrow} = \rho_{ss\downarrow} \) is assumed. (b) Schematic \( d \) density of states \( N_d(E) \) for up- and down-spin bands of a strongly ferromagnetic Fe-Ni or Fe-Ni-B alloy. For sufficient Fe, the Fermi level lies above the divide between Fe and Ni \( s \) bands. (Reproduced from reference [140]).

Figure 1-38(a) shows the main idea of Mott’s two-current model of conductivity in ferromagnetic metals. The conduction proceeds through two parallel channels with the resistivities \( \rho \uparrow \) and \( \rho \downarrow \) corresponding to the spin-up and spin-down conduction electrons, respectively. In the absence of spin-orbit coupling, each channel has series resistivity contributions \( \rho_{ss} \) arising from scattering between like-spin \( s \) states and \( \rho_{sd} \) arising from scattering like-spin \( s \) and \( d \) states; spin mixing can be ignored for high-resistivity materials. Spin-orbit coupling introduces scattering between up- and down-spin \( d \) states[134]. Then the resistivity can be described with the following formula

\[
\frac{1}{\rho} = \frac{1}{\rho_{ss\uparrow}} + \frac{1}{\rho_{ss\downarrow}} + \frac{1}{\rho_{sd\uparrow}} + \frac{1}{\rho_{sd\downarrow}}.
\]
Further developing this two-current model, Marsocci[141] and Thomas et al[142] determined the spin-orbit interaction in NiFe thin films with respect to crystalline axes. The spin-orbit interaction causes non-symmetrical mixing of wave functions and the resultant perturbed wave function is a complex dependence on the angle $\theta$, where $\theta$ is the angle between the current direction and the magnetic field direction. By knowing the wave functions, it is possible to determine respectively: the scattering potentials $V$, the transition probabilities $P_{sd}$, relaxation time $\tau_{sd}$, and conductivity $\sigma_i$ and $\sigma_l$. All these parameters are the complex function of the angle $\theta$[142]. Then the AMR according to Eq. 1.25 can be calculated as

$$\text{AMR} = \frac{\rho_i - \rho_\perp}{\frac{1}{3} \rho_i + \frac{2}{3} \rho_\perp} = \frac{3(\sigma_i - \sigma_\perp)}{\sigma_i + 2 \sigma_\perp}. \quad 1.27$$

Experimentally, the resistivity of a saturated polycrystalline sample is determined by the angle $\theta$ between the electrical current $I$ and the magnetization $M$:

$$\rho = \rho_\perp + (\rho_\parallel - \rho_\perp) \cos^2 \theta. \quad 1.28$$

Here $\rho_\parallel$ is the resistivity for $I \parallel M$ and $\rho_\perp$ is the resistivity for $I \perp M$. Usually $\rho_\parallel$ exceeds $\rho_\perp$. The $\cos^2 \theta$ dependence results from averaging over all crystal orientations[143]. In bulk alloys at low temperature, where only impurity scattering occurs, the magnitude of AMR effect can be several tens of percents, e.g., 20% for NiFe at $T = 20$ K[143]. Phonon scattering in bulk alloys brings the magnitude down to about 5% at room temperature. In thin films the AMR is further reduced to a few percent due to surface scattering and additional structural defects.
In single crystals, contrary to polycrystals, averaging of the AMR resistivity over all crystal orientation is absent. Döring[144] showed experimentally that bulk Ni single crystals have a much more complicated MR than polycrystalline samples. The angular dependence did not obey a behavior involving only the relative orientation of current and magnetization. Instead, the orientation of both current and magnetization with respect to the crystal axes had to be taken into account. Later measurements on single crystal Fe rods and whiskers confirmed Döring’s results[119, 145-150]. The thin film equivalent of a bulk single crystal is epitaxial film, which can be grown on a suitable substrate with modern deposition techniques. MR measurements on epitaxial ferromagnetic films also indicate deviations from the simple $\cos^2 \theta$ behavior and suggest that the directions of both current and magnetization with respect to the crystal axes are important, as for bulk single crystals[151-160].

Figure 1-39: The magnetoresistance of sample A at $H = 10$ kOe as a function of the angle between the applied magnetic field and the electrical current at (a) $T = 4.2$ K, (b) $T = 57$ K, and (c) $T = 150$ K. (Reproduced from reference [161]).
More recently, extensive study on the temperature and angular dependence of the AMR in epitaxial Fe films has been reported by van Gorkom et al[161]. They studied two samples with different angles between the electrical current direction and the epitaxial film [001] direction, sample A and B. In sample A, the [001] direction and the current direction make an angle of $\theta = -20^\circ \pm 3^\circ$, as shown in Figure 1-39. This angle was chosen because it is not one of the high symmetry directions, in which a more regular behavior may be expected. For sample B, the current flows approximately parallel ($\theta = 0^\circ \pm 3^\circ$) to the [001] direction, as shown in Figure 1-40.

![Figure 1-39: Magnetoresistance of sample A as a function of the angle between the applied magnetic field and the electrical current at different temperatures.](image)

Figure 1-39 shows the relative resistance change $(R-R_{\text{min}})/R_{\text{min}}$ of sample A as a function of the angle between the applied magnetic field and the electrical current at $H = 10$ kOe and (a) $T = 4.2$ K, (b) $T = 57$ K, and (c) $T = 150$ K. $R_{\text{min}}$ is the minimum resistance. The resistance is measured by stepping $\phi$ ($\phi$ is the angle between the current...
and magnetization) from -100° to 100° in steps of 5°. The reverse curves from \( \phi = 100° \) to -100° are also measured in order to test the reproducibility, which is good, except for a small temperature drift at higher temperatures. Figure 1-39 confirms that the curves are not symmetric around \( \phi = 0° \) and that the minimum shifts with temperature. Furthermore, the shape is not a simple \( \cos^2\phi \) dependence. For example, in \( T = 4.2 \) K measurement, the minimum of the curve is sharper than the maximum.

The resistance as a function of the angle between the applied magnetic field and the electrical current at \( H = 10 \) kOe for sample B is shown in Figure 1-40. Curves at higher temperatures are shown compared to Figure 1-39, in order to show the change to a nonsinusoidal curve at higher temperatures more clearly. The curves are almost symmetry around \( \phi = 0° \). For \( T = 80 \) K and \( T = 184 \) K a small asymmetry is present. And it is observed that the resistance as a function of the angle is not a \( \cos^2\phi \), as is the case for a polycrystalline sample. This is most clearly visible at \( T = 184 \) K, where an extra minimum is present at about \( \phi = 90° \). The other two curves at \( T = 80 \) K and \( T = 4.2 \) K do resemble a \( \sin^2\phi \), but the curves show a much sharper maximum than minimum, indicating that again it is not a perfect sinusoidal dependence.

### 1.5.3 AMR in Manganites

The AMR in the manganites was found to be similar to transition metal in the magnitude, only a few studies have been published on AMR in the manganites. Ziese and Sena[162] derived an expression for the AMR for the Manganites within a simple atomic state model following the work of Campbell et al[163] and Malozemoff[164]. According
to the double-exchange model, the electric current in the manganites is carried by \( d \) electrons hopping between neighboring manganese sites. The application of a model based on \( s-d \) scattering means that the hopping manganese \( d \) electron is approximated by a plane wave. Although a description by a tight-binding Bloch wave seems more appropriate, Ziese and Sena used the plane wave model as a starting point to understand the magnitude and sign of the observed anisotropic magnetoresistance.

The derivation of the AMR follows the reasoning of Malozemoff[164]. The starting point is a Hamiltonian that includes a crystal-field splitting \( \Delta_{CF} \) and an exchange-coupling energy \( H_{ex} \). The spin-orbit interaction \( H_{so} \) is introduced as a small perturbation with

\[
H_{so} = A \left[ L_z S_z + \frac{1}{2} (L_+ S_- + L_- S_+) \right].
\]  

The ten \( d \)-state wave functions for both spin directions are calculated to second order in the spin-orbit coupling.

Assuming scattering by spherically symmetric impurities, the AMR can be derived by the analysis of the symmetry of the scattering matrix elements. This yields

\[
AMR = \frac{\rho_i - \rho_i}{\frac{1}{3} \rho_i + \frac{2}{3} \rho_i} = \frac{3}{2} \left[ \frac{A^2}{(H_{ex} - \Delta_{CF})^2} - \frac{A^2}{\Delta_{CF}^2} \right].
\]

This expression contains only the local parameters \( \Delta_{CF} \), \( H_{ex} \) and \( A \). With \( \Delta_{CF} \approx 1.5 \text{ eV} \), \( H_{ex} \approx 2.0 \text{ eV} \), and \( A \approx 0.04 \text{ eV} \) a value of \( AMR = -0.85\% \) is found. This is in a good agreement with the experiment value at low temperatures[29].
Angular dependence of the magnetoresistance of epitaxial LCMO films has been studied by some groups[60, 61, 165]. In most cases, the curves can be approximately fit by the $\sin^2 \theta$ dependence, as seen in Figure 1-25, but the AMR ratios are about 10% at most in those studies. Very large AMR ratios have been reported by Li et al[62] in the strained epitaxial PSMO ultrathin films. However, in this case, the MAR was measured by rotating the magnetic field from the in the film plane direction to the out-of-plane direction. The magnetic field is applied always perpendicular to the current, thus there is no change of angle between the $I$ and $M$, and the AMR is due to magneto-crystalline anisotropy. More than 100% AMR has been observed, which will be discussed in detail in the Chapter 4 of this thesis.

Recently, a room-temperature anisotropic magnetoresistive sensor based on manganese perovskite (La$_{0.67}$Sr$_{0.33}$MnO$_3$) thick films has been developed by screen-printing technique[166], which shows the feasibility of using the AMR effect of the magnetite materials for a magnetic sensor.
Chapter 2
Experimental Methods

2.1 Thin Film Preparation

2.1.1 Target and Substrate Preparation

The manganite thin films studied in this thesis were prepared by the pulsed laser deposition (PLD) technique. A pulsed laser beam ablates a dense ceramic target of desired material. In a presence of a background oxygen gas, a plasma is produced and condenses on the heated single crystal substrate.

Almost all the ceramic targets used in this thesis were homemade, synthesized by the standard solid-state reaction method. For example, to make the La$_{0.67}$Sr$_{0.33}$MnO$_3$ ceramic target, high purity La$_2$O$_3$, SrCO$_3$, and MnO$_2$ powders were precisely measured and thoroughly mixed according to desired stoichiometry, and then sintered for four days in an oxygen atmosphere with three intermediate careful grinding and mixings for homogenization. Powder X-ray diffraction measurement was used to examine the synthesized powders to make sure that no impurity is present. Finally, the powders were pressed into the pellet form, and sintered for two days to become the targets.

Three types of single crystal substrates were used in this thesis, namely LaAlO$_3$ (001) LAO, NdGaO$_3$ (110) NGO and SrTiO$_3$ (001) STO, which were bought from the CrsyTech Inc. They were single side polished, and 0.5 mm thick. Before the deposition,
the substrates were carefully cut to desired size using a diamond cutter. Then they were cleaned by sonicating in the Acetone and Methanol for 5 minutes each. Finally they were glued on the substrate heater using the silver paste.

2.1.2 Pulsed Laser Deposition (PLD) Technique

In general, the method of the pulsed laser deposition (PLD) is simple and very flexible. Only a few parameters need to be controlled during process. The targets used in PLD are small compared with the large size required for other techniques such as sputtering techniques. It is quite easy to produce multi-layer film of different materials. By controlling the number of pulses, a fine control of film thickness can be achieved. Thus a fast response in exploiting new material system is a unique feature of PLD among other deposition methods. The most important feature of PLD is that the stoichiometry of the target can be retained in the deposited films. This is the result of the extremely high heating rate of the target surface (~10⁹ K/s) due to pulsed laser irradiation. It leads to the congruent evaporation of the target regardless of the vaporizing temperature of the constituent elements or compounds of the target.

A schematic illustration of a typical pulsed deposition system (PLD) is shown in Figure 2-1. In general, excimer UV lasers are used for deposition. Between the output port of the laser and the laser port of the deposition chamber, optical elements are placed in order to steer and focus the beam. The optical elements that couple the energy from the laser to the target are lenses and apertures, such as mirrors, beam splitters, and laser windows. Once the laser beam passes through the optical elements, it enters the
deposition system and is focused onto the surface of the target. All elements in the target are then rapidly heated up to their evaporation temperature. The emitted materials tend to move towards the substrate, and condense on the substrate.

To prepare the samples studied in this thesis, a Lambda Physik Lex300 KrF excimer laser with the wavelength of 248 nm, the energy density of \(~2 \text{ J/cm}^2\)\), and the repetition rate of 2-5 Hz was used. The growth rates were around 0.5-1Å/second and the thickness of the film was determined by the nominal value measured by a depth profile meter. The substrate temperatures were 750-800 °C and oxygen pressures were 350-800 mTorr during the deposition. The films were then cooled down to the room temperature in the oxygen pressure of 300-750 Torr, and at the rate of 15-40 °C/minute after deposition. The surface and structure of the films were characterized by the X-ray

Figure 2-1: Schematic illustration of a typical pulsed laser deposition (PLD) system.
diffraction (XRD), atomic force microscopy (AFM) and transmission electron microscopy (TEM) measurements.

2.2 Surface and Structural Characterization

2.2.1 X-Ray Diffraction (XRD) Measurements

X-ray diffraction (XRD) $\theta$-2$\theta$, $\phi$ and $\omega$ scans were used to examine the phase purity, crystallographic perfection, orientation relationship, and lattice constants of the manganite thin films prepared by the PLD technique. The scans were performed with a Picker four-circle diffractometer using a Cu $K\alpha$ radiation.

![XRD Patterns](image)

Figure 2-2: XRD patterns of three 20 nm thick LCMO films grown on LAO, NGO, and STO substrates, respectively. The arrows indicate the LCMO 002 peaks.
The focus of this thesis is to study the strain effect on the manganite thin films, and different manganite thin films were grown on the LaAlO$_3$ (001) LAO, NdGaO$_3$ (110) (NGO) and SrTiO$_3$ (001) (STO) substrates to introduce different types of strains into the films. As an example, the psedocubic lattice parameter of bulk La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO) is $a_b=3.867$ Å. The lattice mismatch between the LCMO film and the NGO substrate ($a\sim3.862$ Å) at the room temperature is only $\sim0.1\%$, and therefore the LCMO/NGO films are expected to have little lattice mismatch induced strain. The psedocubic LAO substrate has a smaller (3.794 Å), and the cubic STO substrate has a larger (3.905 Å) lattice constant than the LCMO at room temperature, and hence the LCMO/LAO films are compressed biaxially and the LCMO/STO films are expanded biaxially in the film plane. Correspondingly, the lattice parameters in the film normal axis are expected to expand in the LCMO/LAO films and to compress in the LCMO/STO films.

The XRD measurements show that all the films were epitaxially grown with the $c$ axes normal to the film plane. No impurity phases were found. Figure 2-2 shows the $\theta-2\theta$ scans near the 002 peak of LCMO for three 20 nm thick films grown on LAO, NGO, and STO substrates, respectively. As indicated in the figure, the 002 peaks of the LCMO/LAO and LCMO/STO films are located at 46.1° and 47.9°, and the full width at half maximum (FWHM) of the 002 peak of both LCMO/LAO and LCMO/STO films is $\sim0.6°$. The FWHM of the rocking curve ($\omega$-scan) of the 002 peak of both LCMO/LAO and LCMO/STO films is $\sim0.2°$. This corresponds to $c$ axis lattice parameter of 3.95(±0.01) Å and 3.81(±0.02) Å for 20 nm thick LCMO/LAO and LCMO/STO films, respectively. The diffraction peak of LCMO/NGO film is almost indistinguishable from
the substrate peak due to their close lattice match. The peak positions of LCMO/LAO and LCMO/STO films vary with film thickness. With the thickness decreases, the diffraction peaks become broader and their intensity is reduced, especially for the highly strained films. As shown in Figure 2-3, the XRD $\phi$-scan shows the sharp peaks and almost equal

![Figure 2-3: X-ray $\phi$-scan of the 101 peak of a 16 nm thick LCMO/LAO film. The four peaks indicate that the LCMO film is epitaxial with an in-plane orientation relationship of LCMO[100]//LAO[100], i.e., cube-on-cube. The in-plane lattice parameter of the LCMO is $a=3.78\pm0.06$ Å](image)

peak intensity, indicating high quality in-plane epitaxy and the expected cube-on-cube alignment of the unit cell of the perovskite film with the underlying substrate. The full width at half maximum (FWHM) of the $\phi$-scan of the 002 peak of the LCMO/LAO film is $\sim0.4^\circ$. The in-plane lattice parameter of the LCMO is calculated to be $a=3.78\pm0.06$ Å,
very close to the lattice parameter of the LAO substrate, indicating that the film is fully strained.

### 2.2.2 Atomic Force Microscopy (AFM) Measurements

Atomic force microscopy (AFM) was used to examine the topography of the manganite thin films. The AFM measurements were carried out using both Digital Instrument Nanoscope III and JEOL JSPM-4200 Scanning Probe Microscope. Ultra-
sharp silicon cantilevers from the Mikro Masch were used. The AFM measurements show that the manganite thin films were uniform and flat. As an example, Figure 2-4 shows the AFM topography images of two 25 nm thick LSMO/LAO and LSMO/STO thin films. The image size is 1µ x 1µ, and the mean surface roughness is about 5 nm and 4 nm for LSMO/LAO and LSMO/STO films, respectively. The white particles on the surface are typical for films made by the PLD technique. In fact, particulates deposition on the film is one of the major shortcomings of the PLD technique.

2.2.3 Transmission Electron Microscopy (TEM) Measurements

Some of the manganite thin films have also been studied using the transmission electron microscopy (TEM)[50]. Specimens for TEM observations were made by a standard cross-sectional preparation technique involving gluing two films face to face and then mechanically polishing and dimpling to a thickness less than 30 µm. This was followed by ion-beam thinning, taking care to ensure that the film was not preferentially thinned by the Ar ion beam. Transmission electron microscopy observations were made using a Philips CM200 FEG equipped with a Gatan imaging filter system, using diffraction contrast and high-resolution electron microscopy (HREM) imaging together with selected area diffraction (SAD).

Figure 2-5 shows a HREM image of a 30 nm thick Pr$_{0.67}$Sr$_{0.33}$MnO$_3$ (PSMO) (bulk lattice parameter $a_0=3.867$ Å) thin film and its interface to the LAO substrate (the film is somewhat thinner than 30 nm in this image as some of the surface was milled away in ion beam thinning). The interface is perfectly coherent and no misfit dislocations could be
detected. It shows that the films are highly uniform and defect free, and that they are coherently strained to the smaller lattice parameter of the substrate.

2.3 Physical Properties Measurements

2.3.1 Transport Measurements

Transport property measurements of the manganite thin films were carried out using standard four-terminal method on a Quantum Design PPMS 6000 system. The PPMS 6000 system can conduct the measurements in the temperature range of 1.9-350 K. Temperature sweep capability allows measurements to be taken while sweeping the temperature at a user defined rate (0.01-6 K/min). Continuous Low-Temperature Control
(CLTC) ensures precise temperature control. The PPMS has a superconductor magnet, which can provide a magnetic field up to 9 Tesla with the uniformity of ±0.01% over a 5.5 cm x 1 cm diameter cylindrical volume. The low noise, bi-polar power supply allows continuous charging through zero field with current compensation and over-voltage protection. The resolution of the field control is 0.02 mTesla up to 1 Tesla and 0.2 mTesla up to 9 Tesla. A schematic illustration of the PPMS 6000 probe is shown in Figure 2-6.

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Figure 2-6: A schematic illustration of the PPMS 6000 probe. (Reproduced from Quantum Design).

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The PPMS 6000 system is also equipped with a motorized sample rotator to conduct the angular dependence measurements (see Figure 2-7). Samples are mounted on
removable platforms. A thermometer, in direct contact with the platform, accurately
determines the sample temperature. The rotator can sweep the angular range from -10° to
370°, with the step size of 0.053° for standard resolution.

2.3.2 Magnetic Measurements

The PPMS 6000 system includes the Model P500, AC/DC Magnetometry System
(ACMS), which can perform AC susceptibility as well as DC magnetization
measurements. The ACMS utilizes a DC measurement technique called Extraction
Magnetometry. Moving a magnetized sample through the detection coils induces a
voltage in the detection coil set. The amplitude of this signal is proportional to the
magnetic moment and speed of the sample during extraction. The DC servo motor
employed in the ACMS can extract the sample at a speed of approximately 100 cm per
second, thus significantly increasing the signal strength over conventional extraction

Figure 2-7: Sample rotator with various sample-mounting platforms. (Reproduced from Quantum Design).
system. The greater speed also reduces any error that may result from non-equilibrium time-dependent effects. The ACMS can conduct the DC magnetization measurements at the temperature range of 1.9–350 K, with the magnetization range of $2.5 \times 10^{-5}$ emu to 5 emu.

Some magnetization measurements for very thin films were carried out at the University of Wisconsin-Madison by our collaborators. The magnetization measurements were made in a DC superconducting quantum interference device (SQUID) magnetometer. The diamagnetic background signal from the substrates was minimized by mechanically thinning the substrates to approximately 0.3 mm. For accurate background correction, the susceptibility of blank substrates was measured at different temperatures.

Magnetic force microscopy (MFM) measurements were also carried out for some samples to observe the magnetic domain patterns. The MFM measurements were done using a JEOL JSPM-4200 Scanning Probe Microscope. A Co-Cr coated silicon cantilever was used to pick up the magnetic information on the surface of the manganite thin films.
Chapter 3

Low-Field Magnetoresistance (LFMR) in Manganite Thin Films

3.1 LFMR in La$_{0.67}$A$_{0.33}$MnO$_3$ Thin Films (A=Ca, Sr, Ba)

3.1.1 Introduction

The continually increasing demand for the magnetic information storage and retrieval has driven a significant worldwide effort to improve the performance of relevant hardware components. Modern magnetic recording heads and disk drives utilize a thin magnetoresistive element, made out of permalloy, which senses the slight change in resistance (about 2%) that occurs as the angle of magnetization is changed when the magnetized data bits pass beneath the head. For ultra high recording densities the signal strength produced in the heads diminishes considerably. Therefore, more sensitive materials and innovative structures will be required to detect the decreasing magnetic fringe-fields emanating from the media.

During the last decade, the doped manganite compounds T$_{1-x}$D$_x$MnO$_3$ (where T is the trivalent rare-earth element such as La, Pr and Nd, and D is the divalent alkaline-earth element such as Ca, Sr and Ba) have been studied intensively due to their remarkable colossal magnetoresistance (CMR) effect. As discussed in Chapter 1, it has been found that the electromagnetic transport properties of this perovskite-like structure being very sensitive to the lattice dynamics which can be modulated experimentally by doping at the
T and/or D sites with different cation elements, applying pressure, introducing strain etc.. It is also known that changing the hole concentration (x) will also significantly affect the structural, electronic and magnetic properties of those manganite compounds. Experimental and theoretical studies have suggested that strong electron-phone interaction based on the Jahn-Teller effect plays an important role in the CMR and other properties in the system, together with the well-known double-exchange mechanism. Besides the fundamental science, the studies have also been motivated by the potential field-sensor and device applications of these materials.

The magnetoresistance (MR) of manganites is of unprecedented magnitude; however, the CMR is usually obtained in a high magnetic field (typically a few Tesla), thus severely limiting their practical utility. Reducing the field scale and increasing the operating temperature has been the goal of a number of research groups worldwide. Several groups have reported large low-field MR in multiplayer magnetic tunneling-junctions (MTJ)[84, 86]. Enhanced MR effect was also observed in granular thin films and polycrystalline samples[28, 167, 168], and thin film devices based on grain-boundary effect[33, 35, 95].

On the other hand, one important issue both for physics and for any possible application is the strain dependence of material properties. In particular, many proposed applications involve films, and films typically have large biaxial strains since lattice distortion can be easily introduced in thin films due to lattice mismatch between the film and the substrate. Therefore, the thin film samples provide good candidates for the study of the biaxial strain effect on the electrical and magnetic properties of the materials.
Wang and Li have reported the strain-induced large low-field magnetoresistance in very thin Pr$_{0.67}$Sr$_{0.33}$MnO$_3$ (PSMO) films grown on the LaAlO$_3$ (001) (LAO) substrates[57]. The films are under compressive strain imposed by the lattice mismatch with the substrate. They obtained a MR ratio of -92% at $H=800$ Oe (MR is defined as $[R(0)-R(H)]/R(0)$) and $T=70$ K. They also observed large low-field magnetoresistance anisotropy between magnetic fields applied parallel and perpendicular to the film planes[58]. Although the results were speculated to be due to the strain-induced magnetic anisotropy and domain wall scattering, the origin of the large domain wall resistance is still unclear.

Table 3-1: The lattice constants of the bulk manganite materials (LCMO, LSMO, LBMO) and the substrates (STO, NGO, LAO), and the lattice mismatch between them.

<table>
<thead>
<tr>
<th></th>
<th>LCMO (3.867 Å)</th>
<th>LSMO (3.88 Å)</th>
<th>LBMO (3.897 Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO (3.905 Å)</td>
<td>1%</td>
<td>0.6%</td>
<td>0.2%</td>
</tr>
<tr>
<td>NGO (3.862 Å)</td>
<td>-0.1%</td>
<td>-0.5%</td>
<td>-0.9%</td>
</tr>
<tr>
<td>LAO (3.794 Å)</td>
<td>-1.9%</td>
<td>-2.2%</td>
<td>-2.6%</td>
</tr>
</tbody>
</table>

It is our intention to do a thorough and systematic study to investigate the role of strain in the magnetotransport properties of the manganite thin films and the origin of the large domain wall resistance in the compressive strained manganite thin films. In this section, we will study and compare the LFMR properties in the La$_{0.67}$A$_{0.33}$MnO$_3$ thin films (A=Ca, Sr, Ba). The films were grown on different substrates, namely LaAlO$_3$ (001) (LAO), NdGaO$_3$ (110) (NGO) and SrTiO$_3$ (001) (STO). Due to the different lattice mismatch, different strains will be imposed into the thin films. Table 3-1 shows the lattice constants of the bulk manganite materials and the substrates, and the lattice mismatch between them. As an example, Figure 3-1 shows the schematic illustration of the
structure of LCMO films under tensile strain, almost non-strain, and compressive strain in the film plane by growing the film on different substrates. This structural change has been confirmed by the X-ray diffraction measurements, as seen in Figure 2-2.

We have found that: (1) large low-field magnetoresistance (LFMR) behaviors are observed in La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO) and La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO) thin films on LAO substrates when a magnetic field is applied perpendicular to the film plane, but the maximum LFMR is the largest in LCMO samples (~300% at 1350 Oe and 50 K) and no large LFMR is observed in La$_{0.67}$Ba$_{0.33}$MnO$_3$ (LBMO) samples so far; (2) large domain wall resistance is also observed in the compressive strained LCMO and LSMO thin films, but not in the LBMO thin films; (3) magnetization measurements show that compressive strained LCMO and LSMO thin films have out-of-plane magnetic easy axis, and LCMO
thin films have much larger magnetic anisotropy energy than LSMO thin films; (4) the large low-field MR is strongly dependent on the film thickness, temperature and the composition of the manganites; (5) most of the films grown on STO substrates show positive MR when a magnetic field is applied perpendicular to the film plane, and when the field is parallel to the film plane all films show negative MR regardless of the substrates.

Large magnetic anisotropy energy has been reported earlier in compressively strained Pr$_{0.67}$Sr$_{0.33}$MnO$_3$/LAO thin film[54]. In this section we will present the comparison study of the magnetic anisotropy in LCMO/LAO, LSMO/LAO and LBMO/LAO thin films. The anomalous LFMR effect will be discussed based on strain-induced magnetic anisotropy and unconventional domain wall resistance. We attribute the different behaviors of LFMR and domain wall resistance among the LCMO, LSMO and LBMO films to the difference of the strain-induced magnetic anisotropy energy.

### 3.1.2 LFMR Measurements

Low field magnetoresistance (LFMR) has been studied for both compressive and tensile strained thin films. For the convenience of discussion, in the following part of this chapter, we refer $H_\perp$ for the magnetic field perpendicular to the film plane (the current is always applied in the film plane) geometry, and $H_\parallel$ for the field parallel to film geometry, respectively. In both geometries, the current is always applied in the film plane and perpendicular to the magnetic field. Also we will refer to the films grown on LAO, STO and NGO substrates as LCMO/LAO, LCMO/STO and LCMO/NGO, et al.
Figure 3-2 shows the results of resistance versus magnetic field measurements of the compressive strained LCMO/LAO, LSMO/LAO and LBMO/LAO thin films measured in the $H_{\perp}$ geometry. The magnetic field was scanned from –5 kOe to 5 kOe, and then scanned back to –5 kOe. As seen in the Figure 3-2, large LFMR and MR hysteresis were observed in both LCMO/LAO and LSMO/LAO films. If we define the LFMR ratio as $(R_P - R_0)/R_0$, where $R_P$ is the resistance at the peak of the hysteresis loop, and $R_0$ is the resistance at $H=0$, then the LFMR ratio is largest in LCMO/LAO sample and smaller in LSMO/LAO sample. Such large LFMR effect was only observed in the compressive strained films, and only observed when the field was applied perpendicular to the film.
plane. And this type of large LFMR effect has not been observed so far in the LBMO thin films.

When the field is applied parallel to the film plane, the LFMR effect is much smaller. Figure 3-3 shows the LFMR and MR hysteresis curves of LCMO/LAO, LSMO/LAO, and LBMO/LAO thin films in $H_{//}$ geometry. It is seen that all three films have very small hysteresis loops and LFMR ratios. The MR ratio is largest in the LCMO/LAO thin film, and smallest in the LBMO thin film.

LFMR of compressive strained thin films depends strongly on the film thickness. Figure 3-4 shows the LFMR ratios in the $H_{\perp}$ geometry as a function of the film thickness for LCMO/LAO and LSMO/LAO films. The LFMR ratios shown in this figure are the maximum values of each thickness in the measurements. It is seen that LFMR ratio drops

Figure 3-3: The normalized resistance as a function of magnetic field applied parallel to the film plane of the same samples shown in Figure 3-2.
rapidly as the film thickness increases in both LCMO/LAO and LSMO/LAO films. Large LFMR ratio only exists in a narrow thickness range for both LCMO and LSMO films, but LCMO/LAO thin films have much larger LFMR ratios than LSMO/LAO thin films. For very thin films, both LCMO/LAO and LSMO/LAO show insulating behaviors, and LFMR effect was not available. The thickness dependence of LFMR is related to the strain effect of the films. Our X-ray measurements showed that the lattice parameters of LCMO/LAO films depend strongly on the film thickness. They are almost fully strained.

Figure 3-4: The LFMR ratios in the $H_\perp$ geometry as a function of the film thickness for LCMO/LAO and LSMO/LAO films. The inset shows how LFMR ratio is defined.
when the thickness is below 200 Å. This corresponds to the thickness range where the anomalous LFMR presents.

Figure 3-5: The LFMR ratios in the $H_\perp$ geometry as a function of the temperature for LCMO/LAO and LSMO/LAO films.

LFMR effect also strongly depends on the temperature, as seen in Figure 3-5. The 140 Å thick LCMO/LAO sample shows a maximum LFMR ratio of 300% at 50 K. Below and above this temperature, the magnitude of LFMR ratio is smaller, and as the temperature approaches to the Curie temperature $T_c$ of this sample (~90K), the LFMR ratio vanishes. The LFMR ratio of the LSMO/LAO sample shows similar temperature dependence, which shows the maximum value around 20 K. But the LFMR of the LSMO/LAO sample is much smaller than that of the LCMO/LAO sample. We’d like to
point out here that, all of the LCMO/LAO samples we measured showed the maximum LFMR at temperatures well below their $T_c$'s. This is significantly different from what is observed in grain boundary[172] and the multiplayer tunneling junctions[84, 86]. In those systems, the LFMR shows a monotonous increase with decreasing temperature. This shows that the anomalous large LFMR in our samples has different origin from the grain-boundary spin scattering mechanism. In the system where the grain-boundary scattering is dominant, the largest reported MR is ~30%, while our sample show more than 1000% MR. This again shows the large LFMR effect observed in our samples has a different origin.

Figure 3-6: The normalized resistance as a function of magnetic field applied perpendicular to the film plane for LCMO/STO, LSMO/STO and LBMO/STO films.
Positive MR curves were observed in the tensile-strained samples. Figure 3-6 shows the positive MR in the LCMO/STO, LSMO/STO, and LBMO/STO thin films in the $H_{\perp}$ geometry. It is seen that, for the tensile strained samples, MR is much smaller than that of the compressive strained samples, and they have opposite signs. The LCMO/STO thin film has the largest MR ratio and hysteresis loop, while LSMO/STO and LBMO/STO films have almost no hysteresis loops and very small MR ratios. In our study, the positive MR behavior is only observed when the field is applied perpendicular to the film plane, and in small magnetic fields. When the field becomes larger, MR will become negative.

Figure 3-7: The normalized resistance as a function of magnetic field applied parallel to the film plane of the same samples shown in Figure 3-6.
When the field is applied parallel to the film plane of a tensile strained film, only negative MR has been observed. Figure 3-7 shows the normalized MR hysteresis loops of LCMO/STO, LSMO/STO and LBMO/STO thin films in the $H_{\parallel}$ geometry. The LCMO/STO film has the largest MR ratio and hysteresis loop, and LBMO/STO has the smallest MR ratio and almost no hysteresis.

![Figure 3-7: Normalized MR hysteresis loops of LCMO/STO, LSMO/STO and LBMO/STO thin films in the $H_{\parallel}$ geometry.](image)

It is seen that the LFMR behaviors for the samples with different types of strains in the $H_{\perp}$ geometry are very different. Figure 3-8 shows the normalized resistance as a function of magnetic field in the $H_{\perp}$ geometry for compressive-, non-, and tensile-strained LCMO films. Compressive strained LCMO film show both large hysteresis loop and very

![Figure 3-8: The normalized resistance as a function of magnetic field applied perpendicular to the film plane for LCMO/LAO, LCMO/NGO and LCMO/STO films. The magnetic field was scanned from −5 kOe to 5 kOe, and then scanned back to −5 kOe.](image)
large negative LFMR; non-strained LCMO film show no hysteresis loop and very small negative LFMR; and tensile strained LCMO film show both small hysteresis and small positive LFMR. The fact that LFMR is negative for compressive strained films, but positive for tensile strained films shows that strain effect is one of the dominant factors in the LFMR properties in our sample.

We have shown the results of LFMR in both $H_{\perp}$ and $H_{\parallel}$ geometries. It is obvious that there are significant differences in the LFMR behaviors in these two geometries for both compressive strained and tensile strained thin films.

First, we look at the compressive strained LCMO and LSMO thin films. Comparing Figure 3-2 and Figure 3-3, we can see that it shows very large LFMR with pronounced hysteresis in the $H_{\perp}$ geometry. In the $H_{\parallel}$ geometry, the MR hysteresis is almost invisible and the LFMR ratio is much smaller. In our studies, we find that the above difference becomes smaller as the temperature approaches to $T_c$. As an example, the temperature dependence of LFMR for a 160 Å thick LCMO/LAO sample in both $H_{\perp}$ and $H_{\parallel}$ geometries, and the ratio between the MR in these two geometries are shown in Figure 3-9. It is seen that the LFMR in the perpendicular field is much larger than that in the parallel field at all the temperatures, and the ratio of these two can be as large as 105 at 60 K. Since in both geometries, the current is applied in the film plane and perpendicular to the magnetic field, it means that there is a large out-of-plane LFMR anisotropy in the compressive strained LCMO and LSMO thin films. The difference in both geometries is small for LBMO/LAO thin films. Those results are consistent with the magnetization measurements as will be discussed later, which show large magnetic
anisotropy energies in LCMO/LAO and LSMO/LAO thin films, and small anisotropy energy in LBMO/LAO thin film.

In contrast, the tensile strained thin films of all three compositions show positive LFMF in $H_\perp$ geometry up to about 1 Tesla (see Figure 3-6) and change to negative MR at higher field. In $H_\parallel$ geometry, all three compositions show negative MR (see Figure 3-7). The different signs of LFMR in the $H_\perp$ and $H_\parallel$ geometries can be explained by the domain rotation, which will be discussed in section 3.3.1.

Figure 3-9: The temperature dependence of the LFMR for a 160 Å thick LCMO/LAO sample in both $H_\perp$ and $H_\parallel$ geometries. The ratio of these two LFMR’s is also shown in this figure.
3.1.3 Magnetization Measurements

Magnetization of LCMO/LAO, LSMO/LAO and LBMO/LAO thin films was also measured at different temperature and for different thickness in both perpendicular field ($H_{\perp}$) and parallel field ($H_{||}$).

Figure 3-10 shows the magnetization curves for 200 Å thick LCMO/LAO, 125 Å thick LSMO/LAO and 100 Å thick LBMO/LAO thin films measured at $T=20$ K with the external magnetic field applied in [100] (perpendicular to the film plane) and [001] (parallel to the film plane) directions. When the magnetic field was applied in the film plane, both hysteresis loops of LCMO/LAO film and LSMO/LAO film show zero remanent magnetization and a small coercive field. This suggests that the magnetic easy axis of these two films be perpendicular to the film plane due to the out-of-plane anisotropy induced by in-plane compressive strain, consistent with our previous study of the similar system, PSMO/LAO thin films[54]. The anisotropy energy of these two films has been calculated to be $2.1 \times 10^6$ erg/cc for LCMO/LAO thin film, and $2.5 \times 10^5$ erg/cc for LSMO/LAO film at $T=20$ K. It is seen that the anisotropy energy of the LCMO/LAO thin film is one order of magnitude larger than that of the LSMO/LAO thin film. We also observed zero remanent magnetization in the out-of-plane direction after eliminating the domain pinning effect for both LCMO/LAO and LSMO/LAO films at $T=20$ K. Zero remanent magnetization in both in-plane and out-of-plane directions indicates that the formation of the perpendicular stripe domain structures along z-axis in these two films. Similar results were also obtained for thicker films and at higher temperatures for LCMO/LAO and LSMO/LAO thin films.
Domain patterns on LSMO/LAO sample s observed by several groups using magnetic force microscope (MFM) at room temperature showed that the domains are perpendicular to the film surface with maze like patterns, called “maze domains”[51, 130]. Figure 3-11(a) shows the MFM image of a 1200 Å thick LSMO/LAO film taken in

Figure 3-10: M-H loops of (a) LCMO/LAO, (b) LSMO/LAO and (c) LBMO/LAO thin films, measured in [100] and [001] directions at $T=20$ K.
zero field at room temperature, and the film was cooled down in zero field after deposition. The domains are narrow, long and more ordered in the stripe-like pattern. This is different from the maze domain pattern reported by Kwon et al[51] and Wu et al[130]. Figure 3-11(b) shows the image of the same sample taken in zero field at room temperature.
temperature after the film has been demagnetized with an in-plane magnetic field. Stripe domains become even more ordered along the field direction. Most stripes are long enough to cross the 5 µm image without broken. This is also quite different from the stripe domains observed by Kwon et al. and Wu et al., which were shorter and less ordered. The differences might be due to the different sample preparation process. We estimated the domain wall width of the 200 Å thick LCMO/LAO and 125 Å thick LSMO/LAO films from the magnetic anisotropy energy to be about 10 nm and 30 nm, respectively.

The relationship between the applied magnetic field and domain size was also derived[170] as

$$\frac{1}{d^2} = \frac{1}{d_0^2} - \frac{4}{h^2} H_r^2$$

where $d_0$ and $d$ are the domain size at the applied field $H=0$ and $H$, $h$ is the film thickness, and $H_r = H/(4\pi M_s)$ ($M_s$ is the saturation magnetization) is the reduced applied field. When we increase the external magnetic field, the domain size increases and the domain wall density decreases. This means less domain-wall, which leads to the MR at low field. It is also known that the domain wall width $\delta \sim (T_c/K)^{1/2}$[171], where $T_c$ is the Curie temperature of the ferromagnetic material, and $K$ is its magnetic anisotropic constant. Our measurements show that $T_c$ decreases with decreasing film thickness, and it is reasonable that $K$ would increase with decreasing film thickness since strain will enhance the anisotropy. Therefore, the domain wall width $\delta$ will decrease with decreasing film thickness, which gives larger contribution to LFMR as we discussed earlier. In the thicker films, domain wall width would be thicker, and LFMR is no longer dominated by the
domain wall scattering. LFMR does not depend significantly on the film thickness in thicker films.

As for the hysteresis loops of the LBMO/LAO thin film, zero remanent magnetization was neither observed in the in-plane direction nor the out-of-plane direction at $T=20$ K. This indicates that the magnetic easy axis of this film is tilted, neither perpendicular nor parallel to the film plane. Upon increasing the temperature, the magnetic easy axis was observed to rotate to the in-plane direction. We have not been able to calculate the anisotropy energy of the LBMO/LAO thin film because of the tilting. However, it is smaller than that of LCMO/LAO and LSMO/LAO thin films as it is less than the demagnetization field.

### 3.1.4 Domain Wall Resistance (DWR) Measurements

Since the LFMR is hysteretic, it is natural to relate it to domain rotation as normal MR of a FM material is not hysteretic. To further investigate the origin of LFMR in LCMO/LAO and LSMO/LAO thin films, and to find out the reason of the different LFMR behaviors among LCMO/LAO, LSMO/LAO and LBMO/LAO thin films, domain wall resistance (DWR) was measured for all three kinds of thin films.

The DWR was measured by comparing the resistance of the compressive strained thin films with and without anti-parallel domains. In our measurements, two different types of demagnetized states in the samples were created. (1) Stripe domain state: a sample was cooled in zero magnetic field (ZFC), or a large magnetic field was applied first and then reduced to zero by a damped oscillation mode. In this demagnetized state,
stripe-like domains will be present as shown in Figure 3-11(a). We denote the resistance obtained in these two ways as $R_{ZFC}$ and $R_{MD}$ respectively. (2) Single domain state: a large magnetic field was first applied perpendicular to the film plane (magnetic easy axis of the film), and then reduced to zero linearly. In this case, the sample is in a remanent magnetization state with nearly a single perpendicular domain[54]. We denote the resistance in this single domain (SD) state as $R_{SD}$. By comparing the resistance of the sample at two different demagnetized states, the domain wall resistance can be obtained.

Figure 3-12: The normalized resistance as a function of magnetic field of a 135 Å thick LCMO/LAO film measured from different demagnetized states. The magnetic field was applied perpendicular to the film plane during the measurements.
Figure 3-12 shows the normalized resistance as a function of magnetic field of a 135 Å thick LCMO/LAO sample measured from different demagnetized states. The magnetic field was applied perpendicular to the film plane during the measurements. $R_{SD}(0)$ is the resistance at zero field of the single domain state. As seen in the Figure 3-12, the zero field resistance from stripe domain states (both $R_{ZFC}$ and $R_{MD}$) is much larger than that of a single domain state ($R_{SD}$). This reflects high domain wall resistance in the film. It is also interesting to see that, $R_{ZFC}(0)$ is higher than $R_{MD}(0)$, although both were measured from the random domain states with stripe domain. This is probably because that in the ZFC state, besides the contribution of the domain walls, there are other large contributions to the resistance, such as spin disorder and non-reversible domain walls[169]. Those contributions are suppressed by applying a magnetic field, therefore $R_{ZFC}(0)$ is larger than $R_{MD}(0)$.

At higher field, all three curves coincide together, which is expected as the magnetic field aligns all domains in the field direction and the film reaches the single domain state.

The same measurement was done for LSMO/LAO and LBMO/LAO thin films. The results were shown in Figure 3-13. It was drawn in the same scale as Figure 3-12 in order to compare the DWR ratios. It is seen that similar behaviors were observed in the LSMO/LAO thin film. Both $R_{ZFC}(0)$ and $R_{MD}(0)$ are larger than $R_{SD}(0)$, but the ratio of $R_{ZFC}(0)/R_{SD}(0)$ or $R_{MD}(0)/R_{SD}(0)$ are much smaller than those of the LCMO/LAO thin film. This means that the domain wall resistance of the LSMO/LAO thin film is smaller than that of the LCMO/LAO thin film.
For the LBMO/LAO thin film, all three curves almost coincide together, which indicates that the domain wall resistance in the LBMO/LAO thin films is almost negligible. This is consistent with our LFMR measurements, which show almost no LFMR effect in the LBMO/LAO thin films.

We also want to point out that, the thickness dependence and temperature dependence behaviors of DWR in both LCMO/LAO and LSMO/LAO thin films are also similar to those of LFMR in these thin films. The domain wall resistance decreases

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Figure 3-13: The normalized resistance as a function of magnetic field of 100 Å thick LSMO/LAO and 75 Å thick LBMO/LAO films measured from different demagnetized states. The magnetic field was applied perpendicular to the film plane during the measurements. The figures were drawn in the same scale as Figure 3-12 to compare the DWR ratios.
sharply as the film thickness increases. The temperature where the DWR reaches its maximum is also much below $T_c$ in both LCMO/LAO and LSMO/LAO thin films. Those similarities indicate that in our system, the domain wall resistance is dominant, and the large LFMR is originated from the DWR.

### 3.2 LFMR in Pr$_{1-x}$Sr$_x$MnO$_3$ Thin Films (x=0.2, 0.25, 0.33, 0.4)

**3.2.1 Introduction**

In the last section, we investigated the LFMR in the La$_{0.67}$A$_{0.33}$MnO$_3$ thin films (A=Ca, Sr, Ba). This series has the same hole doping level of x=0.33 but with different divalent cations. This section will focus on the LFMR properties of another manganite series, Pr$_{1-x}$Sr$_x$MnO$_3$ (x=0.2, 0.25, 0.33, 0.4) thin films, which keeps the same cations but varies the hole doping levels. Figure 3-14 shows the phase diagram of the Pr$_{1-x}$Sr$_x$MnO$_3$ series as the function of the hole doping level x. It is seen that for $0.25 \leq x \leq 0.4$, Pr$_{1-x}$Sr$_x$MnO$_3$ is a ferromagnetic metal (FMM), while for x=0.2, it is a ferromagnetic insulator (FMI). But in our studies, for all doping level x (0.2 $\leq x \leq$ 0.4), Pr$_{1-x}$Sr$_x$MnO$_3$ films show metal-insulator transition. However for x= 0.2 and 0.25, the resistivity of the Pr$_{1-x}$Sr$_x$MnO$_3$ films is very high, which indicate that the films at these two doping levels are close to the FMM and FMI phase boundary. The discrepancy between our results and the phase diagram might be because of the slight off-stoichiometry of the oxygen composition of the thin films.
As shown in the last section, non-strained film doesn’t show large LFMR effect. This section will focus on the compressive and tensile strained Pr$_{1-x}$Sr$_x$MnO$_3$ films, which were grown on LaAlO$_3$ (001) (LAO) and SrTiO$_3$ (001) (STO) substrates, respectively. Large LFMR was observed in all compressive strained Pr$_{1-x}$Sr$_x$MnO$_3$ films when the magnetic field is applied perpendicular to the film plane, but the LFMR ratio is larger for the films with lower carrier concentration (x). When the magnetic field is parallel to the film plane, the MR ratio is much smaller. For the tensile strained films, positive MR was observed when the magnetic field is applied perpendicular to the film plane, but the ratio is small. Domain wall resistance (DWR) has also been measured for the compressive strained Pr$_{1-x}$Sr$_x$MnO$_3$ films, and it also showed that the lower the x is, the larger the domain wall resistance.

Figure 3-14: Magnetic phase diagram of the Pr$_{1-x}$Sr$_x$MnO$_3$ series. (Reproduced from reference [178]).
3.2.2 LFMR Measurements

First, we look at the LFMR results of the compressive strained Pr$_{1-x}$Sr$_x$MnO$_3$ thin films grown on LAO substrates. Figure 3-15 shows the normalized resistance as a function of magnetic field applied perpendicular to the film plane for the 60-90 Å thick compressive strained Pr$_{1-x}$Sr$_x$MnO$_3$ films at $T$=30-50 K. The magnetic field was scanned from –5 kOe to 5 kOe, and then scanned back to –5 kOe. Large LFMR and MR hysteresis were observed for all Pr$_{1-x}$Sr$_x$MnO$_3$ thin films (x=0.2, 0.25, 0.33 and 0.4) in Figure 3-15. Using the same LFMR ratio that we defined in the last section, the LFMR

![Image](image.png)

Figure 3-15: The normalized resistance as a function of magnetic field applied perpendicular to the film plane for Pr$_{1-x}$Sr$_x$MnO$_3$ (x=0.2, 0.25, 0.33 and 0.4) ultrathin films grown on LAO substrates. The magnetic field was scanned from –5 kOe to 5 kOe, and then scanned back to –5 kOe. $R_0$ and $R_p(H)$ are indicated in the figure to define the LFMR ratio.
is largest for $x=0.2$ (LFMR~270%), and smallest for $x=0.4$ (LFMR~60%) in Figure 3-15. It needs to point out that for the $x=0.33$ and 0.4, the $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ films grown on the LAO substrates can be made as thin as 45 Å, and the LFMR ratio for the 45 Å thick $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ film could be as large as 300%. But for $x = 0.2$ and 0.25, films thinner than 75 Å would be insulating, and no LFMR can be measured. To systematically compare the LFMR properties, we chose the similar thickness range for all $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ films in Figure 3-15. Due to the larger resistivity for $x=0.2$ and 0.25, the MR loops of these two doping levels are not as smooth as the other two. We also chose different temperatures for different films to show their largest LFMR ratios.

The large LFMR and MR hysteresis are observed in a wide temperature range for all $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ thin films below their zero-field peak-resistance temperature $T_p$. Figure 3-16 shows the temperature dependence of the LFMR ratios. In the perpendicular field, LFMR ratio shows a maximum value where $T/T_p$~0.3-0.5 for all four films. Below and above this temperature, the magnitude of LFMR is smaller, and as the temperature approaches to $T_p$ of the samples, the LFMR almost vanishes. It’s also seen that around this maximum LFMR temperature range, the LFMR ratios are always larger for smaller $x$. As discussed in the last section, this temperature dependence in our system is a very unique compared to the temperature dependence of the CMR effect and LFMR effect observed in other systems. For CMR effect, the maximum effect is usually achieved around $T_p$ of the samples, and decreases as the temperature decreases. For the LFMR observed in the polycrystalline samples and the multiplayer tunneling junctions, the LFMR ratio shows a monotonous increase with decreasing temperature.
LFMR of compressive strained $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ thin films depends strongly on the film thickness. Figure 3-17 shows the LFMR ratios as a function of the film thickness for $x=0.25$ and $x=0.33$ doping levels. The LFMR ratios shown in this figure are the maximum values of each thickness in the measurements. It is seen that LFMR ratio decreases rapidly as the film thickness increases for both $x=0.25$ and $x=0.33$ films. Large LFMR ratio only exists in a narrow thickness range for both doping levels, but films of $x=0.25$ have larger LFMR ratios than $x=0.33$ films in the similar thickness, though the LFMR ratio for the 45 Å thick $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ film could be as large as 300%. For very

Figure 3-16: The temperature dependence of the LFMR ratios of the same films as shown in Figure 3-15.
thin films (<45 Å), films of all doping levels show insulating behaviors, and LFMR effect was not available. The thickness dependence of LFMR is related to the strain effect of the films. Our X-ray diffraction measurements showed that the lattice parameters of strained Pr$_{1-x}$Sr$_x$MnO$_3$ films depend strongly on the film thickness. They are almost fully strained when the thickness is below 200 Å. This corresponds to the thickness range where the anomalous LFMR presents.

![Graph showing the dependence of Max-LFMR (%) on film thickness for Pr$_{1-x}$Sr$_x$MnO$_3$/LAO films with x=0.25 and x=0.33.](image)

Figure 3-17: The LFMR ratios as the function of the film thickness for compressive strained Pr$_{1-x}$Sr$_x$MnO$_3$ (x=0.25 and 0.33) ultrathin films in a perpendicular field.

Such large LFMR effect was only observed when the magnetic field was applied normal to the film plane. When the field was applied parallel to the film plane, the LFMR is much smaller. Figure 3-18 shows the MR measurement in a parallel field of the same
samples as shown in Figure 3-15. It is seen that films of all four doping levels have small MR ratios and almost no hysteresis. Another interesting feature is that the MR ratio is larger for $x=0.33$ and 0.4, and smaller for $x=0.2$ and 0.25, which is quite different from the perpendicular filed measurements.

Figure 3-18: The normalized resistance as a function of magnetic field applied parallel to the film plane for $Pr_{1-x}Sr_xMnO_3$ ($x=0.2$, 0.25, 0.33 and 0.4) ultrathin films grown on LAO substrates. The magnetic field was scanned from $-5$ kOe to 5 kOe, and then scanned back to $-5$ kOe. The dash line and the dotted line are the guide for the eye.

Now we turn to the LFMR results of the tensile strained $Pr_{1-x}Sr_xMnO_3$ thin films. In this case, when a perpendicular field was applied, positive MR was observed, but both the MR ratio and the hysteresis are small. Figure 3-19 shows the MR measurements for $x=0.25$ (200 Å thick) and $x=0.33$ (100 Å thick) tensile strained films in a perpendicular
Figure 3-19: The normalized resistance as a function of magnetic field applied perpendicular to the film plane for $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0.25$ and 0.33) ultrathin films grown on STO substrates.

Figure 3-20: The normalized resistance as a function of magnetic field applied parallel to the film plane for $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0.25$ and 0.33) ultrathin films grown on STO substrates.
field at 70 K and 80 K, respectively. It needs to be pointed out that the positive MR was only observed at lower magnetic field (<1 Tesla) and lower temperatures. When the field or temperature increases, the MR will change from positive to negative. Also, when the magnetic field was applied parallel to the film plane, only negative MR was observed and the MR ratio is much smaller than those of compressive strained films, as shown in Figure 3-20.

3.2.3 DWR Measurements

Domain wall resistance (DWR) for different hole doping levels in the compressive strained Pr$_{1-x}$Sr$_x$MnO$_3$ thin films was also studied. The result of R-H measurements of the same samples as in Figure 3-15 is shown in the Figure 3-21. During the measurement, the magnetic field was applied perpendicular to the film plane. It is seen from Figure 3-21 that the resistance for all doping levels at $H=0$ of the stripe domain state is much higher than that of the single domain state. This is expected since at the stripe domain state, large amount of domain walls exist, and the domain wall scattering will give much higher resistance. By applying a magnetic field of 2.5-5 kOe, all domains will be aligned and the resistance measure at two different states coincide as they all reach the single domain state. It is also clear that at the stripe domain state, the resistance of lower x is larger than those of higher x in the low field range. This means that the DWR of lower x is larger, which is consistent with the LFMR results. For the measurements at the single domain state, all curves of different x almost coincide, showing no significant difference of electronic transport properties at the single domain
state for different hole doping levels. Another feature in Figure 3-21 is that for \(x=0.2\) and \(0.25\), it requires higher magnetic field than \(x=0.33\) and 0.4 to align the domains to reach the single domain state.

Figure 3-21: The resistance versus magnetic field curves for compressive strained \(\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3\) \((x=0.2, 0.25, 0.33\) and 0.4\) ultrathin films in the two different demagnetized states: stripe domain state and single domain state. Please see the text in the last section for more details of the two demagnetized states.

Figure 3-22 shows the temperature dependence of the DWR for \(x=0.25\) and 0.33 samples. Here we define the DWR as \([R_{\text{ZFC}}(0) - R_{\text{SD}}(0)]/R_{\text{SD}}(0)\), where \(R_{\text{ZFC}}(0)\) and \(R_{\text{SD}}(0)\) are the zero field resistance at the zero-field cooled stripe domain state and single domain
state, respectively. It is seen that the DWR reaches the maximum at $T/T_p \sim 0.2-0.25$. Above and below this range, the DWR are smaller, and when the temperature is close to $T_p$, the DWR vanishes. Figure 3-22 also shows that the DWR is much larger for $x=0.25$ than $x=0.33$. The above results are all consistent with the LFMR results we discussed earlier, and indicate that in our system, the domain wall resistance is dominant and the LFMR is originated from the large DWR. We should point out that the DWR is larger than the LFMR at the same doping level for all the films. This may be because that DWR was calculated from the zero-field cooled stripe domain state ($R_{ZFC}(0)$) and the single

Figure 3-22: The temperature dependence of the domain wall resistance for $x=0.25$ and $0.33$. 
domain state \( (R_{SD}(0)) \), while the LFMR was calculated from \( R_p(H) \) and \( R_0 \). The \( R_{SD}(0) \) and \( R_0 \) is almost the same at the same temperature, but the \( R_p(H) \) is obtained when the magnetic field was scanned back from relatively high value. At this state, the domain wall density along the current path is probably less than that of the zero-field-cooled state since a relatively high field was already applied, so \( R_p(H) \) is smaller than \( R_{ZFC}(0) \). Therefore, the LFMR ratio is smaller than DWR ratio.

### 3.3 Discussion and Conclusion

#### 3.3.1 Discussion

First, the comparison of different compositions and strains presented in this chapter indicates that the large LFMR observed in compressive strained LCMO/LAO and PSMO/LAO thin films is not due to the reduced dimensionality, surface effect, the grain boundaries, and the twin structures of the LAO substrates. In our study, LBMO films can be made much thinner (40Å) than the LCMO films on LAO substrates. But LBMO/LAO thin films show almost no LFMR effect. Moreover, even very thin films of all three compositions on NGO substrates show no LFMR effect. Those indicate that the observed large LFMR is not due to the reduced dimensionality of the ultrathin films or the surface effect.

In polycrystalline samples, the enhanced MR up to 30% by spin-polarized tunneling[28] or spin-dependent scattering[172] at the grain boundaries was observed. In both cases, the magnetic domains coincide with the grains. One possible source for grain
boundaries in our samples is the twin structure in the LAO substrate. We have made films of three compositions on LAO substrates, but LCMO/LAO thin films show very large LFMR, while LBMO/LAO thin films show almost no LFMR at all. Furthermore, we have measured samples with current flowing both parallel and perpendicular to the twin boundaries and observed no obvious difference in the MR properties. The magnetic force microscope (MFM) measurements by Kwon et al.[95] on the partially strained La$_{0.7}$Ca$_{0.3}$MnO$_3$ films on LAO substrates indicate that there is no correlation between the growth grains and the magnetic domains. Therefore, pure growth grain boundary effect is not likely the dominant factor in the observed large LFMR effect.

We now consider the effect of magnetic anisotropy and the domain rotation. Our magnetization measurement shows that a compressive strain induced by LAO substrate produces a magnetic easy axis normal to the film plane for LCMO/LAO and LSMO/LAO thin films. Under a large perpendicular field, all magnetic domains are aligned along the field direction, and in this case the resistance is low. When the field is near the coercive field, opposite aligned domains and many domain walls are present, and the resistance is high. The resulting high MR must be due to the large domain wall resistance. When the field is applied parallel to the film plane, a much higher field is required to align all the domains along the magnetic hard axis, and therefore MR ratio is relatively small.

We also observed in the domain wall resistance (DWR) measurements that LCMO/LAO and LSMO/LAO thin films have very large domain wall resistance and the LBMO/LAO thin films have almost negligible effect. This result is consistent with the LFMR of the three systems. The magnetic anisotropy measurements indicate that LCMO films have larger anisotropy energy than LSMO which is larger than LBMO. Therefore,
there seems to be a correlation between magnetic anisotropy energy, thus the domain wall width, and the domain wall resistance (DWR). Table 3-2 shows the summary of the LFMR, DWR, anisotropy energy and the estimated domain wall width of compressive strained PSMO/LAO, LCMO/LAO, LSMO/LAO and LBMO/LAO thin films. It is seen that PSMO/LAO and LCMO/LAO thin films have much larger magnetic anisotropy energy than LSMO/LAO thin film. Consequently, PSMO/LAO and LCMO/LAO thin films have much smaller domain size and domain wall width than LSMO/LSMO thin film. As discussed in the section 1.4.2 and 1.4.3, in general, narrower domain wall width induces larger domain wall resistance. And smaller domain size means larger domain wall density in the film, therefore means even larger domain wall resistance in total. When the film is thicker, both domain size and domain wall width are bigger, which lead to smaller domain wall resistance. And as shown in Eq. 3.1, the relationship between domain size $d$ and the applied field $H$ depends on the film thickness $h$. The $1/h^2$ term might be one of the factors that lead to the thickness dependence of domain wall resistance. This may qualitatively explain our results in the DWR measurements. The origin of the large DWR will be discussed later.

<table>
<thead>
<tr>
<th></th>
<th>PSMO (100 Å)</th>
<th>LCMO (200 Å)</th>
<th>LSMO (125 Å)</th>
<th>LBMO (100 Å)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>42%</td>
<td>0%</td>
</tr>
<tr>
<td>DWR$_{ZFC}$</td>
<td>1800%</td>
<td>7000%</td>
<td>106%</td>
<td>3%</td>
</tr>
<tr>
<td>DWR$_{MD}$</td>
<td>530%</td>
<td>320%</td>
<td>66%</td>
<td>0.3%</td>
</tr>
<tr>
<td>Anisotropy</td>
<td>2.3x10$^5$ erg/cc</td>
<td>2.1x10$^5$ erg/cc</td>
<td>2.5x10$^5$ erg/cc</td>
<td>/</td>
</tr>
<tr>
<td>DW Width</td>
<td>80 Å</td>
<td>100 Å</td>
<td>200 Å</td>
<td>/</td>
</tr>
</tbody>
</table>

Table 3-2: LFMR, DWR, anisotropy energy and the estimated domain wall width of PSMO/LAO, LCMO/LAO, LSMO/LAO and LBMO/LAO thin films. DWR$_{ZFC}$ is defined as $[R_{ZFC}(0)−R_{SD}(0)]/R_{SD}(0)$, and DWR$_{MD}$ is defined as $[R_{MD}(0)−R_{SD}(0)]/R_{SD}(0)$. To compare, all the manganite films are at the x=0.33 doping level.
On the other hand, it has previously been shown that an in-plane biaxial tensile strain induced by an STO substrate is sufficient to make a magnetic hard axis normal to the film plane[53]. When a perpendicular field is applied, the magnetization will rotate out of the plane and be perpendicular to the film plane. As discussed in detail by Eckstein et al[60], the resistance increases with field due to the increasing angle between the measuring current and the magnetization, resulting in a positive MR as the AMR in the transition metal in FM materials. When the field is applied parallel to the film plane, the LFMR hysteresis is due to the domain rotation and movement within the film plane and the negative MR is due to the increased magnetization in the field direction. This explains the LFMR results of the tensile strained LCMO/STO, LSMO/STO and LBMO/STO thin films.

As discussed in section 1.4.2, in conventional ferromagnetic materials the domain-wall scattering does not result in very large MR effect. The results of Yamanaka and Magaosa[126] indicate that domain-wall scattering is ineffective for thick domain walls. However, when the domain-wall width becomes very small, things can change dramatically. Cabrera and Falicov[102] have argue that when the domain-wall width is comparable to the Fermi wavelength of the spin-polarized electrons, the domain-wall scattering can become significant and result in unusually large MR. In our magnetization measurements, the domain wall width was estimated as about 10 nm for the 200 Å thick LCMO/LAO thin film, and about 20 nm for the 125 Å thick LSMO/LAO thin film at $T=20$ K. However, we are not able to observe the domains and domain walls directly using low temperature MFM technique yet. S. J. Lloyd et al[175] recently reported the measurement of the domain wall width of the 2000 Å thick LCMO/NGO film, and the
domain wall width was given as 38±10 nm. Considering the LCMO/NGO film is unstrained with easy axis in the film plane and much thicker than our LCMO/LAO films, our estimation of 10 nm thick domain wall width in our LCMO/LAO thin films should be reasonable.

Quantitatively, the large DWR cannot be explained by the existing models based on spin dependent scattering across domain walls. For example, for the 200 Å thick LCMO/LAO thin film, the domain wall width is about 10 nm, and the lattice constant is about 0.39 nm. One can estimate that the spins on adjacent Mn sites are misaligned by $\theta \approx 7^\circ$ inside the domain wall. In terms of the double exchange model, this corresponds to a reduction in bandwidth by a factor of $\cos(\theta/2)$. Within the Born approximation, carriers scatter at a rate that is proportional to the density of states, and hence inversely proportional to the bandwidth. We can therefore write $R_{DW}/R = 1/\cos(\theta/2)[129]$, where $R_{DW}$ is the absolute resistance of the domain wall and $R$ is the resistance of the same region without domain wall. This gives that $R_{DW}/R = 1.002$, which means the domain wall resistance DWR is less than 1%. Our results are beyond the explanation of the Bloch (or Néel) domain-wall scattering based on existing theories that discussed in section 1.4.3. This may indicate an unconventional domain wall structure in our compressive strained thin films. Very recently, Golosov[176] has investigated the structure of magnetic domain walls in classical double exchange ferromagnet. He predicted three types of domain walls based on Double-Exchange theory: a conventional smooth Bloch wall, an abrupt Ising-type wall, and a stripe wall (as shown in Figure 3-23) which corresponds to the two ferromagnetic domains being separated by a stripe of another, antiferromagnetic, phase. He suggests that our experimental data seems to agree with anticipated conditions...
for the stabilization of the stripe wall. His calculation shows that within a certain range of parameter values, the energy of a stripe wall can be lower than that of a Bloch wall. Due to insulating properties of antiferromagnetic phase, carrier transport across the stripe wall is strongly suppressed, leading to a substantial domain wall contribution to the sample resistance.

Golosov points out that the possibility of stripe wall formation is due to the strain-induced increase of easy-axis anisotropy constant, and also to phase separation which makes formation of stripe walls possible. Large anisotropy energy has been observed in our magnetization measurements for the La$_{0.67}$Ca$_{0.33}$MnO$_3$ and Pr$_{0.67}$Sr$_{0.33}$MnO$_3$ thin films. It has been reported by several groups that phase separation presents in manganites as discussed in section 1.1.7. A. Biswas et al have reported the coexistence of ferromagnetic metallic and charge-ordered insulating phase in strained LCMO thin

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Figure 3-23: Schematic representation of a stripe domain wall in a phase-separated double-exchange magnet. The two ferromagnetic domains with antiparallel directions of magnetization (arrows) are separated by a stripe of antiferromagnetic phase (shaded). In addition, unconnected islands of antiferromagnetic phase are formed within each domain. (Reproduced from reference [176]).
films[177]. Very recently, Murakami et al have directly observed the magnetic microstructure and development of ferromagnetic domains in the mixed-phase state of La$_{1-x}$Sr$_x$MnO$_3$ ($x=0.54, 0.56$) ceramic samples[25] using the electron microscopy, as seen in Figure 1-15. Since our compressive strained thin films already have high resistivity than bulk materials, it is possible that there are phase separation and an antiferromagnetic (AFM) insulating phase at the domain boundaries due to the electronic phase separation. According to the stripe domain wall model proposed by Golosov, the domain wall is formed by the antiferromagnetic phase. Murakami et al have shown that, the magnetization is uniform over the FM region in the mixed-phase state, but that it abruptly diminishes at the interface with the AFM phase. The authors also speculate that the FM island has strong magnetization from the beginning of its formation in the AFM phase. Therefore, in the case of very narrow domain walls of our samples, antiferromagnetic (AFM) phase, such as charge ordering, could form inside the domain walls. Due to insulating properties of AFM phase, the domain wall causes a substantial large resistance. This AFM phase will be melted by applying a magnetic field when it aligns all the domains, resulting lower resistance. The FM domains on the both side of an AFM domain wall should have strong magnetization, and the magnetization abruptly diminishes at the interface with the AFM phase. When domains are antiparallel, spin-polarized tunneling or hopping conduction occurs across the domain walls as in the FM-I-FM ferromagnetic tunneling junctions. Due to the very high spin polarization factor in the manganites, large LFMR is observed. It is seen in Figure 3-14 that $x=0.2$ in the Pr$_{1-x}$Sr$_x$MnO$_3$ series is around the ferromagnetic metal and ferromagnetic insulator phase boundary. Knížek et al[179] have also shown that $x=0.2$ is the boundary between the
antiferromagnetism and ferromagnetism in the Pr$_{1-x}$Sr$_x$MnO$_3$ compound. Therefore, at very low doping level, some AFM insulating phase may be present in the Pr$_{1-x}$Sr$_x$MnO$_3$ thin films, and the phase separation exists. The larger DWR in the lower doping level might be because the stronger tendency of phase separation in the lower doping level since it is closer to the AFM and FM phase boundary. To fully understand the large domain wall resistance in this system, further study (such as using scanning tunneling spectroscopy to detect the phase separation) on the domain wall structure is needed.

Although Golosov’s theory can qualitatively explain the large DWR observed in our samples, some questions still remain. For example, it lacks of an interpretation for the disappearance of DWR in the films thicker than 200 Å. Since the strain relaxation usually takes much larger distance, and such quick thickness dependence is not counted for in the model. Also, there is neither qualitative nor quantitative explanation for the temperature dependence of the DWR. The DWR of our samples reach the maximum well below their Curie temperatures. The temperature dependence is much different than the CMR effect observed in those polycrystalline samples and the multiplayer tunneling junctions, in which the temperature dependence is monotonous with temperature bellow the Curie temperature. It requires more to investigation on the unconventional domain wall structure of those compressive strained thin films to understand the special temperature dependence and thickness dependence.
3.3.2 Conclusion

We have systematically studied the strain-induce low-field magnetoresistance (LFMR) and the domain wall resistance (DWR) in the differently strained La$_{0.67}$A$_{0.33}$MnO$_3$ (A=Ca, Sr, Ba) and Pr$_{1-x}$Sr$_x$MnO$_3$ (x=0.2, 0.25, 0.33, 0.4) thin films. Our results show that the strain effect can significantly affect the LFMR and anisotropy properties of the manganite thin films. Distinctive large LFMR effects have been observed in differently strained thin films. Magnetization measurements show that the anisotropy energy of thin films are dominated by the strain induced anisotropy. In compressive strained films, the strain anisotropy field is larger than the demagnetization field, resulting in the magnetic easy axis perpendicular to the film plane. In the tensile strained films, the strain anisotropy and the demagnetization field both favor an in-plane easy axis. DWR measurements show the similar temperature and thickness dependence as that of the LFMR. Those results indicate that all three are related. To the best of our knowledge, such a large LFMR and DWR has not been observed by any other group.

Our comparison studies show that the MR properties of the manganite thin films depends both on the cation type and the doping levels. Both compressive strained LCMO and PSMO thin films show large anisotropy energy and narrow domain wall width, and they also show large LFMR and DWR. Compressive strained LBMO thin films show smallest anisotropy energy, and they show almost no LFMR and DWR. Pr$_{1-x}$Sr$_x$MnO$_3$ thin films with smaller carrier doping level x show larger LFMR and DWR.

Based on the above results and discussion, we conclude that the large LFMR in the compressive strained thin films is originated from the strain-induced unconventional
magnetic domain walls and the phase separation may play a crucial role in determining the large DWR properties in the compressive strained manganite thin films. The LFMR of the tensile strained thin films can be explained by the domain rotation and movements.

The mechanism of the large domain wall resistance is still not fully understood, and it requires the further study on the unconventional domain wall structure in the compressive strained manganite thin films.
Chapter 4

Anisotropic Magnetoresistance (AMR) in Manganite Thin Films

4.1 AMR in Manganite Thin Films

4.1.1 Introduction

As has been discussed in Chapter 1, it is now commonly accepted that while the well-known double-exchange (DE) theory proposed half century ago is essential in explaining the CMR effect and the ferromagnetic (FM)-paramagnetic (PM) along with a metal-insulator phase transitions in the manganites, it is not sufficient to interpret many experimental results. Strong electron-phone interaction based on the dynamic Jahn-Teller (J-T) effect and spin-orbit interaction[157] related mainly to the static lattice distortions have been found to play important roles in determining the electromagnetic properties of the manganite materials. In reality, both the J-T effect and the spin-orbit coupling are closely related to the structural distortion which can be tuned by doping, applying pressure, introducing strain in the system. Several groups have studied the strain effect on the electromagnetic transport properties of manganite thin film samples. It has been found that the uniaxial strain induced from lattice mismatch can dramatically change the FM/PM transition temperature[45, 180], the CMR effect[38], and the low-field MR effect[57, 58]. In particular, several groups have studied the anisotropic magnetoresistance (AMR) in the manganite thin films and found that the AMR is closely
related to the magnetic anisotropy in the samples[51, 53, 59, 60, 128, 162, 181, 182]. Eckstein et al[60] have reported relatively large in-plane AMR (~8%) in the La$_{0.66}$Ca$_{0.33}$MnO$_3$ thin films. Wolfman et al[128] have studied the out-of-plane AMR of relatively thick Pr$_{0.7}$Sr$_{0.3}$MnO$_3$ films at different magnetic fields and found a correlation between the magnetization and the AMR. They reported a small (<1%) magneto-crystalline AMR. Very recently, Wang et al[57, 58] have shown that the uniaxial strain can strongly affect the low-field MR anisotropy in Pr$_{0.67}$Sr$_{0.33}$MnO$_3$ (PSMO) thin films.

In this section, we present a systematic study of the strain effect on the out-of-plane anisotropic magnetoresistance (AMR) of Pr$_{1-x}$Sr$_x$MnO$_3$ (PSMO) (x=0.2, 0.25, 0.33, 0.4) and La$_{0.67}$A$_{0.33}$MnO$_3$ (A=Ca, Sr, Ba) ultrathin films. The AMR was obtained by measuring the angular dependent magnetoresistance at given magnetic fields and temperatures. Figure 4-1 shows the schematic diagram of the field and current, with respect to the film plane orientation geometry for the out-of-plane and in-plane AMR measurements. In the out-of-plane geometry, the AMR was measured at a given magnetic field $H$ and temperature $T$, by rotating the sample around the axis parallel to the current direction so that the angle $\theta$ between the substrate normal and the magnetic field was changed. There is no change of the angle between current and the field, and the AMR is due to magneto-crystalline anisotropy. In the in-plane geometry, an in-plane magnetic field was applied and the AMR was measured by rotating the sample around the axis parallel to the substrate normal so that the angle $\varphi$ between the magnetic field and the current directions was changed. The data presented in this section are all obtained for $H \geq 0.75$ Tesla where the magnetization is basically saturated known from the magnetization measurements.
We have found several unusual results: (1) very large out-of-plane AMR has been observed in both compressive and tensile strained ultrathin Pr$_{1-x}$Sr$_x$MnO$_3$ films and tensile strained ultrathin La$_{0.67}$A$_{0.33}$MnO$_3$ films with AMR ratio of 550% in Pr$_{0.8}$Sr$_{0.2}$MnO$_3$/LAO and -70% in Pr$_{0.8}$Sr$_{0.2}$MnO$_3$/STO thin films at 1 Tesla; (2) the compressive and tensile strained samples show opposite signs of the out-of-plane AMR, and the MR peak position shift by 90° for the compressive and tensile strained films; (3) the field dependence of the anisotropic MR shows a crossover at the insulating to metallic transition temperatures ($T_p$). At $T<T_p$, AMR decrease with increasing fields. While at $T>T_p$, small AMR exist, but the field dependence follows a more conventional behavior with AMR increase with increasing fields.

Figure 4-1: A schematic diagram of the field and current, with respect to the film plane orientation geometry for: (a) out-of-plane and (b) in-plane AMR measurements.
The out-of-plane AMR results will be the main subject of this section and will be described in detail in section 4.1.2 and section 4.1.3. The anomalous AMR results will be discussed based on the strain-induced orbit ordering and the spin-orbit coupling. The different behaviors for different compositions will also be discussed.

4.1.2 AMR in Pr$_{1-x}$Sr$_x$MnO$_3$ Thin Films (x=0.2, 0.25, 0.33 and 0.4)

Figure 4-2 shows the AMR measurement of compressive strained Pr$_{1-x}$Sr$_x$MnO$_3$/LAO thin films with x = 0.2, 0.25, 0.33 and 0.4 at 1 Tesla. All four curves

![Figure 4-2: The out-of-plane AMR measurement of compressive strained Pr$_{1-x}$Sr$_x$MnO$_3$/LAO thin films with x=0.2, 0.25, 0.33 and 0.4 at $H=1$ Tesla. The arrows indicate the angles where the magnetic field is parallel and perpendicular to the film plane, respectively.](image-url)
follow the same trend for the maximum and minimum resistance positions with AMR ratios positive using our AMR definition. The maximum resistances of all four compositions are obtained at $\theta=90^\circ$ and $270^\circ$, when the magnetic field was applied parallel to the film plane. The $x=0.2$ composition shows the largest AMR ratio, and the $x=0.4$ composition shows much smaller AMR, although it is still quite large in absolute value (~25%).

Figure 4-3 shows the out-of-plane AMR measurements of a 75 Å thick Pr$_{0.8}$Sr$_{0.2}$MnO$_3$/LAO sample measured at $H=1$ Tesla.

Figure 4-3 shows the out-of-plane AMR measurements of a 75 Å thick Pr$_{0.8}$Sr$_{0.2}$MnO$_3$/LAO sample measured at $H=1$ Tesla and at different temperatures. Note
that the angle \( \theta \) is defined from the substrate normal, and the arrows on the figure indicate the position where the magnetic field is parallel or perpendicular to the film plane (\( \theta = 90^\circ \) and \( 180^\circ \) respectively). It is seen from Figure 4-3 that all of the curves are smooth and are 2-fold symmetric with their minimum located at \( \theta = 180^\circ \). One of the most striking features shown in Figure 4-3 is the unusually large magnitude of AMR. If we define the AMR ratio as \( (R_{//} - R_{\perp})/R_{\perp} \times 100\% \), where \( R_{//} \) and \( R_{\perp} \) are the resistance measured when the magnetic field was applied parallel (\( \theta = 90^\circ \) and \( 270^\circ \)) and perpendicular (\( \theta = 0^\circ \) and \( 180^\circ \)) to the film plane respectively, then it is as high as 550\% at \( T = 60 \) K.

\[
\text{AMR} = \frac{R_{//} - R_{\perp}}{R_{\perp}} \times 100\%
\]

**Figure 4-4**: The temperature dependence of AMR ratios for the same thin film as shown in Figure 4-3 measured at different magnetic fields.
The AMR shows strong temperature dependence. The AMR ratio as the function of the temperature measured at different fields for this same sample was shown in Figure 4-4. It is seen that, at low field ($\leq 2$ Tesla), the maximum AMR is obtained around 60 K, well below $T_p$; as temperature increases, the AMR decreases. At higher field, the temperature dependence is weak, and the AMR ratio is small. All curves have a crossover around $T_p$, and above $T_p$ the AMR vanishes.

![Graph showing temperature dependence of AMR ratios for a 5 nm thick Pr$_{0.67}$Sr$_{0.33}$MnO$_3$/LAO sample and measured at different magnetic fields up to room temperature.]

Figure 4-5: The temperature dependence of AMR ratios for a 5 nm thick Pr$_{0.67}$Sr$_{0.33}$MnO$_3$/LAO sample and measured at different magnetic fields up to room temperature.

A more systematic temperature dependence of the AMR for a 50 Å thick Pr$_{0.67}$Sr$_{0.33}$MnO$_3$/LAO thin film and measured at different magnetic fields up to the room
temperature is shown in Figure 4-5. Clearly, below $T_p$, it shows similar features as shown in Figure 4-4, and the AMR is very small at temperatures above 200 K for all the fields applied. The Maximum AMR appears in the temperature range of 30-50 K, slightly depends on $H$. It is more obvious in Figure 4-5 that there is a crossover of the curve at about 110 K, the same temperature as the zero-field $T_p$. That is, below $T_p$, the AMR decreases with increasing $H$ (except for one data point at $T=10$ K and $H=1$ T), while above $T_p$, the AMR increases with $H$. This interesting behavior has also been observed in the PSMO/STO and PSMO/NGO samples as will be shown later. Another worthy noticing point is that in the temperatures between $T_p$ and 200 K, there is still significant AMR effect even it is far above the transition temperatures.

Figure 4-6 shows the AMR results measured at 70 K and at different magnetic fields, for the same sample as shown in Figure 4-3. It is seen that the magnitude of the AMR reaches the maximum at 1.25 Tesla, and the AMR curves become rounded at higher fields. Figure 4-7 shows the field dependence of the AMR measured at different temperatures of the same sample. It is seen that, at low temperatures, below $T_p$, the maximum AMR is obtained around $H=1$ Tesla. When magnetic field $H$ increases, AMR ratio becomes smaller. At higher temperatures, the maximum AMR is shifted to higher fields (e.g. 2 Tesla at 80 K).

The PSMO/LAO samples also drops with increasing thickness of the films. The results show from Figure 4-2 to Figure 4-7 are only observed at the PSMO/LAO films with the thickness less than 200 Å. With increasing film thickness, the AMR not only reduces and reaches the value comparable to the almost strain-free samples, but also changes signs at certain temperatures and magnetic fields. Figure 4-8 shows the AMR
Figure 4-6: The out-of-plane AMR measurements for the same thin film as in Figure 4-3 measured at different fields at $T=70$ K.

Figure 4-7: The field dependence of out-of-plane AMR ratios for the same thin film as shown in Figure 4-3 measured at different temperatures.
ratio as the function of thickness for the $Pr_{0.75}Sr_{0.25}MnO_3$/LAO samples. It is seen that AMR ratio drops sharply as the film thickness increases, and becomes very small above 200 Å.

We now look at the tensile strained ultrathin samples. The tensile strained ultrathin PSMO/STO samples also show very large out-of-plane AMR effect in the thickness range of less than 200 Å. However, in contrast to the compressive strained PSMO/LAO ultrathin films that show positive AMR, the PSMO/STO films show negative AMR. Figure 4-9 shows the AMR measurement of tensile strained $Pr_{1-x}Sr_xMnO_3$/STO thin films with $x=0.2, 0.25, 0.33$ and $0.4$ at 1 Tesla. It is seen that, in this case all four curves show the same trend for the maximum and minimum resistance.

Figure 4-8: The film thickness dependence of out-of-plane AMR ratios for compressive strained $Pr_{0.75}Sr_{0.25}MnO_3$ thin films. The dashed line is a guide for the eyes.
positions and all AMR ratios are negative. The maximum MR of all four compositions are obtained at $\theta=0^\circ$ and $180^\circ$, when the magnetic field was applied perpendicular to the film plane. The $x=0.2$ composition shows the largest AMR ratio, and AMR ratios of the other three compositions are smaller and close.

![Graph showing angular dependent MR](image)

**Figure 4-9**: The out-of-plane AMR measurement of tensile strained $Pr_{1-x}Sr_xMnO_3$ thin films with $x=0.2$, 0.25, 0.33 and 0.4 at $H=1$ Tesla.

Figure 4-10 shows the angular dependent MR of an 180 Å thick $Pr_{0.8}Sr_{0.2}MnO_3$/STO film measured at different temperatures at 2 Tesla. Obviously, the maximum of all the curves appears at $\theta=180^\circ$, corresponding to the minimum of the curve in Figure 4-3. Figure 4-10 shows that there is a sharp peak at $\theta=180^\circ$ in the curves.
measured at low temperatures. However, the curves at around 90° and 270° are rounded. These features are very similar to those shown in Figure 4-3, except that they are shifted by an angle of 90°. This is better seen in Figure 4-11, where for comparison of the effect of strain on the AMR effect, we plot the resistance ratio $R(\theta)/R_\perp$ vs. $\theta$ for a 50 Å thick compressively strained film and a 150 Å tensile strained film for $x=0.33$ ($Pr_{0.67}Sr_{0.33}MnO_3$) composition at different temperatures. It is clearly seen that for the compressive strained films, the resistance minimum is at $\theta=0^\circ$ and 180°, which correspond to the field perpendicular to the film surface direction. However, for tensile

Figure 4-10: The AMR measurements of tensile strained $Pr_{0.8}Sr_{0.2}MnO_3$/STO thin film in the out-of-plane geometry measured at different temperatures and $H=2$ Tesla.
strained PSMO/STO thin films, the resistance minimum is at $\theta=90^\circ$ and $270^\circ$, when the magnetic field was applied parallel to the film plane. This mean the AMR ratio is negative. The absolute value of the AMR is generally smaller for tensile strained films than compressive strained films. However, the value cannot be compared directly by using the same AMR definition. Since we define the AMR ratio as $(R_{\parallel}-R_{\perp})/R_{\perp}$ and $R_{\perp}$ is the resistance minimum for compressive strained films, the maximum AMR has no limit.

Figure 4-11: The AMR curves of compressive and tensile strained Pr$_{0.67}$Sr$_{0.33}$MnO$_3$ thin films in the out-of-plane geometry measured at different temperatures.
While for tensile strained films, $R_{//}$ is the resistance minimum, and therefore the maximum AMR ratio is 100% due to this definition. If we use the minimum $R$ as the denominator for calculating the AMR in both cases, tensile strained films show smaller AMR probably due to the smaller amount of strain in the films resulted from the smaller lattice mismatch with the STO than with LAO substrates.

The AMR of tensile strained films also show strong temperature dependence. Figure 4-12 shows the temperature dependence of the AMR of the same sample in Figure 4-10, measured at different magnetic fields. It can be seen that the maximum AMR ratio is obtained around 60 K, also well below $T_p$. The curves also show the crossover around $T_p$.

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**Figure 4-12**: The temperature dependence of out-of-plane AMR ratios for the same thin film as shown in Figure 4-10 measured at different magnetic fields.
A more systematic temperature dependence of the AMR for a 150 Å thick Pr$_{0.67}$Sr$_{0.33}$MnO$_3$/STO sample and measured at different magnetic fields up to room temperature is shown in Figure 4-13. One can see that there is a maximum on each curve and the maximum is shifted to higher temperatures at high field. The maximum AMR value of -32 % is obtained at $T=130$ K and $H=1$ Tesla. Because of our AMR definition, the absolute number of this value is lower than the 240% for the 50 Å thick Pr$_{0.67}$Sr$_{0.33}$MnO$_3$/LAO sample in Figure 4-5, but it is still very high compared to the AMR.
values of the transition metal FM materials. The relatively smaller ratio in the AMR magnitude of the PSMO/STO samples may also be due to less amount of strain (~1%). In addition, we could not obtain metallic PSMO/STO samples as thin as the PSMO/LAO samples. As mentioned before, one of the interesting features in Figure 4-13 is the crossover of the field dependence of the AMR at temperatures below and above the $T_p$ (190 K for this sample).

Figure 4-14 shows the field dependence of the out-of-plane AMR ratios for the same thin film as shown in Figure 4-10 measured at different temperatures.

Figure 4-14 shows the field dependence of the AMR measured at different temperatures of the same sample as shown in Figure 4-10. It is seen that, at low
temperatures below $T_p$, the maximum AMR is obtained around $H=2$ Tesla. While around and above $T_p$, the field dependence is weak and the AMR ratio is smaller.

Similar to the PSMO/LAO samples, the PSMO/STO samples also show a strong thickness dependence of the AMR. With increasing film thickness, the magnitude of the AMR decreases. It also shows a much weaker field and temperature dependences compared to the thinner samples.

Figure 4-15: The AMR measurements of almost non-strained $Pr_{1-x}Sr_xMnO_3$/NGO thin films with $x=0.2$, 0.25, 0.33 and 0.4 in the out-of-plane geometry at $H=1$ Tesla.

Compared to the highly strained PSMO/LAO and PSMO/STO samples, the less strained PSMO/NGO samples show not only much smaller AMR effect, but also very
weak thickness dependence of the AMR. Figure 4-15 shows the AMR measurement of almost none-strained Pr$_{1-x}$Sr$_x$MnO$_3$/NGO thin films with $x=0.2$, 0.25, 0.33 and 0.4 in the out-of-plane geometry at 1 Tesla. Note that all four curves show a maximum at $\theta=180^\circ$ and the AMR ratios are negative. For the composition of $x=0.2$ and 0.25, the AMR ratios are much larger than those of $x=0.33$ and 0.4.

Figure 4-15: The AMR measurement of almost none-strained Pr$_{1-x}$Sr$_x$MnO$_3$/NGO thin films with $x=0.2$, 0.25, 0.33 and 0.4 in the out-of-plane geometry at 1 Tesla. Note that all four curves show a maximum at $\theta=180^\circ$ and the AMR ratios are negative. For the composition of $x=0.2$ and 0.25, the AMR ratios are much larger than those of $x=0.33$ and 0.4.

Figure 4-16: The temperature dependence of out-of-plane AMR ratios for a 7.5 nm thick Pr$_{0.67}$Sr$_{0.33}$MnO$_3$/NGO sample and measured at different magnetic fields up to room temperature.

Figure 4-16 shows the temperature dependence of the out-of-plane AMR for a 75 Å thick Pr$_{0.67}$Sr$_{0.33}$MnO$_3$/NGO film measured at different magnetic fields up to room temperature. All of the curves show a maximum around 210 K. The largest AMR is
obtained at $H=1$ and 2 Tesla. Similar to the PSMO/LAO (see Figure 4-4 and Figure 4-5) and PSMO/STO (see Figure 4-12 and Figure 4-13) samples, the field dependence of the AMR shows a crossover at about 250 K, which is very close to the $T_p$ of the sample. However, at low temperatures, another crossover appears at about 130 K. That is, below 130 K, the AMR increases with the magnetic field. This is different from the PSMO/LAO and the PSMO/STO samples.

We should mention that the data shown in this section are not corrected for the demagnetization effect. However, demagnetization correction on the AMR was made for some samples by considering that the shape anisotropy always favors an in-plane easy magnetization in thin films. The maximum demagnetization field is $\sim$2-3 kOe at 4.2 K and decreases with increasing temperature, which will reduce the effective field from the measured value for fields perpendicular to the film surface and have no effect for parallel field direction. Experimentally, we reduced the field in the perpendicular direction by $4\pi M$, where the total magnetization $M$ was obtained from the magnetization measurement, then the resistance $R$ were measured again. The effective $R_\perp$ is slightly smaller than what is plotted in the figures. Since most of the data were measured at low temperatures where the resistance does not change very much as a function of field, this correction has a small effect on the AMR data for the field of 1 T, but has little effect on higher fields. Therefore this correction does not change the basic AMR features discussed. In fact, it will make the AMR ratio even slightly larger for compressive strained PSMO/LAO films and smaller for tensile strained PSMO/STO films.

Although compressive and tensile strained PSMO/LAO films show giant out-of-plane AMR, they only show very small in-plane AMR for all the compositions, similar to
the results of other groups[60]. As an example, the in-plane AMR of Pr$_{0.67}$Sr$_{0.33}$MnO$_3$/LAO, Pr$_{0.67}$Sr$_{0.33}$MnO$_3$/STO, and Pr$_{0.67}$Sr$_{0.33}$MnO$_3$/NGO samples measured at $H=1$ T are shown in Figure 4-17. Interestingly, opposite to the out-of-plane cases, the in-plane AMR of the non-strained PSMO/NGO sample is larger than those of the PSMO/LAO and the PSMO/STO strained samples.

![Graph showing in-plane AMR comparison](image)

Figure 4-17: In-plane AMR of Pr$_{0.67}$Sr$_{0.33}$MnO$_3$/LAO, Pr$_{0.67}$Sr$_{0.33}$MnO$_3$/NGO, and Pr$_{0.67}$Sr$_{0.33}$MnO$_3$/STO thin films measured at $H=1$ T. The arrow indicates the angle where the magnetic field is perpendicular to the current.

4.1.3 AMR in La$_{0.67}$A$_{0.33}$MnO$_3$ Thin Films (A=Ca, Sr, Ba)

For complement of the AMR study in the manganite thin films, we also investigated the AMR in the La$_{0.67}$A$_{0.33}$MnO$_3$ thin films (A=Ca, Sr, Ba). Only relative large out-of-plane AMR has been observed in the compressive strained La$_{0.67}$A$_{0.33}$MnO$_3$
thin films (A=Ca, Sr, Ba), but is largest in the LCMO/LAO thin film (27% at 1 T) and smallest in the LBMO/LAO thin film (6% at 1 T).

Unlike the compressive strained films, the tensile strained La$_{0.67}$A$_{0.33}$MnO$_3$ thin films (A=Ca, Sr, Ba) show very large AMR ratios, comparable to the largest ratio observed in the tensile strained PSMO/STO thin films. Figure 4-18 shows the out-of-plane AMR measurement of tensile strained La$_{0.67}$A$_{0.33}$MnO$_3$ thin films (A=Ca, Sr, Ba) at H=2 Tesla.

Figure 4-18: The out-of-plane AMR measurement of tensile strained La$_{0.67}$A$_{0.33}$MnO$_3$ thin films (A=Ca, Sr, Ba) at H=2 Tesla.

Unlike the compressive strained films, the tensile strained La$_{0.67}$A$_{0.33}$MnO$_3$ thin films (A=Ca, Sr, Ba) show very large AMR ratios, comparable to the largest ratio observed in the tensile strained PSMO/STO thin films. Figure 4-18 shows the out-of-plane AMR measurement of tensile strained La$_{0.67}$A$_{0.33}$MnO$_3$ thin films (A=Ca, Sr, Ba) at H=2 Tesla. All three curves show similar behaviors as those of the tensile strained PSMO/STO thin films, with negative AMR ratios. The maximum resistances of all three compositions are obtained at $\theta=0^\circ$ and $180^\circ$, when the magnetic field was applied
perpendicular to the film plane. It is also seen that the LCMO thin film shows the largest AMR ratio, and the LBMO thin film shows smallest AMR. The AMR ratio observed in the LCMO/STO thin film (-67%) is very close to the largest AMR ratio obtained in the PSMO/STO thin films (-80%).

![Graph](image_url)

**Figure 4-19:** The out-of-plane AMR measurements of an 18 nm thick La$_{0.67}$Ca$_{0.33}$MnO$_3$/STO sample measured at $T = 90$ K and at different magnetic field.

The AMR of the tensile strained La$_{0.67}$A$_{0.33}$MnO$_3$ thin films (A=Ca, Sr, Ba) also show similar field dependence as observed in the PSMO/STO thin films. Figure 4-19 shows the out-of-plane AMR measurements of a 180 Å thick La$_{0.67}$Ca$_{0.33}$MnO$_3$/STO
sample measured at $T=90$ K and at different magnetic fields. The maximum AMR is observed around 2 Tesla, but still very large (-40%) even at 9 Tesla.

Figure 4-20: The AMR ratio as the function of temperature measured at different magnetic fields for the same sample as shown in Figure 4-19.

Figure 4-20 shows the AMR ratio as the function of temperature measured at different magnetic fields for the same sample as shown in Figure 4-19. The maximum AMR is observed around 90 K for all the fields except 9 T, and the AMR ratios show the crossover around the $T_p$ of this film. One striking feature of this figure is that at $T=10$ K, AMR change signs at higher fields ($H>2$ Tesla) and the AMR ratio is higher at higher
field. This behavior was also seen in the LSMO/STO thin film at very low temperature ($T=10$ K), but not seen in the PSMO/STO films.

For both compressive and tensile strained La$_{0.67}$A$_{0.33}$MnO$_3$ thin films (A=Ca, Sr, Ba), the AMR show similar thickness dependence as those of the PSMO thin films. The larger AMR ratios were obtained in thinner films, and large AMR ratios were only seen in a narrow thickness range. For LCMO films, since we could not make very thin (i.e., less than 130 Å for compressive strained film and less than 180 Å for tensile strained film) films that are still conducting, this range is smaller than those of the PSMO thin films.

4.2 Discussion and Conclusion

4.2.1 Discussion

The out-of-plane AMR results shown above are interesting in several aspects. First, the magnitude of the AMR is unusually large compared to the reported AMR in conventional ferromagnetic (FM) materials and in other manganites. The AMR of the FM is typically a few percent and is no more than 25% even at very low temperatures[154]. However, those are all related to the angle change between the current and the field. There is no AMR related to crystal axis change. The maximum AMR in our PSMO films is more than a hundred times larger than that of the Ni-Fe films (1-2 %) used the in the magnetic recording devices[185] and it is resulted from the magneto-crystalline anisotropy only.
Second, the AMR of the compressive and tensile strained films show opposite signs. This is interesting both practically and physically. In a practical point of view, this phenomenon indicates that the AMR can be effectively tuned by applying different types of strains. It may provide one more parameter for film and device design. Physically, the effect shows explicitly how strongly can the lattice distortion affect the magnetotransport properties of the manganites. By considering the lattice distortion of the two types of strains and the fact that the $R(\theta)$ curve is just shifted by $90^\circ$ between the compressive and tensile strained samples, we can conclude that the lower resistive state is always achieved when the magnetization (applied field) is parallel to the elongated axis of the MnO$_6$
octahedral, i.e., along the long Mn-O-Mn bond direction as shown in Figure 4-21. The deformation of the MnO$_6$ octahedral due to the strain-induced static J-T distortion splits the degenerated $e_g$ level of the Mn$^{3+}$ into two energy levels, the $d_{3z^2-r^2}$ orbital and the $d_{x^2-y^2}$ orbital. One is occupied and the other is empty. Due to the energy competition, the $d_{3z^2-r^2}$ and the $d_{x^2-y^2}$ orbital levels are occupied for the compressive-strained PSMO/LAO and the tensile-strained PSMO/STO, respectively[186]. Figure 4-22 shows the orbitals of the two strained states. On the other hand, the magnetization direction (and therefore the total spin S direction) relative to the orbital orientation determines the spin-orbit coupling strength which is related to conductivity[161]. As shown in the Figure 4-22, for the PSMO/LAO sample, when $H$ (and in turn $M$) is parallel to the long Mn-O-Mn
bond direction (normal to film plane), S is parallel to the occupied $d_{3z^2-r^2}$ orbital, the resistivity is at minimum. When H is normal to the long Mn-O-Mn axis (parallel to film plane), S is normal to the occupied $d_{3z^2-r^2}$ orbital, the resistivity is at maximum. Similar picture is also true for the tensile strained sample except that the $d_{x'^2-y'^2}$ orbital replaces the $d_{3z^2-r^2}$ orbital and the orbital plane changes from perpendicular to parallel to the film plane. When S is parallel to the $d_{x'^2-y'^2}$ orbital plane (H parallel to the film plane), R minimum is obtained. When S is normal to the orbital plane (H perpendicular to the film plane), R maximum is obtained. This can explain qualitatively why the two types of strained curves in Figure 4-11 (a) and (b) will look similar if we shift one of the curves by 90°. The AMR is determined by the relative direction between S and the orbital plane. This may also imply that the spin-orbital coupling is much stronger when S is parallel to the orbital plane than normal to the orbital plane so that the resistance is lower when they are parallel than when they are perpendicular to each other.

Third, the AMR of both the compressive and tensile strained films show composition dependence. For compressive strained Pr$_{1-x}$Sr$_x$MnO$_3$/LAO films, as seen in Figure 4-2, the smaller the x is, the larger the AMR ratio is. One of the explanations could be the different amount of strains in those films. The smaller the x is, the larger the lattice parameter of the Pr$_{1-x}$Sr$_x$MnO$_3$ is, therefore the larger the lattice mismatch between the Pr$_{1-x}$Sr$_x$MnO$_3$ film and the LAO substrate. However, it also means that the Pr$_{0.8}$Sr$_{0.2}$MnO$_3$/STO films have the smallest tensile strain among the four compositions of Pr$_{1-x}$Sr$_x$MnO$_3$/STO films. But they still show the largest AMR ratios among the four compositions. Therefore, besides strain, some other factors must be involved to affect the
AMR properties in Pr$_{1-x}$Sr$_x$MnO$_3$ films. For example, the phase separation might be one of the possible candidates. It has been shown by Knížek et al.[179] that x=0.2 is the boundary between the anti-ferromagnetism and ferromagnetism in the Pr$_{1-x}$Sr$_x$MnO$_3$ compounds. It is very likely that some phases other than FM presents in the Pr$_{0.8}$Sr$_{0.2}$MnO$_3$ films, and this may enhance the AMR effect in some way. This may be also the reason why the almost non-strained Pr$_{0.8}$Sr$_{0.2}$MnO$_3$/NGO and Pr$_{0.75}$Sr$_{0.25}$MnO$_3$/NGO films show larger AMR ratios than Pr$_{0.67}$Sr$_{0.33}$MnO$_3$/NGO and Pr$_{0.6}$Sr$_{0.4}$MnO$_3$/NGO films. In addition, the AMR is largest in the LCMO thin film and smallest in the LBMO thin film for both compressive and tensile strains. This indicates that the band width change must also be involved in anisotropic spin-orbit coupling and hence enhance the AMR effect.

The physical origin of the observed remarkable out-of-plane AMR effect is not fully understood yet. We can rule out the Lorentz MR effect which is due to the relative orientation between the magnetic moment and the current, since in our measurements, the magnetic field was always applied perpendicular to the current. We can also rule out the reduced dimensionality or surface effect. The almost non-strained PSMO/NGO films as thin as 40 Å didn’t show large out-of-plane AMR at all compared to the thicker but strained PSMO/LAO and PSMO/STO films. This indicates that the observed anomalous out-of-plane AMR effect is not due to the reduced dimensionality of the ultrathin films or the surface effect. Our results show that the out-of-plane AMR of compressive and tensile strained films show opposite signs, and the MR peak positions shift by 90°. The almost non-strained films do not show large AMR effect. This implies that the lattice distortion direction, further, atomic orbital ordering, caused by the strain-induced static Jahn-Teller
distortion and the spin-orbit coupling play crucial roles in the AMR properties. Our survey of current theories on manganites does not show that any models have discussed this effect. Further investigation is then needed to develop the theoretical explanations.

4.2.2 Conclusion

We have systematically studied the anisotropic magnetoresistance (AMR) effect of the strained La$_{0.67}$A$_{0.33}$MnO$_3$ thin films (A=Ca, Sr, Ba) and the Pr$_{1-x}$Sr$_x$MnO$_3$ (PSMO) (x=0.2, 0.25, 0.33, 0.4) thin films grown on different substrates and with different film thickness. Unusually large AMR has been observed in both compressive and tensile strained the Pr$_{1-x}$Sr$_x$MnO$_3$ (PSMO) (x=0.2, 0.25, 0.33, 0.4) thin films. Similarly large AMR has also been observed in tensile strained La$_{0.67}$A$_{0.33}$MnO$_3$ thin films (A=Ca, Sr, Ba), but the AMR is relatively small in the compressive strained La$_{0.67}$A$_{0.33}$MnO$_3$ thin films. The AMR of the highly strained ultrathin PSMO and La$_{0.67}$A$_{0.33}$MnO$_3$ films was found to be much larger than the less strained thick films and the almost strain-free ultrathin films. More interestingly, the AMR of the compressive and tensile strained films show opposite signs. When applying a magnetic field perpendicular to the film plane, the resistance reaches its minimum for the compressive strained film, while it is at the maximum for the tensile strained film. Non-strained films show small AMR in the same conditions. The results can not be explained by the existing models of the AMR effect, but indicate that the strain-induced atomic orbit ordering and the spin-orbit coupling may play crucial roles in the observed AMR properties. In the compressive strained samples, the lowest energy orbital is $d_{3z^2-r^2}$ and in tensile strained samples the orbital is $d_{x^2-y^2}$. In
both cases, the lowest resistance state corresponds to the magnetic moment parallel to the orbital plane. Therefore we believe that the orbital changes when the sample is under strain cause enhanced effect in spin-orbit coupling, which resulted in the unusually large AMR. Further investigation is needed to develop the theoretical explanations.
Chapter 5
MR in Manganite Nanostructures

5.1 Introduction

In chapter 3, we have discussed the large low-field magnetoresistance (LFMR) in compressive strained $\text{La}_{0.67}\text{A}_{0.33}\text{MnO}_3$ ($\text{A}=$Ca, Sr) and $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0.2$, 0.25, 0.33, 0.4) thin films, which has much larger MR ratio than that of GMR and TMR systems as discussed in section 1.3.2 and 1.3.3. The effect is identified to be associated with the magnetic domain walls of the thin films which have magnetization axis perpendicular to the film plane. Specifically, the effect is related to a combination of spin dependent transport across anomalous domain walls and the very high spin polarization in the manganites.

The domain wall width of the PSMO and LCMO films is estimated to be in the order of 10 nm and the domain width about 70-100 nm. But the measurements discussed in chapter 3 are made on large samples in the size of 10 $\mu$m $\times$ 20 $\mu$m $\sim$ 1 mm $\times$ 4 mm, which contain large amount of domains and domain walls. In order to understand the origin of the effect, measurements across a single domain wall is necessary. Therefore, nanostructures containing single domain wall would be the ideal system. In addition, from the practical application point of view, the current MR $vs$ $H$ curve is an average effect of switching of large numbers (in the order of $10^4$) of domains. Due to the distribution of the coercive field for different domains, the MR switch is not very sharp.
It is desirable to have sharp switching of the MR, which can only be accomplished in small size samples containing ideally only two domains.

### 5.2 Experiments and Results

#### 5.2.1 Sample Fabrication

The structure of the manganite samples we studied in this thesis is shown in Figure 5-1. It has a bridge which is made in different length (500 nm – 5 µm) and width (250 nm – 5 µm).

![Schematic illustration of the manganite nanostructure and expected domain wall location (cross section view).](image)

Figure 5-1: Schematic illustration of the manganite nanostructure and expected domain wall location (cross section view).

Manganite nanostructures studied in this thesis were fabricated using photolithography, e-beam lithography and ion beam etching. Figure 5-2 and Figure 5-3
Figure 5-2: Schematic illustration of a fabrication process of the manganite nanostructures. Typical bridge dimension: 250-500 nm long and 1-5 µm wide.
- Photolithography on the PSMO/LAO film, Evaporate Gold and Lift-off

- Spin E-beam Resist (PMMA) on the PSMO/LAO film

- E-beam Writing and Development

- Evaporate Cr and Lift-off

- Ion-milling and remove Cr

Figure 5-3: Schematic illustration of a fabrication process of the manganite nanostructures. Typical bridge dimension: 500-1000 nm long and 250-500 nm wide.
show two different fabrication processes of the manganite nanostructures. While the first process is relatively simple, the second process can make smaller structures comparing with the first process. Both methods use gold as contacts and use two-terminal method to measure the electrical transport properties. Although the structures are very small, due to the high resistivity nature of the manganite material, the gold contact resistance is much smaller than the bridge resistance. So the two-terminal method is a good simplification from the usual four-terminal method.

Figure 5-4 shows an AFM image of a manganite structure fabricated using the process shown in Figure 5-3. The bridge size is about 800 nm long and 500 nm wide. To help to locate the bridge in AFM, the metal layer on the nano-bridge was still on the bridge after ion milling. This layer will be removed afterwards by wet etching.

Figure 5-4: AFM image of a manganite structure fabricated using the process shown in Figure 5-3. The bridge size is about 800 nm long and 500 nm wide.
5.2.2 Experimental Results

Figure 5-5 shows the resistance as a function of the temperature curves at zero field and $H=1$ T in different directions of a PSMO/LAO nanobridge with the length of 500 nm and width of 5 µm. The PSMO film thickness is 100 Å. In zero magnetic field, the $T_c$ of the film was reduced from 150 K to about 60 K probably due to the fabrication process. The resistivity also increases by a factor of 10 at the around $T_c$, and has a huge upturn below $T_c$. But upon applying a magnetic field of $H=1$ T, both $T_c$ increases to 120 K and the resistivity reduces, and the upturn almost disappears. The difference of the resistance in the field shows small dependence on the direction of the field.

Figure 5-5: Resistance as a function of the temperature at zero field and $H=1$ T in different directions of a PSMO/LAO nanobridge with the length of 500 nm and width of 5 µm. $H_{\parallel,\parallel}$ implies the field is applied parallel to both the film plane and the applying current direction, $H_{\parallel,\perp}$ implies the field is applied parallel to the film plane but perpendicular to the applying current direction, and $H_{\perp}$ implies the field is applied perpendicular to the film plane. The PSMO film thickness is 100 Å.
LFMR measurements were conducted for the nanobridges the same way as described in chapter 3 for large samples. Figure 5-6 shows the MR loops at different temperatures for the same nanobridge sample as in Figure 5-5. Large LFMR was observed similar to the large PSMO/LAO thin films, but the ratio is larger comparing to the large samples of the same thickness.

Figure 5-6: The MR loops at different temperatures measured the same way as for the large samples described in chapter 3 for the same nanobridge sample as in Figure 5-5.

Temperature dependence of the LFMR for the nanobridge sample in Figure 5-5 is shown in Figure 5-7. It is seen that it is similar to the large PSMO/LAO film, i.e., the maximum LFMR was obtained at a temperature below $T_c$, and below this temperature or close $T_c$, LFMR drops. Figure 5-6 and Figure 5-7 show that the PSMO nanobridge
maintains the same LFMR property as the un-patterned large PSMO/LAO films, although the $T_c$ and resistivity change due to the fabrication process. Those changes may be caused by the chemicals used during the fabrication, which somehow change the property of the surface layer of the PSMO film and induce a dead layer.

Figure 5-7: Temperature dependence of the LFMR ratios for the same nanobridge sample as in Figure 5-5. LFMR is defined in two different ways, where $R_H$ and $R_0$ are the resistance at $H=5000$ Oe and $H=0$, respectively, in the MR loops as shown in Figure 5-6.

Domain wall resistance (DWR) measurements were also done for the nanobridge samples. Figure 5-8 shows the resistance as a function of the magnetic field measured at the different demagnetized states as described in chapter 3 for the same nanobridge sample as in Figure 5-5 at $T=40$ K. The results are also similar to the un-patterned large
PSMO/LAO samples. Comparing the resistance at the different demagnetized states, it can be seen that the domain wall resistance is very large, comparable to the LFMR. The temperature dependence of the DWR for this sample is also similar to that of the LFMR.

![Resistance plot](image)

**Figure 5-8:** Resistance as a function of the magnetic field measured at the different demagnetized states as described in chapter 3 for the same nanobridge sample as in Figure 5-5 at $T=40$ K.

It is seen that the nanobridge samples maintain the LFMR and DWR properties of the large size thin film samples. But the LFMR and DWR measurements do not show behaviors related to individual domain rotations as we expected, such as a jump or step like behavior in the MR curves. This may prove that, instead of domain rotation, the AFM phase was melted by applied magnetic field, and there is no sudden change in this case.
Figure 5-9: Current as a function of the voltage curves (I-V curves) measured at the temperatures (a) below 100 K, (b) above 100K, in zero magnetic field for the same nanobridge as in Figure 5-5.
To further study the transport properties of the nanobridges, the current as a function of the voltage curves (I-V curves) were measured at the different temperatures and at applied magnetic field in different directions and different demagnetized states. Figure 5-9 shows the I-V curves measured at the different temperatures in zero magnetic field for the same nanobridge as in Figure 5-5. It is seen in Figure 5-9 (a) that below and around $T_c$, the I-V curves are obviously nonlinear. At temperature a little over $T_c$, between 80 K and 100 K, the I-V curves become linear. While at higher temperature, the I-V curves show nonlinear behavior again, as shown in Figure 5-9 (b). This is very different from the un-patterned large PSMO/LAO films, which have linear I-V curves at all the temperatures.

Table 5-1: Barrier height $\phi$ and thickness $t$ obtained from the two-parameter fits to Simmons tunneling model for the same nanobridge sample as in Figure 5-5 at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\phi$ (eV)</th>
<th>$t$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.11</td>
<td>27.7</td>
</tr>
<tr>
<td>20</td>
<td>1.35</td>
<td>24.9</td>
</tr>
<tr>
<td>30</td>
<td>1.64</td>
<td>22.5</td>
</tr>
<tr>
<td>40</td>
<td>1.93</td>
<td>20.9</td>
</tr>
<tr>
<td>50</td>
<td>2.24</td>
<td>19.7</td>
</tr>
<tr>
<td>60</td>
<td>3.14</td>
<td>17.0</td>
</tr>
<tr>
<td>100</td>
<td>15.6</td>
<td>7.66</td>
</tr>
<tr>
<td>150</td>
<td>2.38</td>
<td>17.2</td>
</tr>
<tr>
<td>200</td>
<td>1.36</td>
<td>21.2</td>
</tr>
<tr>
<td>250</td>
<td>1.17</td>
<td>21.4</td>
</tr>
<tr>
<td>300</td>
<td>1.13</td>
<td>20.7</td>
</tr>
</tbody>
</table>

The nonlinear I-V behavior may indicate the tunneling in the nanobridge sample.

We use the two-parameter Simmons tunneling model[194] to fit the nonlinear I-V curves:
\[
\begin{align*}
J(V) &= aV + bV^3 \\
G(V) &= a + 3bV^2
\end{align*}
\]  

and

\[
\begin{align*}
a &= \frac{(2m)^{1/2}}{t} \left( \frac{e}{h} \right)^2 \phi^2 \exp(-A\phi^{1/2}) \\
b &= \frac{(Ae)^2}{96\phi} - \frac{Ae^2}{32\phi^{1/2}} \\
A &= \left( \frac{4\pi}{h} \right) (2m)^{1/2}
\end{align*}
\]

where \(J\) and \(G\) are the current density and conductance, respectively. \(m\) and \(e\) are the mass and charge of an electron, respectively. \(h\) is the Plank constant. \(\phi\) and \(t\) are the barrier height and thickness, respectively. This model shows a good fitting on our \(I-V\) curves, and we obtained the tunneling barrier height and thickness from the fitting.

Table 5-1 shows the barrier height \(\phi\) and thickness \(t\) obtained from the two-parameter fits to Simmons tunneling model for the same nanobridge sample as in Figure 5-5 at different temperatures. It is seen that, below \(T_c\), the barrier height \(\phi\) increases and the thickness \(t\) decreases with temperature; while above 100K, the barrier height \(\phi\) decreases and the thickness \(t\) increases with temperature. There is a jump for both barrier height and the thickness around 100K. This may be because that the \(I-V\) curve is linear around 100 K, and the tunneling model is no longer applicable at this temperature.

Figure 5-10 shows the \(I-V\) curves measured at a perpendicular magnetic field of \(H=1\) T and at different demagnetized states at \(T=40\) K for the same nanobridge as in Figure 5-5. It is seen that at this temperature, below \(T_c\), the \(I-V\) curves are nonlinear in all cases.
**Figure 5-10:** $I-V$ curves measured at perpendicular magnetic field of $H=1$ T and at different demagnetized states at $T=40$ K for the same nanobridge as in Figure 5-5.

**Figure 5-11:** MR ratio as a function of the current obtained from the $I-V$ curves for the nanobridge sample in Figure 5-5 at $T=40$ K.
When applying a perpendicular field or demagnetized by a perpendicular field, the $I$-$V$ curves have large difference from the $I$-$V$ curves in ZFC state, and this shows the effect related to domain walls. The fitted tunneling barrier height reduces in perpendicular field, which may indicates the melting of AFM phase in the sample. When demagnetized by a parallel field, the I-V curves show very small difference from the ZFC state, indicating the sample is in the multi-domain state in those cases. The nonlinear $I$-$V$ behavior at 1 Tesla magnetic field when there is no DW in the sample indicates internal phase separation in the sample. There are insulating phases in the sample at this state and the tunneling behavior is not simply related to the insulating domain walls.

From I-V curves, MR can be calculated as shown in Figure 5-11, and it is seen that the MR ratio is very large, but does not depend on the applied current very much.

Figure 5-12: $I$-$V$ curves measured at the different temperatures in zero magnetic field for a 700 nm long and 300 nm wide PSMO nanobridge.
Smaller PSMO nanobridge samples were also studied. Figure 5-12 shows the $I-V$ curves measured at the different temperatures in zero magnetic field for a 700 nm long and 300 nm wide PSMO nanobridge. It is seen that the $I-V$ curves show nonlinear behaviors below and above the $T_c$, while it becomes linear around $T_c$. This is consistent with the larger nanobridge samples discussed earlier. But this sample doesn’t show large LFMR effect, which may be due to the more damages during the fabrication process since the process is more complicated when the sample size is getting smaller.

### 5.2.3 Discussions

We have presented some preliminary data on the manganite nanostructures in the section 5.2.2. As discussed in section 5.1, the study of the manganite nanostructures is necessary to further understand the nature of the domain and domain wall structure and the magnetization anisotropy, which will help us to understand the large LFMR we observed in the large manganite thin film samples. Our data shows that, while the manganite nanostructure maintains all the LFMR and DWR properties as in the un-patterned manganite thin films, it shows the non-linear $I-V$ characteristics below $T_c$. And the $I-V$ curves were fitted very well with the Simmons tunneling model[194], which indicates that tunneling is a dominant factor in the transport property. This could also be true for the un-patterned manganite thin films, but due to the much larger size of the sample and the distribution of different tunneling directions, the nonlinear $I-V$ characteristics was averaged out, and the large sample shows a linear $I-V$ curve.
Figure 5-10 shows that, even under the magnetic field of 1 Tesla, the $I-V$ curves are still nonlinear. While as seen in Figure 5-8, the sample should be in the single domain state at this high field, and no domain walls exist. Therefore, there are insulating phase in the sample and the tunneling behavior is not simply related to the insulating domain walls. There are FM and AFM islands in the manganite nanobridge below $T_c$. Due to the insulating nature of the AFM island, it may serve as the insulating barrier between two FM islands. Tunneling could happen between the two FM islands through the AFM insulating barrier. Even above $T_c$, phase separation can still exist, and it may cause the nonlinear $I-V$ behaviors well above $T_c$. The dependence of the barrier height and thickness as the function of the temperature is not understood yet. Those values from the fitting may not describe the true barrier physics. Further study on more manganite nanostructures are needed in order to fully understand the nature of the tunneling behavior and its relation with the LFMR and DWR properties.

5.3 Conclusions

We have presented some preliminary data on the manganite nanostructures in this chapter. We found that, while the manganite nanostructure maintains all the LFMR and DWR properties as in the un-patterned manganite thin films, it shows the non-linear $I-V$ characteristics below $T_c$. And the $I-V$ curves were fitted very well with the Simmons tunneling model[194], which indicates that tunneling is a dominant factor in the transport property. The nature of the tunneling is not understood yet, but is believed to be related to the mixed-phase state of the sample. The dependence of the barrier height and thickness
as the function of the temperature is not understood yet. Those values from the fitting may not describe the true barrier physics. Further study on more manganite nanostructures are needed in order to fully understand the nature of the tunneling behavior and its relation with the LFMR and DWR properties.
6.1 Conclusions

This dissertation studied several topics in the manganite thin films aimed at understanding the physics underlying manganite materials and potential application using the manganite materials as the magnetic devices. The study included the low-field magnetoresistance effect and anisotropy magnetoresistance effect of the strained manganite thin films, and manganite nanostructures.

First, we have discussed in chapter 3 the large low-field magnetoresistance (LFMR) in compressive strained La$_{0.67}$A$_{0.33}$MnO$_3$ (A=Ca, Sr) and Pr$_{1-x}$Sr$_x$MnO$_3$ (x=0.2, 0.25, 0.33, 0.4) thin films, which has much larger MR ratio than that of GMR and TMR systems as discussed in section 1.3.2 and 1.3.3. The effect is identified to be associated with the magnetic domain walls of the thin films which have magnetization axis perpendicular to the film plane. Specifically, the effect is related to a combination of spin dependent transport across anomalous domain walls and the very high spin polarization in the manganites. Such a thorough study has not been done by any other group to the best of our knowledge, and these results are important both for fundamental understanding of manganite materials and for potential application using manganite materials as magnetic sensors or memory devices.
Second, we have systematically studied the anisotropic magnetoresistance (AMR) effect of the strained La\textsubscript{0.67}A\textsubscript{0.33}MnO\textsubscript{3} thin films (A=Ca, Sr, Ba) and the Pr\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3} (PSMO) (x=0.2, 0.25, 0.33, 0.4) thin films grown on different substrates and with different film thickness. Unusually large AMR has been observed in both compressive and tensile strained the Pr\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3} (PSMO) (x=0.2, 0.25, 0.33, 0.4) thin films. Similarly large AMR has also been observed in tensile strained La\textsubscript{0.67}A\textsubscript{0.33}MnO\textsubscript{3} thin films (A=Ca, Sr, Ba), but the AMR is relatively small in the compressive strained La\textsubscript{0.67}A\textsubscript{0.33}MnO\textsubscript{3} thin films. The results indicate that the strain-induced atomic orbit ordering and the spin-orbit coupling may play crucial roles in the observed AMR properties. Our survey of current theories on manganites does not show any models have discussed this effect. We believe that the orbital changes when the sample is under strain cause enhanced effect in spin-orbit coupling, which resulted in the unusually large AMR. Although the exact theoretical explanation is still an open question, our results provide very important information on fundamental properties, such as magneto-crystalline anisotropy and spin-orbit coupling, of the manganite materials.

Third, we have presented some preliminary data on the manganite nanostructures. We found that, while the manganite nanostructure maintains all the LFMR and DWR properties as in the un-patterned manganite thin films, it shows the non-linear $I$-$V$ characteristics above and below $T_c$. And the $I$-$V$ curves were fitted very well with the Simmons tunneling model, which indicates that tunneling is a dominant factor in the transport property. The nature of the tunneling barrier is not understood yet, but is believed to be related to the mixed-phase state of the sample below $T_c$. Further study on
more manganite nanostructures are needed in order to fully understand the nature of the tunneling behavior and its relation with the LFMR and DWR properties.

6.2 Future Works

The future work in this topic will consist of three thrusts: studying the strain effect on the MR properties of the manganite thin films by mechanically or electrically controlling the strains; studying the phase separation of the strained manganite thin films in atomic scale; attempts to fabricate the switching device driven by electrical current.

Different strains were introduced into the manganite thin films by choosing different substrates due to the lattice mismatch in this dissertation. The strains can not be controlled in a wide range. To fully understand the strain effect on the MR properties of the manganite thin films, and to utilize the strain effect to improve the MR properties for the magnetic device applications, it is desired to quantitatively control the strains in the manganite thin films. This may be realized mechanically or electrically. By bending the substrate mechanically, we can change the lattice parameter of the substrate. We can increase or decrease the lattice parameter depending on in which direction we are bending the substrate. The advantage of this method is that the substrates for the manganite thin films are readily available. For example, we could use NGO as the substrate for PSMO thin films. Without bending, the lattice mismatch is almost zero, and there is no strain in the film. By bending the NGO substate, we can introduce either the tensile or compressive strain into the PSMO film. The difficulty of this method is the amount of the stress the substrate can stand. Studies on high Tc superconducting films
show that only <1% of binding can be achieved before it breaks. Another method is electrical control by using the piezoelectric materials as the substrate. By applying the electric voltage on the piezoelectric substrate, we can change the lattice parameter of the substrate, so that we can change the strain in the manganite thin film grown on it. The disadvantage of this method is to find a proper piezoelectric material as the substrate and the amount of piezoelectricity of the materials is usually small.

Our results show that the phase separation may play a very important role in the MR properties of the manganite thin films. However, there is no direct evidence of the phase separation at the domain wall in our strained thin films. Recent study has successfully shown the phase separation in the manganite samples with atomic-scale resolution and to review the magnetic microstructures in the mixed phase state using the electron microscopy and holograms. Hence additional experiment should be attempted to examine the micro- or nano-scale magnetic structures in the strained manganite thin films, which can both identify the magnetic structure and also the electronic structure. This work is regarded as important in terms of scientific goals, since it will help to understand the nature of the magnetic domain and domain structures in the strained manganite thin films and therefore to quantitatively explain the large domain wall resistance and the tunneling behavior in the manganite nanostructures.

Finally, additional work can be performed to fabricate the switching device driven by electrical current. Recent interest has focused on switching of magnetic nanoparticles or thin magnetic layers by a spin-polarized current. This concept was originally proposed by Slonczewski[186]. Although the theoretical description is not settled yet[187-189], convincing evidence of current-driven magnetization switching has been presented for
the switching of magnetization in the thin Co layers in Co/Cu/Co pillars[190-192]. When a spin-polarized current passes through a ferromagnetic conductor, the transfer of angular momentum from the current exerts a torque on the magnetic moment of the conductor. At sufficiently high current densities and the torque is large enough, it can reverse the magnetic moment of an individual domain. Therefore, for magnetic nanostructures, the magnetic moment can be reoriented not only by the magnetic field, but also by a current. This effect has been proposed to be a possible choice to improve the magnetic memory and other devices. A large MR effect is expected in the nanostructures of strained manganite thin films. This is because that due to the anomalous domain wall effect, the flipping of the magnetization of a domain will induces a large change in resistance. Therefore, beside the large change of resistance induced by the magnetic field, large switch of resistance states can also be induced by a current. Beside studying the fundamental effect, this will also present a new type of device.


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