Colossal magnetoresistive manganite thin films

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Abstract

Mixed-valence perovskite manganites (Re_{1-x}A_xMnO_3 where Re=rare earth, A=alkaline earth) provide a unique opportunity to study the relationships between the structure and the magnetotransport properties due to an interplay among charge carriers, magnetic coupling, orbital ordering and structural distortion. This makes these compounds very exciting from both the basic research and from the technological viewpoint. As the technology pursued with these materials requires film growth, extensive studies have been made on materials synthesis, structural and physical characterization and device fabrication. In this article, the results of the different experimental techniques and the effects of the deposition procedure of the manganite thin films are first reviewed. Second, the relation between the structural and the physical properties mentioned, and the influence of strains discussed. Finally, possible applications of manganite thin films for spin electronics are presented.

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I. INTRODUCTION

The last decade has seen the emergence of epitaxial metal-oxide films as one of the most attractive subjects for the condensed matter community. The emergence of such interest was primarily stimulated by the discovery of high temperature superconductors (HTSC) and more recently by the discovery of the colossal magnetoresistance (CMR) effect in thin films of manganese oxides Re$_{1-x}$A$_x$MnO$_3$ (where Re is a rare earth and A is an alkaline earth). CMR materials exhibit large changes in electrical resistance when an external magnetic field is applied.

The doped manganites are mixed-valence with Mn$^{3+}$ (3$d^4$) and Mn$^{4+}$ (3$d^3$). For the octahedral site symmetry of MnO$_6$ the configurations become $t_{2g}^3e_g^1$ for Mn$^{3+}$ and $t_{2g}^3$ for Mn$^{4+}$. In the double-exchange mechanism, the $e_g$ electrons are considered as mobile charge carriers interactions with localized Mn$^{4+}$ (S=3/2) spins. The carriers hoping avoids the strong on-site Hund rule exchange energy $J_{ex}$ when the spins are aligned ferromagnetically. (Note that if the Mn spins are not parallel or if the Mn-O-Mn bond is bent, the electron transfer becomes more difficult and mobility decreases). $J_{ex}$ is much larger that the $e_g$ bandwidth and thus, the conduction electrons are highly spin-polarized in the ground state. With this idea, correlations of the half ferromagnetic character of the CMR materials were found. Theoretical and experimental studies indicate that the small polaron effects including Jahn-Teller distorsion also play important roles for the transition and transport measurements as well.

These oxide materials are important from a fundamental point of view since they offer a chemical flexibility that enables new structures and new properties to be generated and, consequently, the relations between the structure, electronic, magnetic and transport properties to be studied.

Since most technological applications require thin films on substrates, the ability to prepare such films and understand their properties is of a prime importance. The synthesis of the first high temperature superconducting oxide thin films almost 15 years ago generated
great interest in the thin films community. This resulted in the development of various
techniques, guided by the importance of preparing high quality thin films of superconductor
compounds, including sputtering, Molecular Beam Epitaxy (MBE) and Metal Organic
Chemical Vapor Deposition (MOCVD), but the most popular technique is probably the
Pulsed Laser Deposition (PLD). This latter method is used extensively to synthesize
cuprates and HTSCs, which are now routinely made in laboratories, and it has been easily
and rapidly adapted for manganites. Another reason for this quick-transfer technology is
that these oxide materials crystallize in a perovskite structure as the HTSCs and in some
sense, they are quite similar. Moreover, the manganite oxides are highly sensitive to the
strain-effect, and this offers the possibility of studying its influence upon various properties
such as insulator-to-metal transition temperature ($T_{IM}$), Curie temperature ($T_C$), structure,
microstructure/morphology, etc... The renewed interest in the manganite materials has re-
sulted in a large volume of published research in this field.

In the present paper, we present a brief review of the experimental work done in the past
7 years. The deposition procedure and its influence (through deposition temperature, oxygen
pressure, post-annealing, substrate type...) upon the magneto-transport properties will be
discussed. In the particular case of thin films, work was mainly devoted to substrate-induced
strain and thickness dependence, and we will describe the experimental situation. Finally,
since much interest in the community of the CMR thin films lies in their use in devices, some
applications of these material will also be presented. Due to an extremely large amount of
research data published in this field, there are unfortunately some missing citations, and we
apologize the authors in advance.

II. DEPOSITION PROCEDURES, STRUCTURE AND PROPERTIES

CMR manganite materials are compounds crystallizing in a perovskite-like structure,
which apart from manganese and oxygen, contain rare earths and/or lanthanide cations.
The prototype compound is La$_{1-x}$Ca$_x$MnO$_3$, but there are many other related structures.
Numerous studies were performed on the hole doped $\text{La}_{0.7}\text{A}_{0.3}\text{MnO}_3$ manganites (where A=Sr or Ca) since these CMR materials exhibit so far the highest Curie temperatures (often associated with an insulator-to-metal temperature transition). Such high transition, close to room temperature, make them suitable for applications. As previously said, there are many different compounds due to the fact that the A-site cation can be a lanthanide or a rare earth. Thus, a number systems have been studied in the form of thin films including: La-Ca-Mn-O, La-Sr-Mn-O, La-Ba-MnO$_3$, La-Pb-Mn-O, La-Mn-O, Nd-Sr-Mn-O, Sm-Sr-Mn-O, Pr-Ca-Mn-O, Pr-Sr-Mn-O, La-Sn-Mn-O, La-K-Mn-O, La-Ce-Mn-O and Bi-Sr-Mn-O. To detail the situation in terms of synthesis, this section is divided into three parts. First, in part A, we will review the parameters that govern the growth of these oxides (temperature, oxygen pressure etc...), and we will consider the progress made in the synthesis of these materials. We will also focus on the different techniques that were are for the growth of thin films. Then in part B, we will discuss the different studies that were carried out to understand the structure and the microstructure of the thin films for the simple perovskite oxides and also for the results of the double ordered perovskites. Finally, some physical measurements will be presented (part C).

A. Synthesis of manganite films

1. Simple perovskite $\text{AMnO}_3$

The manganite thin films have been mainly prepared using the Pulsed Laser Deposition technique. The principle of this technique is relatively simple. A pulsed laser beam ablates a dense ceramic target of the desired material. In the presence of a background gas (usually oxygen), a plasma is produced and condenses on the heated substrate. Typical lasers used for manganite are excimer UV with KrF at $\lambda = 248nm$, XeCl at $\lambda = 308nm$ or ArF at $\lambda = 193nm$. A frequency tripled Nd-YAG at $\lambda = 355nm$ or quadrupled Nd-YAG at $\lambda = 266nm$ may also be used. A cross-beam deposition scheme utilizing two
Nd-YAG lasers was also used to grow Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ thin films on LaAlO$_3$. However, the utilization of high oxygen pressure during the PLD growth prevents the use of Reflection High Energy Electron Diffraction (RHEED) system in order to control in-situ the different stages of the growth. By a more oxidizing gas (atomic oxygen, ozone..) and a differential pumping system, the electron-path in the high pressure oxygen atmosphere can be reduced, and thus the specular beam of the RHEED can be monitored in order to observe the oscillations (see Fig. 1 for a typical experimental setup). High quality manganite thin films were fabricated in this way. A persistent intensity of the RHEED is observed and the roughness of the films is low, around one unit cell.

A second popular deposition technique is magnetron sputtering, which can be RF or DC. Reactive sputtering is particularly useful for large-area films, but the deposition of complex oxides, comprising several cations, is difficult because of a possible change in the material composition between the target and the film. Regardless, in these two techniques (PLD and sputtering) utilize highly-dense ceramic targets, and the configuration is usually ”on-axis”. This means that the plane of the substrate is perpendicular to the particles flux. Samples can also be produced by sputtering and PLD in the ”off-axis” configuration. In the case of PLD, this decreases the surface roughness and avoids the formation of droplets associated with laser deposition. Ion beam sputtering, electron beam/thermal coevaporation and molecular beam epitaxy have also been utilized to make manganite thin films. MOCVD was used to prepare high quality thin films of various compositions. Briefly, metal-organic precursors are dissolved in an ether and injected into the low pressure apparatus. In contrast to the methods previously described, this one does not require a high vacuum but allows deposition at higher oxygen pressure. Others methods used for making manganite thin films are nebulized spray pyrolysis and sol-gel.

Various gases, such as O$_2$, N$_2$O, ozone or a mixture of argon-oxygen atmosphere, result in oxygen-stoichiometric films. The background gas pressure is important for the oxidation process. Thus, the emission of the gas-phase oxidation of Mn
during pulsed laser deposition of manganites in O$_2$ and N$_2$O atmospheres was studied. They shown that both oxidation in the gas phase and at the surface are required in order to obtain the optimized properties. It was found that N$_2$O increases the oxidation of Mn in the plasma plume, leading to an improvement of the magnetic properties of La$_{0.67}$Sr$_{0.33}$MnO$_3$.

The deposition conditions (oxygen pressure $P_{O_2}$, deposition temperature $T_S$, laser fluence...) can drastically influence the properties. For Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ grown on (100)-LaAlO$_3$, the maximum resistivity peak shifts to lower temperatures as the deposition temperature decreases (the optimum $T_C$ of 175K is obtained for $T_S = 615^\circ$C). Yamada et al. have shown that the $T_{IM}$ decreases with either $T_S$ or $P_{O_2}$ in La$_{1-x}$Pb$_x$MnO$_3$. The deposition temperature also strongly influences the microstructure of Pr$_{0.7}$Sr$_{0.3}$MnO$_3$, since films grown at low temperature exhibit a columnar growth with well-connected grains while those deposited at higher temperature are poorly connected with platelet-like crystals.

In addition, it has also been shown that in-situ or ex-situ oxygen annealings is necessary to obtain the optimized properties. In particular, the postannealing of the films can lead to significant modification of the oxygen content and optimizes the physical properties such as $T_{IM}$, $T_C$ and the CMR effect. This annealing effect is necessary to achieve the optimum oxygen concentration of the films. Depending on the nature of the film and on the growth conditions, annealing is used either to fully oxidize the film (oxidative annealing) or to remove extra oxygen (reductive annealing). The effect of annealing was also observed in films annealed in N$_2$ atmosphere (see Fig. 2 for La$_{1-x}$Sr$_x$MnO$_3$). The $T_{IM}$ transition shifts after the annealing to higher temperature and the MR ratio increases slightly. The magnetic transition also occurs at higher temperature after annealing. For example, the Curie temperature, $T_C$, is found to increase from 200K for as-deposited La$_{0.8}$MnO$_3$ film to 320K after the fourth thermal treatment (See Fig. 3). In fact, the changes under annealing can also be seen on the position of the diffraction peak: the out-of-plane parameter decreases, which relates to an increase of the $Mn^{3+}/Mn^{4+}$ ratio. This annealing effect can lead to an improvement in physical properties (like in La$_{0.8}$Ca$_{0.2}$MnO$_3$ where $T_{IM}$ value is higher than that of the bulk) but sometimes the resistivity peak is
lower by more than 100K\textsuperscript{103}. In fact, Prellier \textit{et al.} have shown that the entire phase diagram is different in the ferromagnetic region of La\textsubscript{1-x}Ca\textsubscript{x}MnO\textsubscript{3} (0 < x < 0.5)\textsuperscript{104} as compared to the bulk (in terms of transport and magnetic transitions).

Doping is another method used to improve the magnetic properties. For example, enhancement of the properties (\(T_{IM}\) and \(T_C\)) is observed with silver addition to the La\textsubscript{0.7}Ca\textsubscript{0.3}MnO\textsubscript{3} target (5\%\textit{wt.})\textsuperscript{102} or with La\textsubscript{2/3}Sr\textsubscript{1/3}MnO\textsubscript{3} films doped with Ag and grown by dual-beam PLD\textsuperscript{103}.

\textit{2. Double and triple perovskites: \(A_3Mn_2O_7\) and \(A_4Mn_3O_{10}\)}

Although the majority of studies have been done on simple perovskites AMnO\textsubscript{3}, colossal magnetoresistance also occurs in (La,A)\textsubscript{3}Mn\textsubscript{2}O\textsubscript{7} (A=Ca,Sr). These compounds belong to the Ruddlesden-Popper phases whose general formula is \(A_{n+1}B_{n}O_{3n+1}\). Two parents of this family were synthesized in thin film form with \(n = 2\) and \(n = 3\).

Films of La\textsubscript{2-2x}Ca\textsubscript{1+2x}Mn\textsubscript{2}O\textsubscript{7} (\(x = 0.3\)) were deposited on (001)-MgO by single-target magnetron sputtering\textsuperscript{104,105}. \(c\)-axis oriented films of La\textsubscript{2-2x}Sr\textsubscript{1+2x}Mn\textsubscript{2}O\textsubscript{7} (\(x = 0.4\)) can be grown on (001)-SrTiO\textsubscript{3} under limited conditions (above 900\(^\circ\)C for the deposition temperature and below 100\textit{mTorr} for the oxygen partial pressure, Fig. 4)\textsuperscript{106} which are different from the typical conditions used for (La,Sr)MnO\textsubscript{3} films. On SrTiO\textsubscript{3} substrates, the resistivity curves shows a transition at 100\(K\) which coincides with a magnetic transition for La\textsubscript{2-2x}Sr\textsubscript{1+2x}Mn\textsubscript{2}O\textsubscript{7} films on SrTiO\textsubscript{3}\textsuperscript{106}. Films on MgO are \(a\)-axis oriented, which means that the long parameter is in the plane of the substrate, these films evidence two types of ferromagnetic ordering that possibly result from anisotropic exchange interactions for 0.22 < \(x\) < 0.55\textsuperscript{107}. Magnetoresistance is observed in a wide temperature range below the ferromagnetic transitions on MgO and is accompanied by an hysteresis on SrTiO\textsubscript{3}\textsuperscript{106}. Epitaxial films of (La,Sr)\textsubscript{3}Mn\textsubscript{2}O\textsubscript{7} can also be grown artificially by atomic-layer stacking of SrO and (La,Sr)MnO\textsubscript{3}\textsuperscript{108}.

Contrary to the previous one, the La\textsubscript{3-3x}Ca\textsubscript{1+3x}Mn\textsubscript{3}O\textsubscript{9} (\(x = 0.3\)) compound can be
stabilized, but only in the form of thin films and not in the form of bulk. Features similar to those reported for the double perovskite \( n = 2 \) were also observed for the \( n = 3 \) compound indicating a correlation between the dimensionality (or the c-axis bond configuration) and the magneto-transport properties.

Thus, it appears that the increasing of the c-axis reduces the magnitude of the of the CMR at low temperature and this may be attributed to the increase magnitude of the double-exchange transfer matrix and a better ferromagnetic spin alignment.

3. The particular case of the ordered double perovskite \( \text{Sr}_2\text{FeMoO}_6 \)

This review focuses on manganite thin films, but it is also interesting to present the results on the ordered double perovskite \( \text{Sr}_2\text{FeMoO}_6 \), even though it does not contain Mn, since it exhibits magnetoresistance with a Curie temperature above 370K. Films of \( \text{Sr}_2\text{FeMoO}_{6-y} \) were grown, using pulsed laser deposition on \( \text{(001)-SrTiO}_3 \). They are grown on both \( \text{(001)} \) and \( \text{(111)-SrTiO}_3 \) but in a narrow window near 900°C and \( 10^{-6}\text{Torr} \). Asano et al. have shown that by altering the growth conditions they are able to induce either positive (35%) or negative (−3%) magnetoresistance at 5K under a magnetic field of 8T. The films show metallic conductivity with a ferromagnetic transition above 400K. The experimental magnetic moment is calculated to be 4\( \mu_B \) per formula unit in agreement with the theoretical one. \( \text{Sr}_2\text{FeMoO}_6 \) films also exhibit both an electron-like ordinary Hall effect and a hole-like anomalous Hall contribution. More importantly, an intergrain tunneling type low field magnetoresistance, even at room temperature, has been reported.

B. Structure and microstructure

It is of prime importance to carry out structural characterization of the films, since it has been shown that in the bulk material, a slight variation of the Mn-O bond length or bond
angle drastically modifies the physical properties. Consequently, careful characterization of AMnO$_3$ films is paramount especially from the crystal structure point of view.

One of the best techniques to study the local structure of thin films, as for bulk, is most probably the high resolution transmission electron microscopy (HREM). Van Tendeloo et al. have studied the evolution of the microstructure as function of the thickness in La$_{0.7}$Sr$_{0.3}$MnO$_3$ films on LaAlO$_3$. Close to the interface, both the film and the substrate are elastically strained in opposite directions in such a way that the interface is perfectly coherent. In the thicker films, the stress is partly relieved after annealing by the formation of misfit dislocations. Similar results were found for La$_{1-x}$Ca$_x$MnO$_3$, where the bottom part of the film, close to the substrate, is perfectly coherent with the substrate, suggesting an important strain, while the upper part shows a domain structure. The perfect epitaxy between the film and the substrate can also be viewed on the cross-section of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ deposited on SrTiO$_3$ (Fig.5). This film is grown in the [010]-direction, i.e. $2a_P$, perpendicular to the substrate plane. The cross section along the [110]-direction of the substrate clearly shows the perfect coherence of the interface since the [100] or [001]-directions of the film match the [110]-direction of the substrate. The lattice parameter length in this direction is $a_P\sqrt{2}$.

In general, a strain is observed due to the epitaxial growth in very thin films i.e. lattice parameters adopt those of the cubic lattice (see an example of a compressive strain on SrTiO$_3$). In ultrathin films (60Å) of La$_{0.73}$Ca$_{0.27}$MnO$_3$ on SrTiO$_3$, the crystal structure imposed by the substrate is different than the bulk and leads to disorder effects or the formation of different phases such as $(\text{La}_{0.7}\text{Sr}_{0.3})_3\text{Mn}_2\text{O}_7$ in La$_{0.7}$Sr$_{0.3}$MnO$_3$ films. Microstructural studies also reveal a slight distortion of the La$_{1-x}$Ca$_x$MnO$_3$ film, possibly leading to a breakdown of the symmetry from orthorhombic to monoclinic (due to the presence of spots in the electron pattern that are not allowed in the $Pnma$ space group): this suggests that the structural situation might be different in thin film and in bulk material. In contrast, Teodorescu et al. show that the structure and the stoichiometry of the bulk target are perfectly reproduced in La$_{0.60}$Y$_{0.07}$Ca$_{0.33}$MnO$_{3-\delta}$ thin films.
A comparative study between La$_{2/3}$Ba$_{1/3}$MnO$_3$ (LBMO) and La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LSMO) grown on SrTiO$_3$ shows that thick LBMO presents a perfect epitaxy and grows coherently strained throughout the film thickness, whereas the LSMO films are composed of two layers separated by an intrinsic interface region containing a high density of defects. Sometimes, secondary phases are observed. In Pr$_{0.7}$Sr$_{0.3}$MnO$_3$, the deposition temperature influences the microstructure and is thus, directly connected to the $T_C$, which is depressed maybe due to the role of the grain boundaries.

Returning to the structural characterization of CMR thin films, there are roughly three tendencies that emerge from these studies. The first is that the manganite films are much more sensitive to substrate-induced stress than the analogous cuprate superconductors. The second deals with the presence of two regimes of strain relaxation: one highly strained regime located close to substrate and another above which is more relaxed. It is not clear exactly where the interface is located or even if it exists in every film. The last interesting point that has been shown by several groups is the difference of crystal symmetry (lattice parameters, space group..) between the thin film and the corresponding bulk material.

C. Physical measurements

The standard characterization of CMR thin films consists of resistance measurements versus temperature in zero field and under an applied magnetic field, by using the four probe technique and also in magnetization measurements. Results pertaining to strain effects will be discussed in the next section.

1. Surface measurements

Several groups focussed their studies on the surface. Extensive thin film surface studies were performed using two complementary techniques: Atomic Force Microscopy (AFM) and Magnetic Force Microscopy (MFM). Work was mostly on La$_{1-x}$Sr$_x$MnO$_3$ since this material exhibits the highest Curie temperature. It was also found that the
properties of the surface are different from those of the bulk in both the electronic and
the composition point of view\textsuperscript{127}. For example, the surface termination and the Ca sur-
face concentration depend on the overall Ca concentration in La\textsubscript{1−x}Ca\textsubscript{x}MnO\textsubscript{3} films\textsuperscript{125} (the
La/Ca ratio differs between the surface and in the film). The surface of La\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3}
and La\textsubscript{0.66}Ca\textsubscript{0.33}MnO\textsubscript{3} show a highly ordered grain pattern induced by strains\textsuperscript{126}, and the
La\textsubscript{0.65}Sr\textsubscript{0.35}MnO\textsubscript{3} surface exhibits a surface phase transition at 240K (to be compared to
370K for the bulk)\textsuperscript{127}.

2. Transport across a grain boundary (GB)

Grain boundaries (GB) strongly affect the properties of CMR materials. Low field mag-
netoresistance (LFMR) has been reported and attributed to the spin-dependent scattering
of polarized electrons at the GB\textsuperscript{131}. Researchers tried to enhance this property by artificially
creating an interface between two elements. We will describe here only the intrinsic effect
across natural GB (in polycrystalline thin films) and across artificial GB (in films deposited
on bicrystal substrates). The precise influence of the substrate will be discussed in a sepa-
rated part. Note that another method has been utilized to create artificial GB by scratching
the LaAlO\textsubscript{3} substrate before the deposition of the LCMO film\textsuperscript{132}. The MR is subsequent in
a field of 2kOe and varies with the field orientation with respect to the GB.

The simplest way of creating a natural GB is to grow the film on polycrystalline sub-
strates\textsuperscript{133}. Most of this work was done by IBM\textsuperscript{133,134} on La-Ca-Mn-O (LCMO) and
La-Sr-Mn-O (LSMO) films. The ρ − T curve of such films depends on the grain size, as
shown on Fig. 6: resistivity in zero field decreases when the grain size increases, but the
peak temperature of approximately 230K is almost independent of the grain size\textsuperscript{133}. Gu et al.
show that the Low Field Magnetoresistance at low temperature has a dramatic dependence
on the nature of the in-plane GB\textsuperscript{133}. The reduction of zero-field low-temperature resistivity
is might be explained by the spin-polarized tunneling across half-metallic grains. Another
possibility to obtain polycrystalline samples is to decrease the deposition temperature. The
resulting GB results from a lower crystalline quality of the film\textsuperscript{136}.

Bicrystal substrates having a single GB have also been used to study the transport across a GB. LCMO and LSMO thin films were deposited on bicrystalline SrTiO\textsubscript{3} substrates having a specific misorientation angle\textsuperscript{137,138}. To measure the properties of the GB only, the film was patterned into a Wheatstone bridge. The GB resistance and its magnetic field dependence is strongly dependent on the misorientation angle\textsuperscript{138} (See Fig. 7). The MR increases with an increase of the misorientation angle of the bicrystal\textsuperscript{138}. The change of resistance is 3\% under 2\textit{mT} magnetic field at 300\textdegree{}K for La\textsubscript{0.7}Sr\textsubscript{0.3}MnO\textsubscript{3}. At 77\textdegree{}K, a large bridge resistance (27\%) is observed during magnetic field sweeps between \pm{}200\textit{mT} over a temperature range down to 77\textdegree{}K. Steenbeck \textit{et al.} utilized La\textsubscript{0.8}Sr\textsubscript{0.2}MnO\textsubscript{3} films grown on SrTiO\textsubscript{3} bicrystals with a misorientation angle of 36.8\textdegree{}\textsuperscript{139} or 24\textdegree{}\textsuperscript{140}. They found that the GB magnetoresistance occurs at low temperature, separated from the intrinsic MR near \textit{T}_C, and that the sign of the MR at the GB depends on the domain structure and \textit{H}\textsuperscript{139}. Moreover, current-voltage measurements show that the field dependence might not be related to tunneling\textsuperscript{141}.

3. Irradiation effects

Irradiation, varying the ions dose\textsuperscript{142,144}, was used to look at the effect of columnar defects upon the thin films’ properties\textsuperscript{129,142}. On irradiated La\textsubscript{0.7}Sr\textsubscript{0.3}MnO\textsubscript{3} samples, the MFM shows the existence of magnetic domains in different magnetization directions, suggesting that the defects can be considered as pinning centers for the magnetic domain walls\textsuperscript{129,143,144}. The effect of irradiation (with 90 Mev\textsuperscript{16}O) by was studied La\textsubscript{0.75}Ca\textsubscript{0.25}MnO\textsubscript{3}. At a low dose of \num{10^{11}} ions/cm\textsuperscript{2}, the irradiation induces an increase of both the Curie temperature and of the resistive temperature transition \textit{T}_\text{IM}, whereas for high doses a decrease is observed\textsuperscript{145} due to enhancement of pinning for the magnetic domains walls. The film becomes insulating and does not show any resistivity peak when the dose is higher than \num{10^{14}} ions/cm\textsuperscript{2} (see Fig.8\textsuperscript{143}). Irradiation with 250\textit{MeV} Ag\textsuperscript{17+} induces phase transformation in La\textsubscript{0.7}Ca\textsubscript{0.3}MnO\textsubscript{3} thin films\textsuperscript{144} indicating that the nature of the ions plays also a role.
4. Phase separation

Phase separation was suspected in La$_{0.4}$Ba$_{0.1}$Ca$_{0.5}$MnO$_3$ films and confirmed by the noise probe method in La$_{2/3}$Ca$_{1/3}$MnO$_3$ films; in this work the authors attribute the origin of the random telegraph noise to a dynamic mixed-phase percolative process, where manganese clusters switched back and forth between two phases that differ in their conductivity and magnetization. This spatial inhomogeneity in doped manganite thin films was also investigated in La$_{1-x}$Ca$_x$MnO$_3$ using Scanning Tunneling Microscopy. The phase separation is observed below the Curie temperature where different structures of metallic and more insulating areas coexist and are field dependent. This suggests that the insulator to metal transition at $T_C$ should be viewed as a percolation of metallic ferromagnetic domains.

5. Other experiments

Magneto-optical measurements reveal the onset of the ferromagnetic transition via the coercive field increase and the Kerr rotation. Using this technique, the spontaneous formation of twins in La$_{2/3}$Ca$_{1/3}$MnO$_3$ films below 105K was also observed.

III. EFFECTS OF STRAINS

The CMR manganites are sensitive to all types of perturbations. In particular, it has been shown in bulk that the internal (through the average size of the A-site cation) or external pressure (via hydrostatic pressure) can strongly influence the magnetotransport properties. Since the beginning of the rediscovery of the CMR effect in Mn-based compounds, many studies have been focussed on the strains in thin films. This is due to the fact that Mn $eg$ electrons, which determine most of the physical properties, are coupled to the lattice degrees of freedom through the Jahn-Teller trivalent manganese. Thus, strains affect the properties of the manganite thin films, and, in consequence, one needs to correctly understand the effects in order to obtain the desired properties. The following section will discuss the two...
types of strains: in-the-plane (i.e. substrate-induced strains, part A) and out-of-plane strain (i.e. thickness dependence, part B).

A. Substrate-induced strains

The first important parameter for successful thin film growth is undoubtedly the substrate. For CMR materials, the same substrates as used for the HTSC compounds were utilized. The most commonly used substrates to grow manganite perovskites are MgO (cubic, \(a = 4.205\,\text{Å}\)), SrTiO\(_3\) (STO, cubic, \(a = 3.905\,\text{Å}\)), LaAlO\(_3\) (LAO, pseudocubic, \(a = 3.788\,\text{Å}\)), NdGaO\(_3\) (NGO, orthorhombic with \(a = 5.426\,\text{Å}, b = 5.502\,\text{Å}\) and \(c = 7.706\,\text{Å}\)) and Si (cubic, \(a = 5.43\,\text{Å}\)). Many authors have investigated the strain-effects of the substrate by growing various films on different substrates. They have experimentally or theoretically studied the effect of strains on the magnetoresistive properties of La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) and La\(_{0.7}\)Ca\(_{0.3}\)MnO\(_3\) or on the surface flatness for many substrates. The physical properties of these materials depend on the overlap between the manganese \(d\) orbitals and oxygen \(p\) orbitals, which are closely related to the Mn-O-Mn bond angle and the Mn-O distance. As the unit cell of the thin film is modified with respect to the bulk material, the Mn-O distances and Mn-O-Mn angles are altered, inducing variations in the electronic properties. We will review the main characteristics, such as the structure and the physical properties, which are affected by the substrate-induces strains.

1. Modification of the structure and the microstructure

The influence of the substrate upon the microstructure/structure, the lattice parameters, the texturation and also the orientation of the film is discussed in this section.

Using Magnetic Force Microscopy, Kwon et al. showed on La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) a ”feather-like” pattern, indicating an in-plane magnetization on (100)-SrTiO\(_3\), while on (100)-LaAlO\(_3\), a ”maze-like” pattern corresponding to a perpendicular magnetization anisotropy is seen.
This kind of study was confirmed and extended recently by Desfeux et al. on other substrates.\textsuperscript{162}

The influence of the substrate can principally be deduced from the lattice parameters of the film and the effect of strain on lattice parameters has been studied by many groups. These measurements lead to different spin-structures. This is evident in La$_{1-x}$Sr$_x$MnO$_3$ for which the spin-orbital phase diagram was obtained in the plane of strain-field ($c/a$ ratio) vs. doping $x$ using the density-functional electronic-calculation.\textsuperscript{163} The phase diagram of La$_{0.67}$Sr$_{0.33}$MnO$_3$ was also plotted for different substrates.\textsuperscript{157} A strong dependence of anisotropy and Curie temperature on lattice strain is observed. The effect of uniaxial strain was studied theoretically by Ahn et al.\textsuperscript{164} Uniaxial strain produces changes in the magnetic ground state, leading to dramatic changes in the band structure and optical spectrum.

Both in-plane and out-of-plane lattice parameters are often modified by stain effects when various substrates are used.\textsuperscript{157,163,165,68} This is evidenced in Fig.9 for 300Å thin films of Pr$_{0.7}$Sr$_{0.3}$MnO$_3$ (PSMO) grown on LaAlO$_3$, SrTiO$_3$ and NdGaO$_3$.\textsuperscript{163} The 002 peaks of the PSMO/LAO and PSMO/STO films are at 46.2° and 47.8°, corresponding to an out-of-plane parameter of 3.93 and 3.81 Å, respectively (the diffraction peak of the PSMO film on NGO is almost invisible from the substrate peak due to the small mismatch). These values have to be compared to the lattice parameter close to 3.87Å found in the bulk PSMO. They indicate that the films are under tensile stress on STO (decreasing in the growth direction and expanding in the plane) and under compressive stress on LAO (decreasing in the plane and expanding in the out-of-plane direction) due to the lattice mismatch between the film and the substrate at room temperature (Fig.10). The strain effects on the out-of-plane lattice parameter of La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO), are enhanced with annealing:\textsuperscript{103} the lattice expansion is 2-3 times larger in LCMO/STO than in LCMO/NGO. The stress also influences the bond lengths and bond angles. Miniotas et al. have evaluated the Mn-O and Mn-Mn distances in La$_{1-x}$Ca$_x$MnO$_3$ films grown by MBE. The Mn-O bond length was found to be fixed at 1.975Å, independent of the substrate types while the Mn-Mn distance (and subsequently the Mn-O-Mn bond angle) was calculated to be 3.93Å for STO and 3.84Å for...
Lattice mismatch (i.e. the difference of parameters between the film and the substrate) influences not only the parameters of the film but also the texturation (or epitaxy), i.e. the in-plane alignments. Usually, changes in the in-plane orientation is observed only when the mismatch is small (e.g. LCMO on LAO and is not realized on YSZ or on MgO). Textured La$_{2/3}$Sr$_{1/3}$MnO$_3$ films were obtained on Si when buffer layers are used. La$_{0.7}$Ca$_{0.3}$MnO$_3$ was grown using a buffer layer of CeO$_2$ and LSMO with a buffer of YSZ or a double layer Bi$_4$Ti$_3$O$_{12}$/SiO$_2$. A highly conducting diffusion barrier layer of TiN has also been utilized recently as a buffer layer. This progress is interesting for technological reasons especially when using Si substrates.

A surprising effect of lattice mismatch is related to the orientation of the films, especially those that crystallizes in an orthorhombic perovskite cell. This was first seen on YMnO$_3$ which is [010]-oriented on SrTiO$_3$, but [101]-oriented on NdGaO$_3$ or LaAlO$_3$. Similar results were obtained with Pr$_{0.5}$Ca$_{0.5}$MnO$_3$, Pr$_{0.7}$Sr$_{0.3}$MnO$_3$, or Pr$_{0.7}$Sr$_{0.3-x}$Ca$_x$MnO$_3$. It seems that this orientation can be generalized for every compounds that crystallize in an orthorhombic structure. This dependence on the orientation with the substrate is explained by the lattice mismatch ($\sigma$) which should favor one orientation. Indeed, the mismatch between the film and the substrate can be evaluated using the formula $\sigma = 100\ast(a_S-a_F)/a_S$ (where $a_S$ and $a_F$ respectively refer to the lattice parameter of the substrate and the film).

For Pr$_{0.5}$Ca$_{0.5}$MnO$_3$, the smaller mismatch on LaAlO$_3$ is obtained for the [010]-axis in the plane ($\sigma_{LAO} = -0.4\%$), i.e. the [101]-axis perpendicular to the substrate plane. In contrast, the smaller mismatch on SrTiO$_3$ ($\sigma_{STO} = 2.2\%$) is found for the [101]-axis is in the plane and thus the [010]-axis normal to the surface of the substrate as found experimentally.

2. Influence on the physical properties

Much work has been done on the influence of strain on the transport properties, but we will also describe how the magnetic properties can be changed. Many groups have focussed...
their studies on the modification of the physical properties\cite{175,176} by the strain effects since the most common properties such as the insulator-to-metal ($T_{IM}$) transition and the Curie temperatures ($T_C$) are affected. In Fig.11, Koo et al. show this clear correlation between the substrate and the physical properties for La$_{0.7}$Ca$_{0.3}$MnO$_3$ films: the $T_{IM}$ and maximum MR shift to a higher temperature when changing a SrTiO$_3$ to a LaAlO$_3$ substrate\cite{159}.

Since the crystallinity of these films can be changed, as previously discussed, Gillman et al.\cite{168} have prepared La$_{1-x}$Ca$_x$MnO$_3$ ($x=0.41$) films on substrates with different lattice parameters by liquid delivery metalorganic chemical vapor deposition. Films on LaAlO$_3$, closely lattice matched with the substrate, exhibit a high degree of crystallization and a high magnetoresistance ratio as compared to films deposited on Al$_2$O$_3$ or Y-ZrO$_2$. Similar results were reported for La$_{0.67}$Sr$_{0.33}$MnO$_3$ which is epitaxial when grown on (100)-LaAlO$_3$ and polycrystalline when grown and (100)-SrTiO$_3$. Moreover, the $T_{IM}$ increases by 20K when using (011)-LaAlO$_3$ rather than (001)-LaAlO$_3$. Similar results have been reported for La$_{2/3}$MnO$_3$-δ films grown on both Al$_2$O$_3$ and SrTiO$_3$\cite{342} and also for La$_{0.67}$Ca$_{0.33}$MnO$_3$\cite{177}. The $T_{IM}$ is higher and the transition is sharper for material grown on STO (300K) than on ALO (200K). Even if the $T_{IM}$ varies a lot, the Curie temperature is found to remain almost constant, independent of the substrate, for many compounds such as La$_{2/3}$MnO$_3$-δ\cite{342} or La$_{0.7}$Sr$_{0.3}$MnO$_3$\cite{177}.

The above evidence implies that the $T_{IM}$ is directly connected to the substrate. Often, the transition is at higher temperature and sharper when the mismatch between the film and the substrate is smaller, probably due to a high degree of epitaxy.

Strain not only influences the transport transitions, but the direction of the magnetization as well (via lattice deformation): it is found to be in-the-plane for films under tensile stress (for example on SrTiO$_3$) and out-of-plane for compressive stress (as in the case of LaAlO$_3$)\cite{128,177}. Using a wide-field Kerr microscope, magnetic domain orientation and contrast of La$_{0.67}$Sr$_{0.33}$MnO$_3$/SrTiO$_3$ suggest a magnetic anisotropy with <110>easy axes\cite{178}. The easy direction is along [110] of the pseudocubic unit cell, i.e. diagonal to the O-Mn-O bond direction for La$_{0.7}$Ca$_{0.3}$MnO$_3$ film grown on untwinned paramagnetic NdGaO$_3$ (001)\cite{179}.
The substrate-induced strain can also influence the optical properties, as for La$_{0.67}$Ca$_{0.33}$MnO$_3$. This can be explained by the fact that the substrate-induced strain result in modification in the Mn-O bonds and Mn-O-Mn bond angles and thus, in both the corresponding phonon modes and electron-phonons interactions leading to changes in the phonon frequencies and optical conductance. Note that the strains can also induce a surface magnetization as for La$_{0.7}$Sr$_{0.3}$MnO$_3$.

3. Low Field Magnetoresistance (LFMR)

The strain effects on the low field magnetoresistance (LFMR) was first studied on polycrystalline La$_{0.67}$Sr$_{0.33}$MnO$_3$. It was also extensively studied by Wang et al. in Pr$_{0.67}$Sr$_{0.33}$MnO$_3$. Films with compressive strains (on LaAlO$_3$) show a large LFMR when the field is applied perpendicularly to the substrate plane (Fig.12), while they exhibit a positive MR when the film is under tensile stress (on SrTiO$_3$). Almost no LFMR is observed when the film is stress-free (on NdGaO$_3$). O’Donnel et al. confirm that the LFMR depends on the strains and the orientation of the field, by studying highly crystallized La$_{0.7}$Ca$_{0.3}$MnO$_3$ thin films made by Molecular Beam Epitaxy. It was also shown that the LFMR is dominated by the grain boundaries and its sign can be explained by a simple atomic $d$-state model. This idea of anisotropic MR was evidenced by La$_{0.7}$Sr$_{0.3}$MnO$_3$ deposited on (001)-SrTiO$_3$, (110)-SrTiO$_3$ and (110)-LaGaO$_3$. Magnetic anisotropy was also seen recently on La$_{0.7}$Ca$_{0.3}$MnO$_3$ films grown on (001)-NdGaO$_3$.

4. Charge-ordered (CO) manganites

Most of the experimental studies were done on manganites showing an insulator-to-metal transition without field, but it was also shown that substrate-induced strain can affect the properties of charge-ordered (CO) compounds. CO is a phenomenon observed wherein electrons become localized due to the ordering of heterovalent cations in two different sublattices ($Mn^{3+}$ and $Mn^{4+}$). The material becomes insulating below the CO transition.
temperature, but it is possible to destroy this state and render the material metallic by, for example, the application of a magnetic field\textsuperscript{192} but, an electric field can also induced insulator-metal transitions in thin films of CO manganites\textsuperscript{51}. Pr\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3} is an example of such a compound. In this case, a tensile stress can decrease the melting magnetic field\textsuperscript{56} whereas a compressive strain induces a locking of the structure\textsuperscript{57} at low temperature (i.e. under cooling, when the in-plane parameters of the film are equal to the parameters of the substrate, they are kept at this value). This idea of locking was confirmed in Pr\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} where the structural and physical transitions are suppressed under cooling\textsuperscript{193}, as compared to the bulk (note that, even if the compound Pr\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} is not a typical CO, it has some similarities in the physical properties). In this material, the A-type antiferromagnetic phase with the \textit{Fmmm} structure, which is obtained at low temperature (below 135K) in the corresponding bulk compound, is not observed in the thin film. The consequence of the absence of structural transitions is that magneto-transport properties are affected. There is no antiferromagnetism (i.e. the A-phase) at low temperature. The material only becomes ferromagnetic insulating. This is one of the very few examples of substrate-induced strain upon the film structure. These results show that the strain effect can destabilized the charge-ordered state for CO materials but, surprisingly, it seems also possible to induce a CO state when the film composition is not a CO type (i.e. if the film has an insulator-to-metal transition without the presence of a magnetic field). This has been shown in a normally metallic La\textsubscript{0.7}Ca\textsubscript{0.3}MnO\textsubscript{3} compound where the lattice-mismatch strain effects leads to a strain-induced insulating state\textsuperscript{194}. This insulating behavior is related to the coexistence of a metallic state with a possibly charge-ordered insulating state\textsuperscript{193,195}.

B. Thickness dependence
1. Lattice parameters

The influence of the thickness \((t)\) is primary seen upon the lattice parameters of the films (in-plane and out-of-plane parameters). Usually, the volume of the unit cell is conserved in the thin film as compared to the bulk. In order to verify this result, the evolution of the three-dimensional strain states and on crystallographic domain structures was studied on epitaxial \(\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3\) as a function of lattice mismatch with two types of (001)-substrates, \(\text{SrTiO}_3\) and \(\text{LaAlO}_3\). Surprisingly, it was shown, using normal and grazing incidence x-ray diffraction techniques, that the unit cell volume is not conserved and varies with the substrate as well as the film thickness (Fig. 13).

But the main result is that for a tensiled film (under expansion in the plane of the substrate), the out-of-plane and in-plane parameters gradually increases and decreases, respectively, as a function of the film thickness. For example, in the case of \(\text{Nd}_{2/3}\text{Sr}_{1/3}\text{MnO}_3\) grown on \(\text{SrTiO}_3\), the out-of-plane parameter increases from a value of 3.8Å for a 200Å thick film to 3.86Å for a 1000Å film, which is close to the bulk value (Fig. 14). The scenario is the opposite when the film is compressively strained as in \(\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\) on (100)-\(\text{LaAlO}_3\): the out-of-plane parameter decreases from 3.94Å for a 300Å thick film to 3.9Å for a 4500Å thick film, while at the same time the in-plane parameter changes from 3.82Å to 3.88Å. The film is not completely relaxed until it reaches a thickness on the order of 1000Å. In \(\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3\) deposited on (001)-\(\text{LaAlO}_3\), two regimes were observed using XRD: one which was strained (close to the substrate), and a quasi-relaxed component in the upper part of the film, the latter increasing with film thickness.

As previously reported, increasing film thickness leads to a change of the symmetry of the film. This was systematically studied by looking at various film compositions vs. thickness by Yu et al. They found a strong tetragonal lattice strain using HREM and XRD characterization. This is more important for a composition in which the bulk structure is orthorhombic, as in \((\text{La}_{1-x}\text{Pr}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3\), as compared to \(\text{La}_{1-x}\text{Na}_x\text{MnO}_3\) or \(\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\) where the structure is rhombohedral.
2. Physical properties

The physical properties of manganites such as insulator-to-metal transition, magnetoresistance, coercive field, or microstructure are strongly dependent on the thickness. As an example, the MR value calculated as \( \Delta R/R(H) \) for \( H = 6T \) exhibits a strong dependence on film thickness as shown in Fig. 15 for \( \text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \). The curves show a maximum MR for a thickness near 1100Å with a value of 10\(^6\)% and, on either side of the peak, the MR ratio is drastically lower. Transport properties are mostly affected and the magnetization is only moderately changed with thickness as seen for \( \text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3 \) deposited on \( \text{MgO} \) or \( \text{SrTiO}_3 \). At an intermediate thickness around 1000Å, the films usually recover the properties of the bulk compounds. Even when the film is under low epitaxial stress (case of NGO), \( T_{IM} \) varies greatly from 182\( K \) (35Å) to 264\( K \) (1650Å), as seen in Fig. 16 for \( \text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \).

Films thinner than 1000Å have properties different from the bulk and are most of the time unusual. For example thin \( \text{La}_{1-x}\text{Ba}_x\text{MnO}_3 \) films (\( t<1000\AA \)) exhibits a \( T_C \) higher than in the bulk due to an anomalous tensile strain effect when deposited on \( \text{SrTiO}_3 \). Consequently, the resulting film shows room temperature ferromagnetism and an enhancement of the magnetoresistance. In \( (\text{La},\text{Ca})\text{MnO}_3 \) films, the thinnest films which present full magnetization, grow with the \( b \) axis of the structure perpendicular to the substrate, whereas the thicker films grow with the \( b \)-axis in the plane of the substrate and do not present full magnetization. Another example of the thickness dependence is seen in \( \text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3 \) on \( \text{SrTiO}_3 \), which is ferromagnetic around 150K but remains insulating. Biswas et al. have explained this behavior by the coexistence of two different phases, a metallic ferromagnet (in the highly strained region) and an insulating antiferromagnet (in the low strain one). This nonuniformity induces, under a magnetic field, an insulator-to-metal transition resulting in a large CMR effect. But, the metallic behavior of the bulk \( \text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) can be retained for a thickness down to 60Å when the \( \text{SrTiO}_3 \) substrate is treated to obtain an atomically flat \( \text{TiO}_2 \) terminated surface. For \( \text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3 \) (\( t<50\text{nm} \)) on
(100)-SrTiO$_3$, Razavi et al.$^{119}$ reported an unexpected insulator-to-metal transition, most probably due to La-deficiency. Nevertheless, Sun et al.$^{166}$ have estimated the "dead-layer" for La$_{0.67}$Sr$_{0.33}$MnO$_3$ to be around 30Å for NdGaO$_3$ and 50Å for LaAlO$_3$ (Fig. 17). The magnetic, transport and structural properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$ deposited were MgO was interpreted recently in terms of a magnetic (10Å) and an electrical (insulating) dead layer (respectively of 10Å and 4Å thick)$^{207}$.

More recently, the robustness of the charge-ordered (CO) state was studied by Prellier et al.$^{174}$. In Pr$_{0.5}$Ca$_{0.5}$MnO$_3$, the thicker film induced the less stable state, i.e. a small magnetic field as compared to the bulk is required to destroy the CO state and induce a metallic behavior (Fig.18). In Nd$_{0.5}$Sr$_{0.5}$MnO$_3$, the (110)-films show a strained and a quasi-relaxed layer. The latter increases with film thickness whereas the strained one has a constant thickness$^{5}$. The coexistence of two strain regimes inside the same film was also seen in La$_{0.66}$Ca$_{0.33}$MnO$_3$ films on SrTiO$_3$ and LaMnO$_3$ deposited on NdGaO$_3$ at the interface a cubic-like dense layer (50Å thick) is observed while the upper layer shows a columnar growth. These two distinct thickness ranges behave differently with respect to the thickness-dependence of the magnetotransport properties$^{63}$; the upper range ($t > 200\text{Å}$) is weakly thickness-dependent whereas the lower one not. These results$^{63,163}$ show the evidence for the effect of Jahn-Teller type distortion and confirm theoretical explanations$^{160}$. In Nd$_{2/3}$Sr$_{1/3}$MnO$_3$ films, the release of the strain as the thickness increases$^{198}$ results in a first-order phase transition.

Thus, these results show the thickness-dependence of the physical properties of the film, but it seems difficult to estimate these changes precisely. For example, considering a Pr$_{0.7}$Sr$_{0.3}$MnO$_3$ film deposited on NdGaO$_3$, is it possible to evaluate the $T_{IM}$ and the $T_C$ for 2000Å thick film? There is no report of such calculations, and one of the reasons is that the properties of the film depend not only of the substrate, but also on the growth conditions. It will be necessary to answer this question in the future.
IV. POTENTIAL OF THIN FILM GROWTH: THE DESIGN.

The improvement in controlled heterostructures and multilayers is a necessary stage for the realization of many devices and circuits. Structures with new properties such as superlattices were also widely studied.

A. New structures

Thin film methods offer a powerful and versatile technique for growing new structures, as previously seen for example in cuprates. This is due to strain effects that can stabilize structures which do not exist under classical conditions of pressure and temperature. For example, various metastable perovskites, which can not be formed in bulk or can only be prepared under high pressure, such as BiMnO$_3$\cite{5}, YMnO$_3$\cite{7}, atomically ordered LaFe$_{0.5}$Mn$_{0.5}$O$_3$\cite{8}, are synthesized via a pulsed laser method or by using injection MOCVD like NdMn$_7$O$_{12}$\cite{10}.

Also interesting is the construction of new compounds, such as artificial superlattices, that show unique physical properties since different types of magnetism can be combined by building the desirable structure at the atomic layer level\cite{211}. Growth conditions such as the oxygen pressure or the deposition temperature are easy to control in the thin film process, allowing the synthesis of metastable phases.

Another approach to obtain exotic properties via new phases is the method of artificial superlattices. Preliminary films were grown by stacking a magnetic layer (La$_{0.7}$A$_{0.3}$MnO$_3$ with A=Sr, Ba...) and another perovskite, usually insulator (such as SrTiO$_3$)\cite{212}. This allows a continuous variation of the in-plane coherency strain in the films\cite{213}-\cite{215}. High quality films showing a clear chemical modulation by the presence of satellite peaks around the main diffraction peak were obtained\cite{213}-\cite{214}. In the case of La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO), the metallic transition is suppressed and the MR enhanced at low temperature when the thickness of the LCMO layer is decreased to 25Å\cite{214}. The MR ($MR = 100 \times [R(0) - R(H)]/R(0)$) is calculated to be 85% at $H = 5T$ over a wide temperature range (10 − 150K) (Fig.
A systematic study of La$_{0.7}$Ba$_{0.3}$MnO$_3$/SrTiO$_3$ superlattices shows that the decrease of the La$_{0.7}$Ba$_{0.3}$MnO$_3$ (LBMO) layer thickness results in the broadening of the MR peak vs. temperature. Such studies also confirm the importance of strains and the relevance of Jahn-Teller electron-phonon coupling in doped manganites, as pointed out by Lu et al. Following the same idea, La$_{2/3}$Ba$_{1/3}$MnO$_3$/LaNiO$_3$ multilayers were synthesized. Magnetization measurements show evidence of antiferromagnetic coupling between LBMO layers when the thickness of the LaNiO$_3$ spacer is 15Å or less.

The magnetic exchange interactions have been extensively studied in La(Sr)MnO$_3$/LaMO$_3$ (M=Fe, Cr, Co, Ni). The authors showed that the ferromagnetism is systematically affected by the adjacent magnetic layers via the interface, and, they propose an expression of $T_C$ on the basis of the molecular field image. The magnetotransport properties of superlattices such as La$_{0.6}$Pb$_{0.4}$MnO$_3$/La$_{0.85}$MnO$_3$ or La$_{0.7}$MnO$_3$/Pb$_{0.65}$Ba$_{0.05}$Ca$_{0.3}$MnO$_3$ were also investigated. An enhancement of the magnetoresistance is obtained in these materials. c-axis YBa$_2$Cu$_3$O$_7$/La$_{0.67}$Ba$_{0.33}$MnO$_3$ superlattices were also grown. Above $T_C$, the CMR persists up to room temperature, and below $T_C$ the superlattices exhibit a quasi-two-dimensional superconductivity of the YBa$_2$Cu$_3$O$_7$ layers coexisting with magnetism in the La$_{0.67}$Ba$_{0.33}$MnO$_3$. An increase in the thickness of the antiferromagnetic La$_{0.6}$Sr$_{0.4}$FeO$_3$ layer in between La$_{0.6}$Sr$_{0.4}$MnO$_3$ layers induces a strong magnetic frustration around the superlattice interfaces, leading to a reduction of the magnetic temperature transition and of the ferromagnetic volume.

Salvador et al. used the PLD technique to create A-site ordering in films of (LaMnO$_3$)/(SrMnO$_3$) superlattices. An increase of the superlattice period leads to a decrease in the $T_C$ and in $T_{IM}$ or in a low magnetization value.
B. Some Devices

The intense efforts of the condensed matter community in the area of CMR thin films have led to a more precise understanding of the growth of thin film oxides even if the utilization of the materials into devices has not proven to be viable yet. The aim of this article is to give an overview of the manganite thin films and, for this reason, we will not go into details of the realization of devices. A more comprehensive description of the devices made using CMR materials can be found elsewhere\textsuperscript{13}. Examples of devices include magnetic field sensors, electric field devices\textsuperscript{224}, uncooled infrared bolometers\textsuperscript{225} or low temperature hybrid HTSC-CMR devices\textsuperscript{226}. Some of these are briefly discussed below.

A magnetic tunnel junction is a structure composed of two ferromagnetic (FM) layers separated by an insulator barrier (I) and have attracted attention due to their properties of tunneling magnetoresistance (TMR). However, to obtain TMR (FM/I/FM junction) with 100% efficiency, it is necessary to have a perfect half-metal (i.e. a 100% spin polarization). Such a property was confirmed by spin resolved photoemission measurements in the case of the La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) compound\textsuperscript{227}. Junctions with LSMO which show a TMR effect\textsuperscript{228}–\textsuperscript{233}. A large MR in 83% at a low field of 10Oe at 4.2K in a trilayer film of LSMO/STO/LSMO was observed\textsuperscript{234} (Fig. 20). Note that the top layer can also be Co\textsuperscript{233}, half-filled ferrimagnetic Fe$_3$O$_4$\textsuperscript{231,232} or La$_{0.7}$Sr$_{0.3}$MnO$_3$\textsuperscript{228,229}. Using Fe$_3$O$_4$, a positive MR is observed which could be attributed to the inverse correlation between the orientations of the carrier spins in the two FM layers\textsuperscript{231}.

The electric field effect has been investigated, in which the top layer can be paramagnetic, such as STO\textsuperscript{229}, or ferroelectric layer, such as PZT (PbZr$_{0.2}$Ti$_{0.8}$O$_2$\textsuperscript{224}), and the bottom layer is a CMR material. but the changes are more profound in the case of PZT where only 3% change in the channel resistance is measured over a period of 45min at room temperature which makes this attractive for nonvolatile ferroelectric field effect devices\textsuperscript{224}.

The large temperature coefficient of resistance (TCR, calculated as $(1/R)(dR/dT)$) just below the resistivity peak makes these CMR materials interesting for bolometric
detectors. However, for a given material the TCR decreases as $T_C$ or $T_{IM}$ increase. A TCR of 7%/K is obtained for LCMO at 250K.

Hybrid structures consisting of HTSC-CMR have also been made for use in spin injection devices.

V. CONCLUSION

The structural, magnetic and transport properties of manganite thin films have been presented in this article. As seen, the colossal magnetoresistive oxides display an exciting diversity of behavior in the form of thin films, and an extremely large amount of work has been carried out on thin films showing the great potential of their magnetic and transport properties. It has been shown that the structural and physical properties of these oxides are strongly dependent on the deposition procedure, chemical composition and applied strain. For this reason, the direct comparison of data between a thin film and a bulk material (ceramic or single crystal) is difficult due to the stress in the thin film.

It has also been shown that devices are interesting and potentially useful for magnetic sensors. Prior to the fabrication of such devices, it will be necessary to characterize the materials more comprehensively, in particular from the view point of the structure and the microstructure. This is clearly evidenced by the fact that intrinsic phenomena such as the substrate-induced strain and the thickness dependence, which are directly related to the thin film process, strongly affect the magnetotransport properties. These results suggest that the local lattice distortions of the Mn-O bonds in the manganite thin films contribute to changes in the physical properties.

There are two main ideas that should be considered in the future based on the recent results. It is now recognized that the strains directly affect the lattice parameters. In addition, researchers have noted that there is a clear relation between the oxygen content (or indirectly the Mn$^{3+}$/Mn$^{4+}$ ratio) and the lattice parameters of the unit cell of the film. Thus, one should ask the following question: what is the relation between the oxygen content and
strain? This triangular connection must be investigated precisely and explained in the future. The second main direction is related to the stress, because despite the large amount of work published on manganite thin films, there is still no direct proof of substrate-induced strains: researchers have only found indirect correlations at room temperature. More sophisticated mechanisms going beyond classical concepts (i.e. by looking at the evolution of the structure under cooling) and theoretical work, in particular by quantifying the stress for these oxide films, are required to understand the nature of this class of compounds.

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Figure Captions

Fig. 1: Typical experimental setup of a Pulsed Laser Deposition system used for growing oxides.

Fig. 2: $\rho(T)$ and MR ratio of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ thin films is zero field and a field of 5T for as-grown (top) and annealed at 950°C for 10h in pure N$_2$ gas (bottom). (a): $x=0.33$, (b): $x=0.2$ and (c): $x=0.16$ (reproduced from ref. 98).

Fig. 3: $M(T)$ for as-deposited and post-annealed $\text{La}_{0.8}\text{MnO}_3-\delta$ films. Annealing 1-600°C, 3h; Annealing 2-600°C, 24h; Annealing 3-700°C, 3h; Annealing 4-800°C, 3h (Reproduced from Ref. 99).

Fig. 4: Map of the reaction conditions for different manganite thin films on SrTiO$_3$. The growth conditions for the $c$-axis oriented (La,Sr)$_3$Mn$_2$O$_7$ films (type 3) is restricted to the hatched region. Detailed structure of films with type 1 (open circles) and type 2 (open triangles) are not identified (Reproduced from Ref. 106).

Fig. 5: [010]-cross-section of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ deposited on SrTiO$_3$ taken at room temperature.

Fig. 6: $\rho(T)$ under different magnetic fields for polycrystalline La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO) films with different grain sizes and an epitaxial film. The inset shows the zero-field resistivity at 10K as a function of the average grain size for and La$_{0.75}$MnO$_3$ (LXMO) (Reproduced from Ref. 133).

Fig. 7: Normalized GB MR as a function of the applied field for different bicrystal angles measured at room temperature. The inset shows the (a) low and (b) high field dependences for the 24°device. The applied magnetic field is in plane and perpendicular to the GB (Reproduced from Ref. 138).

Fig. 8: $\rho(T)$ for as-deposited films and irradiated films at different ion doses (Reproduced from Ref. 147).

Fig. 9: XRD pattern in the range 45-50° of 300Å thick Pr$_{0.67}$Sr$_{0.33}$MnO$_3$ films on LaAlO$_3$, NdGaO$_3$ and SrTiO$_3$. The arrows indicate the 002 peaks of Pr$_{0.67}$Sr$_{0.33}$MnO$_3$ (Reproduced
Fig. 10: Schematic structure of a film grown under tensile and compressive stress in the plane. Note the compression or the elongation of the out-of-plane parameter depending on the nature of the stress.

Fig. 11: (a) $\rho(T)$ of La$_{0.7}$Ca$_{0.3}$MnO$_3$ on various substrates under 0 and 1T magnetic field. (b) MR defined as $(\rho(0) - \rho(1T))/\rho(0)$ normalized to the value at $T=317K$ (Reproduced from Ref. 159).

Fig. 12: Normalized $R(H)$ curves of 75 Å thick Pr$_{0.7}$Sr$_{0.3}$MnO$_3$ films on LaAlO$_3$ measured with the field applied parallel (H//) and perpendicular (H⊥) to the plane of the substrate. In the H⊥ geometry, a very sharp hysteresis loop and large MR ratio are observed. Arrows indicate the scanning sequence of the magnetic field (Reproduced from Ref. 183).

Fig. 13: Thickness dependence of the perovskite unit cell volume of epitaxial La$_{0.8}$Ca$_{0.2}$MnO$_3$ films on (001)-LaAlO$_3$ (triangles) and (001)-SrTiO$_3$ (circles). Large deviations of the lattice parameters from those of the bulk are observed. As film thickness increases, both in-plane and out-of-plane lattice parameters tend to deviate away from those of the substrates towards the bulk value (Reproduced from Ref. 196).

Fig. 14: $c$-axis lattice parameter of Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films deposited on SrTiO$_3$ as a function of the thickness (Reproduced from Ref. 198).

Fig. 15: Thickness dependence of the MR for La$_{0.67}$Ca$_{0.33}$MnO$_3$ thin films grown on (100)-LaAlO$_3$ (Reproduced from Ref. 155).

Fig. 16: $\rho(T)$ of La$_{0.7}$Ca$_{0.3}$MnO$_3$ grown on (110)-NdGaO$_3$ vs. film thickness (Reproduced from Ref. 201).

Fig. 17: (a) Temperature dependence of the resistivity for La$_{0.67}$Sr$_{0.33}$MnO$_3$ films with varying thickness on NdGaO$_3$ and LaAlO$_3$. (b): Thickness dependence of the conductance of films at 14K (Reproduced from Ref. 166).

Fig. 18: $\rho(T)$ under varying magnetic fields for different thickness of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ thin films grown on SrTiO$_3$. Arrows indicate the direction of the temperature dependence
Fig. 19: MR (MR=100×[R(0T)-R(5T)]/R(0T)) vs. temperature for a LCMO (55Å)/STO (160Å) superlattice (20 periods) and a single LCMO layer. Note the broadening of the MR peak and the MR of 85% at 5T from 10K to 150K (Reproduced from Ref. 212).

Fig. 20: MR vs. applied magnetic field at different temperatures for a tunnel junction with a rectangular 2.5 × 12.5µm top electrode. The moments of both electrodes are shown at various fields. Magnetic field is applied is applied along the easy axis of the rectangle (see inset) (Reproduced from Ref. 234).