3.3 Magnetotransport through artificial grain boundaries

3.3.1 Grain boundaries created by the atomic saw method

Up to now, we have focussed on the effect on the magnetotransport properties of growth-controlled grain boundaries in thin films of LCMO on MgO(001) substrates.

We have identified electrical contact between misaligned grains to constitute a resistive GB while the electrical contact between well aligned grains has been shown to be less resistive and does not show the granular behaviour characteristics described in previous sections.

In order to check the above hypothesis, we have elaborated a experimental model system with artificial and well controlled grain boundaries obtained from an epitaxial film. It is a result of a collaboration with the Laboratoire the Physique de la Matière Condensée, UMR (Toulouse) which developed the atomic saw method which mechanically induces planar defects in the film.

The atomic saw method

The atomic saw method was first developed by Peyrade et al. [108] on semiconductor heterostructures. It is based on a dislocation slipping process induced by plastic deformation of the substrate. Dislocations start at the defects on the surface of the sample and they slip through the single crystal. Each dislocation creates a lattice shift and at the surface of the sample, steps are evidenced. When a thin film is deposited on top of the single crystal substrate (before the dislocation creation), the thin film will also be cut or crossed by dislocation slipping.

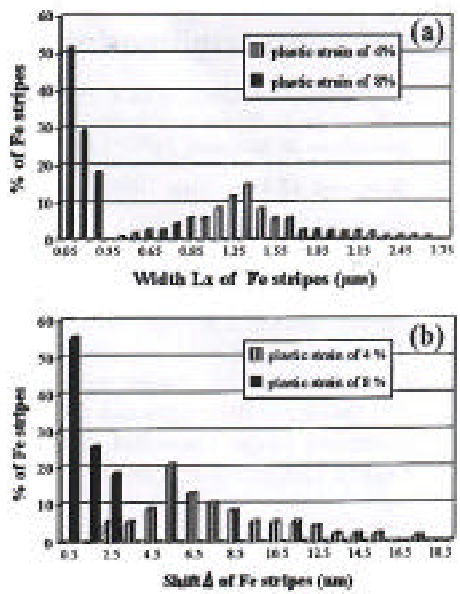

Fig. 3-65 *Statistics on the dispersion of the width and amplitude of the steps on MgO (001) substrates from [107]*

0.5mm thick MgO substrates can be plastically deformed at room temperature. Some authors [107] deduced that the (100) planes are not likely to be activated at room temperature. The compression of the MgO (001) substrate in the [100] direction creates stripes in the [010] direction with lattice shifts in the [101] and [10$\underline{1}$] directions.

This method applied to Fe films on MgO(001) [109] revealed the existence of a distribution of stripe widths (L) and heights (Δ) of the steps at the surface of the sample while the crystal periodicity was restored in the volume. The statistics performed by the same group on the dispersion of the width and amplitude of the steps on MgO(001) substrates demonstrates that the distribution is always peaked at a certain value but depending on the strain performed when deforming the system the distribution is more or less wide. Hence, a plastic strain of 4% gives rise to broader stripes (1.5µm) with higher amplitudes (8nm) than a strain of 8% (L=50nm and Δ=0.5 nm) [107](Fig. 3-65).

Artificial grain boundaries in manganite system

The system consists in a 15nm thick $La_{2/3}Ca_{1/3}MnO_3$ epitaxially grown film (texture in the three directions) on a single crystalline MgO (001) substrate. X-Ray θ-2θ measurements have confirmed that the film was textured along (001) (Fig. 3-66). After deposition, the film has been cut in three stripes of about 2mm wide and 7mm long. One stripe has been conserved as deposited. On the other two stripes the atomic saw method was applied.

The LCMO film on MgO (001) substrate was submitted to a uniaxial compression along the [100] direction at a constant speed of 1µm/min at RT. After such compression at 300K, the substrate and the film were plastically deformed.

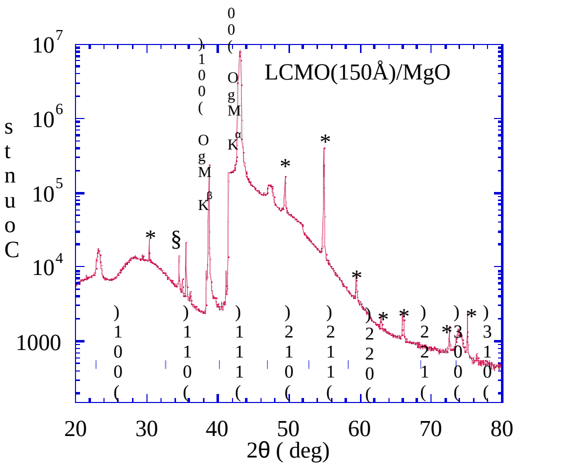

Fig. 3-66 *XRD of the 150 Å thick LCMO film on MgO substrate used to perform the atomic saw.*

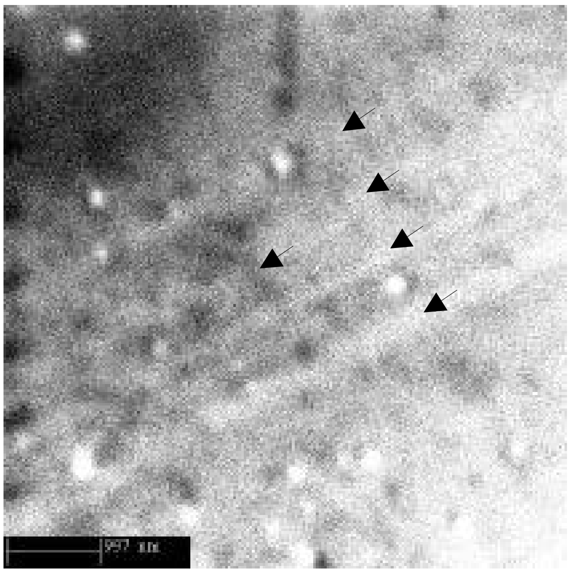

Fig. 3-67 *SEM observations on the film cut by the atomic saw.*

AFM measurements on the non-compressed film showed an averaged rms roughness of about 2nm. The effect of the compression on the LCMO film is the creation of stripes parallel to the [010] direction. The distance between the dislocations is around 1µm as deduced from SEM observations (Fig. 3-67). The amplitude Δ of the stripes ranges from 50 to 175 Å as extracted from contact AFM measurements (Fig. 3-68).

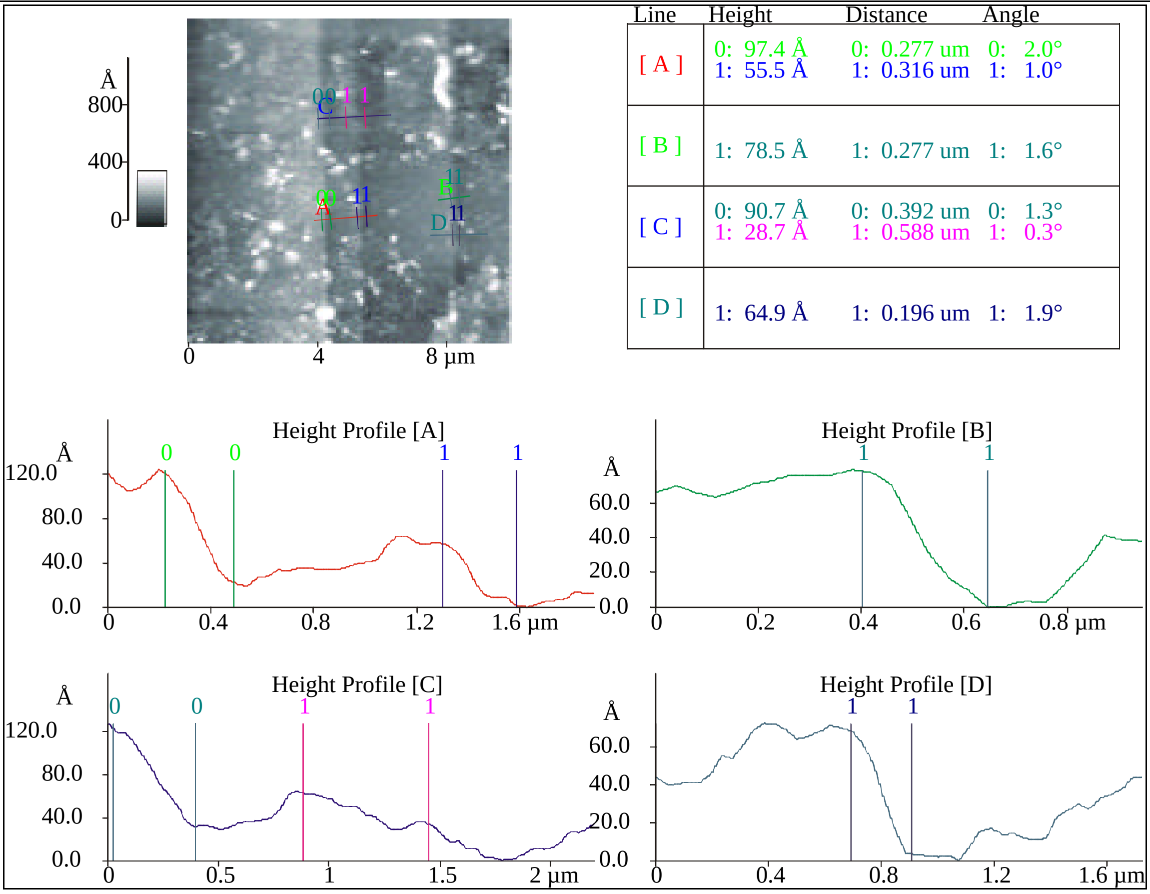

Fig. 3-68 *AFM observation of the striped film.*

3.3.2 Magnetotransport

Transport measurements performed using the four probe method in applied magnetic fields up to 8T on the non-deformed film show the classical features of an epitaxial continuous LCMO films on MgO(001) substrate (Fig. 3-69). The shift towards lower temperatures of the metal-insulator transition can be understood to be a signature of a residual stress in the film as shown in chapter 4.

The residual resistivity in the epitaxial continuous film is about 800μΩcm, which is about seven times larger than the value in single crystals (140μΩcm). The large value of the residual resistivity can be associated to the existence of a great number of dislocations at the interface between the substrate and the film, which are created to release the strain induced by the lattice mismatch between the film and the substrate (as inferred from HREM studies reported in [110])

The maximum value of the MR in the epitaxial and non deformed film is similar to that measured reported in thicker epitaxial films, around 80%, and it occurs close to T_C.

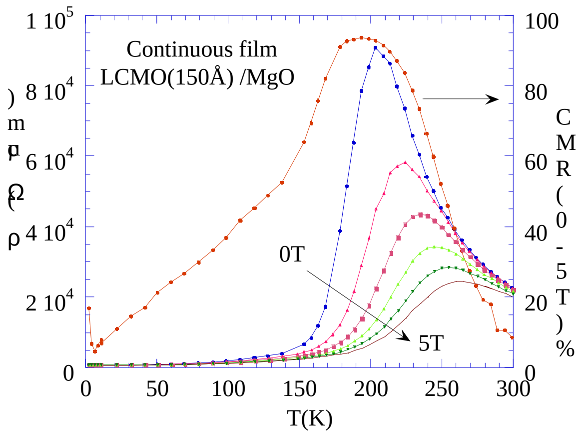

Fig. 3-69 *Thermal evolution of the CMR and resistivity for 15nm thick film on MgO substrate before performing the atomic saw method*

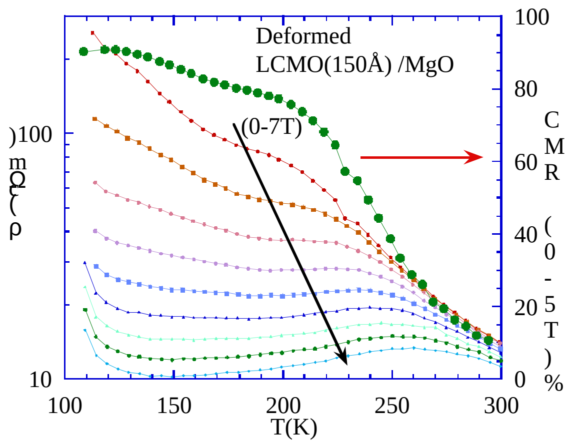

Fig. 3-70 *Magnetotransport measurements performed on the deformed film*

Magnetotransport measurements performed on the deformed film through the dislocation network are shown in Fig. 3-70. The results were reproducible indicating that the observed behaviour is characteristic of the deformed film.

Deformed film display the following features:

I) A huge increase of the resistivity at any temperature (due to the extremely high values of the resistance presented by the film we have been unable to measure at temperatures below 100K). A difference of two orders of magnitude in the value of the resistivity at 200K exists between the deformed and non-deformed film that can be attributed to the existence of dislocations. An estimation of the grain boundary resistance has been made assuming a periodic dislocation lattice (period=1μm). Thus between the 3mm of distance separating the voltage contacts, there should exist about 3000 dislocations. Hence, the estimated resistance of one GB is about 2000Ω. Consequently, we deduce that the film is crossed by dislocations but tunneling between grains is possible. From the microstructure point of view, our deformed film corresponds to a 4% plastic strain. Therefore, the distribution of amplitudes and widths of the stripes is important. Taking into account that the film thickness is about 15nm (as obtained from the in situ 670nm reflectivity measurements), the film displays a state shown in (Fig. 3-71).

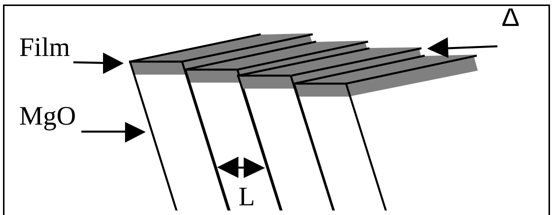

Fig. 3-71 *Schematic representation of the state of the 150Å thick LCMO film after deformation.*

II) The deformed film does not show the metal-insulator transition at T_C. However, a feature is observed around 200K in the resistivity measurements. This feature shifts toward higher temperatures under an applied magnetic field similarly to the metal-insulator transition temperature of the continuous film.

III) The behaviour of the CMR in the deformed film is striking. On the one hand, its value is very close to the value obtained in continuous epitaxial films (around 80%). On the other hand, it does not exhibit a maximum at T_C and the MR slightly increases at low temperature as in the case of polycrystalline films. In polycrystalline films on MgO, the values of the CMR at 5Tesla never reached more than 50% (Fig. 3-13).

IV) The low temperature resistivity indicates a tendency towards low temperature localisation as in the case of polycrystalline films.

V) In addition to these features, the LFMR of the deformed film at 140K, (Fig. 3-72) is very small. In polycrystalline films, LFMR drops very fast with temperature and often it disappears at temperatures below T_C but in most of the cases at 140K there is still some LFMR (≈5%) (Fig. 3-39). However, in epitaxially grown films on bicrystal substrates, for low misalignment angles LFMR is also small [81](Fig. 3-73).

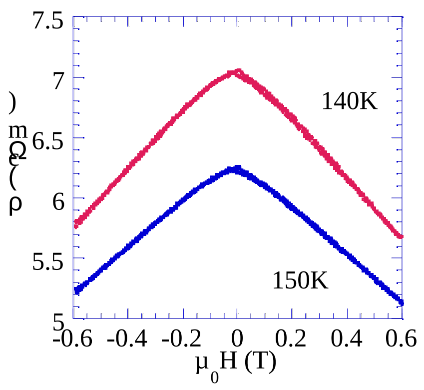

Fig. 3-72 *Magnetotransport measurements at low fields on the deformed film displaying the absence of LFMR*

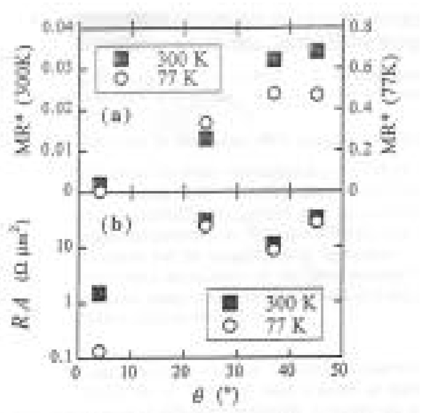

Fig. 3-73 ***LFMR measured on $La_{2/3}Sr_{1/3}MO_3$ films grown on bicrystalline $SrTiO_3$ substrates as a function of the misalignment angle****[81]*

In the following we will focus on the effect of the atomic saw method on the microstructure of the film. From crystallographic considerations, it is energetically unfavourable to have dislocations, which do not allow a correct alignment of the planes of neighbouring stripes. Nevertheless, we recall that the film has dislocations because they appear first in the MgO substrate. Taking into account that the cell parameter of MgO is about 4.2 Å, the height of the steps should be proportional to this value.

As the film has a different cell parameter than the substrate, that suggests that the correct alignment in the film of the crystallographic planes is not possible for neighbouring film stripes (Fig. 3-74). Hence, the dislocations created at the MgO substrate induce a zone of crystallographic disorder in the film and grain boundaries are formed in the film consistent with zones where the crystal symmetry is broken.

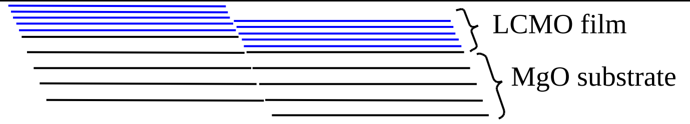

Fig. 3-74 *Schematic representation of the effect on the manganite film of dislocations created in the MgO substrate.*

In ordinary metals, the existence of dislocations would only induce an increase of the residual resistivity. However, manganites do not behave as ordinary metals because the electrical conduction is mainly governed by first neighbours hopping. Hence, in manganites, these dislocations give rise, in addition to the increase of residual resistivity, to a localisation at low temperatures. An electrical barrier is created at the dislocation in manganite films.

The grain boundary formed by atomic saw cannot be associated to a chemical intergranular phase because cation migration as often supposed for grain boundaries formed by other methods. The reason is that the film exhibits the correct perovskite phase before the deformation at room temperature and the possibility of cation diffusion is very reduced and no new chemical phase is expected.

In our opinion the above magnetotransport measurements can be explained due to the creation of an electrical GB at the dislocation position because of the existence of crystallographic disorder. That can explain the increase of the resistivity by two orders of magnitude in the deformed film, and also the constant magnetoresistance at low temperature.

A comparison can be performed between the deformed film and the scratched film described in section 0. The most remarkable difference between the two systems is that in the deformed film all the possible percolative paths have to cross the GBs. In addition, the grains are crystallographically textured along the same direction but constitute zones of crystallographic symmetry breaks in contrast to the scratched film where the grain boundary is constituted by crystallographically disordered zones.

The difference between the textured films on MgO and the deformed film is that while in textured films the grains are created at high temperature and thus GB recrystallisation giving rise to metallic electrical contact between certain grains is possible, in the artificial GB no recrystallisation at the GB is possible and no percolative path is possible.

From the magnetotransport point of view, the most remarkable differences between the deformed and the scratched films are that in the scratched film (Fig. 3-27) the resistivity diminishes below T_C while in the deformed film (Fig. 3-70) it increases monotonously upon cooling. The application of a magnetic field turns the deformed film metallic below T_C and reveals a M/I transition.

3.3.3 Conclusions

In this section we have presented the microstructural and magnetotransport study on artificially created grain boundaries. These GB consist in zones of crystallographic disorder due to the existence of dislocations. The GB are expected to have the same composition than the film because the dislocation creation is performed through the atomic saw method at 300K. Hence, atomic diffusion is ruled out.

All the standard features characteristic of the granular behaviour are found in our model system with the artificially created GBs.

The large value of the resistance at low temperatures did not permit to check the low temperature localisation phenomena. However, a certain tendency towards localisation is observed upon cooling.

Grain boundaries dominate the transport behaviour of the manganite films when no percolating paths are possible as we have shown in the deformed film. The global behaviour of films with grain boundaries corresponds to the combination of two different behaviours: the behaviour inside of the grains (transport measurements it was possible to observe a kink at the T_C of the film) and the behaviour at the grain boundaries

3.4 Discussion and Conclusions

From the results of this chapter we conclude that what has been called granular behaviour or PMR in the literature is an extrinsic transport mechanism and we have now contributed to get more insight in the origin of the granular characteristic behaviour. Electrical GB appear when crystallographic disorder is created. It can be induced during the thin film growth (tuning deposition temperature) or after deposition (mechanically induced grains). .

In the following, we will proceed to analyse the magnetotransport particularities of granular behaviour and to discuss its origin using the new results presented in this thesis.

Electrical Grain Boundaries in manganites

Electrical GB in manganites has been shown to consist in zones of crystallographic disorder. We have shown that the GB are not constituted by a secondary chemical phase as argued by other authors. The hypothesis of badly oxygenated GBs has been ruled out due to the fact that scratched films deposited at the same deposition conditions than the epitaxial films and the film cut by the atomic saw method, display the granular behaviour. In addition, electrical GB have been created at 300K thanks to the atomic saw method and at this temperature, cation diffusion seems unlikely.

Not all the GBs exhibit the granular type behaviour. Some of the GBs in textured $La_{2/3}Ca_{1/3}MnO_3$ film on MgO do not exhibit it, even if the rocking curves show at least 1.5° of crystallite misalignment in the in-plane direction. However, the film cut by the atomic saw method display large MR up to low temperatures. In both systems, there is conduction mechanism through GB between two crystallographically textured grains. The reason for this difference can be the deposition temperature. It is high enough in the epitaxial deposition region to allow the recrystallisation of certain crystallographic grain boundaries, suppressing any electrical barrier. The atomic saw method is performed at room temperature and the induced GB are not annealed, keeping their electrical barrier character.

So the symmetry breaking created by a crystallographic disorder (existence of a planar defect as dislocations or the grain surface) seems to be the origin of the weakening of the FM interactions between Mn ions close to the surface of the grains. Some authors predicted the magnetic interactions at the ordered surface to be AF [111].

An estimation of the value of the grain boundary specific resistivity, R_g, has been performed assuming a uniform current flow between the metallic contacts. In order to calculate the grain boundary specific resistivity, the in-plane grain radius (Fig. 3-16) is used and the height of the grains is the film thickness. The values obtained are about $3\ 10^{-3}\Omega\mu m^2$ to $0.1\ \Omega\mu m^2$ of the same order of magnitude than the ones reported by Isaac et al [81] ($0.1\text{-}10\Omega\mu m^2$ depending on the misalignment angle) on a film grown on a bicrystal. They are smaller than the values given by Balcells et al.[98] for thin powders which were of the order of $50\ \Omega\mu m^2$.

In our case, the randomness of the crystallite orientation in polycrystalline films gives rise to an extended distribution of angles between the crystallites, which tends to increase the grain boundary specific resistivity. In epitaxial films, there exist only one possible crystallite orientation, so all the grain boundaries join equally oriented crystallites and metallic percolating paths are possible.

The approximations used to calculate the grain boundary specific resistivity suppose the current path to be straight lines but polycrystalline systems on MgO substrates are found to be percolating systems as extracted from the low temperature I(V) measurements and the current path could be a meander. In this case, its length could be several times the distance between the point contacts and the number of grain boundaries would be larger than our simple estimation.

We have begun a collaboration with the DPMC (Geneve) and scanning tunneling microscope in potentiometry mode (STP) has been used to study our epitaxial films on MgO. The measurements performed by B. Grevin et al at the DPMC on a $La_{2/3}Sr_{1/3}MnO_3$ epitaxial films on MgO substrate at room temperature.

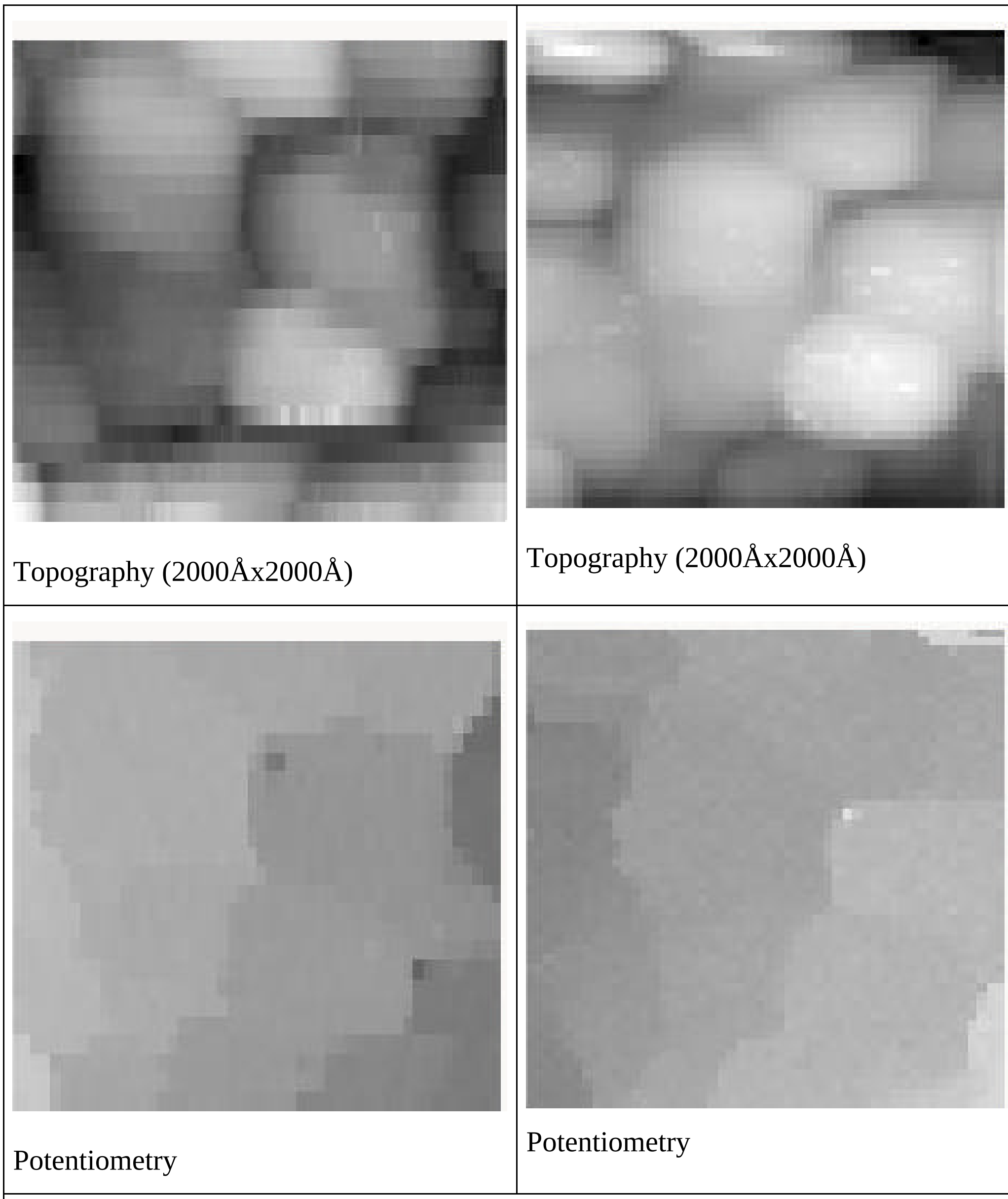

Fig. 3-75 *Topographic and potentiometric gray scale 2000x2000Å images of $La_{2/3}Sr_{1/3}MnO_3$ epitaxial thin films acquired simultaneously. The electric field is about 17.6V/mm and the gray scale in the topography covers a range of 177Å from black (low) to white (high) with rms value of 33 Å. The absolute scale for potentiometric data is 4mV from Black (low potential) to white (high potential)*

The measurements demonstrate that films exhibiting the so called epitaxial or single crystal transport behaviour and deposited on non matched MgO substrate are constituted by grains as shown in the topographic images (Fig. 3-75), corroborating our AFM precedent observations. In addition, the sharp potential steps in the potentiometry mode, coincide always with the grain boundaries. However, some grains in the epitaxial films are electrically well connected (Fig. 3-75). Hence, in epitaxial films deposited on non matched MgO substrate, the potential drop is always situated at the edges of the grains (GB) and less resistive paths do have a percolative nature [112].

Hence, when controlling the substrate temperature during deposition, the average misorientation angle between the grains can be tuned as well as the crystallites connection. Below percolation threshold, the macroscopic magnetotransport properties are dominated by intergranular transport. This is consistent with the unexistance of an intermediate regime between the epitaxial-like and the granular magnetotransport behaviour when changing the substrate deposition temperature.

In addition, if the GB length is considered to be the zone where the voltage drops in the potentiometric measurements, GB are observed to be less than 10-20nm.

Low Field Magnetoresistance

From the measurements on the film cut by the atomic saw method we deduce that LFMR is related to the existence of tunneling between non exchange coupled grains.

Polycrystalline films obtained by PLD thanks to low or high temperature deposition always showed LFMR. In addition, in reported films grown on bicrystalline substrates, LFMR depends on the misalignment angle (Fig. 3-73) and for low misalignment angle the LFMR is highly reduced. Hence, even if GB exist in epitaxial films, no LFMR is observed when the grains are well electrically connected and thus magnetically exchange coupled.

LFMR has been found to be independent of the grain size (Fig. 3-40). The relationship between LFMR and the grain size only applies when there exist an electrical barrier between the grains and they are non-exchange coupled.

The linear dependence of the LFMR with the coercive field, has been often explained on the basis of the mesoscale magnetoresistive response (MMR) theory reported by Evetts and Blamire [78]. We suggest that H_C is a scaling parameter in the measure that in a polycrystalline system, close to H_C we can find neighbouring grains with asymmetric magnetic orientation. The MMR model is unable to explain the low temperature localisation and ruled out the tunneling through the grain boundary as the mechanism at the origin of the granular behaviour.

The fact that LFMR decreases faster than M^2 has been interpreted as a probe that the intergrain conduction mechanism is not spin tunneling. However, in order to apply Helmans theory to polycrystalline samples the polarisation and the magnetisation of the electrodes as well as the magnetic behaviour of the electric barrier has to be taken into account. We have shown that the transport mechanism at the GB is dominated by inelastic spin tunneling. Moreover, we have shown that GBs are certainly magnetic, and thus carriers will be scattered by the moments in the barrier when tunneling, as in the case of $Fe/GdO_x/Fe$ heterostructures [113].

Our explanation of the LFMR consists in the following: the inside of the grains in polycrystalline samples and in the FM regime behaves as in the single crystal. However, the exchange coupling between grains is weak through a GB due to the structural disorder at the interfaces (Fig. 3-76).

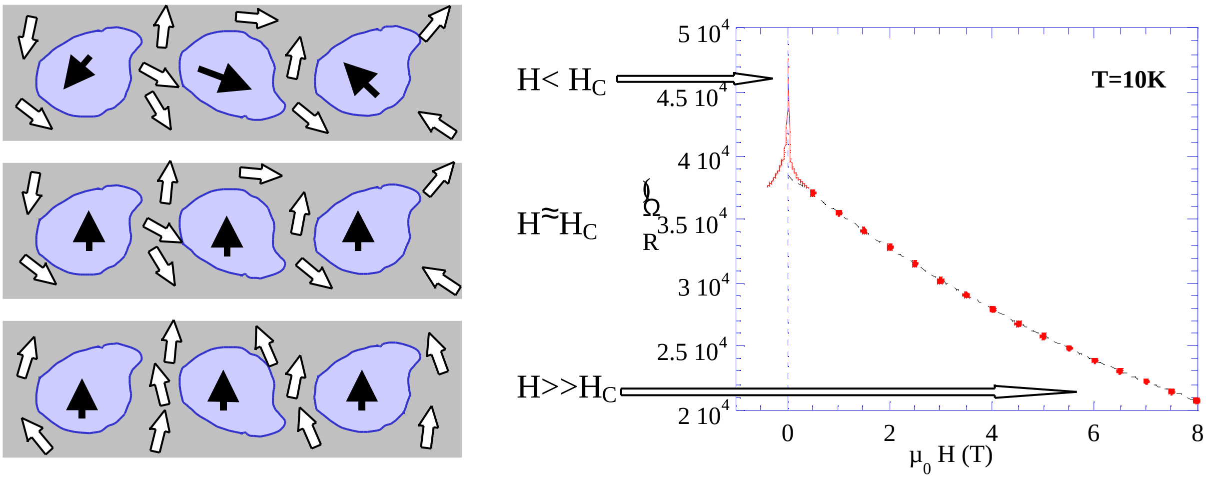

Fig. 3-76 *Schematic explanation of the MR observed in polycrystalline films.*

In the FM state, the direction of the magnetisation of each grain is determined by the shape or magnetocrystalline anisotropy (small in manganites but larger because of strain, see chapter 4) and the minimisation of the magnetostatic energy. The application of an external magnetic field, aligns the magnetisations in neigbouring grains and tunneling or activated hopping through magnetic impurities at the GB is possible between neighbouring grains so there exist a reduction of the resistance once the grains are FM aligned. The characteristic magnetic field is the coercive field.

Higher applied magnetic fields align the misaligned moments at the interfaces (GB) as has been concluded from high magnetic fields ($\mu_0H<30T$) measurements on polycrystalline films.

The reason for the strong influence of the grain boundaries on the transport behaviour in manganites should be searched in the mechanism controlling the electric conduction in manganites. In manganites, the “conduction band” is formed by the hybridisation of Mn 3d and O 2p orbitals and the carrier transport is first neighbours hopping. Hence, if there is a crystallographic disorder, the Mn-O-Mn chains are cut and the carrier transport is highly reduced.

In order to understand the effect of non FM aligned Mn moments at the grain boundaries (GB), we will consider that in polycrystalline films there exist two zones: a) inside of the grain. FM and with T_C given by the kink in the resistivity around 250K. b) The GB which may contain magnetic ions.

The effect of the existence of the two zones should be more important in the transport measurements than in the magnetisation because in the basis of the DE model such zones should behave as an insulator barrier. In order to detect some differences in the magnetisation measurements like the saturation magnetisation using standard VSM or SQUID techniques, very accurate magnetisation measurements and film volume determination should be done and large number of GB should be present. In this sense, measurements in the polar geometry seem to be more accurate (dead layer if it exist at the film-substrate interface will not be seen). We have performed Kerr measurements in polar geometry. Our measurements revealed differences in the magnetisation of polycrystalline films compared to epitaxial films at temperatures about 170K while no evident differences were observed at 5K. This indicates the existence of different temperature evolution of the magnetisation in these systems.

The effects of the large magnetic fields on the resistivity of polycrystalline films is nearly constant up to low temperatures (Fig. 3-19). This agrees with GB being not fully saturated FM regions.

Low temperature localisation

Low temperature localisation has also its origin in the GB barrier. The carriers, thermally activated through the barrier at high temperatures, are localised upon cooling down below 15K. Electrical transport in the low temperature region has been demonstrated to be very inhomogeneous in polycrystalline and epitaxial films and the existence of percolating paths has been evidenced when measuring with different µ-contacts and using potentiometry mapping.

In a percolating system, the behaviour observed for a group of contacts can be representative of the most resistive GB of the path. The electrical barrier at low temperatures has been shown to be magnetically active. For lower temperatures (≈30mK) the application of a magnetic field has been interpreted as increasing the number of channels which contribute to the electrical transport, which is equivalent to an energy barrier decrease(Fig. 3-59).

Therefore, spin transport through the barrier has been found to be thermally assisted inelastic hopping through misaligned Mn ions at the GB. Upon cooling, hoping is less favourable and tunneling through magnetic impurities seems to be at the origin of the low temperature localisation as sketched by Guinea [114]. In such model, the electrons tunnel from one grain to the other through an intermediate state (misaligned magnetic ions at the grain boundary). If the electrodes consist in Mn ions strongly coupled to the conduction electron, there exist a probability for this electron to tunnel to the impurity state (misaligned magnetic ion at grain boundary) and later on to the other grain. In Fig. 3-77 is represented by M_L,M_R the magnetisation of the left and

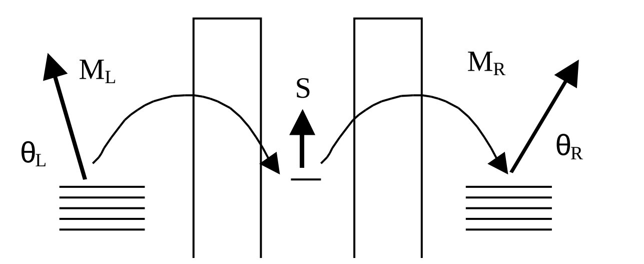

Fig. 3-77 *Schematic representation of tunneling through a magnetic impurity as sketched by Guinea et al.*

right hand side grains, and θ_L, θ_R the relative orientations of the grain magnetisation with respect the manganese at the grain boundary.

Considering that resonant tunneling through magnetic impurities process determines the conduction, Guinea et al. concluded that the magnetoresistance should be reduced compared to the case were no spin flip of the electron spin is possible. This model also predicts that for an impurity with S=3/2 as in Mn^{+4}, the current flowing when the moments of the neighbouring grains are distributed randomly compared to the current flowing when the three electrodes are aligned is about 5/16. That means, in terms of magnetoresistance, that if it were possible to align ferromagnetically the manganese moments at the surface of the grains, the expected magnetoresistance would be 68% which is smaller than the experimentally found (MR(30T)≈90% in polycrystalline films).

Magnetocoulomb effects, and direct as well as thermally activated tunneling through magnetic ions in the barrier have been observed in granular films in very low temperature measurements. The effect of an applied magnetic field in the magnetocoulomb effects has been interpreted as increasing the size of the charging grain which can be understood as an increase of the magnetically ordered zone in the GB. This result is in agreement with the image of a canted FM GB being FM aligned with the external magnetic field.

The fact that at low temperatures the transport measurements display non linear I(V) curves shows that the GB are insulating in the whole range of temperatures. This result contrast with the photoemission measurements where the surface of a manganite films is shown to be collinear FM at low temperatures and exhibits a faster drop of the magnetisation with temperature compared to the bulk sample or to the XMCD measurements [37]. Unfortunately, these photoemission experiments are difficult to interpret because, photoemission is highly surface sensitive and the authors did not give any explanation of the procedure followed to obtain a clean surface for photoemission measurements with ex-situ deposited films.

High field MR

The existence of the high field MR down to low temperatures in polycrystalline films can be associated to the effect of aligning the magnetic ions at the surface of the grains. Moreover, the maximum MR obtained is about 90%, which is larger than the value estimated by [76] and explained in section 2.2.4.

In addition, it is interesting to remark that the high field measurements performed up to 30T revealed that the maximum MR in polycrystalline films has the same value than in epitaxial films (about 90%). However, the MR at low temperatures is always larger in polycrystalline films than in epitaxial films indicating the existence of non FM ordered regions which are polarised under the application of the magnetic field.

At 50K, the high fields magnetotransport measurements revealed that the MR of LCMO thin films on MgO does not saturate under magnetic fields of 30T and that it scaled rather well with the microstructure of the film (Fig. 3-30).

Kink at T<TC in resistivity measurements

We have interpreted the maximum of resistivity in granular systems for temperatures below T_C on the basis of a model which takes into account the existence of weakened FM interaction at the surface of the grains and their huge influence on the transport properties.

Previously to this work, other authors explained the kink at $T<T_C$ based on the existence of a second FM phase at the surface with different T_C which is very unlikely to happen. In addition we have demonstrated that no second phase exist at the GB.

It has been observed on ferromagnets that surface magnetisation drops faster than the bulk magnetisation for temperatures far below the transition temperature and behaves as [115, 116]:

$$M_S = M_S(0)\left[1 - B_S T^{\frac{3}{2}}\right] \qquad \textbf{Eq. 3-10}$$

were B_S is seen to be twice the bulk value. That means that, at the surface, the polarisation should be different from the bulk value. Thus, the polarisation of the electrons at the surface of the material drops faster than in the bulk. As tunneling electrons are supposed to come from the first layers from the surface between the metal and the insulator, they should reflect the surface properties and, hence, their polarisation is expected to follow the temperature dependence of the surface magnetisation: $P = P_0\left(1-\alpha T^{\frac{3}{2}}\right)$ with α larger at the surface than in the bulk due to surface exchange softening. α has been also reported to depends on surface contamination. Such assumption of the temperature change of polarisation with temperature also means that for high T_C materials the loss of polarisation will be less rapid than for low T_C materials [60]. This fact could be the origin of a faster drop of the magnetisation in films.

Studies based on mean field approximation and numerical Monte Carlo simulations deduced that the surface magnetisation varies with temperature as $(T_C-T)^{\beta}$ with β between 1 and 0.8 instead of _ or 1/3 predicted for bulk magnetisation. That means that close to the transition temperature, the drop is still faster in the surface than inside of the grains.

The fact that the magnetisation at the surface of the grains is highly reduced and drops faster is at the origin of the magnetic susceptibility that needs high magnetic fields to saturate (Fig. 3-30).

Our model is based in the following assumptions:

a) GB are the surfaces of the grains were the crystallographic symmetry breaks

c) GB can have some crystallographic disorder due to the existence of a free surface (ex. surface reconstruction)

d) GB constitute electrical barriers which contain the Mn ions which are not collinear-FM aligned

e) Electrical transport through the GB is done by tunneling (mainly inelastic or through localised states in the barrier). In direct tunneling, as the barrier is magnetic spin filtering effects should occur.

That means that the magnetisation of the surface highly influences the transport through the electrical barrier.

Experimentally, Park et al.[37] reported the surface magnetisation extracted from Spin Resolved Photoemission Spectroscopy (SPES) measurements. Surface magnetisation was reported to decrease faster with temperature than the bulk (Fig. 3-78). We have extracted their magnetisation data and fitted the normalised magnetisation (M $(T_C-T)^{\beta}$) in a certain range of temperatures close to the transition. The magnetisation within the first 50 Å drops with a exponent of 1.3, while within 200Å the critical exponent is reduced to 0.68 and finally to 0.5 for the bulk magnetisation (Fig. 3-79).

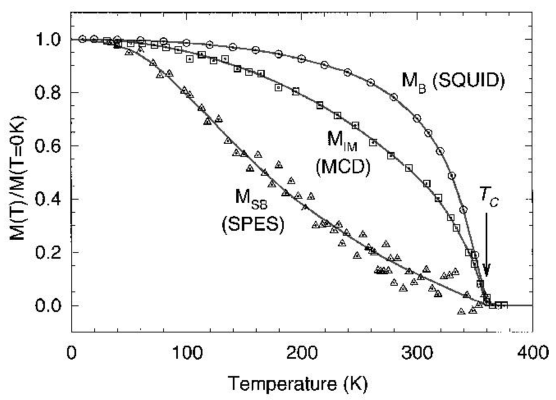

Fig. 3-78 *Temperature dependence for the magnetisation at different length scales. M_B is the bulk magnetisation (SQUID), M_{IM} is the intermediate magnetisation (Magnetic X-Ray circular dichroism), and M_S is the surface magnetisation (Spin Resolved Photoemission Spectroscopy) from ref [37]*

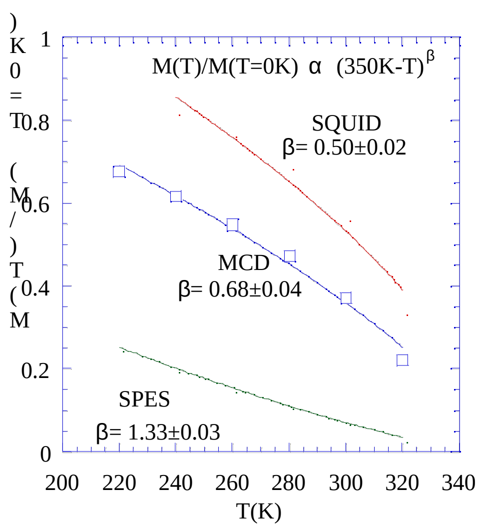

Fig. 3-79 ***Fit around the critical temperature of the normalised magnetisation data extracted from ref*** *[37]*

In order to find out the role of the surface magnetisation in the behaviour of granular films we have used the value of β found above, to parameterise the temperature dependence of the surface magnetisation ($M_{surface}$) in a LCMO film (T_C=265K).

Transport through the surface is not only dependent on the surface magnetisation but also on the difference with bulk magnetisation in such a way that when the surface and the bulk have the same magnetisation, the surface contribution should disappear. So the scaling parameter seems to be the difference: M_{Bulk}-$M_{Surface}$ as shown in Fig. 3-80. The difference between the calculated surface magnetisation and the bulk magnetisation of the film gives a curve which exhibits a maximum around 150K which corresponds to the temperature of the experimentally observed maximum of the resistance.

So conveniently mixing both contributions, considering the mixing parameters to reproduce the degree of good connectivity between the grains the resistance of the sample should be reproduced. In this sense, following the model given by [117] considering the resistance to depend on temperature and magnetisation of the material in the domains in a hopping type model (VRH):

$$\rho \qquad \exp\left(A\left(\frac{1-\left(M/M_S\right)^2}{k_B T}\right)^{1/4}\right) \qquad \textbf{Eq. 3-11}$$

The resistivity parameterising function can be constructed considering a network of parallel resistors and the resistivity is roughly well fitted. The function containing of M_{Bulk} will give rise to the kink at T_C and the function of (M_{Bulk}-$M_{Surface}$) disappears as T_C and gives rise to the maximum at $T<T_C$.

Therefore, considering that the thermal evolution of the resistance and taking into account the contributions of the inside of the grain which magnetisation behaves as M_{bulk} and the contribution due to the GB which magnetisation we approach to the value of $M_{Surface}$ extracted previously we could reproduce the resistance at 0T without any requirement based on the existence of another phase at the GB.

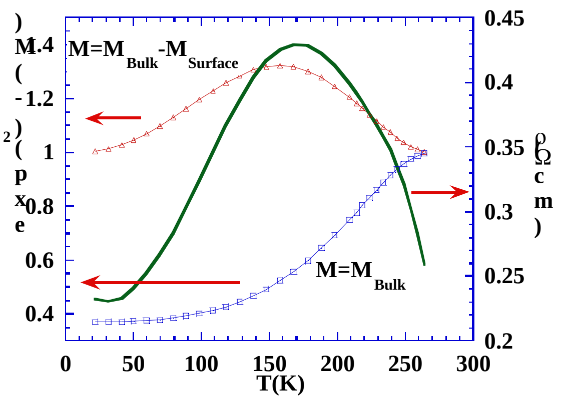

Fig. 3-80 *Calculated value of the thermal evolutions of the surface and the bulk magnetisations and the resistivity in a polycrystalline sample.*

Final remarks

In the present study of the granular behaviour on manganite films we have succeeded in developing systems which revealed the relationship between the different phenomena associated to granular behaviour. New systems have been reported as for example the films cut by the atomic saw method which revealed interesting features. In addition, high magnetic field ($\mu_0H<30T$) measurements performed at the SNCMP (Toulouse) were also important for the understanding of granular behaviour. Measurements at very low temperatures and under an applied magnetic field had never been performed before on manganite thin films. In addition, a fruitful collaboration permitted to obtain potentiometric and topographic measurements using a STM set-up that agreed with our conclusions.

To conclude, it is evident from the experimental point of view that the grain boundary in manganese perovskites, due to crystallographic symmetry breaking or disorder, constitutes a real electrical barrier because transport in manganites is a first neighbour conduction. Percolation phenomena have been evidenced in manganite epitaxial polycrystalline films on MgO substrates. The existence of free surfaces alters the Mn surroundings and is DE interaction that has been said to be responsible of the FM coupling. We have also ruled out the existence of a secondary phase at the GB. Only the different thermal evolution of the magnetisation at the surface of the grains is needed to account for the maximum of the resistance at temperatures below T_C.