Nanoscale Structural Correlations in Magnetoresistive Manganites

V. Kiryukhin

(Rutgers University)

A. Borissov, T.Y. Koo, H. Ishibashi, S. Grenier, S-W. Cheong (Rutgers),
J.P. Hill, D. Gibbs, C.S. Nelson, Y.J. Kim (BNL), Q. Huang, J.W. Lynn (NIST)

Supported by the NSF and DOE

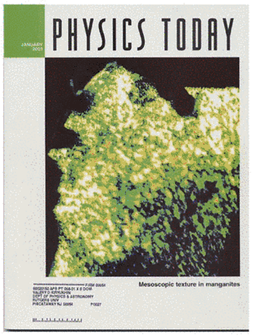
Inhomogeneities dominate the physics of a large number of correlated materials.

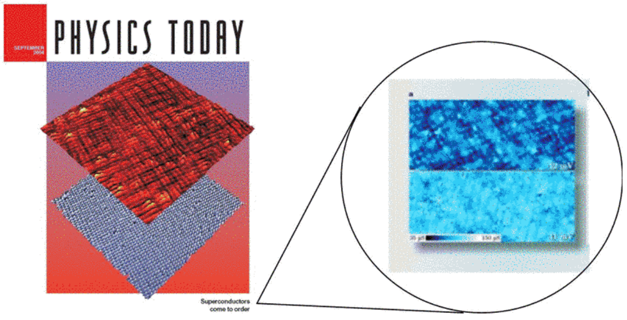
- Nanoscale inhomogeneities appear to be of particular importance.

- The inhomogeneities are commonly observed in a number of chemically uniform materials.

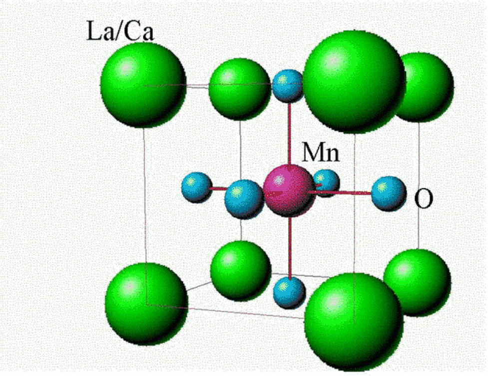
- Their presence leads to new physical phenomena.

The self-organization of clustered structures appears to be a characteristic of many interesting materials.

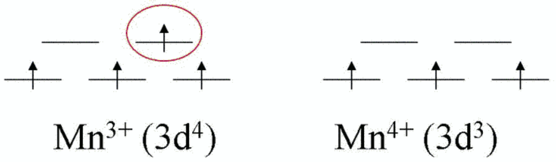




Perovskite Manganites $A_{1-x}B_xMnO_3$



- Electron-electron
- Electron-lattice
- Superexchange
- Long-range elastic strain



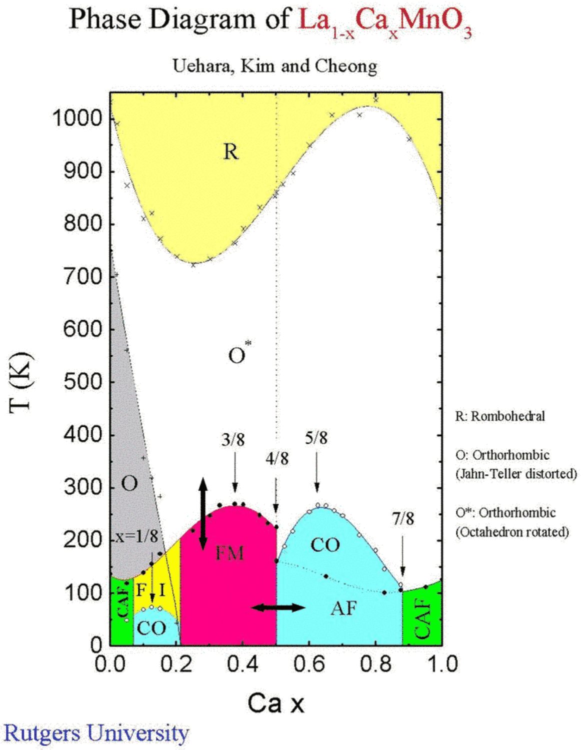
e_g: $d_{x^2-y^2}$, $d_{3z^2-r^2}$

t_{2g}: d_{xy}, d_{yz}, d_{xz}

CMR Effect

↕ PI to FM

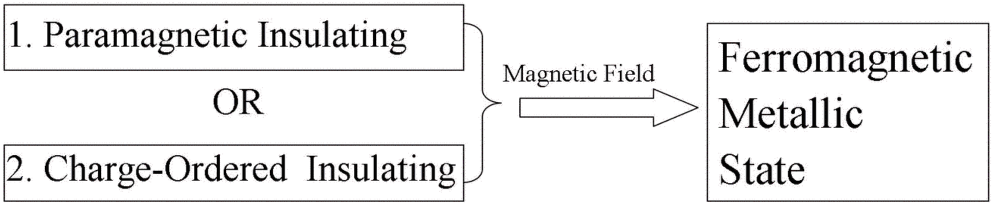
↔ CO to FM


Phase Diagram of $La_{1-x}Ca_xMnO_3$

Uehara, Kim and Cheong

Rutgers University

Colossal Magnetoresistance (CMR)



1. Paramagnetic Insulating

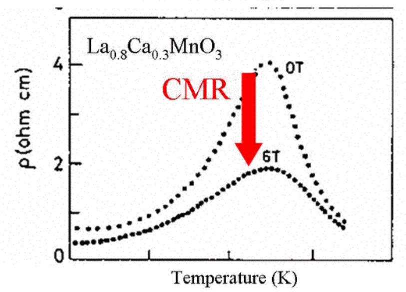
OR

2. Charge-Ordered Insulating

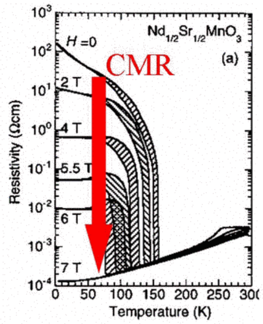
Magnetic Field

Ferromagnetic Metallic State

1. PI to FM



2. CO to FM



R. Mahendrian, et al., (1996)

H. Kuwahara, et al. (1995)

CMR and Inhomogeneous States

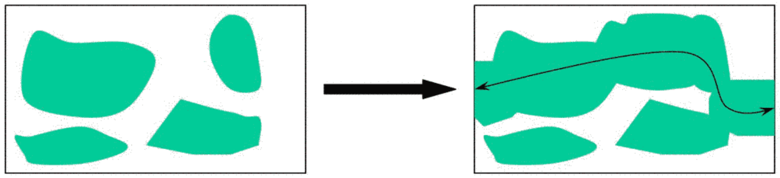
A Variety of Length Scales:

- martensitic states (hundreds of microns)
- “phase-separated” states (submicron)
- nanoscale correlations

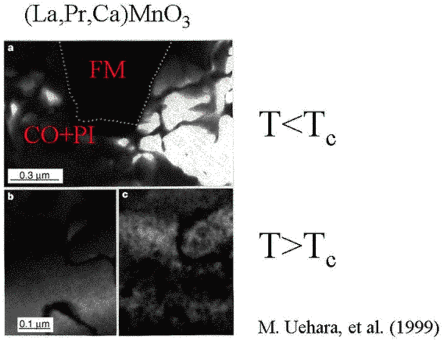
The balance between the phases in the inhomogeneous states can often be readily influenced by varying physical parameters (magnetic field, pressure, radiation), producing various “colossal” effects.

CMR and Inhomogeneous States

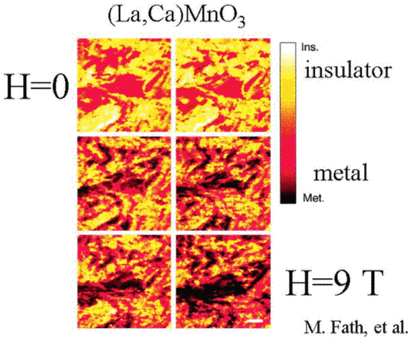
1. Phase separation between metallic and insulating phases (~1μm).



Percolative phase transition



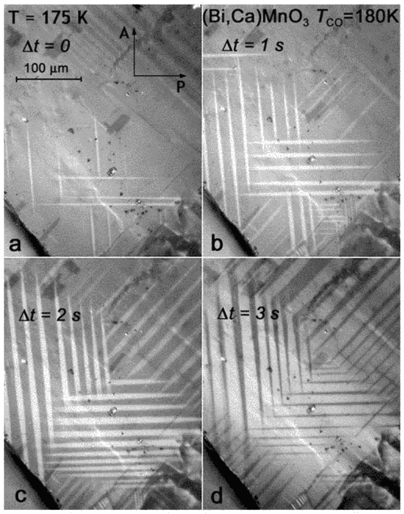
M. Uehara, et al. (1999)



M. Fath, et al. (1999)

CMR and Inhomogeneous States

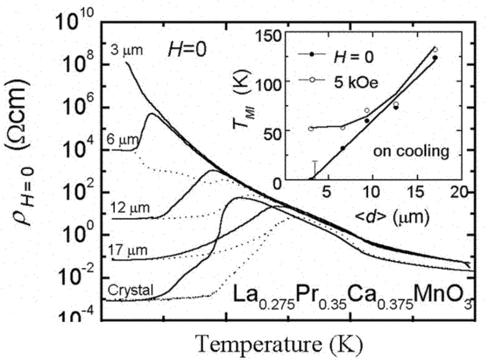
2. Martensitic States (1-100μm).



V. Podzorov, et al. (2001)

Martensitic accommodation strain stabilizes inhomogeneous states and nonequilibrium phases.

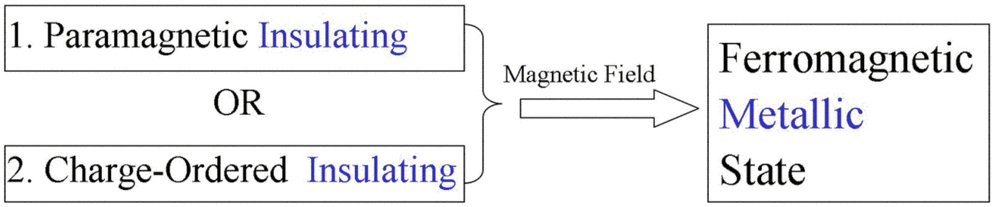
It plays a significant role in ceramic samples.



CMR and Inhomogeneous States

Inhomogeneous states are ubiquitous in manganites. In many cases, they explain the character of various transitions in the manganites, as well as the sensitivity of their properties to the change of external conditions.

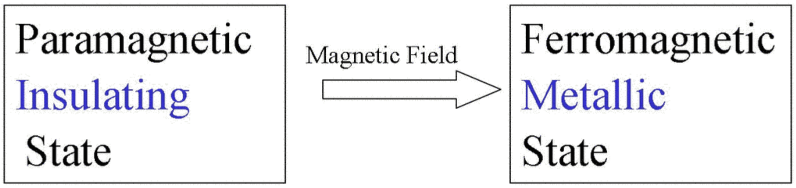
Q: How do these inhomogeneities affect the magnitude of the CMR?



CMR and Inhomogeneous States

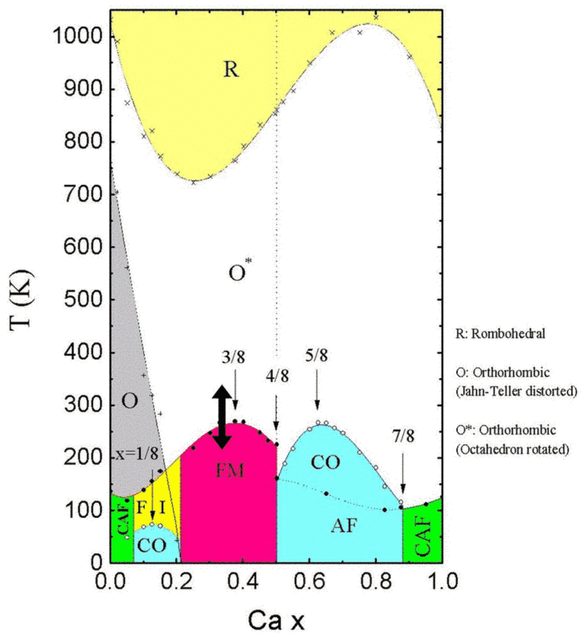
Inhomogeneous states are ubiquitous in manganites. In many cases, they explain the character of various transitions in the manganites, as well as the sensitivity of their properties to the change of external conditions.

Q: How do these inhomogeneities affect the magnitude of the CMR?



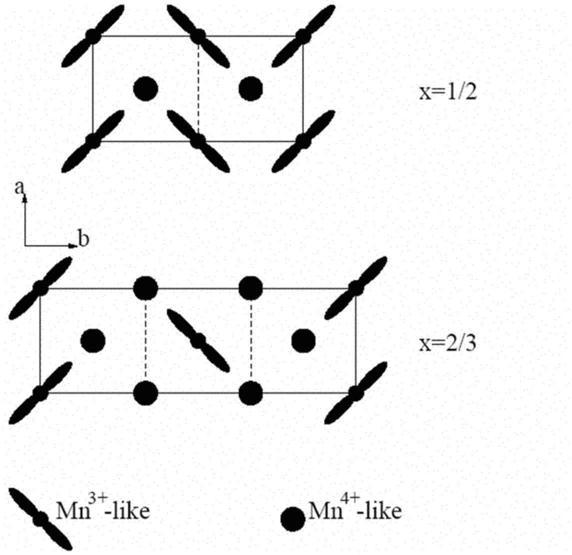
Phase Diagram of $La_{1-x}Ca_xMnO_3$

Uehara, Kim and Cheong



Rutgers University

Charge and orbital order in manganites. Goodenough’ model. Stripes.



Resonant x-ray scattering shows that

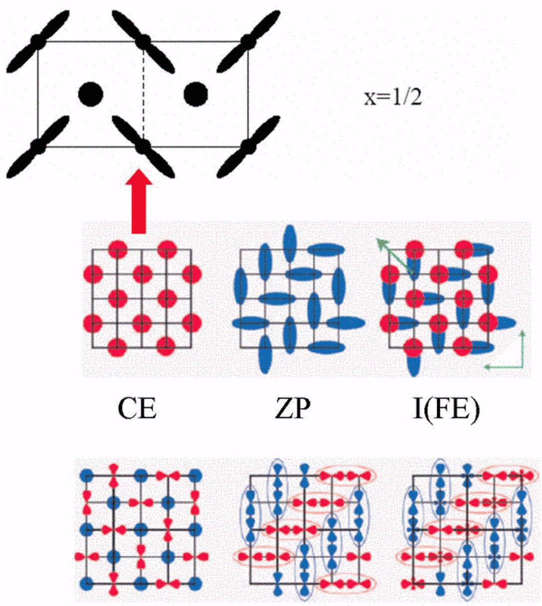
(1) Charge disproportionation is small, and the Mn valence is close to 3.5.

(2) The basic checker-board arrangement of distinct Mn ions is correct.

S.Grenier, at al., PRB, 2004.

Charge and orbital order in manganites. Goodenough' model. Stripes.

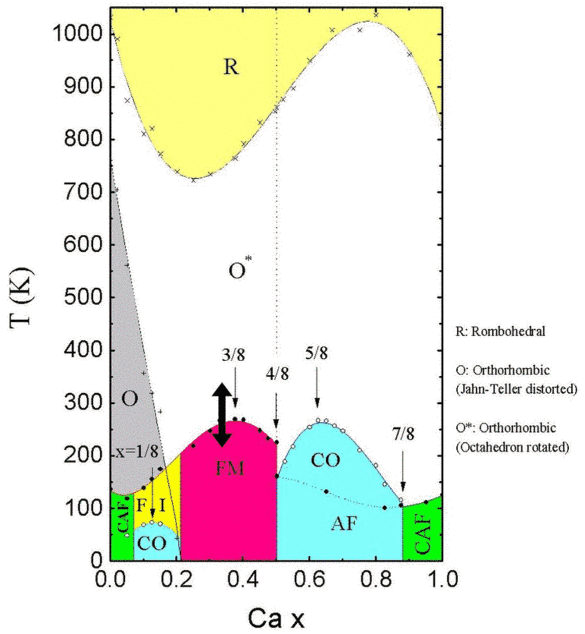
Manganites as Multiferroics (Magnetoelectrics) ?



Efremov, V.d.Brink, Khomskii (2004)

Phase Diagram of $La_{1-x}Ca_xMnO_3$

Uehara, Kim and Cheong



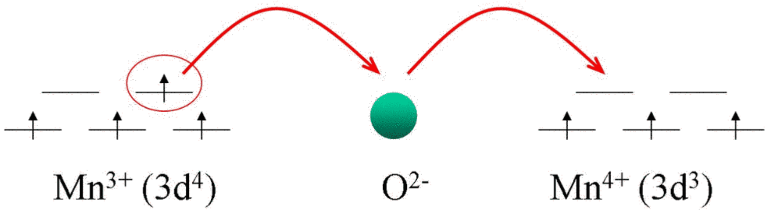
R: Rombohedral

O: Orthorhombic (Jahn-Teller distorted)

O*: Orthorhombic (Octahedron rotated)

Rutgers University

Colossal Magnetoresistance (CMR)



e_g: $d_{x^2-y^2}$, $d_{3z^2-r^2}$

t_{2g}: d_{xy}, d_{yz}, d_{xz}

Double exchange mechanism: $t_{ij} \sim \cos(\theta_{ij}/2)$, where θ_{ij} is the angle between the core Mn spins 3/2. (Strong Hund's rule coupling).

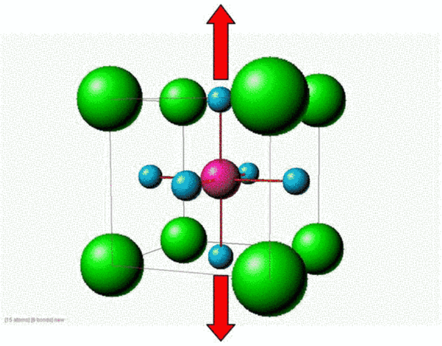
Zener (1951), Anderson and Hasegava (1955)

The AF CO state is insulating. The FM state is more conducting than the PI state. In reality, the PI state is not as good a conductor as the DE mechanism predicts.

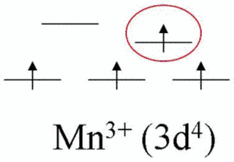
FM: $\rho \sim 10^{-3}$ Ωcm

PI: ρ as large as 1 Ωcm ???

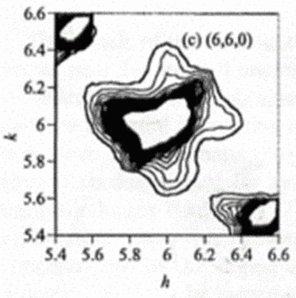
Colossal Magnetoresistance (CMR)



Polarons play a role (Millis, 1995)



Jahn-Teller Effect

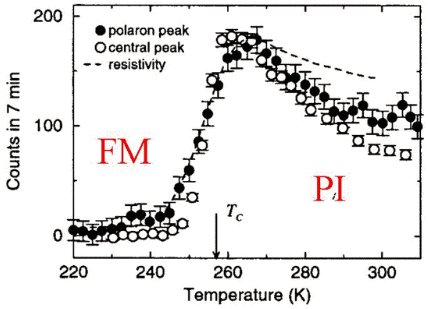


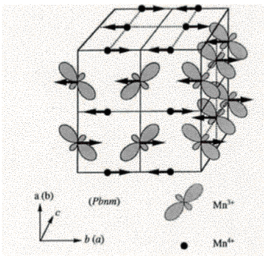
X-ray scattering from uncorrelated polarons (Huang scattering) in the PI phase is observed (Shimomura, et al., 1999)

Nanoscale Correlations and the CMR

Nanoscale correlated (CO?) regions play a role!

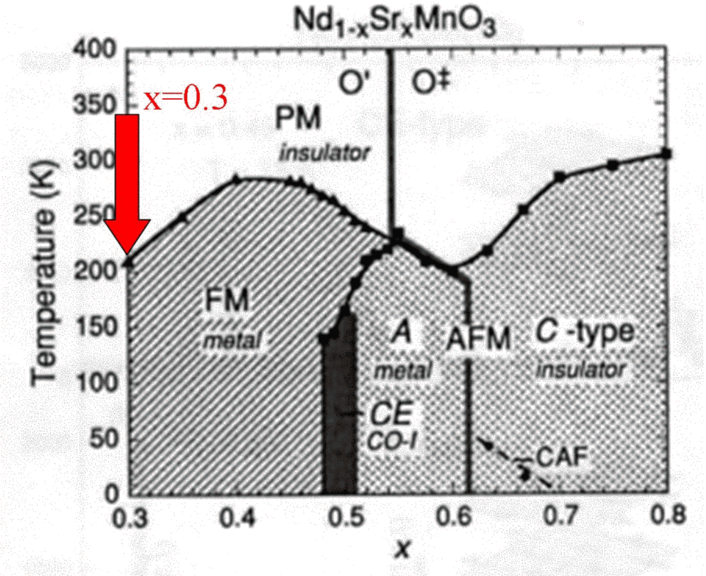
Broad peaks are observed in neutron scattering experiments at the wavevector characteristic to the CE-type charge/orbital order in the PI phase of $La_{0.7}Ca_{0.3}MnO_3$ and other manganites (Adams, et al.; Dai, et al.; Tokura, et al.; Nelson, et al., 2000).





C. P. Adams, et al., (2000)

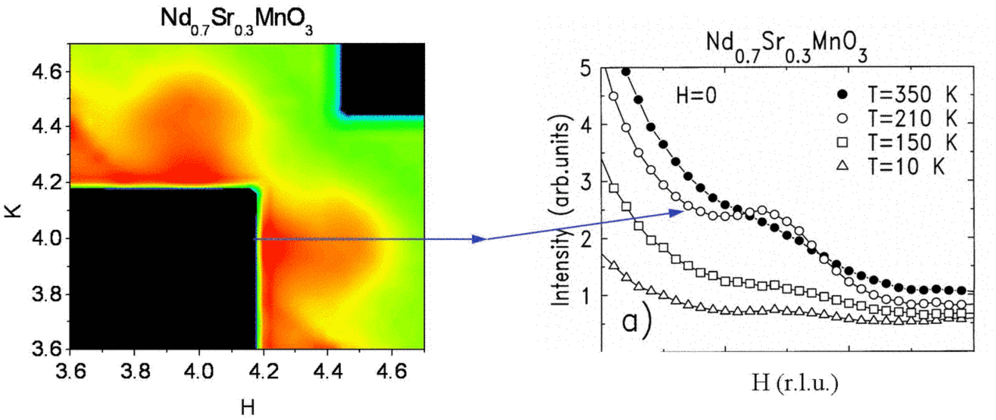
Nanoscale Correlations and the CMR



Kajimoto, et al., 1999

Nanoscale Correlations and the CMR

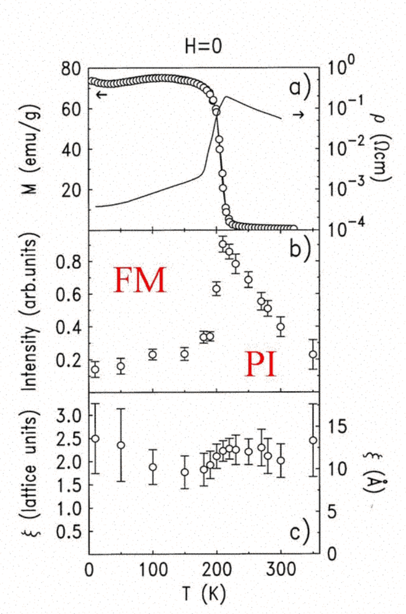
x=0.3 samples



Broad peaks at the CE-type position in the PI$^{(*)}$ phase

Nanoscale Correlations and the CMR

x=0.3 samples



Temperature dependences

-remnant correlations in the FM phase

- temperature-independent correlation length

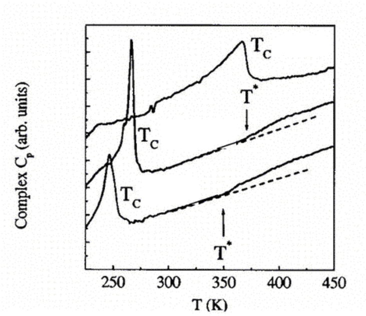
- evidence for *T** ?

V. Kiryukhin, at al., PRB (2002)

Nanoscale Correlations and the CMR

x=0.3 samples

Evidence for *T** ?

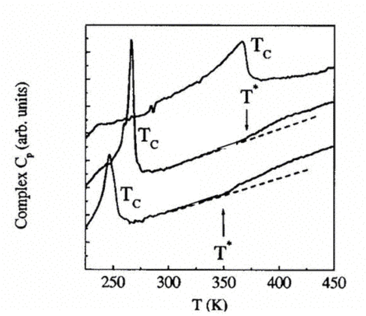


Heat capacity in $La_{2/3}Ca_{1/3}MnO_3$ and in $La_{2/3}Sr_{1/3}MnO_3$ (J. Mira et al., 2001)

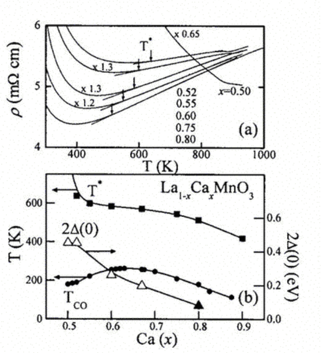
Nanoscale Correlations and the CMR

x=0.3 samples

Evidence for *T** ?



Heat capacity in $La_{2/3}Ca_{1/3}MnO_3$ and in $La_{2/3}Sr_{1/3}MnO_3$ (J. Mira et al., 2001)

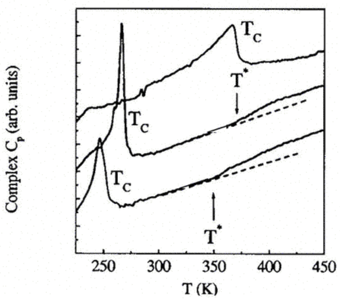


Electrical resistivity and optical conductivity in $La_{1-x}Ca_xMnO_3$, x>0.5 (K. H. Kim, et al., 2002)

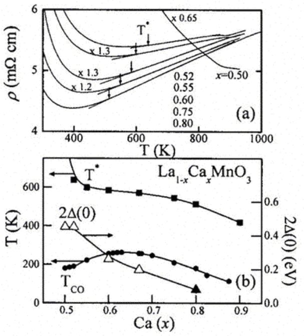
Nanoscale Correlations and the CMR

x=0.3 samples

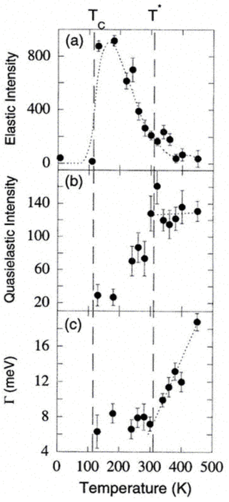
Evidence for *T** ?



Heat capacity in $La_{2/3}Ca_{1/3}MnO_3$ and in $La_{2/3}Sr_{1/3}MnO_3$ (J. Mira et al., 2001)



Electrical resistivity and optical conductivity in $La_{1-x}Ca_xMnO_3$, x>0.5 (K. H. Kim, et al., 2002)



Neutron scattering, layered $La_{2-2x}Sr_{1+2x}Mn_2O_7$ manganite, x~0.4 (Argyriou, et al., 2002)

Nanoscale Correlations and the CMR

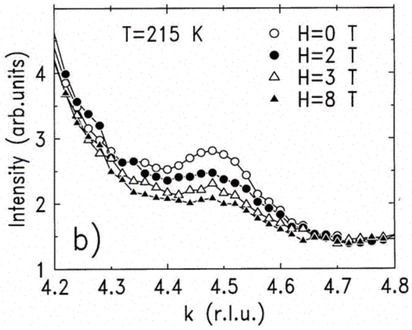
x=0.3 samples

CMR Effect

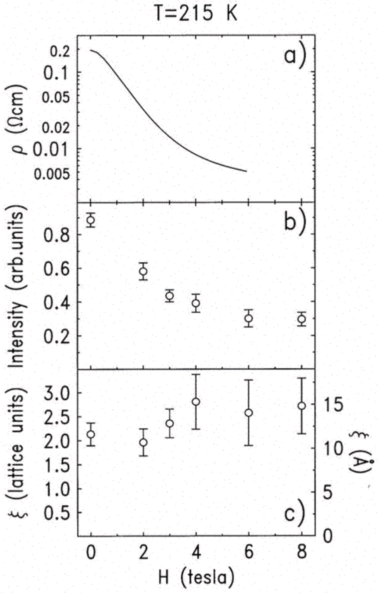
- correlations suppressed by the field

-inhomogeneous high-field state

- field-independent corr. length

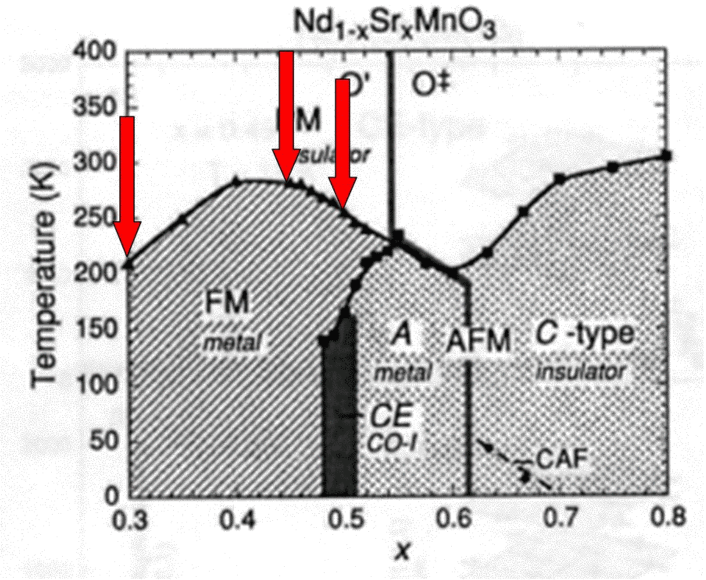


T.Y.Koo, et al., PRB ((2001)



Opposite behavior to the FM clusters observed by SANS

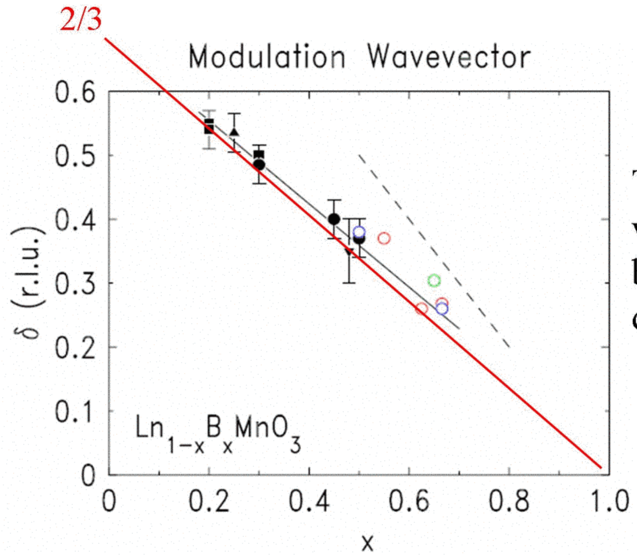
Nanoscale Correlations and the CMR



Kajimoto, et al., 1999

Nanoscale Correlations and the CMR

Doping dependence



The lattice modulation wave vector appears to be determined by a single parameter – the divalent metal concentration *x*.

V. Kiryukhin, et al., PRB (2002)

Nanoscale Correlations and the CMR

Doping dependence

Nanoscale structural correlations play an important role in the CMR phenomenon. They are associated with the higher-resistivity PI state, and they are different from the ferromagnetic clusters observed in the small-angle neutron scattering experiments.

- specific correlation length (10-15 A)[1]; object of a well-defined size?

- linear dependence of the lattice modulation period on *x*

- "Griffith" temperature T* (?). The nanoclusters may become dynamic above T* [Nelson, at al., (2001); Argyriou, at al., (2002)]

Q: physical mechanism responsible for the correlations
Q: the structure of the correlated regions; static or dynamic
Q: the role of uncorrelated polarons

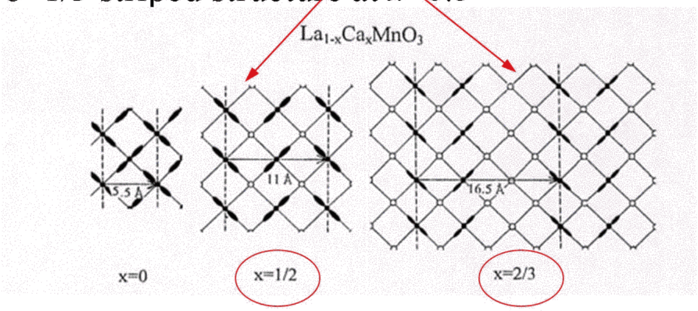
[1]) The actual volume of the correlated regions can be as large as $(2\xi)^3$~100 unit cells

---

Nanoscale Correlations and the CMR

Doping dependence

Possible structures: CE-type at *x*=0.3, other CO/OO structures at larger *x*, δ~1/3 striped structure at *x*=0.5



The correlated regions are electron-depleted ?

-numerous theoretical predictions (Khomskii et al., Dagotto et al., . . .)

-Coulomb forces should not prevent charge redistribution in the *nanoscale* regions (but can be a factor limiting the region size)

Nanoscale Correlations and the CMR

Doping dependence

Separate treatment of the localized classical t_{2g} electrons (S=3/2), and the e_g electron.

$$H = H_{kin} + H_{Hund} + H_{AF} + H_{el\text{-}ph} + H_{el\text{-}el}$$

1. One orbital (Ferromagnetic Kondo, or Double Exchange) Model

- no electron-phonon interaction, no Coulomb interaction for e_g

- JT provides a static splitting of the e_g orbitals – one active orbital

$$\hat{H} = -t \sum_{\langle ij\rangle,\sigma} (a^\dagger_{i,\sigma} a_{j,\sigma} + H.c.) - J_{\mathrm{H}} \sum_{i,\alpha,\beta} a^\dagger_{i,\alpha} \sigma_{\alpha\beta} a_{i,\beta} \cdot \mathbf{S}_i + J_{\mathrm{AF}} \sum_{\langle ij\rangle} \mathbf{S}_i \cdot \mathbf{S}_j$$

Nanoscale Correlations and the CMR

Doping dependence

2. Two-orbital Models

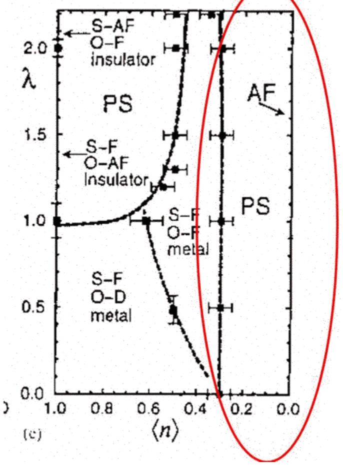
- two e_g orbitals coupled to JT phonons

- argument: large J_H allows to drop the Hubbard U and the electron-electron coupling

$$\begin{aligned} H &= H_{kin} + H_{\mathrm{Hund}} + H_{\mathrm{AF}} + H_{el-ph} \\ &= -\sum_{\mathbf{ia}\gamma\gamma'} t^{\mathbf{a}}_{\gamma\gamma'} a^\dagger_{\mathbf{i}\gamma} a_{\mathbf{i}+\mathbf{a}\gamma'} - J_{\mathrm{H}} \sum_{\mathbf{i}\gamma} \mathbf{s}_{\mathbf{i}\gamma} \cdot \mathbf{S}_{\mathbf{j}} + J_{\mathrm{AF}} \sum_{\langle\mathbf{ij}\rangle} \mathbf{S}_{\mathbf{i}} \cdot \mathbf{S}_{\mathbf{j}} \\ &\quad -2g \sum_{\mathbf{i}} (Q_{2\mathbf{i}} T^x_{\mathbf{i}} + Q_{3\mathbf{i}} T^z_{\mathbf{i}}) + (k_{\mathrm{JT}}/2) \sum_{\mathbf{i}} (Q^2_{2\mathbf{i}} + Q^2_{3\mathbf{i}}). \end{aligned}$$

Typical Parameter Values for Manganites (eV)

U	J_{H}	CFS	t	λ	J_{AF}
6	2	1	0.5	1-1.5	0.05

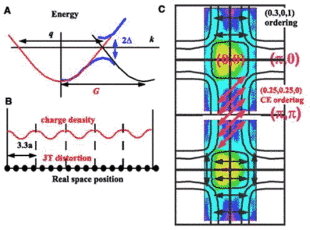


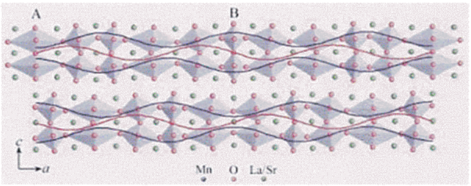
Nanoscale Correlations and the CMR

Doping dependence

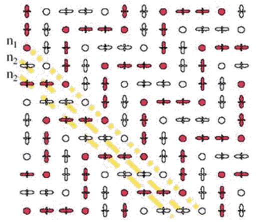
Other scenarios?

- Fermi surface nesting, as in 2D manganites (Chuang, et al.; Campbell, et al., 2001,2002) – unlikely (?) in these 3D materials





- Continuously-modulated (diagonal) phases (Brey, 2004); “electronic soft matter states” (Littlewood et al, 2005)



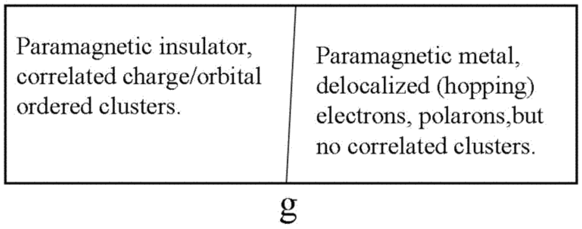
Nanoscale Correlations and the CMR

Nanoscale correlations and uncorrelated polarons vs. metallicity in manganites.

Experiment shows: ferromagnetic metal – no correlations
paramagnetic insulator – correlations present.

Q: What about the uncorrelated polarons?

Q: Does the presence of the correlations distinguish metal from insulator in the paramagnetic state? Is there a metal-insulator transition in this state, perhaps associated with electron localization in correlated clusters?



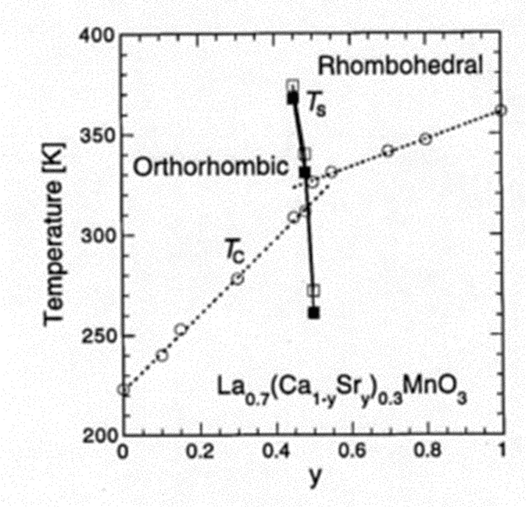
Paramagnetic insulator, correlated charge/orbital ordered clusters.

Paramagnetic metal, delocalized (hopping) electrons, polarons,but no correlated clusters.

g

Nanoscale Correlations and the CMR

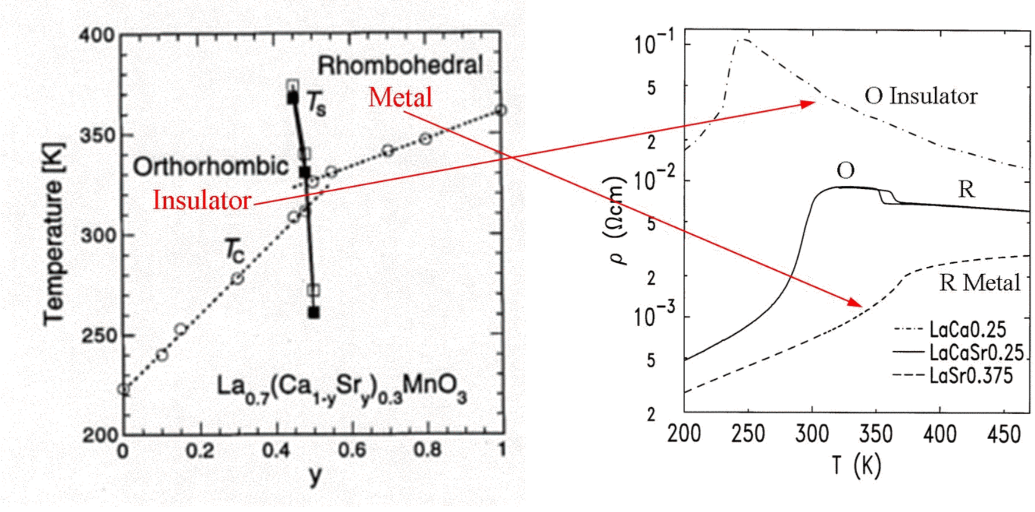
Nanoscale correlations vs. metallicity in manganites.



Tomioka, et al., 2000

Nanoscale Correlations and the CMR

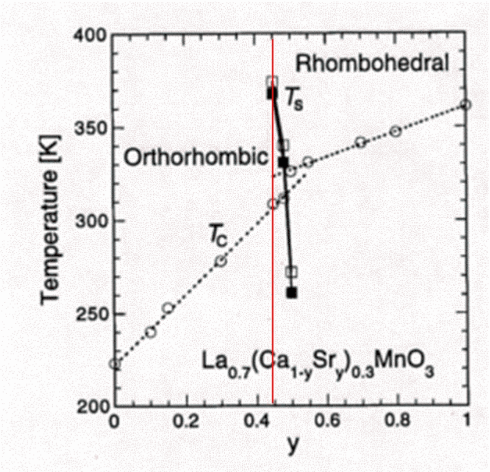
Nanoscale correlations vs. metallicity in manganites.



Tomioka, et al., 2000

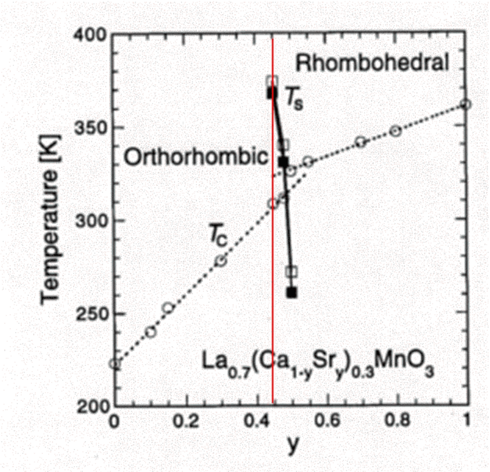
Nanoscale Correlations and the CMR

Nanoscale correlations vs. metallicity in manganites.

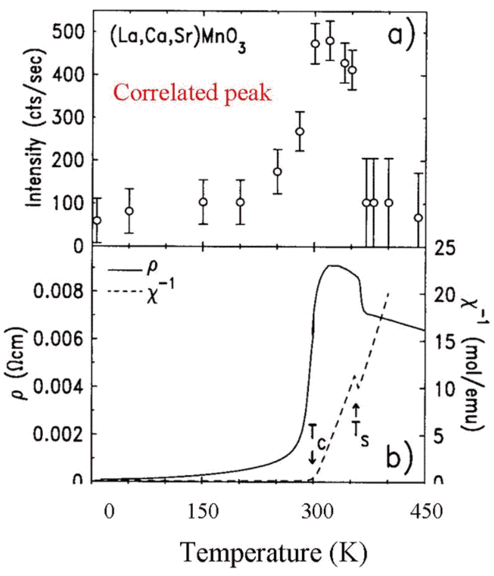


Nanoscale Correlations and the CMR

Nanoscale correlations vs. metallicity in manganites.



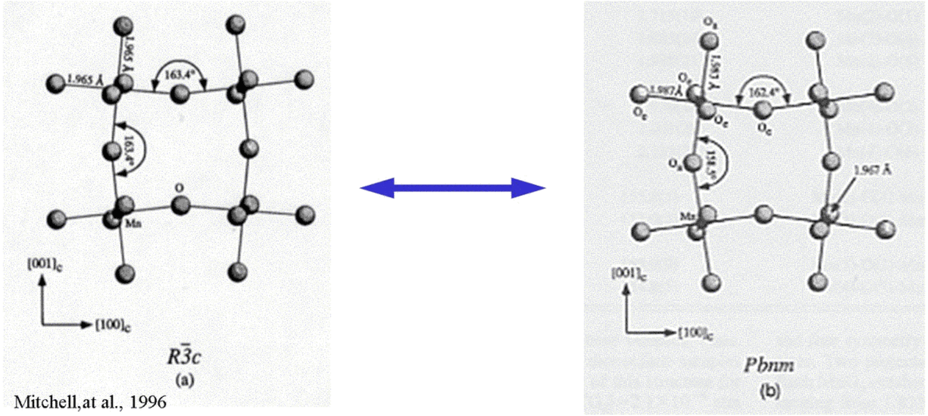
$La_{0.75}(Ca_{0.45}Sr_{0.55})_{0.25}MnO_3$



V. Kiryukhin, et al., PRB (2003)

Nanoscale Correlations and the CMR

Nanoscale correlations vs. metallicity in manganites.

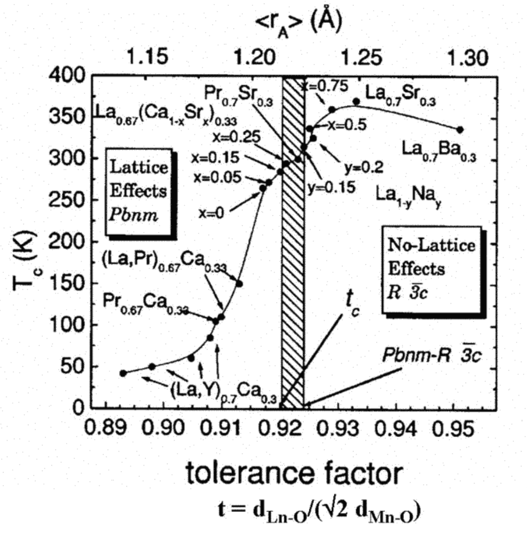


Mitchell,at al., 1996

Paramagnetic Metal	Paramagnetic Insulator
No Correlated Clusters	Charge/Orbital Ordered Clusters
Undistorted MnO_6 Octahedra	Distorted MnO6 Octahedra (similar to the charge-ordered phases)

Nanoscale Correlations and the CMR

Nanoscale correlations vs. metallicity in manganites.

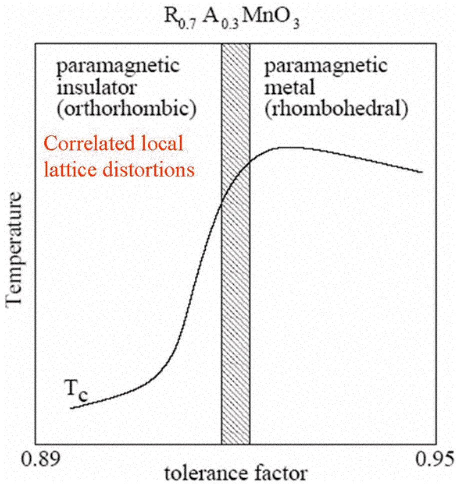


Calorimetric, thermal expansion, resistivity, and magnetisation measurements provide evidence that “lattice effects” are important in the orthorhombic manganites, while their influence is strongly reduced in the rhombohedral phase.

J. Mira, et el. (2001)

Nanoscale Correlations and the CMR

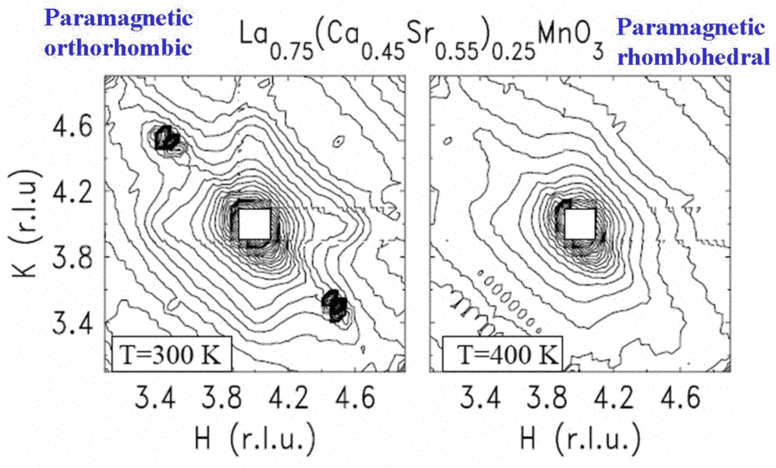
Nanoscale correlations vs. metallicity in manganites.



Q: But still, what about the uncorrelated polarons?

Nanoscale Correlations and the CMR

Nanoscale correlations vs. metallicity in manganites.

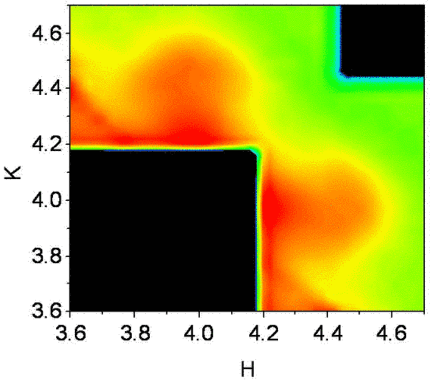


Uncorrelated polarons are present in the both paramagnetic phases.

Q: Do they exhibit any temperature-dependent anomalous behavior?

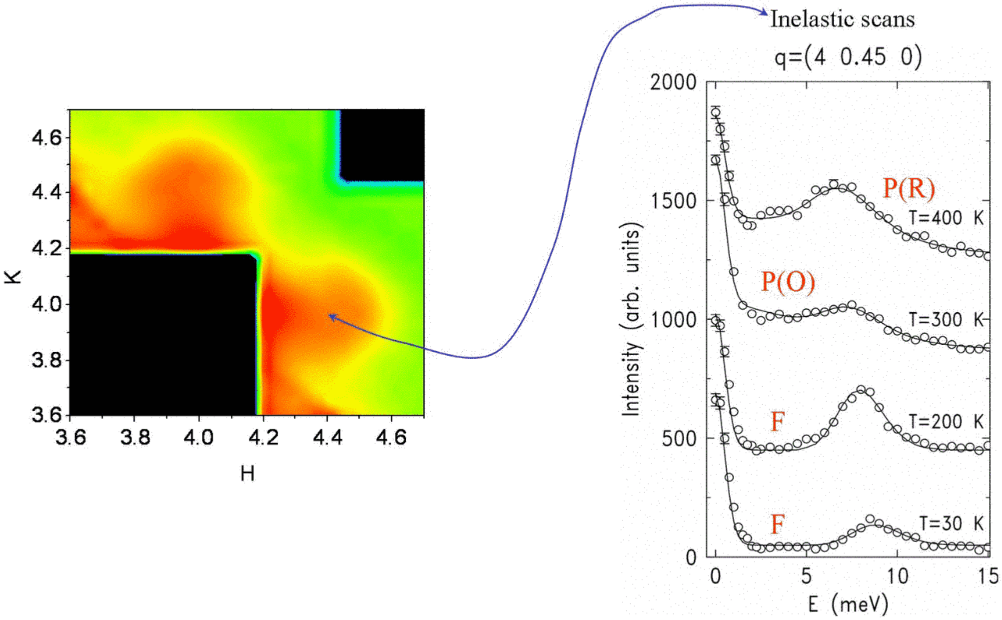
Nanoscale Correlations and the CMR

Nanoscale correlations vs. metallicity in manganites.



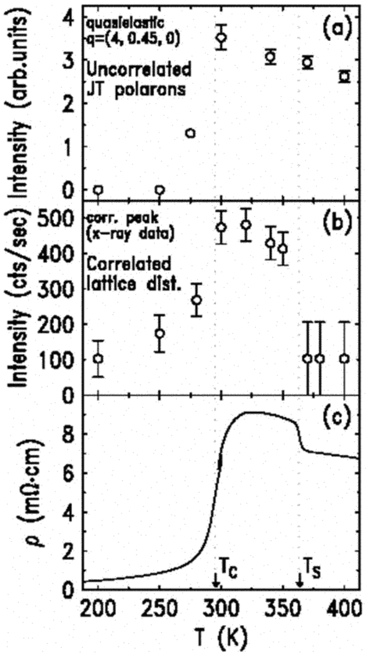
Nanoscale Correlations and the CMR

Nanoscale correlations vs. metallicity in manganites.



Nanoscale Correlations and the CMR

Nanoscale correlations vs. metallicity in manganites.



No anomalies at the structural transition in the behavior of the uncorrelated dynamic polarons. No significant bandwidth changes due to the structural transition (powder refinement).

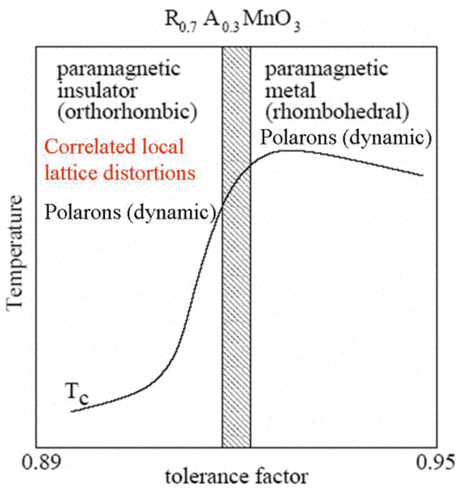
Slowly-fluctuating correlated polarons disappear at T_S

Analysis of the neutron data (q-scans at various energies) shows that single polarons are dynamic with lifetime ~120 fs, while the structural correlations fluctuate much more slowly (lifetime>600 fs).

V. Kiryukhin, et al., PRB **70**, 214424 (2004)

Nanoscale Correlations and the CMR

Nanoscale correlations vs. metallicity in manganites.



Paramagnetic phase:

- Dynamic polarons. Anomalous DW factors, acoustic phonon damping.

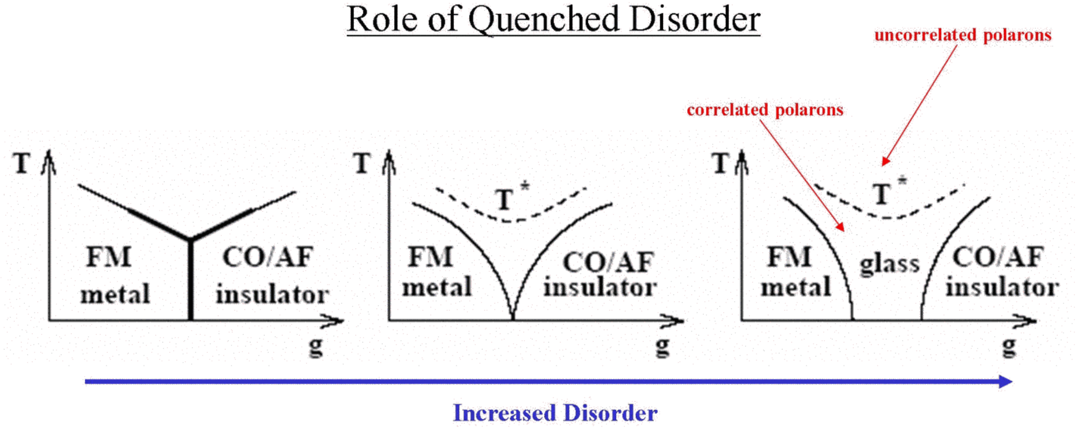
- Correlated nanoscale lattice distortions (slowly-fluctuating). O-phase only.

Presence of the correlated lattice distortions (not single polarons) distinguishes the metallic and the insulating paramagnetic states in CMR manganites.

Q: Is this transition driven by the localization of the carriers into charge/orbital ordered clusters?

Nanoscale Correlations and the CMR

Role of Quenched Disorder

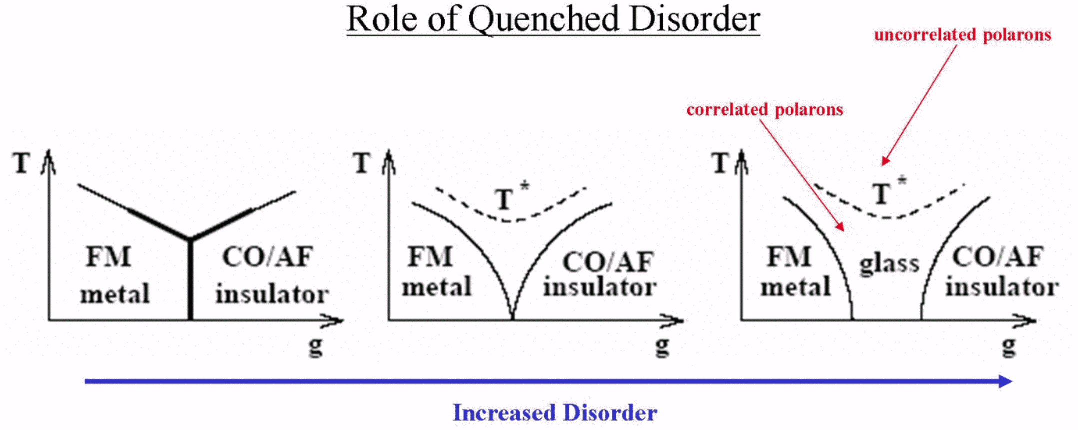


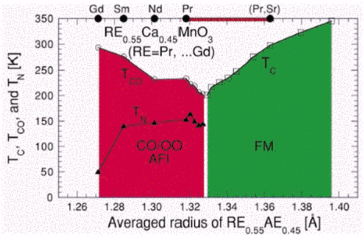
Generic picture for systems with competing phases and quenched disorder?

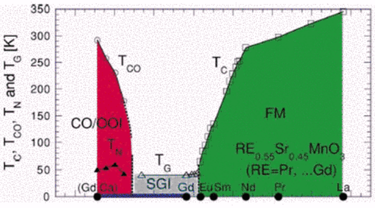
Dagotto, 2002

Nanoscale Correlations and the CMR

Role of Quenched Disorder







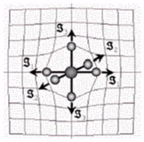
Tomioka, Tokura, 2004

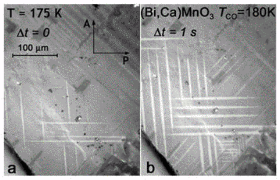
Nanoscale Correlations and the CMR

Role of Long-Range Strain

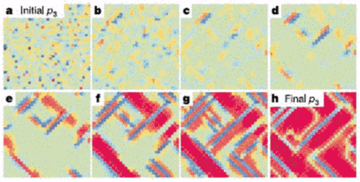
- quneched disorder is not the entire story as it does not explain the effects of O-to-R transition on the nanoscale correlations in LSCMO. Effects of long-range strain might play a key role in the stabilization of the correlations in the O phase.

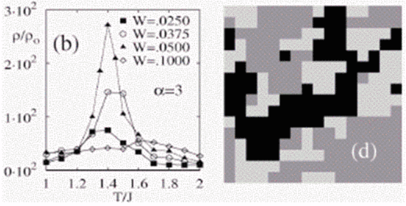
- polaronic distortions are long-range. Effects of strain are well known in manganites. E.g.: martensitic accommodation strain; stabilization of the CO state. (Littlewood 1999, Podzorov et al. 2001, Khomskii & Kugel 2001, Campbell et al. 2003.)





- preliminary theoretical studies (toy models) support the importance of the long-range strain (Burgy at al. 2004, Ahn at al. 2004). Realistic models are yet to be constructed, however.



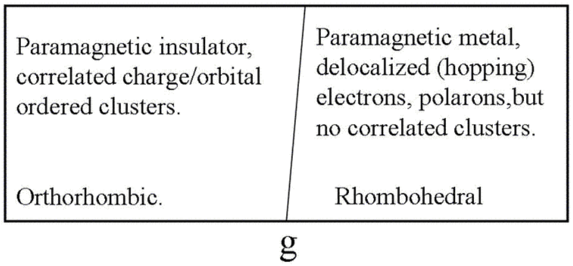


Conclusions

- The insulating character of the orthorhombic paramagnetic state in CMR manganites stems from the presence of the nanometer-scale correlated lattice distortions. Thus, nanoscale inhomogeneities play a key role in the CMR effect.

- The correlations have common correlation length (10-15 A), their lattice modulation vector has a common linear dependence on the doping level. The correlated regions probably possess charge/orbital order, and are electron-depleted

- It appears that the presence of the correlated regions distinguishes the metallic and the insulating phases in the paramagnetic state. A new type of phase transition?



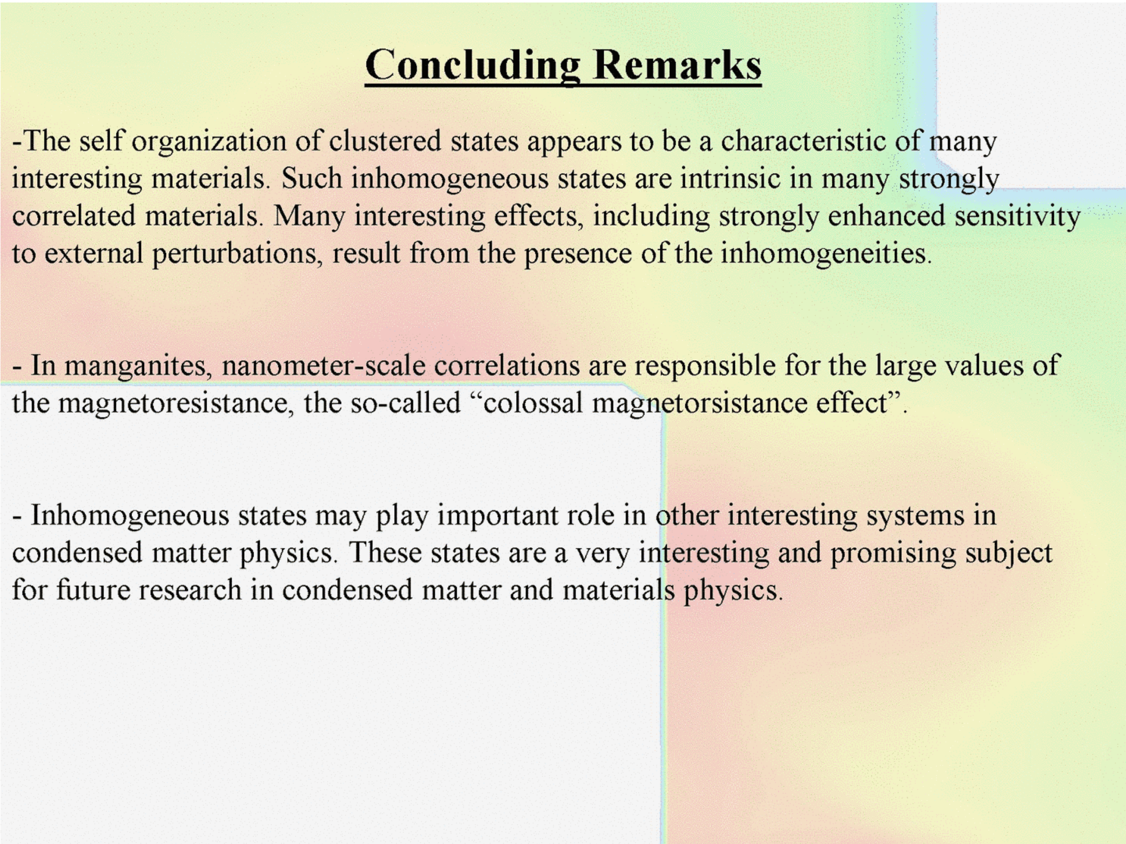
Paramagnetic insulator, correlated charge/orbital ordered clusters.

Orthorhombic.

Paramagnetic metal, delocalized (hopping) electrons, polarons,but no correlated clusters.

Rhombohedral

g



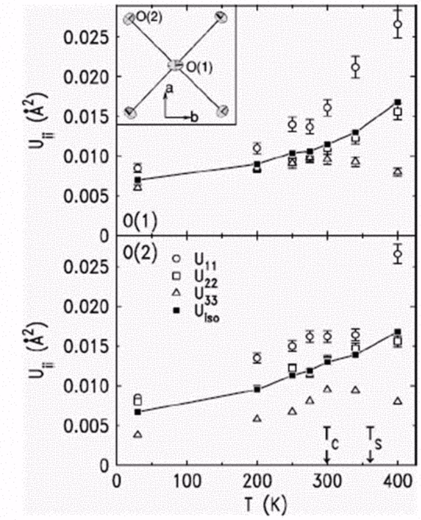
Concluding Remarks

-The self organization of clustered states appears to be a characteristic of many interesting materials. Such inhomogeneous states are intrinsic in many strongly correlated materials. Many interesting effects, including strongly enhanced sensitivity to external perturbations, result from the presence of the inhomogeneities.

- In manganites, nanometer-scale correlations are responsible for the large values of the magnetoresistance, the so-called "colossal magnetorsistance effect".

- Inhomogeneous states may play important role in other interesting systems in condensed matter physics. These states are a very interesting and promising subject for future research in condensed matter and materials physics.

Neutron powder diffraction results, LSCMO.

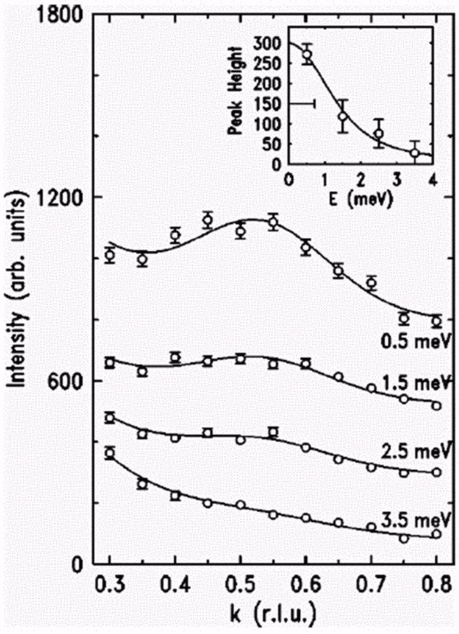


W~cos(ω)/d$^{3.5}$, where

ω=(π-<Mn-O-Mn>)/2, d is Mn-O length.

From powder diffraction refinements of the O and R structures, we obtain that the difference between the bandwidths of the O and R states is less than 0.3%.

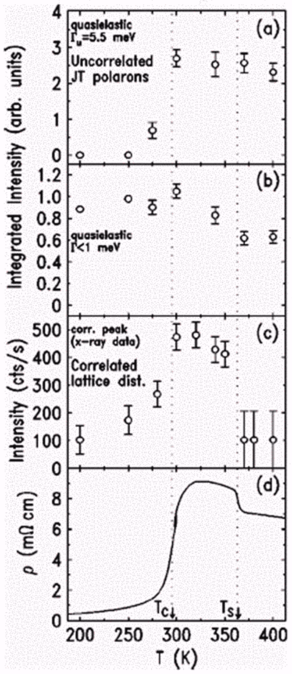
Single-crystal LCSMO neutron results.



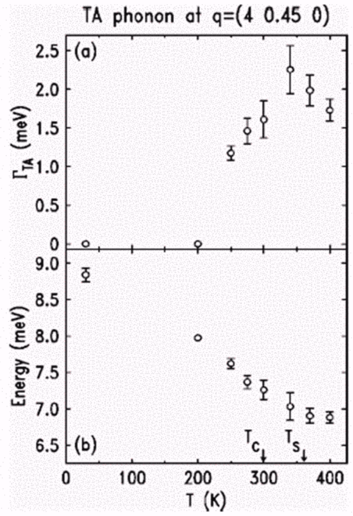
The lifetime of the structural correlations is larger than 600 fs.

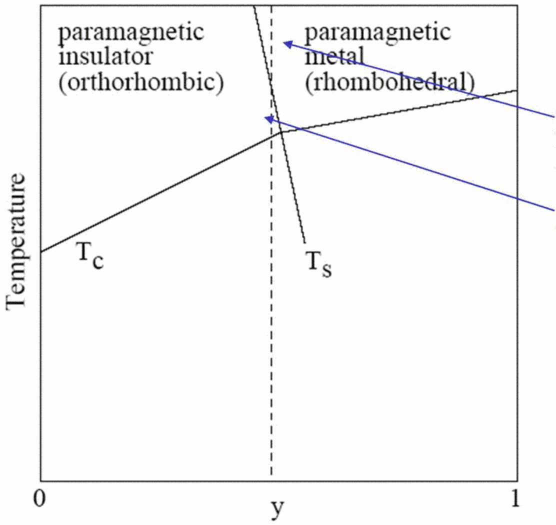
Single-crystal LCSMO neutron results.

Summary



TA Phonon





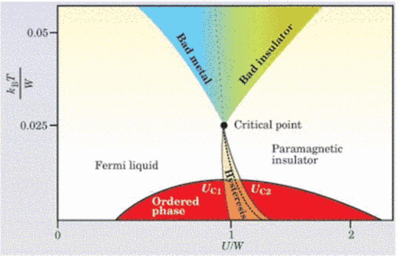
Paramagnetic Phase:

Metal: Single polarons present (dynamic). Rhombohedral average symmetry.

Insulator: Static correlated nanoscale lattice distortions present. Dynamic polarons also present. Orthorhombic average lattice symmetry.

Q: But is the rhombohedral paramagnetic phase a metal ?

PA: Yes, at a significantly large doping level x. The doping level x=0.25 of our sample may be quite close to the critical doping level for a possible bad metal – bad insulator crossover.



Kotliar & Vollhardt, 2004.