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Strain and disorder effects on inhomogeneous states of manganites

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- Inhomogeneities and role of disorder and strain

- Model for manganite films: effects of thickness, strain and el-ph coupling

- Role of disorder at low temperatures
- Phase separation in films of $La_{1-x}Ca_xMnO_3$ and $La_{1-x.}Sr_xMnO_3$
- Preliminar analysis about STM experimental data on LSMO films:

features of multiphase modulation?

Manganites: $Re_{1-x}A_xMnO_3$

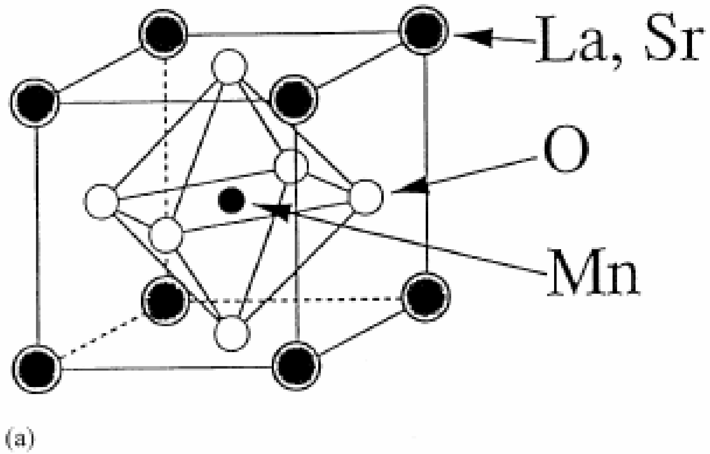
Re-Rare earth (La or Nd trivalent) A- Alkali (Sr or Ca divalent)

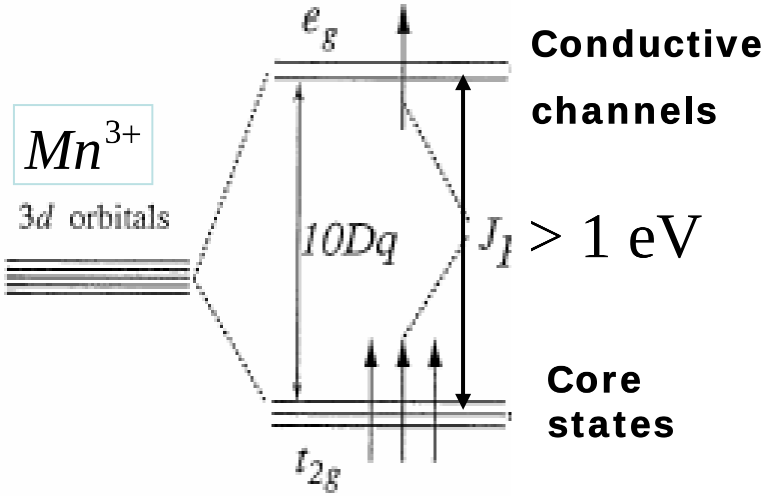
Mixed valence compounds:
Mn^{4+} instead of Mn^{3+} depending on hole doping x

Compounds kwown for their colossal magnetoresistance properties

CMR features in correspondence with metal-insulator ferro-para transition

Perovskite structure



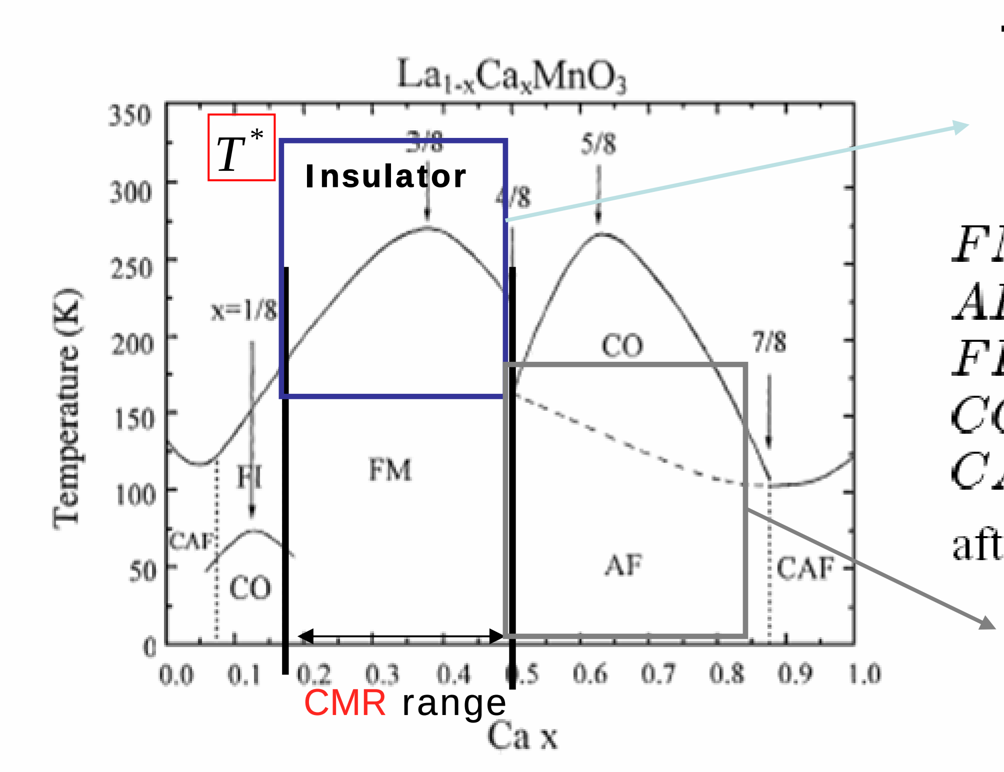


Half-metallic systems with strong Hund’s rule coupling and double-exchange mechanism

Classification of manganites

I) Large bandwidth (weak el-ph and disorder strength) → (LSMO) $La_{1-x.}Sr_xMnO_3$

II) Intermediate bandwidth (intermediate el-ph and disorder strength) → (LCMO) $La_{1-x}Ca_xMnO_3$



Nano and/or meso inhomogeneities

FM stands for Ferromagnetic metallic
AFM for Antiferromagnetic insulating
FI for Ferromagnetic Insulating
CO for Charge-Ordered
CAF for Canted Antiferromagnetic

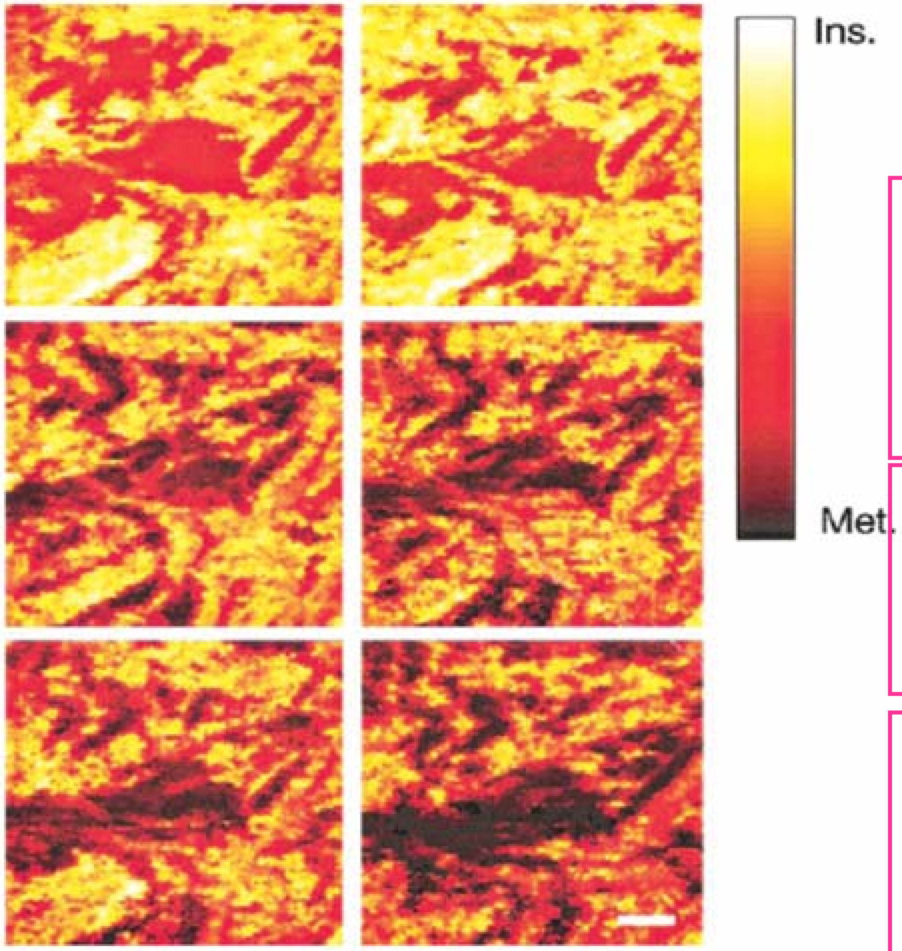
after S.-W. Cheong and H.Y. Hwang (1999)

Inhomogeneities on the nanoscale

III) Small bandwidth (large el-ph coupling and disorder strength)

Inhomogeneities in manganites

STM data in LCMO film for x=0.3 just below the critical temperature



Fath et al., Science **285**, 1540

As the Curie temperature is approached from below, diffuse scattering from lattice polarons develops along with short range polaron correlations that are consistent with stripe formation in LCMO.
C.P. Adams et al., PRL **85**, 3954

Presence of lattice polarons and their short-range correlations with populations of correlated and uncorrelated polarons related to the transport in LCMO,
P. Dai, PRL **85**, 2553

Short-range polaron correlations are completely dynamic at high *T*, but then freeze from a characteristic temperature,
D.N. Argyiou et al, PRL **89**, 36401

In LCMO with Pr (single crystal) insulating domains in the metallic host at least an order of magnitude larger in size compared to previous estimates and memory effects probably due to long-range strains,
D.D. Sarma et al. PRL **93**, 97202

Mechanisms of phase separation

Role of disorder (mainly electron mechanism)

Numerical studies through MonteCarlo simulations on double-exchange models characterized by first order transitions. Quenched disorder is important to smear the transition between competing states and induce clustered states crucial for CMR -> Prediction of characteristic temperature $\boxed{T^*}$ (E. Dagotto “Nanoscale phase separation”, Springer Verlag, 2003)

Role of (intrinsic) strain (mainly lattice mechanism)

Strong coupling between electronic and elastic degrees of freedom gives long-range strains. Natural mechanism for self-organized inhomogeneities over nano- and micrometre scale (K.H. Ahn et al., Nature 2004). Prediction of **Multiscale phase modulations** at high T with nanometer-scale polaron correlations(Cheong et al.)

Intrinsic and Extrinsic

Disorder + Strain ⟶ Thin films for experiments

Hamiltonian for manganites

Single orbital model

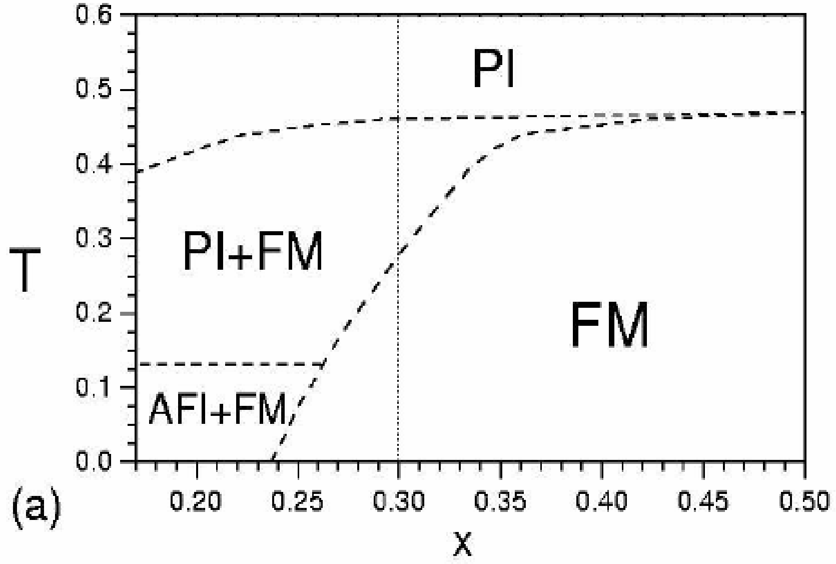
$$
\begin{aligned}
H = &-t \sum_{<i,j>} \left(\frac{S_0^{i,j} + 1/2}{2S+1} \right) c_i^\dagger c_j - \mu \sum_i c_i^\dagger c_i \\
&+\omega_0 \sum_i a_i^\dagger a_i + g\omega_0 \sum_i c_i^\dagger c_i (a_i + a_i^\dagger) \\
&+\epsilon \sum_{<i,j>} \vec{S}_i \cdot \vec{S}_j - g_s \mu_B \textstyle\sum_i \vec{h}_{ext} \cdot \vec{S}_i
\end{aligned}
$$

- Double-exchange term for strong Hund's rule coupling,

with $(\vec{S}_0^{i,j})^2 = (\vec{S}_i + \vec{S}_j + \vec{s})^2$.

- Electron-phonon term.
- Super-exchange term.
- External magnetic field h_{ext}.

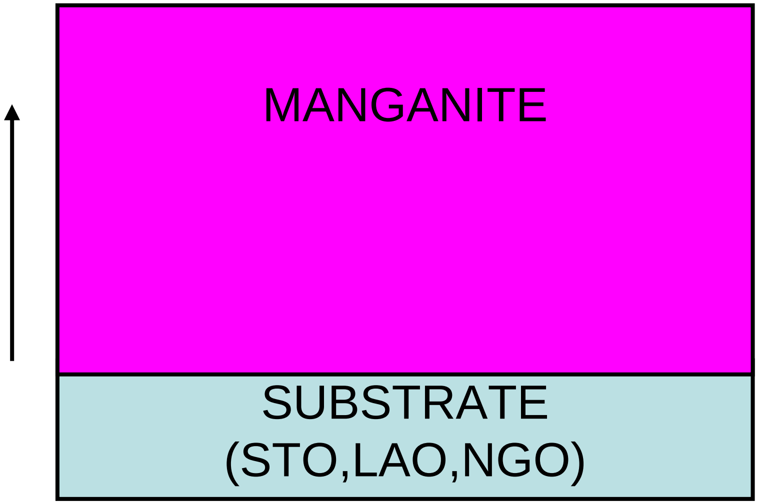
Mean-field phase diagram (bulk)



- Qualitative agreement with experimental phase diagram for $0 < x < 0.5$
- Evidence of phase separation

Films: confinement along the growth axis

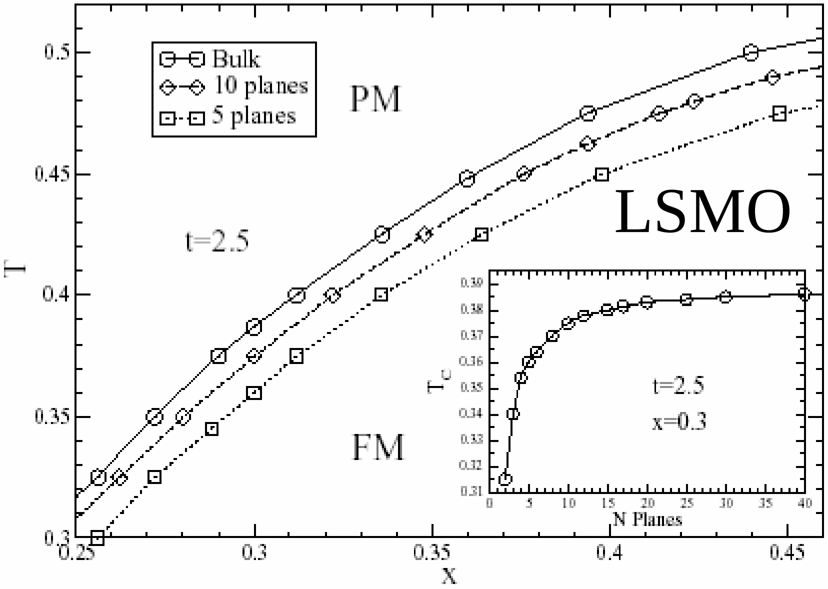
C.A. Perroni et al., PRB **68,** 224424 (2003)

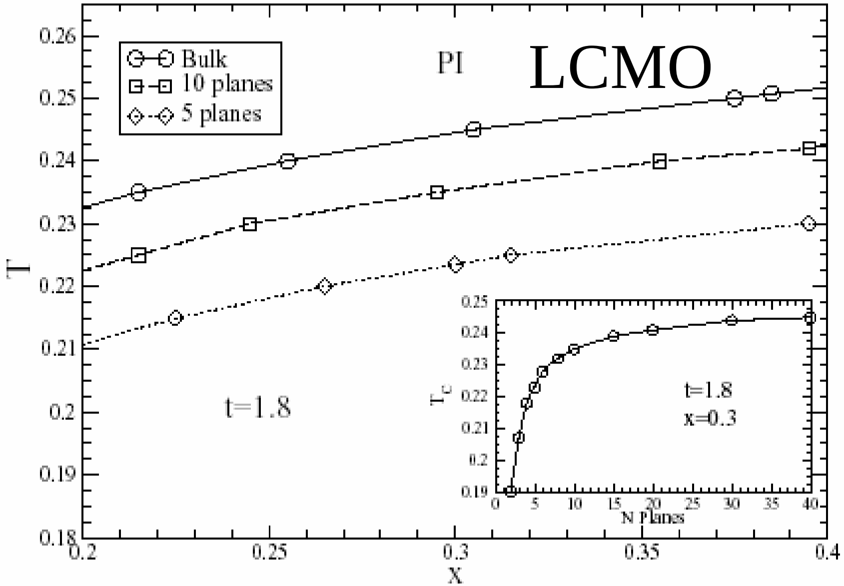

MANGANITE

SUBSTRATE
(STO,LAO,NGO)

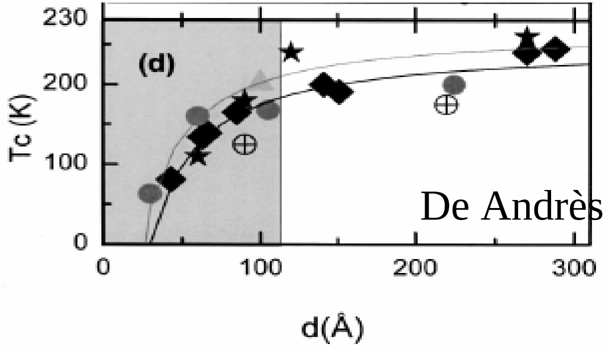
Manganite Films

Size effects



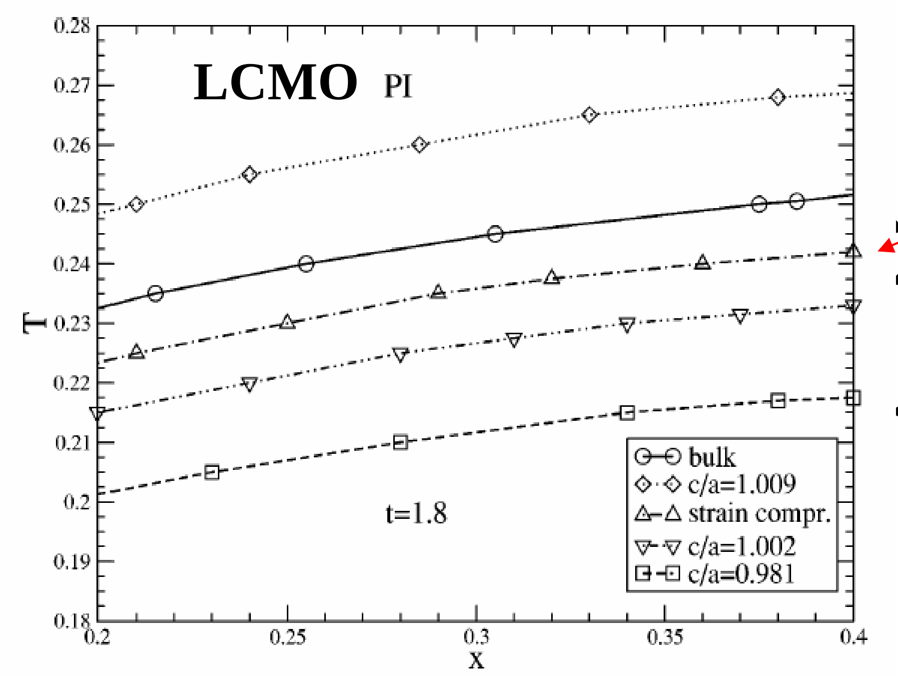


The M-I transition as a function of x for different bandwidth and couplings: the transition temperature decreases with film size



De Andrès et al. APL (2003)
LCMO

Strain effects due to mismatch with substrate



Compressive strain $\frac{c}{a} > 1$ on (LAO) $LaAlO_3$

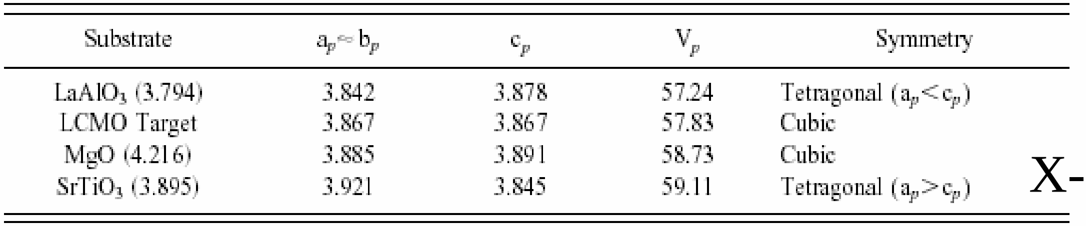
Dependence on the Mn-O-Mn bond angle (EXAFS)

$\frac{c}{a} \cong 1$ MgO

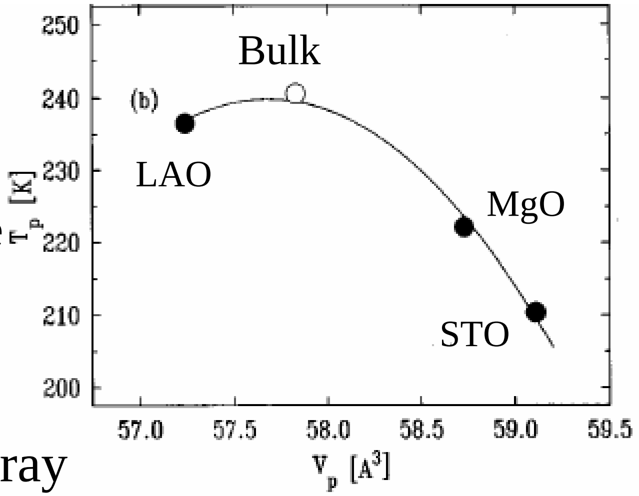
Tensile strain $\frac{c}{a} < 1$ on (STO) $SrTiO_3$

$$t_x = t_y \cong \cos(\phi_{in-plane})/d_{in-plane}^{3.5}, \quad t_z \cong \cos(\phi_{out-plane})/d_{out-plane}^{3.5}$$

d Mn-O-Mn bond length, $\phi = \frac{\pi - \vartheta}{2}$, θ Mn-O-Mn bond angle

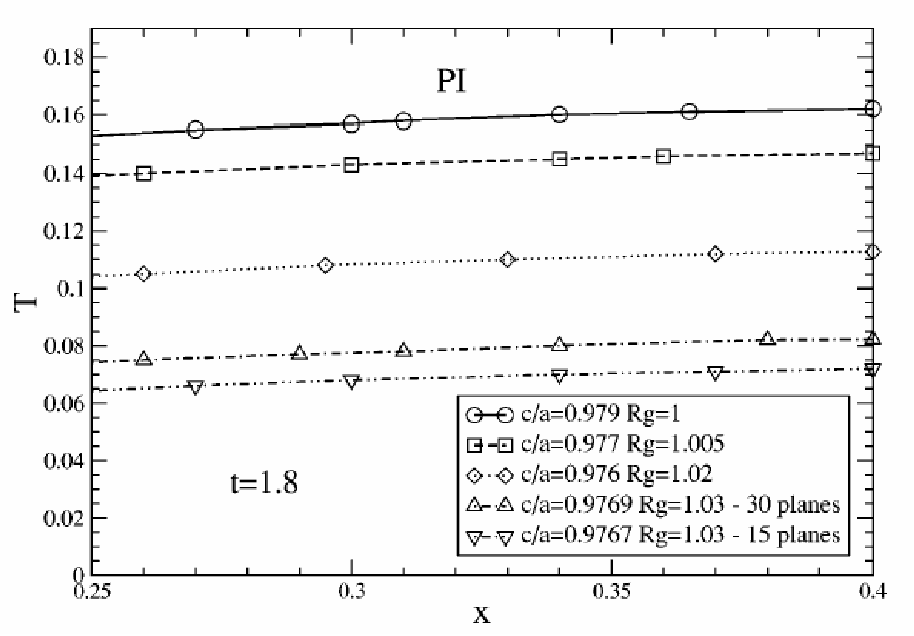


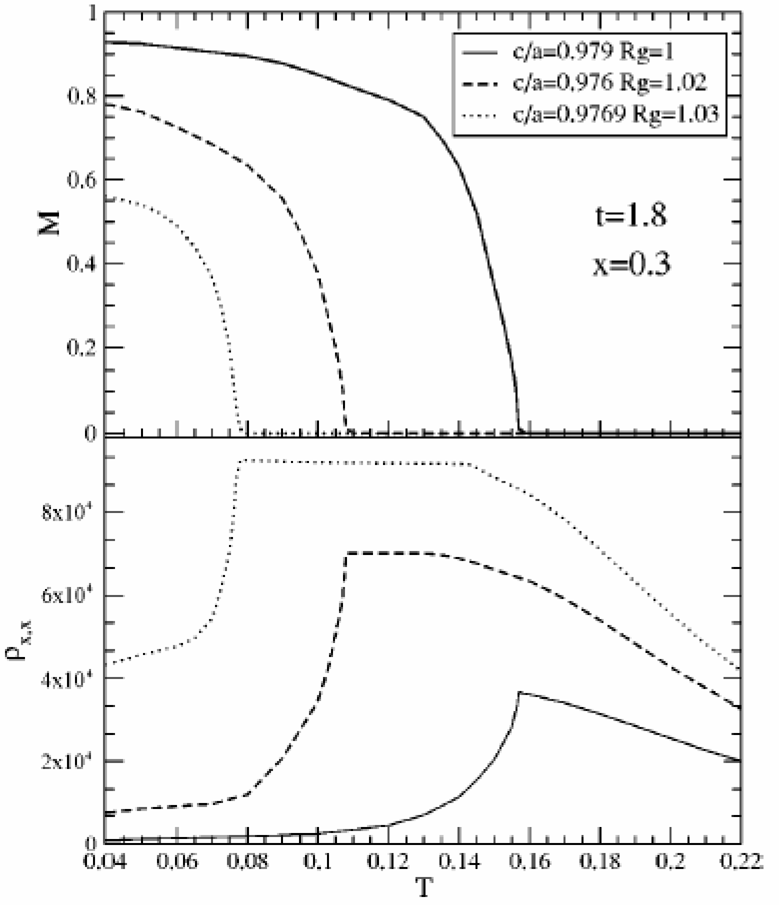
Substrate	$a_p \approx b_p$	c_p	V_p	Symmetry
$LaAlO_3$ (3.794)	3.842	3.878	57.24	Tetragonal ($a_p < c_p$)
LCMO Target	3.867	3.867	57.83	Cubic
MgO (4.216)	3.885	3.891	58.73	Cubic
$SrTiO_3$ (3.895)	3.921	3.845	59.11	Tetragonal ($a_p > c_p$)



X-ray

Role of size, strain and el-ph effects

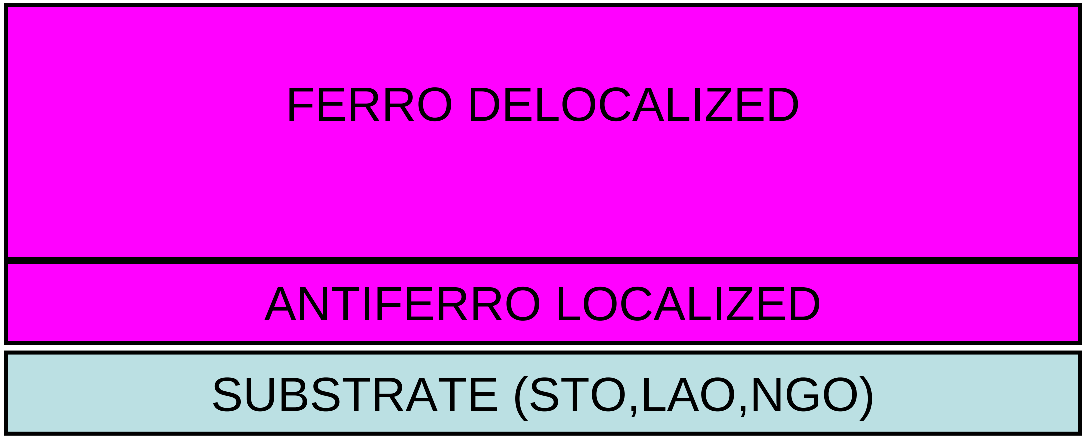




Reduction of critical temperature, magnetization and increase of the resistivity up to

dead layer

Role of interfaces and dead-layer



FERRO DELOCALIZED

ANTIFERRO LOCALIZED

SUBSTRATE (STO,LAO,NGO)

You can take into account the surface term between ferro and antiferro layers when the thickness of the film is small.

With decreasing the size, the thickness of Antiferro layer increases. With small sizes, only the antiferro layer can become stable.

C.A. Perroni et al., to be submitted

Interesting issue within a collaboration with experimental groups

Low T transport: signature of disorder effects

Different mechanisms for resistivity: $\rho \propto T^{\alpha}$

α =2: Fermi liquid or spin-flip (prohibited in truly half-metallic samples) mechanism (I. Mannari, 1959) (single crystals)

α =2.5: finite density of states of the minority spins at Fermi energy due to disorder inducing spin-flip scattering (X. Wang et al. PRL 1999)

α =3: anomalous single magnon scattering at finite temperatures through non rigid behavior of the bands due to spin fluctuations (T. Akimoto et al. PRL 2000) .

Relevance of single-magnon scattering

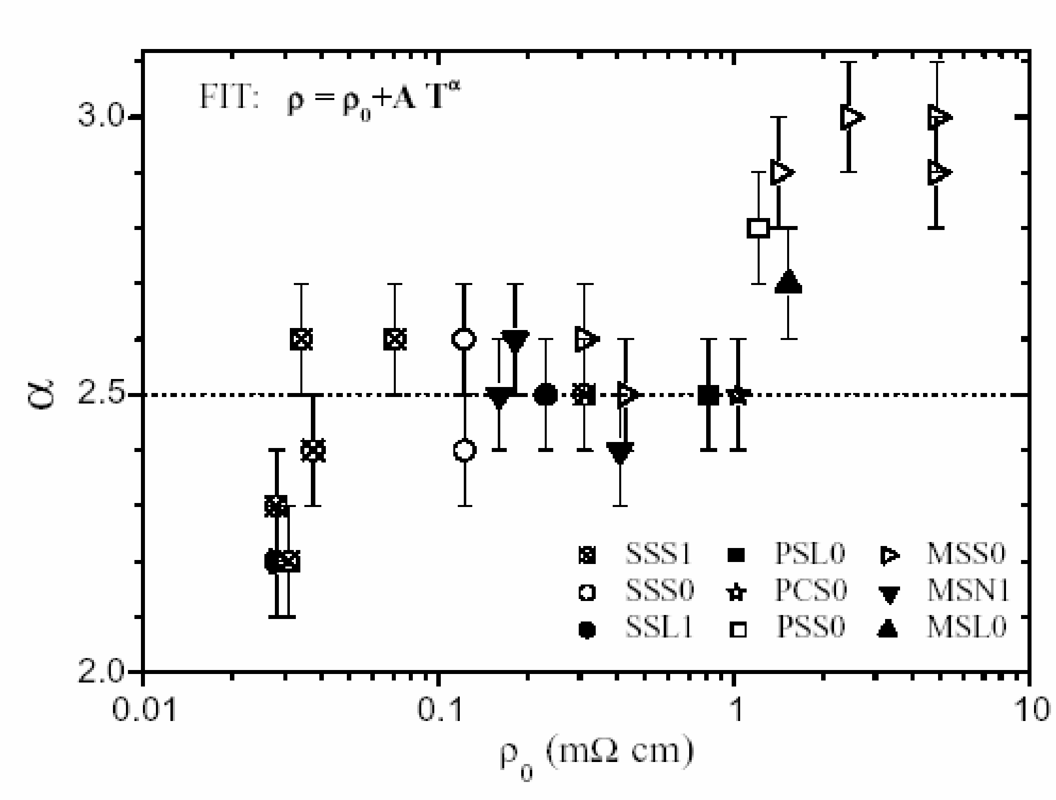
$$\boxed{\rho_{LT} = \rho_0 + AT^{\alpha}}$$

$\boxed{\rho_0}$ measures the strength of the disorder

S. Mercone, C.A. Perroni et al., PRB **71,** 64415 (2005)

Analysis on many optimized films grown with different techiques

Correlation between residual resistivity and the exponent α seen in experimental data



α =2: Fermi liquid or spin- flip (no in good half-metals)
α =2.5: minority spins at Fermi energy due to disorder
α =3: anomalous magnon scattering

α =3 dominant as effective bandwidth decreases. With increasing disorder, the energies available to delocalized states get reduced.

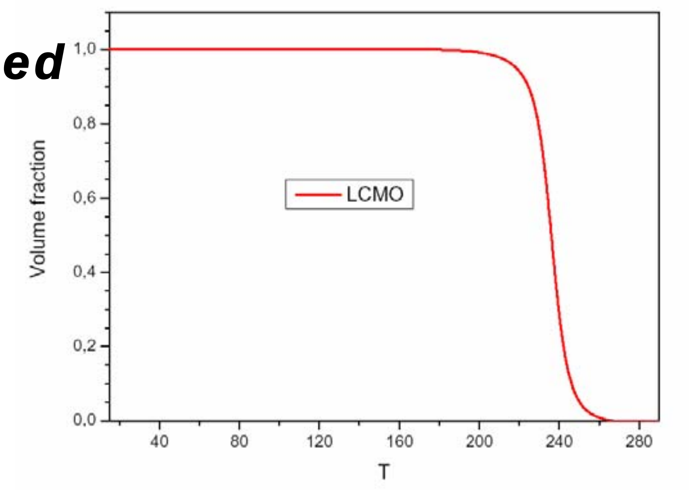
Phase-separation in LCMO and LSMO films
Experimental resistivity $\rho_{EX}(T)$

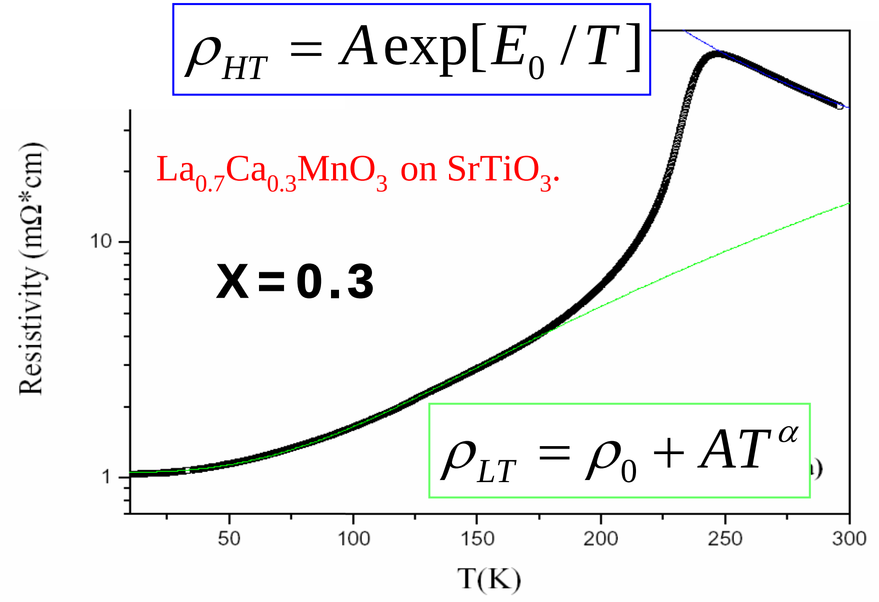
G. Balestrino, M. Angeloni and coworkers

L. Maritato, S. Mercone and coworkers

F. Miletto, U. Scotti di Uccio and coworkers

Extracted f(T)



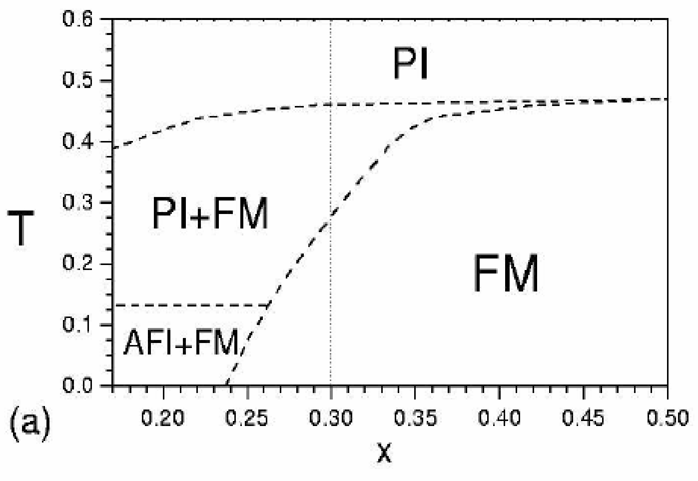


$$\rho_{HT} = A\exp[E_0 / T]$$

$$\rho_{LT} = \rho_0 + AT^{\alpha}$$

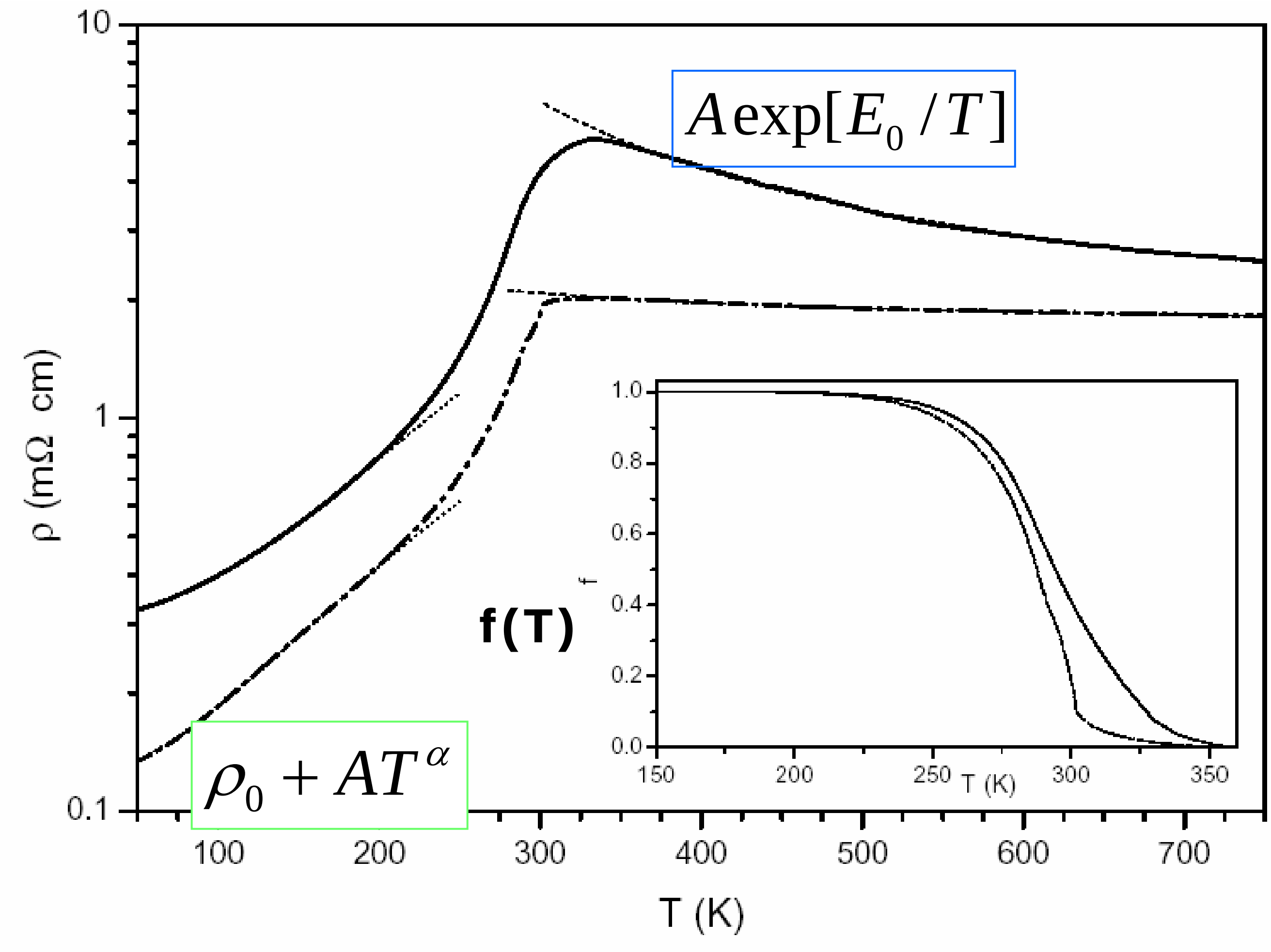
$$\rho_{EX}(T) = \rho_{LT}(T) f(T) + \rho_{HT}(T)[1 - f(T)]$$

$f(T)$: metallic volume fraction



S. Mercone, C.A. Perroni et al., PRB **71,** 64415 (2005)

$La_{0.7}Sr_{0.3}MnO_3$ film on substrate on STO with different orientations



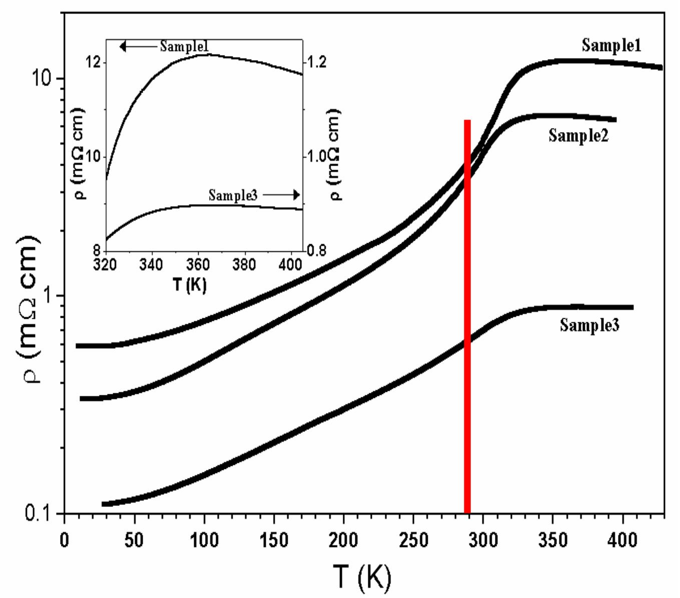
$$A\exp[E_0/T]$$

$$\rho_0 + AT^{\alpha}$$

f(T)

For LSMO bulk (single crystal) there is no metal-insulator transition

STM analysis in LSMO films with x=0.3 at room and nitrogen liquid temperature in collaboration with Coherentia –INFM STM group (R. Di Capua, M. Salluzzo, R. Vaglio)



Name	Substrate	Thickness (nm)	T_p (K)	T_c (K)
Sample1	STO (110)	10	350	310
Sample2	STO (100)	40	350	300
Sample3	NGO (110)	40	370	305

Nanoscale correlations at room temperature

No inhomogeneities at nitrogen liquid temperature!

Features compatible with multiphase modulation

In addition to stress fields, amounts of disorder can tune the behavior of inhomogeneity and consequently CMR, see J. Burgy et al., PRL **92**, 97202 (2004).

R. Di Capua, C.A. Perroni, et al. to be submitted

Conclusions

- The role of thickness, strain and el-ph interaction are relevant in affecting the properties of manganite thin films and their tendencies toward “phase separation” regime.
- The role of disorder is important in influencing the transport properties.
- Open questions:: Nanometric and/or micrometric scale inhomogeneity. Feasibility of multiphase modulation?
- Perspectives: STM experiments and analysis at temperatures larger than MI transition temperature.