STUDY OF COLOSSAL MAGNETORESISTANCE AND PRESSURE EFFECTS IN La$_{2/3}$Ca$_{1/3}$MnO$_3$ THIN FILMS

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

in
THE FACULTY OF MATHEMATICS AND SCIENCE
DEPARTMENT OF PHYSICS

We accept this thesis as conforming
to the required standard

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BROCK UNIVERSITY

June 1998

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Abstract

The main purpose of this thesis is to study properties of La$_{2/3}$Ca$_{1/3}$MnO$_3$, both polycrystalline ceramics and thin films. This material has striking related electrical and magnetic properties. Thin films show colossal negative magnetoresistance (CMR) near transition from an insulating to a metallic state accompanied closely by transition from a paramagnetic to a ferromagnetic state. The double exchange mechanism (DE) and the Jahn-Teller deformations play an important role in CMR effect. Applied pressure has a very similar effect as does an applied magnetic field, except, at low temperatures (T<T$_c$) the field suppresses the resistivity more than pressure.

In our study we performed x-ray diffraction analysis, resistivity and magnetization measurements, as well as measurements of resistivity under applied pressure. The origin of strong resistivity change at low temperatures can be explained by the intergranular spin-dependent scattering of DE electrons. Oxygen stoichiometry plays an important role in the magnitude and position of MR(T) maximum. The distortions of structure and Mn-O-Mn bonds in applied pressure are discussed.

The fabrication of La$_{2/3}$Ca$_{1/3}$MnO$_3$ thin films by pulsed laser deposition was successfully developed. The films grown on (100) SrTiO$_3$ substrate are c-axis oriented and exhibit negative magnetoresistance $\Delta\rho/\rho(H)$ of over 400% at 245°C and 4200% at 90 K.
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Acknowledgement

My first great 'thank you' belongs to Dr. F.S. Razavi, my supervisor, who was my main advisor and supporter throughout my stay at Brock with patience, stimulating research guidance, helpful discussions and valuable suggestions. I thank Dr.T. Jenkyns, Dr.S.K. Bose, Dr.E. Battala and Dr.B. Mitrovic, members of my committee, for their careful reading of my thesis. I am grateful to all faculty members and staff of the department for their friendship, support and helpful hints.

I highly appreciate the machine shop and electronics shop experts for their endeavor, great job, and endless sense of humor. I am thankful to all my fellow students for their support and help. I also wish to thank the people in Ontario who made my stay in St. Catharines so pleasant and to all my friends overseas for their long-distance encouragement.

I would like to thank Mr. Harrison for his support through the Thompson–Harrison Graduate Scholarship and the Open Society Fundation Bratislava, Slovakia, for providing a travel grant for my study at Brock.
Chapter 1

Introduction

Solid state physicists remember very well the broad research response when high temperature superconductivity was discovered in cupric oxides. Since YBCO appeared on the stage, complex oxides have attracted more attention suggesting the possibility of their usage in standard electronics and tailoring with silicon technology. Recently mixed valence perovskite-type manganite oxides $A_{1-x}B_xMnO_3$ (A=La, Pr, Y, Nd; B=Ca, Sr, Ba, Pb) have attracted considerable interest because of their very large negative magnetoresistance (MR) in the vicinity of the magnetic phase transition temperature $T_c$.

This effect has been known since 1950 when Jonker and van Santen [1] for the first time synthesized and characterized a series of compound $La_{1-x}Ca_xMnO_3$. For the doping level of $x \approx 0.3$ the compound undergoes a magnetic phase transition from low temperature ferromagnetic metal (FMM) to a paramagnetic insulator (PMI) at high temperatures. Soon afterwards Zener [2] explained the properties of this material by the *double exchange* mechanism. In the novel type of magnetic interaction he assumed that the only way charge transfer could happen was via the simultaneous hopping of electrons from Mn$^{3+}$ to O$^{2-}$ and from O$^{2-}$ to Mn$^{4+}$. By the strong Hund’s rule coupling ferromagnetism is induced via the parallel orientation of both the traveling spins and magnetic moments of the Mn$^{3+}$ and Mn$^{4+}$ ions. Then Anderson and Hasegawa [3] explicitly formulated this mechanism and it was applied to the $La_{1-x}Ca_xMnO_3$ system by de Gennes [4].

In the past few years this material attracted many researchers, as a consequence of increasing demands for higher density information storage and therefore the new magnetic
recording heads, memory chips and sensor materials. Lanthanum manganites displaying colossal magnetoresistance (CMR, the new acronym since 1994 [5]) are a noticeable challenge for heterogeneous ferromagnetic multilayers and cluster alloys with giant magnetoresistance (GMR). The renewal of interest started gradually with the first studies of LaPbMnO [6], Pr$_{1-x}$Ca$_x$MnO$_3$ [7], Nd$_{0.5}$Pb$_{0.5}$MnO$_3$ [8] followed by the unexpected discovery of CMR in thin films of (LaSr)MnO$_3$ [9], (LaBa)MnO$_3$ [10], (LaCa)MnO$_3$ [10, 5, 11]. Since the structure and chemical character of manganite perovskites are so like high temperature superconductors, knowledge and experience in preparation and characterization of superconducting films can be applied to the manganites.

Recently Millis [12] realized that the basic double exchange interaction itself is not sufficient to explain such large negative MR. The importance of lattice degrees of freedom and electron-phonon coupling originating from Jahn-Teller distortions leads to several theories of CMR [13, 14, 15]. Besides the strong interaction between spin, charge and lattice, there appear to be further critical parameters: the average ionic radius of the A-site atoms, the Goldschmidt tolerance factor, Mn$^{3+}$/Mn$^{4+}$ ratio, and others. It might be necessary to take these into account when explaining possible inhomogeneous, or local effects, as a polaron formation [44, 46, 64] and the charge ordering [28, 21], the large Debye-Waller factors [20], the sound velocity anomalies in the charge ordered state [21], and the large isotope effect of the ferromagnetic Curie temperature [40].

Research was not concentrated only on perovskites. Strong anisotropy in transport properties and even higher MR are exhibited by layered manganites, for example the compounds La$_{2-2z}$Sr$_{1+2z}$Mn$_2$O$_7$ [16] and La$_{2-2z}$Ca$_{1+2z}$Mn$_2$O$_7$ [17], corresponding to the Ruddlesden-Popper series having the generic formula $(A_{1-x}B_x)_{z+1}Mn_zO_{3z+1}$, for $z=2$. CMR has also been observed in polycrystalline Tl$_2$Mn$_2$O$_7$ of pyrochlore structure [18] and Fe$_{1-x}$Cu$_x$Cr$_2$S$_4$ chalcogenide spinels [19], which have neither mixed valence for a DE magnetic interaction nor a Jahn-Teller (JT) effect. Therefore the CMR effect remains
unclear, the JT effect combined with DE seems not to be the only cause of CMR.

The objective of my research is the fabrication of La$_{2/3}$Ca$_{1/3}$MnO$_3$ thin films and their characterization in terms of pressure effects, magnetoresistance, magnetization and resistivity. The second chapter outlines basic theoretical knowledge necessary for discussion of measured results, presented in fourth chapter and discussed in fifth chapter. Third chapter describes the experimental techniques and sample preparation procedures.
Chapter 2

Review of Present Theoretical and Experimental Work

2.1 Structural and electronic characteristics

Among the variety of examples of cubic perovskite structure ABO$_3$ only a few are perfectly cubic. The large ion A, for example La$^{3+}$, Ca$^{2+}$, Y$^{3+}$, Ba$^{2+}$, Sr$^{2+}$, is located at a cube center, the small ion B represented by Mn$^{3+}$, Mn$^{4+}$, Co$^{3+}$ or Ti$^{4+}$ is situated at cube corners, and oxygen ions are the midpoints of the cube edges (Fig. 2.1).

![Figure 2.1: La$_{1-x}$Ca$_x$MnO$_3$ perovskite structure. Arrows indicate spin magnetic structure.](image)

The parent compound LaMnO$_3$ shows the orthorhombic structure and mixed crystals transfer to the distorted cubic structures A$_{1-x}$$^{3+}$A$_x^{2+}$(Mn$_{1-x}^{3+}$Mn$_x^{4+}$)O$_3^{2-}$, where A and A'
are a trivalent rare earth and divalent alkaline earth ions, respectively. This can be explained by the increase of Goldschmidt [22] tolerance factor \( t = (r_O + r_A)/\sqrt{2}(r_O + r_B) \) in which \( r_A, r_B, r_O \) are the radii of the ions A, B, and O of the perovskite compound ABO\(_3\). For \( 0.8 < t < 0.9 \) monoclinic perovskite structures are formed, and for \( t > 0.9 \) cubic ones. Therefore for LaMnO\(_3\) with the \( t \) value 0.89 only a slight increase in \( t \) induced by substituting larger ions Ba or Sr for La is needed for a transition to a cubic structure. Alternatively a larger amount of Ca is needed to reduce the \( r_B \) value. The \( T_c \) value increases with the tolerance factor above 0.96. There is a strong positive magnetic interaction between Mn\(^{3+}\) ions and Mn\(^{4+}\) ions in comparison to very weak Mn\(^{3+}\)–Mn\(^{3+}\) and Mn\(^{4+}\)–Mn\(^{4+}\) interactions [1]. Then ordered structures with an increased number of Mn\(^{3+}\)–Mn\(^{4+}\) neighbors may indeed be expected below the Curie temperatures.

The correlation between magnetic order and conductivity has been known since the early fifties when very high conductivity was observed in ferromagnetic region for (LaM)MnO\(_3\) (M=Ca doping 25-35%) by Jonker and van Santen [1].

Wollan and Kohler [28] first used neutron diffraction to study the magnetic order and magnitude of the magnetic moments of the La\(_{1-x}\)Ca\(_x\)MnO\(_3\) (LCMO) system. They observed that the parent compounds \( x = 0 \) and \( x = 1 \) are insulating antiferromagnets, but in the region \( 0.2 < x < 0.5 \) they are ferromagnetic at low temperature with almost metallic conductivity for divalent dopants Ca, Sr or Ba. In the range \( 0.2 < x \leq 0.4 \) the structure is rhombohedral. It was suggested that the spin configuration need not be homogeneous and magnetic clusters of trapped charge carriers could form a spin glass below \( T_c \) in the range \( 0.1 < x \leq 0.2 \) [27]. In the range \( 0.4 < x \leq 0.5 \), \( T_c \) decreases with \( x \), as a result of a long-range antiferromagnetic ordering.

The parent LaMnO\(_3\) shows ferromagnetic ordering in the \( a-b \) plane and antiferromagnetic ordering along the \( c \)-axis under the Néel temperature. The ferromagnetically
ordered Mn–O layers of the $a$–$b$ plane are separated by a nonmagnetic La(Ca)–O monolayer (Fig. 2.1).

The free Mn ion outer state is split up into twofold and threefold degenerate levels in the cubic crystal field of Mn–O octahedra (six-coordinated structure). The twofold upper $\Gamma_3$ level $e_g$ electrons suffer a greater electrostatic repulsion from the negative anion O$^{2-}$ than the $t_{2g}$ electrons of $\Gamma_5$ level, so that the $\Gamma_3$ state is at a higher energy. In our system, further splittings due to distortions from cubic symmetry are greater than the spin-orbital splittings. When $t < 1$ stresses in the structure are relieved by cooperative rotation of the MnO$_6$ octahedra and thus Mn–O–Mn bond is bent slightly from 180°.

Lanthanum manganite compounds have very complicated structural, electronic and magnetic phase diagrams [1, 28, 23]. In ceramics first it has been found that the exact structure is dependent on the oxygen content, or equivalently on the valence state of the Mn ion. In the doping level $x \approx 0.33$ the optimum CMR effect occurs (the lowest resistance and highest $T_c$). At high temperatures a paramagnetic insulator with activated behavior undergoes a magnetic first-order phase transition to a ferromagnetic metal as the material is cooled through the Curie temperature $T_c$ (Fig. 2.2) in the range $0.96 \leq t \leq 0.98$. The peak of MR occurs close to $T_c$. However $T_c$ increases with applied magnetic field. The MR ratio is defined here as $(R(0) - R(H))/R(H) = \Delta R/R(H)$. When the Mn magnetic moment is increased by either lowering the temperature or applying a magnetic field the resistivity decreases. For samples with smaller $T_c$ the magnetoresistance MR($T_c$) is generally larger.

Recently, the second-order ferromagnetic transition was indicated, when the linear thermal-expansion coefficient $\beta(T)$ exhibited an asymmetric peak at the $T_c$ [61].

In the following sections the properties mentioned above are given in more detail and other interesting phenomena are introduced. Our research is concentrated on Ca doping ($x \approx 0.33$).
Figure 2.2: La$_{2/3}$Ca$_{1/3}$MnO$_3$ typically displays an insulating to metallic phase transition accompanied by paramagnetic to ferromagnetic phase transition near $T_c$. (film sample # 11)
2.2 Double exchange

Zener first attempted to study the correlation between magnetic order and conductivity identifying a double exchange process [2]. The end point (x=0) LaMnO₃ shows an absence of conductivity at low temperatures. Semicon ductivity at higher temperature is a result of the thermally activated ionization and direct hopping of the Mn³⁺ ions. Therefore the description of the electronic states in terms of the customary band representation is inappropriate and he tried an alternative description in terms of localized orbitals as reviewed below.

By replacement of La³⁺ ions by, say Ca²⁺ ions, it is necessary, that the corresponding number of Mn³⁺ ions (3d⁴) be replaced by Mn⁴⁺ ions (3d³). It was suggested [1] that the conductivity is accomplished by the migration of Mn⁴⁺ holes as Mn⁴⁺ ion captures an electron from a neighboring Mn³⁺ ion. Since Mn ions are too far apart to have an appreciable overlap the hopping must occur somehow via the closed shell oxygen ion O²⁻. According to Hund’s rule Zener presumed that each Mn ion is in its configuration of the highest multiplicity.

The wavefunctions before and after the electron transfer are degenerate and represent configurations:

$$\psi_1 : Mn^3+O^2-Mn^4+,$$

$$\psi_2 : Mn^4+O^2-Mn^3+.$$

The exchange energy $\epsilon$ is given by $\int \psi_1^*(H - \epsilon_0)\psi_2 d\tau$, where $H$ is the Hamiltonian of the whole system and $\epsilon_0$ is the energy of the initial states $\psi_1$ and $\psi_2$. The predominant term in the integrand contains the product: $(Mn^4+|1)^*(O^2-|1)(O^2-|2)^*(Mn^3+|2)$. The “Bra” sides of the brackets are the wavefunctions of the valence electron in ions. Here the electron transfer between adjacent Mn³⁺ can be visualized as an electron hopping from the central O²⁻ onto a Mn⁴⁺ simultaneously with an electron hopping onto the oxygen ion from the Mn³⁺ ion. This type of transfer was given the name double exchange (DE).
It should be pointed out that the double exchange integral is nonvanishing only if the spins of the two Mn d-shells are parallel. The energy has the lowest value for a parallel alignment of the spins of the two Mn ions.

This is different from Kramer's superexchange [32] where excited states are degenerate leading to an antiferromagnetic ordering of spins. Here the system is inherently degenerate because of the presence of Mn ions of two different charges. Therefore the alignment of spins of adjacent Mn d-shells leads to ferromagnetism accompanied by an increase in the electrical conductivity through Mn$^{4+}$ migration. Because of degeneracy more appropriate eigenfunctions are linear combinations $\psi_+ = \psi_1 + \psi_2$ and $\psi_- = \psi_1 - \psi_2$ with higher energy associated with $\psi_+$ and lower energy with $\psi_-$ by the effect of the double exchange. Therefore by a parallel alignment of spins, the energy of the system will be lowered at low temperatures, regardless of the sign of the exchange integral. It was experimentally verified, that antiferromagnetic superexchange is too weak to compete with the ferromagnetic Mn$^{4+}$-O$^{2-}$-Mn$^{3+}$ interaction, e.g. in the LaMn$_{1-x}$GaxO$_3$ system [47].

The DE mechanism was investigated in greater detail by Anderson and Hasegawa [3] using considerably more general assumptions. They approximated their results by a simple semiclassical model using configurations: 

\[
\begin{array}{ccc}
\text{Mn}_1 & \text{O} & \text{Mn}_2 \\
\text{I} & d_1' d_1 & p^2 d_2' \\
\text{II} & d_1' & p^2 d_2 d_2' \\
\text{III} & d_1' d_1 & p d_2 d_2' \\
\end{array}
\]

where $d_1', d_2'$ are fixed and $d_1, d_2$ mobile $d$-electrons. For two ions which have very large spins $S$ one can assign them definite directions in space and a definite angle between them. The first atom has spin $\vec{S}_1$ with spin eigenfunctions $\alpha$ and $\beta$, the second (Mn$_2$) atom has spin $\vec{S}_2$ with eigenfunctions $\alpha'$ and $\beta'$, and $\theta$ is the angle between $\vec{S}_1, \vec{S}_2$. The eigenstates $d_1 \alpha$ and $d_1 \beta$ on atom 1 have energies: $E(d_1 \alpha) = -JS$, $E(d_1 \beta) = J(S + 1)$. Here $J$ is an
intra-atomic exchange integral by which the valence electron’s spin is coupled to the rest of the ion spin. Similarly the energies on atom 2 are: \( E(d_2\alpha') = -JS, \quad E(d_2\beta') = J(S + 1) \).

To write the transfer matrix properly, \( \alpha \) and \( \beta \) must be expressed in terms of \( \alpha' \) and \( \beta' \) by a rotational transformation. Then the secular equation (using \( S_1 = S_2 = S \) )

\[
\begin{pmatrix}
    d_1\alpha & d_1\beta & d_2\alpha' & d_2\beta' \\
    d_1\alpha & -JS - E & 0 & t \cos(\theta/2) \sin(\theta/2) \\
    d_1\beta & 0 & J(S + 1) - E & -t \sin(\theta/2) \cos(\theta/2) \\
    d_2\alpha' & t \cos(\theta/2) & -t \sin(\theta/2) & -JS - E \\
    d_2\beta' & t \sin(\theta/2) & t \cos(\theta/2) & J(S + 1) - E
\end{pmatrix} = 0
\]

has the complete solution \( E = \frac{1}{2} \pm \sqrt{J^2(S + \frac{1}{2})^2 + t^2 \pm 2Jt(S + \frac{1}{2}) \cos \theta/2} \). Here \( t \) represents the Zener’s transfer integral \( t = \int \psi_1(1)\psi_p(1)H\psi_2(2)\psi_2(2)d\tau \). By exact quantum calculation \( \cos(\theta/2)_{\text{exact}} = (S_0 + \frac{1}{2})/(2S + 1) \), where \( \bar{S}_0 = \bar{S}_1 + \bar{S}_2 \).

In Zener’s case \( (J \gg t) \) the solution can be simplyfied by ignoring high eigenvalues to

\[
E \approx -JS \pm t \cos \theta/2 = -JS \pm t[(S_0 + \frac{1}{2})/(2S + 1)].
\]

For \( J \ll t \) we get \( E \approx J/2 - [t \pm J(S + \frac{1}{2})] \cos \theta/2 = -t + J/2 \pm J/2(S_0 + \frac{1}{2}) \).

In the first case the two eigenstates are the symmetrical and antisymmetrical combinations of the localized orbitals where the electron has a spin parallel to \( \bar{S}_1 \) or \( \bar{S}_2 \), respectively. In the latter case the two states of the traveling electron correspond to spin up or down with respect to the total spin \( \bar{S}_1 + \bar{S}_2 \).

In both cases there is linear dependence in total spin \( S_0 \), and for every \( S_0 \) there are two states, high and low energy. The carrier energy is dependent on the angle \( \theta/2 \) between the different ionic spins. Particularly, because of orbital degeneracy and the motion of the electron as an extra degree of freedom we did not obtain an \( \bar{S}_1 \cdot \bar{S}_2 \) interaction.

P.G. de Gennes [4], in his tight binding approximation, found that all antiferromagnetic or ferromagnetic spin arrangements are distorted as soon as some Zener carriers are
present \((0 < x < 1)\). The carrier energy is lowered if the sublattices become canted. This is because energy gain from electron transfer is of the first order in the distortion while the increase of antiferromagnetic exchange energy is only of second order. Then the results are: a nonzero spontaneous moment in low fields, a lack of saturation in high fields, possible simultaneous occurrence of ferromagnetic and antiferromagnetic characteristics in neutron diffraction and spin wave spectra. For free DE carriers, the distortion corresponds to uniform canting of the sublattices, and if they are bound, the spin distortion is inhomogeneous. As proposed by de Gennes, the canted arrangement could be stable up to a definite temperature, above which the system becomes anti- or ferromagnetic (dependent on \(x\)).

Goodenough [23] predicted the intensity of magnetization and the phase diagram for the \([\text{La}(\text{Ca}^{2+})]\text{MnO}_3\) system in terms of a semicovalent exchange model. Based on \(d - p\) hybridization he studied magnetic structures of different doping levels and successfully predicted the \(T_c(x)\), crystal structure and qualitative resistance vs. doping level \(x\) dependences. For example, phase \(\beta\) \((0.25 < x < 0.375)\) is cubic (rhombohedral possible) with low resistivity and ferromagnetic below Currie temperature \(T_c\) which has its maximum at \(x = 0.31\) and double exchange is optimized.

In the works [3, 4] mentioned above an effective Hamiltonian of the DE mechanism can be represented as

\[
H_{DE} = \sum_{ijab} \frac{t_{ij}^{ab}}{\sqrt{2}} \sqrt{1 + \frac{\vec{S}_i \cdot \vec{S}_j}{S^2}} (c_{ia}^\dagger c_{jb} + H.c.)
\]

where \(\vec{S}_i\) are classical spins for regime near \(T \sim T_c\), \(c_{ia}^\dagger\) is the creator of the spin polarized electron on site \(i\), and \(t_{ij}^{ab}\) is the DE transfer integral (the hopping matrix element for given pair of ions \(i, j\) dependent on orbitals \(a\) and \(b\)). The Hamiltonian describes the hopping of spinless fermions with dependence on the relative orientation of the total \(d\)-electron spin on neighboring sites \(i\) and \(j\).
Band theory calculations have shown that the electronic structure of manganites are intimately coupled to the underlying magnetic structure because of the large Hund’s coupling [41]. The Hamiltonian can be written together with the Hund’s coupling $J_H$ as

$$H = \sum_{ijab\sigma} t_{ij}^a c_{ia\sigma}^+ c_{j\sigma} - J_H \sum_{i\sigma \sigma'} \vec{S}_i \cdot \vec{S}_{ia\sigma} \sigma_{\sigma'} c_{ia\sigma}$$

where the outer electron is aligned to a core spin $S_i$.

The resistivity and magnetoresistance implied by this formula have been previously calculated by Saerle and Wang [6], Kubo and Ohata [39], and recently by Furukawa [15]. The theoretical calculations based on the Kondo–lattice many-body model with ferromagnetic coupling can give an essential account for the large MR observed near $T_c$. They showed that the transition from ferromagnetic to paramagnetic state is accompanied by a change in the temperature dependence of the resistivity which results in a very large magnetoresistance near the transition. But their quantitative results (e.g. constant resistivity above $T_c$) do not agree with observed data.

Other authors studied the electronic correlation effect in the DE model using the slave–boson picture and considering Coulomb interaction [43]. At a sufficiently low density $x$ and a very weak on-site Coulomb interaction the phase separation might take place. The magnetization and the Curie temperature reach maxima near $1/3$ doping.

Large MR near $T_c$ can originate from spin–dependent electron scattering when the manganese spins change the canting angle with the magnetic field and from electron scattering by partially formed magnetic ordering or spin fluctuations [11]. Just above $T_c$, the canting angle is changed easily by the applied field. By lowering the temperature below $T_c$ the canting angle becomes stable, fluctuations decrease and MR gradually decreases. The strong peak of MR is due to the enhanced magnetic scattering and the possible dynamic Jahn–Teller distortions near $T_c$ with trapping out and releasing polaron holes [12, 5, 27], which is discussed in next section.
2.3 Importance of electron–phonon interaction and Jahn-Teller distortions

Recent theoretical and experimental studies [12, 14, 40, 46] have suggested that, in addition to the double exchange theory, some other effects, such as those relating to static or dynamic lattice distortions of the MnO$_6$ octahedra, are needed to understand the interplay between the carriers' transport and the spin arrangement.

The double exchange model does not provide a satisfying representation of the physics in the LCMO. Especially there is a great difference between the observed and calculated value of T$_c$, the calculated resistivity (T > T$_c$) is consistent with data only qualitatively, with magnitude several orders lower. It has incorrect behavior in magnetic fields and also at low temperatures. Therefore, some other mechanism must be involved in reducing the electron kinetic energy around T$_c$. Millis [12] suggested the mechanism of polaron effect due to a very strong electron-phonon coupling induced by Jahn-Teller splitting.

**Jahn-Teller effect** is a distortion of the highly symmetrical molecule in degenerate electronic state, which reduces its symmetry and lowers its energy by removing the degeneracy. In our case distortion to tetragonal symmetry leads to splitting of e$_g$ $\sigma$-bonding orbitals. Particularly at higher temperatures distortion can resonate between two stable configurations c/a > 1 and c/a < 1, which is known as the **dynamic Jahn-Teller effect**. The special coupling between vibrational modes and low-frequency electron motion develops.

For the octahedral oxygen coordination (Fig. 2.1), the three $t_{2g}$ d-states with symmetry $xy, yz, zx$ are split in energy from the two $e_g$ states $x^2 - y^2, z^2$ by the cubic crystal field. Figure 2.3 shows the ground state occupancies of Mn ions in the case when Jahn-Teller orthorhombic distortion splits the degenerate $e_g$ energy levels. The Mn$^{3+}$ ions have three localized electrons in the $t_{2g}$ orbitals and one electron in the $e_g$ orbital which is strongly hybridized with the neighboring oxygen 2p states [23].
Figure 2.3: Crystal-field splittings and ground state orbital occupancies of Mn ions in orthorhombically distorted oxygen octahedra. Adapted from Ref. [29]

The Mn$^{4+}$ ion has a vacant $e_g$ orbital.

In the orthorhombic parent compound LaMnO$_3$, the cooperative Jahn–Teller distortions are static and long-range in (001) planes [27]. By doping, at high enough concentrations, the structure is rhombohedral which allows short-range-cooperative breathing-mode displacements of oxygen atoms on either side of a localized Mn atom. Goodenough [47] concluded that the ferromagnetic coupling was due to a strong dynamic $e_g$-electron coupling to the oxygen displacements along the Mn–O–Mn bond axis.

Kusters [8] recommended a magnetic polaron model. This might be hindered by very week carrier–spin interaction. But JT coupling is very strong with the onset at least at 800K for LaMnO$_3$. Indeed, the polaron picture was favored by recent direct polaron observations in electron paramagnetic resonance [46], and by study of O$_{18}$ substitution [40]. Direct oxygen displacements studied by ion channelling [45] found very strong correlation of transport with local lattice distortions of Mn sites. Measured distortion decreased and reached a steady state below $T_c$. The neutron powder–diffraction data [64] showed,
that polarons start to form below and close to $T_{MI}$ (maximum resistivity temperature) and they have been attributed to a static breathing mode distortion of oxygen around manganese of magnitude $\delta \sim 0.012$ nm.

J.B. Goodenough proposed [27], that the colossal magnetoresistance reflects a progressive trapping out of mobile small-polaron holes with decreasing temperature in the paramagnetic phase and their progressive release with decreasing temperature below $T_c$.

So far (1997) there are not many comprehensive books about the topic published. However, some papers with reviewed information have appeared [30, 31, 41, 44, 27].
Chapter 3

Experimental Methods

3.1 Preparation and properties of the ceramic targets

Ceramic targets of La$_{2/3}$Ca$_{1/3}$MnO$_3$ were prepared by the standard solid state reaction as well as the sol-gel technique. Here the names C1, C2 and SG2 refer to three batches of material prepared differently. Each batch supplied about two-three tablets of identical properties. The samples were prepared as follows.

Appropriate amounts of starting materials La$_2$O$_3$ (3.2580 g), CaCO$_3$ (1.0004 g), and MnCO$_3$ (3.4483 g) powder were mixed using mortar and pestle. Initial powders for sample C2 were mixed in absolute ethanol and dried overnight. Prior to calcination the mixture was heated to 100°C for 2 h. The mixture was slowly heated up for 10 h and calcinated at 1220°C for 6h in O$_2$, then pulverized, mixed in the ball mill and sintered in an Al$_2$O$_3$ crucible at 1300°C in O$_2$ for 15 h two more times and finally at 1375°C, then cooled to room temperature slowly (1.4°C/min). Before the last firing the powder was formed under 10 tons pressure into 5 mm diameter pellets 1 mm thick (sample C2). Preparation conditions for all ceramic samples (3 batches) are summarized in Table 3.1.

The ceramic sample C1 was prepared under different conditions. The starting powder was mixed with MnO$_2$ and not MnCO$_3$ using the Al$_2$O$_3$ ball mill. The calcination went 20 h at 1050°C and the last firing was at 1350°C with the final cooling at the rate 1.28°C/min. All the annealing was performed in air flow. Most likely, the air contained oil vapor contaminants.
Table 3.1: Solid state treatment.

<table>
<thead>
<tr>
<th>sample</th>
<th>C1</th>
<th>C2</th>
<th>SG</th>
</tr>
</thead>
<tbody>
<tr>
<td>mixing</td>
<td>ball mill 1h</td>
<td>abs. ETOH</td>
<td>citrate-gel</td>
</tr>
<tr>
<td>calcination(^a)</td>
<td>(O_2) RT / 1050(^\circ)C (\Delta) RT 2(h) (f_c)</td>
<td>air RT / 1220(^\circ)C (\Delta) RT 10(h) 6(h) 6(h)</td>
<td>air RT / 1100(^\circ)C (\Delta) RT 24(h) (f_c)</td>
</tr>
<tr>
<td>reground(^b)</td>
<td>mortar 5min</td>
<td>ball mill 15min, press 8t</td>
<td>mortar 5min, press 10t</td>
</tr>
<tr>
<td>sintering</td>
<td>air RT / 1300(^\circ)C (\Delta) RT 2(h) 21(h) 1(h)</td>
<td>O(_2) RT / 1300(^\circ)C (\Delta) RT 6(h) 15(h) 10(h)</td>
<td></td>
</tr>
<tr>
<td>reground</td>
<td>mortar 10min</td>
<td>mortar 15min, press 9t</td>
<td></td>
</tr>
<tr>
<td>sintering</td>
<td>air RT / 1300(^\circ)C (\Delta) RT 2(h) 20(h) 1(h)</td>
<td>O(_2) RT / 1300(^\circ)C (\Delta) RT 2(h) 12(h) 6(h)</td>
<td></td>
</tr>
<tr>
<td>reground</td>
<td>mortar 10min, press 11t</td>
<td>mortar 20min, press 11t</td>
<td></td>
</tr>
<tr>
<td>final sintering</td>
<td>air RT / 1350(^\circ)C (\Delta) RT 1.5(h) 16(h) 13(h)</td>
<td>O(_2) RT / 1375(^\circ)C (\Delta) RT 3(h) 13(h) 12(h)</td>
<td>O(_2) RT / 1350(^\circ)C (\Delta) RT 3(h) 20(h) 10(h)</td>
</tr>
</tbody>
</table>

\(^a\)RT—room temperature; \(\Delta\)—warming and cooling; \(f_c\)—furnace cooling  
\(^b\)press—tablets formed under pressure in tons

Extensive grinding increases the homogeneity of the material, but the minimum obtainable particle size of the starting oxides is not less than 1 \(\mu\)m. Citrate synthesis is a fast and simple technique which offers the unique advantage of low temperature synthesis, high purity and precise composition control. Therefore, some targets (batch SG) were prepared by the sol-gel process in combination with pyrolysis (e.a. citrate gel method) to obtain a homogeneous and very fine powder mixture. The MnCO\(_3\), La\(_2\)O\(_3\), CaCO\(_3\) powders of proper molar ratio (La:Ca:Mn) were dissolved in nitric acid (65%) and all put together with citric acid, then aged at room temperature for several days. Details of citrate gel preparation are reviewed in Table 3.2.

The liquid of low pH value was neutralized with ammonia (NH\(_4\)OH) up to pH= 6.81. The solution (< 50 ml) was put on a hot plate in an oversized 2l beaker. Upon heating the brown solution became more transparent and yellow while boiling slowly, then it turned dark and viscous by evaporating the solvent. At a certain moment (after about 50min), spontaneous combustion was initiated resulting in a powder of very fine particles.
Table 3.2: Citrate–gel preparation of $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ precursor.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass (g)</th>
<th>HNO$_3$ (ml)</th>
<th>H$_2$O (ml)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCO$_3$</td>
<td>1.7242</td>
<td>+ 3</td>
<td>+ 7</td>
<td>(heated)</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>1.62905</td>
<td>+ 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>0.50044</td>
<td>+ 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ citric acid 6.3</td>
<td>+ 3</td>
<td>+ 4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

which has the correct stoichiometry because the mixing of components occurred at the molecular level. The risen powder filled approximately half of the vessel. It is important that all the liquid undergo the combustion uniformly. After the pyrolysis the compound was calcinated at 1100°C for 24 h with subsequent furnace cooling. The powder was reground, pelletized into three tablets, and sintered at 1350°C for 20 h in O$_2$ flow, then it was cooled down at the rate 1.66°C/min.

Generally, in standard solid state technique the chemical reactions are diffusion limited, and they can be speeded up by prior production of fine, well mixed particles. During the calcination initial powders heated below their melting point, decompose and react to form ternaries such as $\text{CaCO}_3+\text{MnO} \rightarrow \text{CO}_2+\text{CaMnO}$. In sintering, the grains in adjacent particles react and bond. Therefore, surface contact between particles is maximized by pressing the powders before sintering. Repeated grinding, mixing and re-heating are needed so as to form single-phase lanthanum manganite oxides. In the case of the citrate-gel route the decomposition and reaction of initial powders may already appear during pyrolysis.

The final tablets are hard ceramics. Carbon contamination can derive from many sources such as incomplete decomposition of carbonate starting powders, incomplete combustion of organics used as solvents, precursors in sol-gel technique or from gaseous CO$_2$ retained in intergranular spaces. The gas is released during PLD. Contamination could derive from solvents used in mixing initial powders or from wear of the milling
and grinding media which then go into the final solution or forms second phases, usually intergranular.

Before the four-contact dc resistivity measurement the ceramic pellets were cut into rectangular shape and four golden strip contacts were evaporated onto the flat surface of the samples. Then platinum wires were soldered onto the evaporated contacts by use of indium solder. When passing a current of known magnitude the dc resistivity is determined by the voltage drop across the sample inner voltage terminals. Magnetoresistance was measured in a 50 kG magnetic field.

Powder x-ray diffraction was used to check the phase purity and structure of the target material. Our ceramic targets' structure is assigned to the cubic cell. The x-ray diffraction patterns were recorded using CuKα radiation by Guinier-Haag film camera and by the standard rotating detector diffractometer. Energy dispersive x-ray diffraction revealed the desired representation of La and Mn.

The crystal structure depends not only on the Ca doping level but also on the oxygen stoichiometry. The degree of variation in oxygen content is not known.

3.2 Pulsed laser deposition of La$_{2/3}$Ca$_{1/3}$MnO$_3$ thin films

Manganite thin films were grown by the pulsed laser deposition (PLD) method similar to that for high-temperature superconductors. An excimer laser operates at 308 nm (XeCl) with a variable pulse duration and repetition rate with the energy fluence about 0.2 J/cm$^2$. The pulse width used was 5 ms with 0.6 s repetition rate. In the case of YBCO, films ablated at shorter laser wavelengths and low laser fluence were observed to be smoother [25]. Deposition with such a low power is possible only because the instantaneous power density is high. In order to maintain the laser power constant the laser was regularly evacuated, flushed and cleaned by He gas (55 psi) and refilled once
every two weeks or after 50000 pulses.

The laser beam is reflected by 45° mirror through a quartz lens and window on the target in a high-vacuum chamber (Fig. 3.1). Pulses of a laser beam generate a plume of ejected particulates (clusters of atoms and ions) perpendicular to the target surface regardless of the angle of incidence. By modification of the equipment geometry the angle of incidence of the laser beam on the target is 16° and the target to substrate axis is 25° off vertical. This can eliminate micro-sized particulate density on the substrate, because the heavy particulates with smaller velocity component perpendicular to the main flow tend to concentrate in the central region of the plume [24].

One surface of each substrate was polished using an automatic polisher in a clean dustless environment. The substrate was first ground with 600 grit sandpaper, and then polished with 6 micron and 1 micron diamond aerosol spray with intermediate cleaning in an ultrasound bath of water and soap. Eventually the substrate was polished with 0.05 micron alumina particles suspended in distilled water and washed in an ultrasound bath of distilled water. It was subsequently cleansed in acetone and flushed by argon gas the substrate was placed into the PLD chamber.

The MgO (100) or SrTiO₃ (100) substrate is placed on a (stainless steel) holder-heater facing the target at a distance of 3.8 cm. Target was first glued to the brass holder by silver epoxy DYNALOY™ and dried for 1 hour above 100°C. The target is rotated with the target holder during the deposition to obtain uniform surface removal and to minimize the density of heavy particles. Oxygen pressure was maintained at 300 mTorr. Deposition substrate temperature (Tₛ) varied in the range from 650°C to 900°C. The deposited film was postannealed at 900°C for 1h at about 950 mbar O₂ and cooled down to room temperature. The substrate temperature is very important not only for the film’s structural perfection but also for the preservation of the stoichiometry of the complex oxides.
Figure 3.1: Schematic drawing of the PLD system. Legend: A—roughing/backing pump; B—turbomolecular pump with a throttle valve; C—vacuum valves; D—mirror; E—lens; F—quartz window in vacuum chamber; G—vacuum gauge; H—spinning target fastened to target holder on target changer assembly; J—plume of particles ablated from target; K—oxygen gas inlet; L—quartz thickness monitor; M—driving motor for target spinning; N—substrate holder in the heater, fixed on ceramic rod; O—spiral of resistive heating element; P—thermocouple; R—variable leak valve for fine adjustment of O₂ partial pressure; S—substrate on the holder
Chapter 3. Experimental Methods

Research on various materials has shown that there is a critical substrate temperature, \( T^* \), below which the structure of the films is not completely monocrystalline and the film composition deviates significantly from the desired stoichiometry [35]. By increasing the substrate temperature above \( T^* \), the cooling rate increases and subsequently the rate of crystalization increases together with the mean \( adatom \) (deposited atom) diffusion distance. The increasing structural perfection of the deposited film is characterized by lower carrier concentrations and higher mobilities (PbSe [24], see p.262). In case of LCMO the resistivity decreases with the film perfection [38]. Decreasing the deposition rate (target-substrate distance, laser-pulse energy) has the similar effect as the increase in \( T_s \).

The background gas (O\(_2\)) plays an important role in producing the atomic and molecular precursors required for the growth of the compound phase. It helps to form and stabilize the desired crystal phase of oxide films at the deposition temperature. The O\(_2\) gas interacts with the ablated material and undergoes photon and electron-impact dissociation during the ablation process, especially near the target by producing highly active atomic oxygen ([24], see p.267). Contrary to high-\( T_c \) superconducting cuprates, for lanthanum manganites to get results similar to those for a single crystal one needs to post-anneal films in an oxygen atmosphere at higher temperature. Apparently the most volatile element in the molecule during growth is oxygen. High temperatures increase adatom surface mobility. Then enhanced nucleation and annealing of defects during growth result in improvements in film-surface morphology.

3.3 Characterization of films

The film preparation conditions are later summarized together with their properties in Table 4.3. The film thickness was measured by the fringe shift in the standard multibeam
interference method observed on the edge of the film patterned by chemical lithography. The fringe pattern is governed by the relation \( d = m \frac{\lambda}{2} \), where \( \lambda \) is the wavelength of monochromatic light, \( m \) the relative shift fringes and \( d \) is the thickness of the film (height of the edge). In order to get this step we coated the surface of the film sample with resist solution. Then the film was masked and exposed to UV light. Developer removed resist from all the exposed area. When immersed into HCl acid the film from the exposed area dissolved, leaving a sharp enough film step on the substrate.

Electrical resistivity was measured by the standard four-contacts method. Before the measurement four parallel strips of gold layer were evaporated on the film. Then four gold wires were attached to the strips by use of indium solder in order to achieve ohmic contacts.

The sample was connected to the probe and all put into the liquid nitrogen dewar. Usually all the measurements were performed during warming up after fast cooling to \( \approx 80 \text{ K} \). Measurements at lower temperatures were performed by immersing the probe into the Helium dewar or by the automatic Quantum Design Magnetic Property Measurement System (MPMS).

The MPMS system consists of a Helium dewar with a superconducting magnet, SQUID detection system and probe assembly connected to control systems. Automatic control and data acquisition are provided by a PC computer and subsystem controllers for the high-performance control of gas, temperature, magnetic field and sample transport. The modular design of the system allows the probe to be refit for various types of measurement. The electrical resistivity and magnetoresistance were measured as a function of temperature between 4.3 K and 300 K using 10 – 100 \( \mu \text{A} \) sample current. The Resistivity versus magnetic field measurements were performed for fields up to 50 kG at several temperature points (10 K, 77 K, \( T_c \), 300 K).

Magnetization measurements were performed in the same temperature range using
a conventional dc SQUID magnetometer in an applied field of 0.01 T. The sample is moved through the magnet while signals detected in the second-derivative (wound in opposition) coils are coupled into the SQUID sensor through a superconducting insulation transformer. The output voltage of the SQUID detector as a function of position is used to compute automatically the magnetic moment of the sample by regression methods.

To measure magnetoresistance of thin films van der Pauw technique [36] was used as well. The rectangular film on the substrate was contacted on the four corners A,B,C,D using indium solder and thin gold wire. Van der Pauw has shown that the resistivity could be determined using the relation: 
\[ \exp(-\pi R_{AB,DC} \frac{d}{\rho}) + \exp(-\pi R_{BC,AD} \frac{d}{\rho}) = 1 \]
where \( \rho \) is the specific resistivity of the material and \( d \) is the thickness of the sample. The resistance \( R_{AB,DC} \) can be defined as the ratio of potential difference between D and C point contacts and the current through the A and B contacts. Analogically we define the resistances \( R_{BC,AD} \) and \( R_{BD,AC} \).

Some of the samples were made using PLD and their resistivity and magnetization measurements were performed in Max-Planck Institut, Stuttgart. The characterization and properties of the samples are reviewed in Table 4.3.

### 3.4 Measurement under external pressure

Pressure effects were measured by increasing pressure up to 1.5 GPa using a self-clamping type pressure cell (Fig. 3.3). Pushing force applied to the cell at room temperature by a conventional press was transmitted to the sample region by a tungsten-carbide push rod and then locked in by tightening a copper-beryllium bolt. The sample is placed in a high pressure region inside the nylon cup filled with with a 1:1 2-Methylbutane 3-Methyl - 1 - butanol ratio or kerosene as a pressure transmitting medium.

The pressure was determined at room temperature using the pressure dependence
of the resistance of lead as an internal pressure manometer (Fig. 3.2). Using the four-point resistivity technique to achieve good contacts the lead strip was spot-welded to four copper leads. The nylon cup is sealed at one end by a hardened steel piston through which electrical leads (4 for lead, 4 for sample) were brought out of the high pressure region using STYCAST™ epoxy sealant. In order to eliminate thermoelectric effects the reading was performed for positive and negative (switched) current direction and averaged.

The pressure cell was placed inside a 3-volume cryostat. First the outer dewar of a cryostat was evacuated. The middle dewar was filled with liquid nitrogen and a small amount of nitrogen was transferred into the inner dewar in order to increase the cooling rate. When the temperature reached about 90 K the liquid helium was slowly transferred into the inner volume until the cell was cooled down to the temperature of 4.3 K. The measurements of resistivity were taken during slow spontaneous warming up.

As temperature decreases, there is always a pressure reduction due to the thermal

---

Figure 3.2: Detail of the sample attachment in the pressure cell. Legend: 1–sample with evaporated four gold strips for four-point measurement; 2–lead strip, four-point technique; 3–piston; 4–nylon cup; 5–electrical Cu leads sealed in STYCAST™ through the piston
Figure 3.3: Schematic drawing of the pressure cell. Legend: 1–W-C push rod; 2–Be-Cu pressure-clamping bolt; 3–Be-Cu springs; 4–Be-Cu cell body; 5–W-C piston; 6–antiextrusion ring; 7–nylon cup (sample space: 20 mm long, 7 mm inside diameter); 8–hardened steel piston; 9–Cu leads for data acquisition; 10–thermometer
contraction of the pressure medium. In a wide temperature range one has to take into account this drawback. The pressure determined at room temperature decreases reversibly in going from room to liquid-nitrogen temperatures with a nearly constant drop of value $\Delta p \approx 0.3$ GPa independent of the exact cell construction. To remedy this problem, the temperature dependence of pressure was determined using the calibrated pressure dependence of the normalized resistance of the lead strip. Then, from the grid of temperature, pressure, and resistivity points the curves of constant pressure were acquired. Deviations in the pressure data are about $\pm 0.03$ GPa.
Chapter 4

Results and Discussion

4.1 Polycrystalline samples

Ceramic samples were prepared under different conditions as viewed in Table 3.1. Some of the physical properties are shown in Table 4.1. The ceramic sample consists of small monocrystallites, grains. Their mean size can be estimated by Scherrer formula [34]

\[ b = 0.9\lambda / \Delta(2\theta)\cos\theta \]

where \( \Delta(2\theta) \) is the width of the x-ray diffraction peak at half of its maximum intensity (the sharpness of the peak). The results are shown in the second column of the Table 4.1. All ceramic samples were pressed into hard pellets with resulting density 80-85% of theoretical value.

Sample C1 was prepared very first. As seen in Figure 4.1, the resistance dependence exhibits a very sharp increase at low temperature and then a local minimum at 34.5 K. The peak resistance is very high in comparison to the room temperature value of 3.6 Ωm. The transition Curie temperature \( T_c \), determined as the temperature at 5% change of M when magnetization abruptly increases, is much higher than the peak of

<table>
<thead>
<tr>
<th>set</th>
<th>mean grain size (nm)</th>
<th>( T_c ) (K)</th>
<th>( T_{MI} ) (K)</th>
<th>( \rho_{max} ) (Ωcm)</th>
<th>( \rho_{5K} ) (Ωcm)</th>
<th>( T^{ST}_{MI} ) (K)</th>
<th>( \rho^{ST}_{max} ) (Ωcm)</th>
<th>MR(^{ST}_{max} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>42</td>
<td>188.6</td>
<td>50.8</td>
<td>142000</td>
<td>190000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>33</td>
<td>202.7</td>
<td>3.3</td>
<td>0.19</td>
<td>226</td>
<td>0.77</td>
<td>386</td>
<td></td>
</tr>
<tr>
<td>SG</td>
<td>52</td>
<td>267</td>
<td>220.8</td>
<td>2.5</td>
<td>0.75</td>
<td>222</td>
<td>1.5</td>
<td>81</td>
</tr>
</tbody>
</table>
resistance $T_{MI}$. The magnetization saturation occurs below $T_{MI}$. It signifies a strong contribution of inhomogeneities in the fully established ferromagnetic state. Data were obtained using four indium contacts made directly on the clean surface of the sample and passing 1 $\mu$A sample current. The inset shows the result of resistance measurement of the same sample using evaporated gold contacts and indium solder with sample current 10 mA. This measurement was performed a year before the measurement in the main body of Fig. 4.1. Clearly, because of power dissipation, the lower current is more appropriate in case of such high resistivities and the recent measurement gives more reliable results. In addition, there might be a possible change in electrical properties of LCMO when it is exposed to humid air, due to the rare-earth oxides sensitivity to moisture. To our

Figure 4.1: Resistance (•) of La$_{2/3}$Ca$_{1/3}$MnO$_3$ (C1) in zero field. Solid line is a fit through $R(T)$ data. Magnetization (○) was measured at 200 Gauss. Inset shows $R(T)$ of the same sample using 10mA sampling current.
knowledge, there were no reports on time instability of properties in LCMO.

Figure 4.2 shows colossal magnetoresistance \( \log \rho(H) \) of the C1 sample at 10 K when cooled from room temperature at a zero magnetic field. Prior to measurement the remnant magnetic field was removed by cycling the magnetic field with decreasing amplitude of \( H \) to zero. First, there is a large decrease of resistance with increasing magnetic field. Then, as the magnetic field is reduced to zero value and increased in the opposite direction the magnetoresistance has only a small hysteresis. The anomalous hysteretic behavior between the unmagnetized and magnetized states could be a consequence of the strong connection of magnetotransport with magnetization [48]. It may be caused by a spin-glass state at the low temperature with localized carriers in the unmagnetized state. Similar behavior was observed in spin glass perovskite \( \text{La}_{0.66}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3 \)
[49]. In our case most likely oil contaminants from "air" flow or chemical reactions with the Al₂O₃ crucible could essentially affect the nominal stoichiometry. The presence of impurities and a lower oxygen content lead to decrease of $T_{MI}$, $T_c$ and increase of maximum resistivity.

Figure 4.3 shows magnetoresistance $R(H)/R(0)$ well above $T_{MI}$ at 190K. Again, there is hysteresis, but after one cycle resistance is 1.25 times higher due to positive MR. This behavior is not intrinsic to a LCMO system and can be the result of an inhomogeneous system.

The sample C2 was prepared from initial powders mixed in ethanol. This guaranteed homogeneity of the resulting material by improved mixing in a volatile medium. However, the carbon contaminants could be a major drawback. Therefore before the
first calcination the solution was dried and then heated slowly. Resistance vs. temperature dependence together with magnetoresistance as measured in zero and 50 kG magnetic fields is in Figure 4.4. The maximum of resistivity occurs at a sharp peak at

\[ T_{MI} = 203 \text{K} \]

which is shifted to higher temperature (226K) in the applied field. The shift of \( T_{MI} \) to higher values and decrease of resistance particularly around the maximum with increase of magnetic field is the basic characteristic inherent in LCMO [5].

Magnetoresistance (MR) is calculated from measured sets \( R(0G, T), R(50kG,T) \) as:

\[ MR(T) = (R(0, T) - R(H, T))/R(H, T). \]

The MR maximum (385\%) at temperature 200K is very close to the metal–insulator transition temperature. At low temperatures the MR is almost constant down to about 100\% at 5K. The magnitude and temperature dependence of MR are consistent with the literature [50]. Below 25K the resistivity shows

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**Figure 4.4:** Resistance at zero H (●), at 50kG (○) and MR (□) of the target C2.
upward rise up to 7%.

Figure 4.5 shows results of $R(H)/R_0$ ratio measured at three different temperatures. $R_0$ is an initial resistance value when the sample was unmagnetized in zero H. The magnetic field H was first increased ($H>0$), then decreased ($H<0$), and finally brought to $H=0$. When $T>T_c$, the normalized resistance $R(H)/R_0$ shows quadratic dependence on H. Just below $T_c$ and at low temperatures, the H dependence is different. Measured at 5K, it is divided near $\pm 2kG$ into two nearly linear regions with slopes $d(R(H)/R_0)/dH=-0.128kG^{-1}$ and $-0.0066kG^{-1}$. It was observed that the residual $\rho_{5K}$ almost linearly increases as a function of the reciprocal of grain size [38]. Therefore, polycrystalline samples of smaller
grain size (<1μm) exhibit high resistivity with a slow decrease and significant MR below $T_{MI}$, essentially independent of $T$. At low temperature $\rho$ is considerably influenced by scattering of charge carriers on grain boundaries. The $H$ dependence of normalized resistance is different at 5K and 190K.

As proposed in Ref.[38], at low temperature the conduction electrons have aligned neighboring spins through the DE mechanism inside the magnetic domains, which are defined by the grains. When traveling across grains, the electrons suffer strong spin-dependent scattering at the boundaries leading to a higher zero $H$ resistivity than for epitaxial films and monocrystals. First, the low-field substantial MR (steeper leg in Fig.4.5 at 5K) is due to parallel alignment of the domains in the lower magnetic field. Then as the field increases, the canted spins in disordered regions near the grain boundaries are aligned and magnetization increases slowly. Therefore, significant contribution to large MR in polycrystalline samples could emerge from extrinsic effects, tunable by the sample preparation process.

The results of thin film deposition using the C2 target are reviewed in section 4.2, page 50. The films characteristics are of lower quality compared with those prepared using the SG ceramic (target prepared by sol-gel method).

The magnetoresistance measurement of SG sample shows interesting results in Fig.4.6. With decreasing temperature the magnetoresistance has a steep onset around 265-270 K from negligible MR = 2% up to 67% and remains around that value down to 110K when a moderate increase to 81% is observed. The magnitude of MR is usually observed at minimum for polycrystalline LCMO and for this nominal composition ($x=0.33$) the magnetoresistive behavior is unusual. In an applied field there is an almost uniform, strong suppression of the magnitude of the resistivity below the transition. The temperature dependence of resistivity in a zero-field and a 50kG magnetic field below $T_{MI}$ is not typically metallic. The sample has higher resistivity about $0.4 \, \Omega cm$ over the entire
Figure 4.6: Resistivity and MR (□) of the SG sample. Resistivity (○) at 0kG, (●) at 50kG.
temperature range. Note the upward rise is about 5% below 20K.

The charge carriers cannot be described as classically free. High resistivity at low temperature refers to somehow localized carriers, e.g. by disorder, impurities, or by glassy-state. It has been suggested [27] that below $T_{MI}$ the possible existence of a heterogeneous electronic state within the single phase structure is analogous to the one found in similar mixed-valence systems. These effects could be results of intragrain spin-polarized tunneling as was observed in layered $La_{3-3x}Ca_{1+3x}Mn_3O_{10}$ through the insulating $Mn-O-O-Mn$ bond [37], which would suggest the presence of a layered phase. The high MR at low temperature could result also from spin-dependent scattering at the grain boundaries [51].

The upward slope of $\rho(T)$ and MR as temperature decreases ($T \ll T_c$) was observed in recent research [52] and attributed to the extrinsic effect of grain-boundary transport. However, further work is needed to determine the influence of different scattering mechanisms at temperatures below 5K and we cannot automatically assume that this is a result of the intrinsic electron-electron and electron-magnon or extrinsic intergrain scattering only. This phenomenon may originate from the Kondo effect as temperature approaches zero. A strong scattering of magnetic ions may occur when superexchange wins the competition. It should be noted, that, if the doping level deviates from $x = 0.33$, the $R(T)$ behavior could significantly deviate from the nominal one [53]. The results of our $\rho(T)$ and MR(T) are almost the same as those observed on $La_{0.7}Ca_{0.3}Mn_{0.95}Fe_{0.05}O_3$ [54]. But the resistivity of SG is lower in comparison to other ceramic samples and it is of the order of the resistivity for polycrystalline LCMO ($x \sim 0.3$).

In Fig.4.7 the magnetic moment $M$ measurement revealed the ferromagnetic transition at 267K, more than 40K higher than $T_{MI}$. The transition to the magnetically ordered state is quite abrupt over 10K which is characteristic of a homogeneous sample. In comparison to the narrow width of the slope at transition, the resistivity maximum has
Figure 4.7: Magnetic moment of the SG sample (ZFC).
a very broad peak, measured in zero and 50 kG magnetic field.

Magnetization vs. temperature shows a gradual increase approaching the low temperature (T < T_c) due to the small changes in the spin canting angle or domain motion.

Our magnetization measurement did not display a significant AF contribution and neither a spin-glass phase. There may not be complete saturation. Even in the FM phase the slight canting of the magnetic moments can affect the resistivity.

Because of the high T_c and lower resistivity we decided to use SG and C2 samples as targets for PLD.

To determine the crystallographic symmetry and unit cell parameters TREOR, a general trial-and-error autoindexing software for x-ray diffraction patterns, was used. Powder indexing works well on good data, but with poor data it did not work at all. A zero point error due to the instrument misalignment is much more serious than statistical errors of the same magnitude. A systematic error was observed in the x-ray diffraction patterns. The spectra show a uniform shift of the peak positions +1.5° in addition to the reading error ±0.025°. Therefore, the measurement of silica powder was used for calibration. Diffraction patterns measured by the x-ray film camera did not have this problem, but resolution ±0.1° is rather worse. In the Fig. 4.8 there is a typical powder diffraction pattern of La_{2/3}Ca_{1/3}MnO_3. The position and height of the peaks for our LCMO samples match well with those of the literature [50]. In Table 4.2 are the strongest lines of x-ray diffraction pattern for polycrystalline samples of SG and C2. All peaks can be assigned to the cubic perovskite structure with a lattice constant a = 0.3852 nm for SG, and a = 0.3851 nm for C2. Our estimated lattice constants are lower compared to a = 0.3863 nm reported for La_{0.67}Ca_{0.33}MnO_3 [51]. Typically, reported values vary from 0.385 to 0.389 nm. The structure is not perfectly cubic as seen on Fig.4.8. Peaks of higher indices are split because of tetragonal or rhombohedral distortions. Lines (120) and (100) are weak and most pronounced only for C1. Notice that the sample SG was annealed
Chapter 4. Results and Discussion

Figure 4.8: X-ray diffraction patterns of C1 and SG.

Table 4.2: X-ray powder diffraction lines ascribed to cubic perovskite

<table>
<thead>
<tr>
<th>h k l</th>
<th>110</th>
<th>111</th>
<th>200</th>
<th>211</th>
<th>220</th>
<th>310</th>
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<tr>
<td>SG</td>
<td>2θ obs.</td>
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<tr>
<td></td>
<td>32.8</td>
<td>40.5</td>
<td>47.15</td>
<td>58.65</td>
<td>68.9</td>
<td>78.47</td>
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<td></td>
<td>2θ calc.</td>
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<td></td>
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<tr>
<td></td>
<td>32.857</td>
<td>40.532</td>
<td>47.152</td>
<td>58.662</td>
<td>68.893</td>
<td>78.455</td>
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<td>C2</td>
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<td></td>
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<td>32.88</td>
<td>40.53</td>
<td>47.18</td>
<td>58.71</td>
<td>68.88</td>
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</tr>
<tr>
<td></td>
<td>32.863</td>
<td>40.540</td>
<td>47.161</td>
<td>58.674</td>
<td>68.907</td>
<td>78.472</td>
</tr>
</tbody>
</table>
only once, without repeated grinding and sintering as the other samples prepared by the conventional method to reach homogeneity. It was difficult to use indexing software for the C1 diffraction pattern, because of an undetermined zero point shift. However, we estimated the cubic perovskite lattice parameter $a = 0.382\text{nm}$. The lower value of the lattice parameter, and hence the smaller volume of a unit cell, means that the compound has higher content of smaller size Mn$^{4+}$ ions or missing O$^{2-}$ ions. The involved effective ionic radii of the 6-fold coordination in nanometers [55] are:

$$\begin{align*}
\text{O}^{2-} & : 0.138 \\
\text{Mn}^{4+} & : 0.053 \\
\text{Mn}^{3+} & : 0.0645 \\
\text{Ca}^{2+} & : 0.106 \\
\text{La}^{3+} & : 0.132
\end{align*}$$

4.2 Magnetoresistance, Magnetization and Resistivity of Thin Films

Most of the thin film samples were prepared by use of the SG target material. The choice followed from the optimal parameters of the SG sample (high $T_c$, low $\rho$). In Table 4.3 the properties of the thin films as they were fabricated in chronological order are listed. All the films were deposited on SrTiO$_3$ (100) substrate (except #13) and show a shiny black surface. Samples LCM29 — LCM28 (last 6 rows in Table 4.3) were made in the Max-Planck Institut, Germany using pulsed laser deposition with laser energy 300 mJ, at $\lambda = 230\text{nm}$, pulse frequency 5 Hz, target-substrate distance 40-41 mm, and partial oxygen pressure 0.5 mbar.

We found that optimum deposition conditions for our LCMO thin films are $T_S = 700 - 850^\circ\text{C}$, $P_{O_2} = 0.3 \text{Torr}$ and postannealing treatment at $900^\circ\text{C}$, at a partial pressure of 950 mbar O$_2$ for 1h. Films #4-13 were deposited by 5000 laser pulses except #12 was exposed to 25000 pulses. (See more results on #12 on page 67).

The film #13 was deposited on TiO$_2$ substrate. TiO$_2$ has orthorhombic structure $a = 0.5456$, $b = 0.9182$, $c = 0.3143\text{nm}$. After deposition, the white color substrate
Table 4.3: Preparation conditions and properties of La$_{2/3}$Ca$_{1/3}$MnO$_3$ thin films.

<table>
<thead>
<tr>
<th>film #</th>
<th>$T_S$ [°C]</th>
<th>Thickness [nm]</th>
<th>postannealing in $O_2$ [°C]</th>
<th>$T_{MI}$ [°C]</th>
<th>$\rho_{max}$ [mΩcm]</th>
<th>$\rho_{5K}$ [mΩcm]</th>
<th>$\rho_{80K}$ [mΩcm]</th>
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<tr>
<td>4</td>
<td>760</td>
<td>50-100±30</td>
<td>760</td>
<td>249</td>
<td>1160Ω</td>
<td>9.7</td>
<td>1.8Ω</td>
</tr>
<tr>
<td>5</td>
<td>760</td>
<td>450±50</td>
<td>-</td>
<td>188.5</td>
<td>587</td>
<td>3.8</td>
<td>0.7</td>
</tr>
<tr>
<td>6</td>
<td>760</td>
<td>300±50</td>
<td>900</td>
<td>247.2</td>
<td>67.7</td>
<td>0.49</td>
<td>0.7</td>
</tr>
<tr>
<td>7</td>
<td>570</td>
<td>240±30</td>
<td>900</td>
<td>268.3</td>
<td>19.3</td>
<td>8.4</td>
<td>3.8</td>
</tr>
<tr>
<td>8</td>
<td>625</td>
<td>370±30</td>
<td>900</td>
<td>265.2</td>
<td>27.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>705</td>
<td>400±30</td>
<td>900</td>
<td>275</td>
<td>12.88</td>
<td></td>
<td></td>
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<tr>
<td>10</td>
<td>840</td>
<td>150-240±30</td>
<td>900</td>
<td>276.3</td>
<td>14.1</td>
<td>0.26</td>
<td>0.37</td>
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<tr>
<td>11</td>
<td>900</td>
<td>270±15</td>
<td>815</td>
<td>260.1</td>
<td>15.5</td>
<td>0.16</td>
<td>0.23</td>
</tr>
<tr>
<td>12</td>
<td>800</td>
<td>1000-1600±300</td>
<td>780</td>
<td>275.1</td>
<td>280.9</td>
<td>11.4</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>750</td>
<td>250±15</td>
<td>900</td>
<td>205.8</td>
<td>23700</td>
<td>8600</td>
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<tr>
<td>LCM29</td>
<td>720</td>
<td>265±10</td>
<td>700</td>
<td>103.8</td>
<td>48700</td>
<td>1860</td>
<td>24250</td>
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<tr>
<td>LCM27</td>
<td>790</td>
<td>240</td>
<td>690</td>
<td>209.5</td>
<td>946</td>
<td>3.1</td>
<td>6.16</td>
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<td>RP3c</td>
<td>850</td>
<td>85</td>
<td>750</td>
<td>177</td>
<td>750</td>
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<td>RP4a</td>
<td>850</td>
<td>14</td>
<td>750</td>
<td>155</td>
<td>1120</td>
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<td>530</td>
<td>240</td>
<td>700</td>
<td>118.6</td>
<td>24.8</td>
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<tr>
<td>LCM28</td>
<td>630</td>
<td>270±20</td>
<td>700</td>
<td>214</td>
<td>77</td>
<td>0.11</td>
<td>0.19</td>
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</tbody>
</table>

changed its color to brown indicating strong interdiffusion or chemical reaction with film material or perhaps loss of oxygen. Three orders of magnitude change in resistivity was observed.

Films #6–10 were prepared systematically under the same conditions, only the substrate temperature $T_S$ was varied. As seen in Table 4.3 the thickness ($d$) of the films differs with variation in $T_S$ as shown in the Fig. 4.9. Because $T_{MI}$ and $R_{max}$ did not show any monotonic dependence on $T_S$, the thickness may be another important parameter. With further improvement in thickness monitoring during deposition, we can keep our films of nearly constant thickness $d$.

A sample of the electrical resistivities of a LCMO thin film as a function of temperature under different magnetic fields is shown in Fig.4.10, which is in good agreement with
Figure 4.9: Upper – Thickness vs. substrate temperature of the films #6–10. The dashed line is interpolated fitting curve. Lower – Monotonic dependence of $\rho_{\text{max}}(T_{MI})$ of the films #6–10. The fitted slope: $\partial \rho_{\text{max}}/\partial T_{MI} = -1.92 \, \text{m}\Omega \text{cm}K^{-1}$
results for La$_{0.67}$Ca$_{0.33}$MnO$_3$, based on sol-gel preparation [42]. A transition temperature $T_{MI} = 260.1\, K$ is just below the magnetic ordering temperature $T_c = 262\, K$. The temperature $T_c$ here was determined at the 5% change in magnetization on the slope of the paramagnetic to ferromagnetic phase transition. The $T_c$ is not well defined because short range ferromagnetic order can exist above $T_c$ continuously turning into long range magnetic order below $T_c$.

For film #5, $T_c = 245.7\, K$ is above $T_{MI} = 188.5\, K$. In the Figure 4.10, the MR ratio and $\rho$ are shown as a function of temperature. The peak MR ratio was about 400% around 245K for #11, above 800% at 175K for #5, 1200% at 195K for LCM27 and 4000% at 90K for LCM29. We note that the CMR effect is most pronounced near $T_{MI}$ and it nearly disappears completely as $T$ approaches zero (1.4% at 5K) only for film #11. Note, that the maximum of MR increases as it shifts to lower temperature.

In the magnetization measurement (Fig. 4.11) the samples were cooled to 5K in a zero field and the measurement was performed by warming the samples #11 and #5 in an applied magnetic field of 200 and 500 gauss, respectively. Both curves exhibit maxima at about 150K and 40K with a subsequent decrease of magnetization with decreasing temperature. This is not a typical behavior for a ferromagnet, one would expect sharp increase at $T_c$ and almost no temperature dependence below $T_c$. Similar observations (a drop in the ZFC magnetization) in Ref. [59] were attributed to the spin freezing (spin–glass) behavior, the result of frustration of the ferromagnetic clusters (grains) from competing superexchange (page 9) and DE interactions. However, it is possible that some parts of the sample are less rich in Ca causing the antiferromagnetic ordering in these parts and the drop in magnetization. To examine this picture, a complementary field cooling (FC) magnetization measurement is necessary. The broad transition for nonannealed sample #5 indicates less homogeneity of the magnetic structure than for #11.
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Figure 4.10: Resistance at zero $H$ (•), at 50 kG (○) and MR (□) of the films #11 and #5.
Figure 4.11: Magnetization of the films #5 (○) and #11 (●). The arrows indicate $T_c$. Approximate mass of the films #5 and #11 are $3.5 \times 10^{-5}$ g and $3.6 \times 10^{-5}$ g, respectively.
Figure 4.12 shows normalized resistance $R(H)/R(H=0)$ vs applied field at different temperatures for film #11 with $T_{MI} = 260K$. The applied magnetic field $H$ is perpendicular to the surface of the film. After zero field cooling to 5K the magnetic field was increased to 50kG and brought back to zero, then the sample temperature was increased to 100, 225 and 300K and the resistance measured by the same tracing of the magnetic field. Since we did not perform demagnetization or quenching of the superconducting magnet, some remnant magnetic field could be present and affect low field results. This may be the reason for positive MR (1.5%) in the measurement at 100 K after increasing and decreasing magnetic field of 50 kG.

Figure 4.13 shows the same measurement on the film #5 with magnetic field in the plane of the film. At low temperature sample #11 shows a slow linear decrease with the applied field, whereas film #5’s behavior is nonlinear and hysteretic at 5K. As observed in polycrystalline samples (Sec. 4.1), at higher temperatures just below and above the peak in $R(H)$, the resistivity is a strong function of the applied field. Above $T_{MI}$ the $R(H)$ dependence exhibits sublinear and below $T_{MI}$ superlinear behavior. Near the Curie temperature in the ferromagnetic region it is easier for the magnetic field to align Mn ion spins and conduction electrons can hop between Mn sites of parallel spins according to the DE mechanism. This gives rise to higher MR just below $T_{MI}$.

The temperature dependence of normalized resistivity $R(T)/R_{max}$ at zero field of LCMO films #5 and #6 is shown in Fig. 4.14.

The annealed film (#6) exhibits a resistivity peak of 0.068 $\Omega cm$ at 247 K, whereas the as-deposited one (#5) 0.59 $\Omega cm$ at 189 K. Most likely, the postannealing process shifts the resistivity maximum to higher temperatures and lowers its magnitude significantly. In Ref.[57], the authors observed that the oxygen stoichiometry changed from 3.03 to 2.99 as the substrate temperature was varied from 500 to 900°C. Then the oxygen content increased when the films were annealed at 900°C in O$_2$. The excess or depletion of O$_2$
Figure 4.12: $R(H)$ dependence of the film #11 at various temperatures.
Figure 4.13: R(H) dependence of the film #5 at various temperatures.
alters the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio, because an increase in oxygen content leads to the formation of $\text{Mn}^{4+}$ ions. Then an increase in the carrier concentration leads to the reduction of resistivity and to the upward shift in the ferromagnetic transition temperature $T_c$.

Almost monocrystalline epitaxial films usually have a magnitude of resistivity of the order of $10^{-4} \, \Omega \text{cm}$. Our last films #9,10,11 have $\rho_{5K}$ values of the same order suggesting epitaxiality. In comparison to polycrystalline samples, films exhibit sharp drop in $\rho$ at lower temperatures, where $\rho$ can be more influenced by the presence of grain boundaries, scattering regions for conduction electrons [38].

Films #(7–11) were measured in a van der Pauw configuration. The van der Pauw technique works well if a) the contacts are at the circumference of the sample, b) the contacts are sufficiently small, c) the sample is homogeneous in thickness, and d) the

Figure 4.14: Comparison of postannealed (900°C) (•) and as-deposited (○) films #5 and #6 deposited at 760°C.
surface of the sample is singly connected, i.e. the sample does not have isolated holes. An example, where the last requirement is not fulfilled, is shown in Fig. 4.15. The film #7 had a few small holes etched by the acid when it was prepared for thickness measurement. It is a result of dust particles being deposited on the film surface before or during the resist etching process. The second major problem was inhomogeneity in thickness up to ±40% observed in films #4, #10 and #12.

The first attempts to make LCMO films are characterized by low values of $T_{MI} < 100$K and very high peak resistance of the order of $10^6 \Omega$. Examples are shown in Fig. 4.16. Both films #1 and #3 were deposited at 4.5 cm target-substrate distance, using target material C2 and at substrate temperature 850°C and 800°C respectively. The film #3

![Graph showing temperature vs. resistance and p/d](image)

**Figure 4.15:** Problems in van der Pauw measurement. Resistance $R_{AB,DC}$ (•) and $R_{BC,AD}$ (○) shows asymmetry of measurement, result due to inhomogeneity and holes in the film.
Figure 4.16: $R(T)$ of LCMO films at zero field deposited from C2. Film #1 (○) on MgO and film #3 (●) on SrTiO$_3$ substrate.
was postannealed 15 min at 800°C. While depositing #1, the substrate temperature accidentally dropped to 770°C after half of deposition time. Film #1 was especially thin and transparent. The shiny surface of the first test films indicated that we were close to the conditions necessary for the production of good films. It was suggested [56], that the maximum of resistance in thin films is function of thickness. Resistivity increases with decrease of peak temperature. The thinner film RP4a has the lower value of $T_{MI}$ than the film RP3c. This applies for thickness below 100 nm. We did not observe this behavior in our films #4-13 grown at different $T_5$. Other films were deposited only from the SG target with the properties shown in the tables and graphs above.

High-quality lanthanum manganite thin films should have properties approaching those measured in single crystals [63, 38]. Some differences might occur due to the mesoscopic and two-dimensional effects. The composition (oxygen stoichiometry) of the compound formed during pulsed laser deposition depends on partial oxygen pressures [24]. One of the most important considerations in fabrication of good films is the choice of substrate material. Substrate and film should match lattice parameters, be chemically compatible (Cf. film #13, p.40), match coefficients of thermal expansion, have high dielectric constant, and show no phase transitions in temperature range from annealing or deposition temperature down to the minimum temperature used in measurements. The mismatch of lattice parameters leads to strain in the film and subsequently to cracks and defects. Pinholes, surface roughness and other defects are usually observed. Depending on the sizes of the defects they can affect electrical and magnetic properties.

The crystallographic order of the film can be significantly influenced by the substrate if there is some degree of matching between them along the interface. The surfaces and interfaces have an excess energy per unit area, $\gamma$, because any interruption of crystal symmetry increases potential energy $E_p$ [33]. During deposition of a film on a single-crystal substrate it is energetically favorable to merge the symmetries of the two crystals,
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and to match the substrate's bonding symmetry and periodicity. This alignment of the film is *epitaxy* or *epitaxial growth*. The interfacial energy, $\gamma$, is minimized by maximizing the density of bonds of appropriate length and angle across the interface.

Therefore, most of our films were deposited on SrTiO$_3$ cubic (perovskite) substrates $a=0.39\text{nm}$ with the dielectric constant $\varepsilon > 1000$, thermal expansion coefficient $\alpha = 10\text{ppm}$, and thermal conductivity $k = 0.06\text{ W/cm.K}$ at $700^\circ$. Films grown on MgO of cubic (NaCl) structure $a=0.4213\text{nm}$ showed poor results (e.g. #1).

The films LCM29 and LCM27 were studied more systematically. Some of data were measured in both perpendicular and parallel configuration of the applied field and film surface orientation. To our knowledge there is one reference [62] which claims that the low-field MR ($H < 300G$) is dependent on the angle between the magnetic field and the current. At higher fields MR is assumed and claimed to be isotropic [63, 5, 11]. In thin films this effect may not be accurate. In our measurements of LCM29 an LCM27 we used only a parallel orientation of the magnetic field and current in the in-plane configuration.

Figure 4.17 displays temperature dependences of $\rho$ at different H. The temperature of the resistance peak $T_{MI}$ is driven to a higher value with increasing H especially for LCM27. Notice an increase of resistance as the $T_{MI}$ is lower for LCM29.

The MR curve calculated from $\rho(H = 0, T), \rho(H = 50kG, T)$ shows the CMR effect (Fig 4.18) most pronounced at temperatures near $T_{MI}$. The low temperature deviation of MR for LCM29 in perpendicular position to the field implies some anisotropic effects or spin scattering on grain boundaries.

The Curie temperature was determined from magnetization measurement (Fig. 4.18, 4.19). As for ceramic samples (Sec. 4.1), the ferromagnetic–paramagnetic transition seen in the magnetization measurement was very broad, different $T_c$ for film LCM27 occurred with parallel and perpendicular applied field.

Figure 4.20 shows the $R(T)$ dependence for sample LCM29 which was first cooled to
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Figure 4.17: R(T) dependence of LCMO films LCM29 and LCM27 in various magnetic fields. The magnetic field direction is in the plane of the film surface.
Figure 4.18: Magnetoresistance MR(T) of LCMO film LCM29 at 50kG field perpendicular (○) and in-plane (●) of the film is shown together with (perpendicular) magnetization M(T) (□). The lower figure shows magnetoresistance of LCMO film LCM27.
Figure 4.19: Magnetization of LCMO film LCM27 in perpendicular (○) and parallel (●) orientation to the magnetic field. Mass of the film is $1.3 \times 10^{-8}$ g.
5K in zero field and measurement was taken during warming up at 20 kilogauss. Then the sample was cooled to 5K in the same field and measured again. The low tempera-

ture deviation may indicate superexchange overcoming DE interaction. However, the magnetization measurement does not show a significant transition from FM state at this region. The magnetization M was measured when the film was perpendicular to the field and it might not be saturated. The same measurement was taken on LCM27 and no visible temperature hysteresis was observed.

We have measured resistance as a function of H at various temperatures. The results of normalized resistance R(H)/R(H=0) are shown in Fig. 4.21. The measurement was taken at two different positions: the magnetic field direction in plane of the film (parallel
Figure 4.21: \( R(H) \) dependence of LCMO film LCM29 when \( H \perp surface \) (a), (c), and \( H \parallel current \) (b), (d).
to the current), and the field perpendicular to the film surface. The results are similar to those of #5 and #11. The R(H) curves below $T_{MI}$ show cusp-like behavior across H=0G. The same set of measurements was performed on LCM27 with results in Fig. 4.22. Particularly below $T_{MI}$ the R(H) behavior is different for LCM29 and LCM27. The latter sample exhibits small positive MR up to 10kG below 90 K and then turns to negative MR at higher field perpendicular to the film. This can be the effect of a remnant magnetic field as already mentioned (see p.46) and an anisotropic magnetoresistance effect [62] on the orientation of the magnetization from its zero-field orientation in the plane of the film to perpendicular to the film.

Figures 4.24 (upper panel) and 4.25 show the magnetic hysteresis curves at 20, 150 and 280 K for LCM27 thin film. The large difference between the parallel and the perpendicular orientation of the field and film surface typically comes from anisotropy effects and superposition of FM and AF components, resulting in a canted spin state. The magnitude of M is determined by the spin canting angle and the increase of M is due to field induced change of the spin canting angle.

We estimated the demagnetization factor contribution to the change to be about 10% of M. X-ray data are not available for this sample. Most likely the film is oriented as the other films from the same supply. This means, the axis of easy magnetization lies in the plane of the film. If the film is oriented with c-direction normal to the surface, the planes of ferromagnetic ordering $a-b$ are parallel to the substrate and it is easier for spins to be aligned along the $a-b$ plane. Indeed, our results support this picture. Particularly for the end-point compound LaMnO$_3$ the $a-b$ plane has ferromagnetic ordering and antiferromagnetic coupling is along the $c$ direction. Our material ($x \sim 0.3$) contains quasiferromagnetic order with slight canting of the magnetic moment along $c$. This suggests the film LCM27 to be (100) c-oriented.

Figure 4.24 (lower panel) shows the correlation between resistivity and magnetization
Figure 4.22: R(H) dependence of LCMO film # LCM27 when $H \perp surface$ (a), (c) and $H \parallel current$ (b), (d).
Figure 4.23: M(H) dependence of the film LCM29 at 20 K. Inset shows M(H) dependence at 150 K. Mag. field parallel (o) and perpendicular (●) to the film surface. Mass of the film is approximately $1.4 \times 10^{-5}$ g.
Figure 4.24: Magnetization of LCMO film LCM27 at 20 K (upper panel). The magnetic field direction is parallel (o) and perpendicular (●) to the film surface. Lower panel shows M(H) ($H \perp surface$) together with $R(H)/R_0$ at 20K.
Figure 4.25: Magnetization of LCM27 at 150 K (upper panel) and 280 K (lower panel). The magnetic field direction is parallel (o) and perpendicular (●) to the film surface.
as functions of the magnetic field in perpendicular orientation to the surface at 20 K. In parallel orientation, typical $H_c$ was about 370 G for LCM29 and 65 G for LCM27. A distortion of the hysteresis loop (Fig. 4.25, lower panel) is due to demagnetization or uniaxial anisotropy effects.

Film LCM29 in Fig. 4.23 does not indicate significant changes between parallel and perpendicular orientations of the applied field. This would suggest a lower AF contribution and nontextured structure. Resistivity $\rho$ two orders of magnitude higher than for LCM27 further endorses this view. (The abrupt change in the body of the Figure seems to be the result of a flux jump in SQUID.)

For all films, low T resistivity slightly increases with decreasing temperature. This may be due to the presence of an AFM phase which competes with the FM phase in this region. Whether the $e_g$ electrons are mobile or localized depends on the local spin orientation. If the local spins are ferromagnetically aligned, the $e_g$ electron will be mobile, kinetic energy and resistivity are reduced effectively by DE. In antiferromagnetic regions the strong intra–atomic exchange of local spins would not allow the electron to transfer, resulting in a charge localization. The transport properties are very sensitive to the type and change of magnetic structure. (See the note on the upward slope of $\rho$ for SG ceramic, page 36.)

### 4.3 X–ray measurement

If the film is not polycrystalline but preferentially oriented we can measure the degree of preferential orientation by measuring the x-ray $2\theta$ scan. From the values of $2\theta$ and the Bragg condition we can calculate $a$, the periodicity of the atomic plane parallel to the film surface. The intensity of the peak increases with the degree of texturing, the number of crystallites with atomic planes parallel to the surface. If the grains in the film
are smaller then the film thickness their size can be estimated by the Scherrer formula (page 28).

An x-ray diffraction pattern of the film #10 grown on SrTiO$_3$ (100) substrate at 840°C is shown in Fig. 4.26. The strong (200) and (300) lines indicate the (100) oriented growth of LCMO film on the SrTiO$_3$ substrate.

Figure 4.26: X-ray diffraction pattern of a 200 nm thick LCMO film #10 (LCM) grown on SrTiO$_3$ (STO) at 840°C.

Figure 4.27 shows detail of the $2\theta$ scan in the vicinity of the peak (200) for the three samples. The presence of CuK$_{\alpha 2}$ radiation was not observed. The peaks are indexed on the pseudocubic cell. The diffraction peak widths for LCMO film were of the same order as substrate peak width. It means that the film is of good quality. Figure 4.28 shows detail around peak (300) for film #10. The fringes just the above peaks (300) and (200) may indicate a smooth film. The number of fringes indicates the smoothness of a film [66].

The full width at half the maximum intensity of the (300) peak of #10 film was about 0.14°. It is important to note, that the Sherrer formula can be used to estimate the particle size of very small crystals ($< 100$ nm). Notice, that the line width for SrTiO$_3$ substrate does not correspond to the crystal of at least 0.1 mm. In any real diffraction experiment the incident rays are not perfectly parallel and in a beam of x-rays
Figure 4.27: Details of X-ray diffraction peak (200) of LCMO films grown on (100) SrTiO$_3$.

Figure 4.28: Detail of X-ray diffraction peak (300) of LCMO film #10.
divergent and convergent rays occur. These contribute to the width of the diffraction line [34] together with an instrumental broadening. The strong CuK\(_a\) component is superimposed on the continuous spectrum and it itself has a width of about 10\(^{-4}\) nm, leading to an increase in line width up to 0.08°. Another source of peak broadening may be a mosaic structure, crystal imperfection when the lattice is broken up into a number of slightly misoriented small blocks. The small angle of misorientation appears in the line width. Most likely in our case the broad lines may have been produced by nonuniform strain in the film and small crystallites perfectly aligned on the substrate. Similar results were obtained on high quality LCMO [66] and YBCO perovskite films [65].

The lattice mismatch is about 1.2% for films #5,10,11 and 2% for film #12. The lattice constant was estimated for the pseudocubic perovskite unit cell 0.3859 nm, 0.3860 nm, 0.3858 nm and 0.383 nm for films #5,10,11,12 respectively. The values are higher then for polycrystalline targets (a= 3.85 Å) due to the deformation induced by SrTiO\(_3\) substrate with lattice constant a= 3.905 Å or due to the oxygen stoichiometry closer to the nominal one. Of course the crystal structure is not perfectly cubic. It can be distorted, stretched in the \(ab\) plane and our lattice parameters are mere estimates. Obviously, the crystallographic order of our films was significantly influenced by the substrate with some degree of matching along the interface (see page 53) [33].

The splitting of the line (111) around 41° for #10 can be due to tetragonal or orthorhombic splitting of the strained film structure (Fig. 4.26). Only a single line was observed for #5 at that region. Since the film #5 was not postannealed, the oxygen pressure and post–deposition heating treatment may be important for epitaxial growth.

The lower value of the lattice parameter of #12 is an exception. The diffraction pattern of film #12 contained weak lines of (110), (211) and (311) indicating a perovskite–type structure with some disorientation from (100) orientation dictated by the SrTiO\(_3\) substrate. These peaks were not observed in the other films we measured. Most likely,
1 \mu m thick film #12 was not grown epitaxially.

As thickness increases the preferred orientation of film growth may deteriorate to polycrystalline growth. An order of magnitude higher $\rho$ confirms our suggestion. Dependent on substrate temperature $T_S$ there might be a critical thickness for epitaxy, $h_e$, above which the film collapses into an amorphous phase as was recently found in Si grown by MBE ($\ln h_e \propto 1/T_S$) [26]. Most likely it is induced by the increasing roughness of the substrate and initiated by the thermally activated process. Visible to the naked eye, the distinct regions of various thickness and shade of black color have formed, reminiscent of a liquid surface. Our x-ray profile shows diffraction crystalline lines and we did not observe a significant broad maximum of amorphous phase.

4.4 Pressure Results

In Figure 4.29 we present an example of resistivity data from the film sample RP3c. All samples exhibit the same qualitative behavior with different parameters given in Table 4.4. The temperature $T_{MI}$ of the maximum in $\rho(T)$ is very close to $T_c$. As it has been reported previously [58], $T_{MI}$ is higher for samples (RP3c, RP4a), deposited at higher substrate temperatures. Applied pressure depresses the peak resistance, and $T_{MI}$ monotonically increases for all samples (Fig. 4.30) with $\partial T_{MI}/\partial P$ given in Table 4.4. The observed values are significantly larger than those for conventional ferromagnets such as Ni ($\partial T_c/\partial P = 3.2 K/GPa$), Co, Fe ($\partial T_c/\partial P = 0$) [67].

The $T_{MI}(P)$ dependence observed is linear without saturation up to measured 1.4 GPa. The decrease of resistivity across the whole temperature range measured with increasing pressure is qualitatively similar to the effect of an applied magnetic field Fig. 4.17,[68]. However, with applied pressure, the onset of the resistivity drop shifts to higher temperatures.
Figure 4.29: RP3c R(T,P); Temperature dependence of resistivity $\rho(T)$ under various pressures for sample RP3c.

Table 4.4: Properties of $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ thin films under pressure.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{MI}$ (K)</th>
<th>$\partial T_{MI}/\partial P$ (K/GPa)</th>
<th>$\rho(280K,0Pa)$ (m$\Omega$cm)</th>
<th>$\rho(T_{MI},0Pa)$ (m$\Omega$cm)</th>
<th>$PR_{max}$ P=1GPa</th>
<th>$PR(273K)$ P=1GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCM26</td>
<td>119</td>
<td>33.6</td>
<td>120</td>
<td>24900</td>
<td>9270%</td>
<td>32.3%</td>
</tr>
<tr>
<td>RP3c</td>
<td>177</td>
<td>22</td>
<td>97</td>
<td>750</td>
<td>3840%</td>
<td>41.8%</td>
</tr>
<tr>
<td>RP4a</td>
<td>155</td>
<td>33.7</td>
<td>55</td>
<td>1120</td>
<td>16800%</td>
<td>39.3%</td>
</tr>
<tr>
<td>LCM28</td>
<td>214</td>
<td>18.5</td>
<td>19</td>
<td>77</td>
<td>660%</td>
<td>47.4%</td>
</tr>
</tbody>
</table>
Figure 4.30: Pressure dependence of $T_{MI}$ for the samples given in Table 4.4.
The colossal change of resistivity with pressure is very noticeable around its maximum. Above $T_{MI}$, the slope of the $\rho(P)$ curves decreases linearly with pressure ($\partial \rho / \partial P \approx -2m\Omega cm/GPa$, at room temperature), whereas below $T_{MI}$ a nonlinear dependence of $\rho(P)$ occurs to some saturation value. This is most observable for sample LCM26. Likewise in polycrystalline samples, hydrostatic pressure increases $T_{MI}$ and decreases the resistivity at all temperatures. A similar rate was found for measurements on La$_{1-x}$Ca$_x$MnO$_3$, La$_{1-x}$Sr$_x$MnO$_3$, Pr$_{1-x}$Ca$_x$MnO$_3$ [70].

Figure 4.31 shows the temperature dependence of the pressure ratio defined as $PR = (R(0) - R(P))/R(P)$ where $R(0)$ is the zero-pressure resistance and $R(P)$ the resistance under hydrostatic pressure. The PR curves are very similar to the magnetoresistance curves MR (Fig. 4.10). For higher temperatures $T \gg T_{MI}$, PR shows little pressure

![Graph showing temperature dependence of $(R(0) - R(P))/R(P)$ for sample RP3c.](image)

Figure 4.31: Temperature dependence of $(R(0) - R(P))/R(P)$ for sample RP3c.
dependence.

The epitaxial films RP3c and RP4a were prepared under the same conditions, only with different thickness. RP3c ($d = 85 \text{ nm}$) has higher $T_{MI}$ and lower $\rho(T_{MI})$ than RP4a ($d = 14 \text{ nm}$). The thinner film has a remarkably higher $PR_{\text{max}}$ than the thicker one. The thickness may have an important role when applied pressure competes with substrate induced strain. Thin films are always under biaxial stress, because they are being pulled on by the substrate in two dimensions. In our case, SrTiO$_3$ has a greater lattice parameter causing a tensile strain distribution in the film. The thinner film has a greater strain energy stored per unit area which can enhance the effects of applied pressure. The films are (100) oriented on SrTiO$_3$ (100) substrate and therefore the applied hydrostatic pressure could be anisotropic.

The expression $\rho(T) = C \exp(-B/T^\alpha)$ was found to give a good fit to our high temperature results at all hydrostatic pressures up to 1.4 GPa with $\alpha$ varying from 0.8 to 0.5. This may correspond to a combination of the semiconductor behavior $\rho = C \exp(E_g/k_BT)$, Mott's variable-range hopping $\rho = C \exp([T_0/T]^{1/4})$ and other thermally activated mechanisms of hopping and scattering. Figure 4.32 shows the pressure dependence of the semiconducting gap determined from the high temperature data of Fig. 4.29 (240-280K), using only the expression $\rho(T) \propto \exp(E_g/k_BT)$. The contribution of the $C \exp([T_0/T]^{1/4})$ term is at least an order of magnitude smaller in this temperature range. The semiconducting gap energy $E_g$ depends very weakly on pressure with a slope $dE_g/dP \approx 10 \text{ meV/GPa}$. We were not able to fit the data using the small polaron hopping model [72] on its own.

The low-temperature resistivity (10-50K) under pressure has been fitted to the empirical expression $\rho(T) = \rho_0 + \rho_1 T^\alpha$. The $\rho_0$ term represents resistivity due to domain and grain boundaries, nonstoichiometry and other temperature-independent scattering mechanisms. The power term is responsible for the combination of electron-electron,
Figure 4.32: Pressure dependence of the semiconducting gap energy above $T_{MI}$ for samples LCM26 (○), RP3c (●), RP4a (□).
electron-magnon and electron-phonon scattering. As seen in Fig. 4.33, the pressure affects $\rho_1$ more than $\rho_0$. Far below the phase transition temperature in the FM region, the magnetic field mainly affects $\rho_0$ Fig. 4.17[68]. Figure 4.34 shows examples of high temperature and low temperature (inset) dependence of resistance under a fixed pressure 0.9 GPa.

The DE conduction occurs via the $e_g$ electrons between Mn ions which is expressed through the transfer integral $t_{eff} = t_0 \cos(\theta_{ij}/2)$. Here, $\theta_{ij}$ is the angle between neighboring Mn spins and the overlap integral $t_0$ is a parameter dependent on the angle and length of the Mn-O bond (p. 10). Thus, the parameter $t_0$ could be highly pressure dependent. In turn, the term $\cos(\theta_{ij}/2)$ relating to the magnetic order would be affected by the magnetic field. Under pressure, in all samples, an enhancement of the DE interaction is
Figure 4.34: Example of the low temperature fit of $\rho(T) = \rho_0 + \rho_1 T^{-2.46}$ in the region 4-70 K for LCM28. Lower panel shows the high temperature fit of $\ln(\rho) \sim 1/T$ for the film RP4a under pressure 0.9 GPa.
responsible for the shift of $T_{MI}$ towards higher temperatures. To increase $t_0$ by external pressure and to reduce $\rho$, the Mn-O-Mn bond angle should increase close to the ideal 180° and the Mn-O bond length should decrease. The same scenario has been proposed and recently demonstrated in the $PrNiO_3$ perovskite structure by neutron diffraction measurements under pressure[73].

By substituting the A-site ion La with the smaller Pr ion [71] this chemical pressure suppresses $T_{MI}$. In other words, $T_{MI}$ is increasing with a tolerance factor. Since $\partial T_{MI}/\partial P > 0$ we expect the tolerance factor to increase with pressure, making the Mn–O bond much softer than A–O. Goodenough [27] explained this using the classical Virial theorem $2\langle T \rangle + \langle V \rangle = 0$ as follows:

If there is a discontinuous increase in the mean kinetic energy $\langle T \rangle$ of the electronic system when crossing the transition from localized to itinerant electrons, there should be a corresponding discontinuous decrease in the mean potential energy $\langle V \rangle$ of the $t^3$ antibonding electrons and hence a decrease in the mean equilibrium Mn–O bond length. Therefore on the transition the mean Mn–O bond length becomes soft and abnormally compressible.

Indeed, recent synchrotron radiation and neutron powder diffraction work on the orthorhombic $La_{0.75}Ca_{0.25}MnO_3$ structure showed that the cell volume and the lattice parameters have a sharp anomaly at $T_{MI}$ implying a rearrangement of the internal structural parameters [74]; similar effects were measured for several orthorhombic samples of different values of doping level $x$ and A-site ionic radius $<r_A>$. Decreasing the temperature across $T_{MI}$ causes the Mn–O bond lengths and the oxygen anisotropic Debye-Waller factors to suddenly drop [20, 74].
Chapter 5

Conclusions

In conclusion, we have successfully fabricated polycrystalline LCMO by the sol-gel and standard solid state techniques. We have shown that good-quality LCMO films can be prepared by PLD using conditions similar to those for copper oxide superconductors. By using appropriate depositing conditions it is possible to obtain films which have better parameters than the ceramic targets. Thin films show large MR ratios of up to 400% in 50 kG at 250 K, which can be shifted to higher values.

Residual resistivity ($\rho_{5K}$) is close to the upper limit of metallic resistivity. The lower the resistivity, the fewer defects on the films and properties closer to those of single crystals. Almost monocrystalline epitaxial films usually have a resistivity of the order of $10^{-4}$ $\Omega$cm. Our last films #9,10,11 have $\rho_{5K}$ values of the same order suggesting epitaxiality, as demonstrated by x-ray diffraction results. In comparison to polycrystalline samples, films exhibit a sharp drop in $\rho$ at lower temperatures, where $\rho$ can be more influenced by the presence of grain boundaries which are scattering regions for conduction electrons [38]. We demonstrated that the postannealing process is able to change resistance, resulting in large MR probably because of a change in oxygen stoichiometry.

The low temperature subtle increase of resistance as T decreases to zero for both polycrystalline and film samples is not understood completely at this moment. Most likely the transport is polaronic due to strong electron–phonon coupling.

The thickness of the thin films plays an important role in the temperature and the magnitude of maximum MR and PR.
Part of this study has demonstrated the large pressure sensibility of the resistance in LCMO. The increase in the transition temperature with pressure can be interpreted as a consequence of pressure induced contraction and alignment of the Mn-O-Mn bonds. This leads to a delocalization of the charge-carriers and the formation of the FMM phase. Changes in lattice constants will affect the interatomic distance and the bond angle between Mn$^{3+}$ and Mn$^{4+}$, thus influencing magnetic exchange interactions between the manganese cations.

The CMR lanthanum manganites with all the interesting features are very promising as a base for novel applications. From the point of view of a future magnetoresistive detector, the main technological requirement is the strong MR around room temperature with linear or no temperature dependence. The strong pressure dependence of the resistivity and the accompanying effects in thin films have potential for application in pressure-sensing devices. The large magnetic entropy change near $T_c$ makes manganese oxides promising candidates for magnetic refrigeration [60].
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