

LOCAL PROBE STUDIES IN MANGANITES AND COMPLEX OXIDES

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OUTLINE

Manganites and intrinsic complexity

Charge-ordering scenarios, phase separation
Multiferroic systems

Local Probe Studies

Hyperfine technique: Perturbed Angular Correlations

Probing electric fields in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ system

Phase separation, polaron dynamics in $\text{LaMnO}_{3+\delta}$ and $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$

Multiferroics: RMnO_3

Other oxide systems

Perspectives

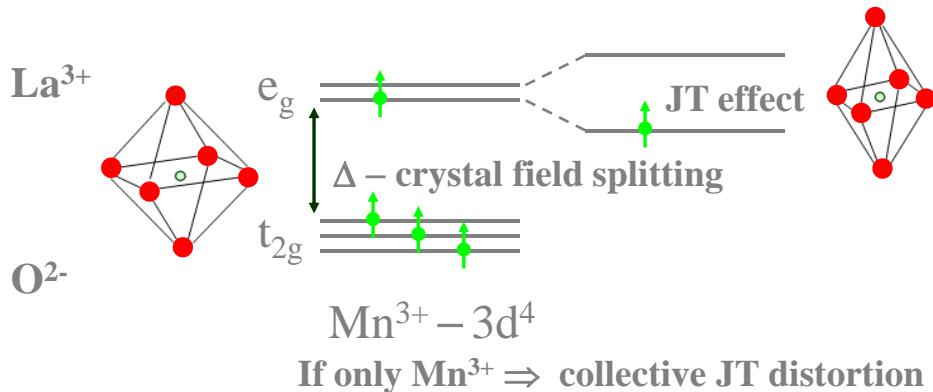
Introduction to Manganites

$AMnO_3$ (A=La, Pr, Nd & Ca, Sr ...)

Doping with divalent ions

(R-D) MnO_3

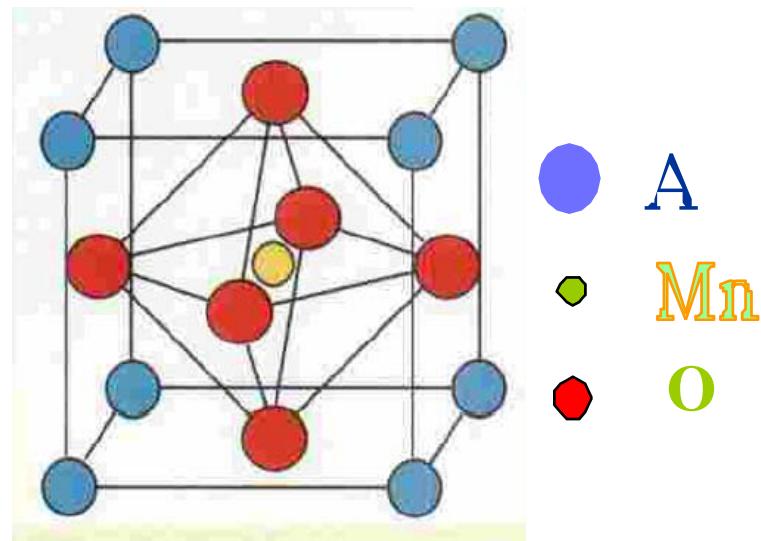
Mixed valence: $Mn^{3+} : Mn^{4+}$



$Mn^{3+} - 3d^4$
If only $Mn^{3+} \Rightarrow$ collective JT distortion

Manganites

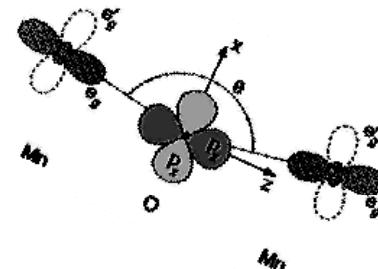
base structure perovskite



{

- Electron doping (charge and orbital)
- Structure
- Magnetic Interactions

Introduction to Manganites



Small Ionic radii

$$\text{Pr}^{3+} = 1.30 \text{ \AA}, \text{Ca}^{2+} = 1.34 \text{ \AA}$$

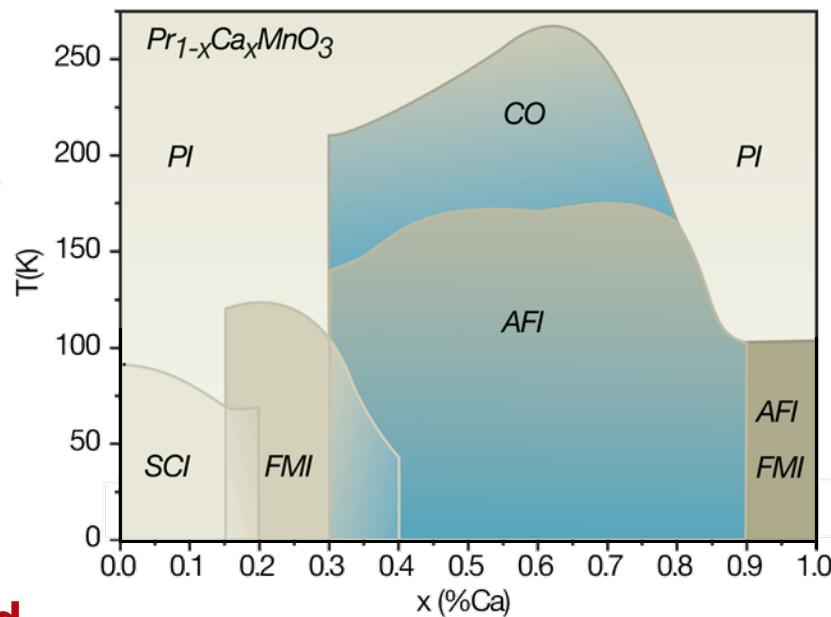
- Orthorhombic structure for all x

Small overlap between Mn & O orbitals

- Insulator for all x

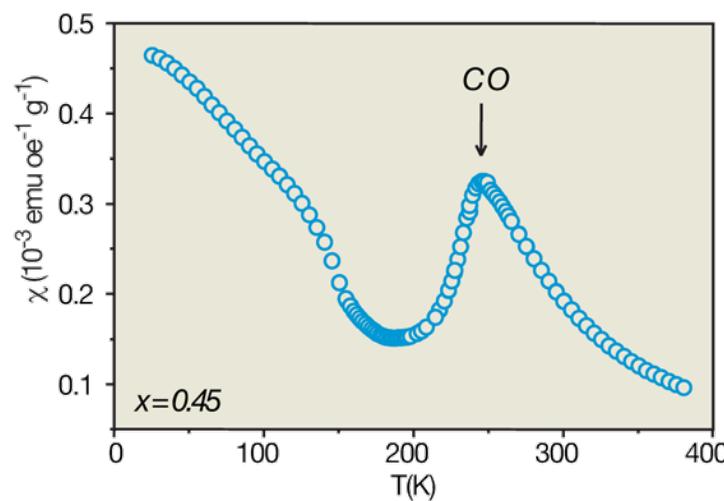
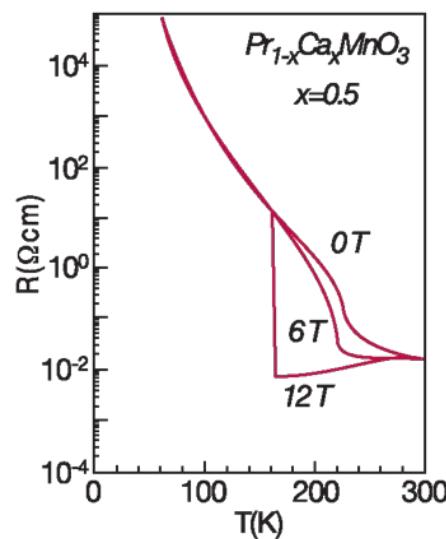
Charge Order is stabilized over a broad range of compositions

Magnetic - Electric Phase Diagram



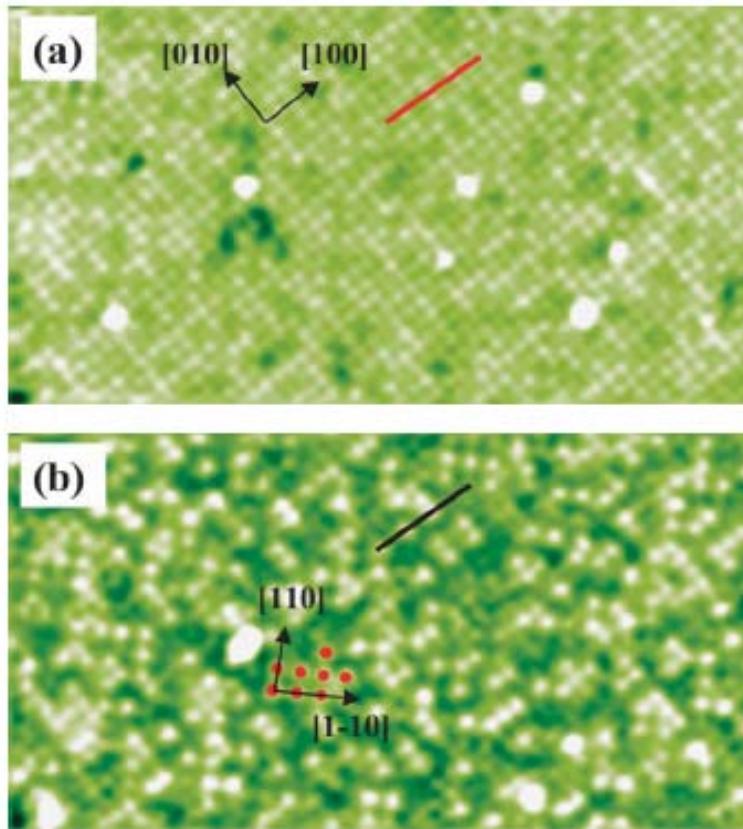
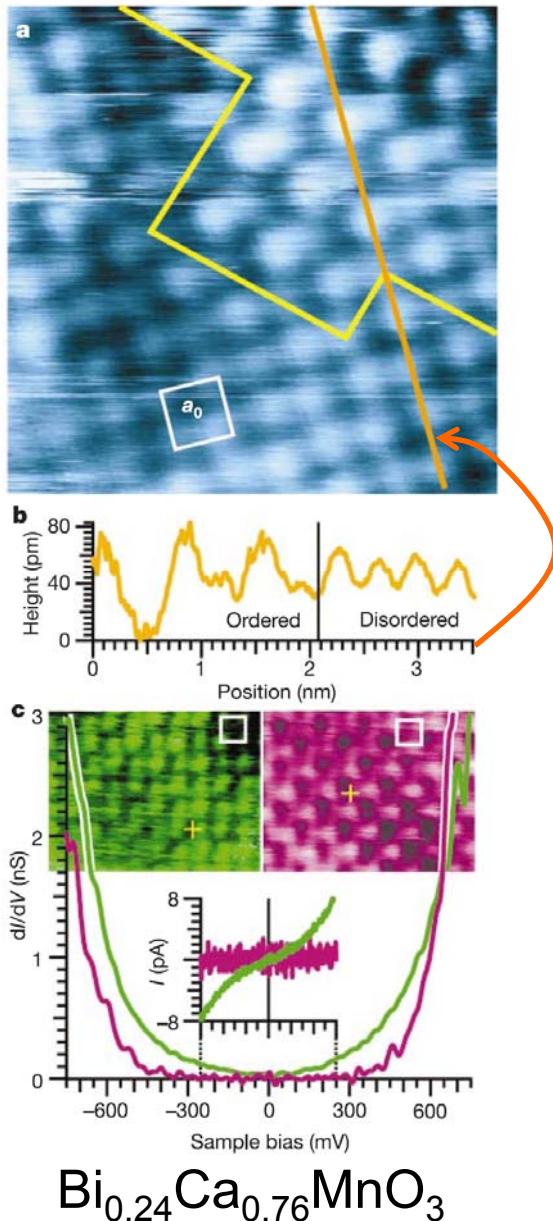
Mn³⁺/Mn⁴⁺ localization in a ordered way

CO/FO signatures

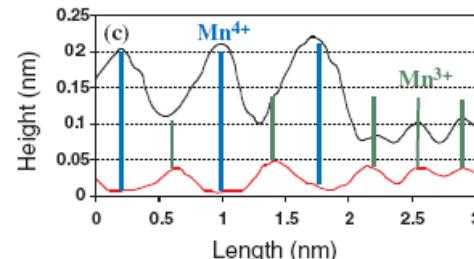


Phase separation and complexity

Atomic-scale coexistence



Renner et al, Nature 416,
518 (2002)



Ma et al,
Phys Rev. Lett
95, 237210 (2005)
 $(\text{La},\text{Pr})_{5/8}\text{Ca}_{3/8}\text{MnO}_3$

Charge contrast:
occupied and
unoccupied states
Clusters with CT
type arrangement
in the
paramagnetic
phase

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Multiferroic materials

- Inversion symmetry breaking (charge-orbital related)
- Dislocated spin density waves
- Magneto-electric coupling

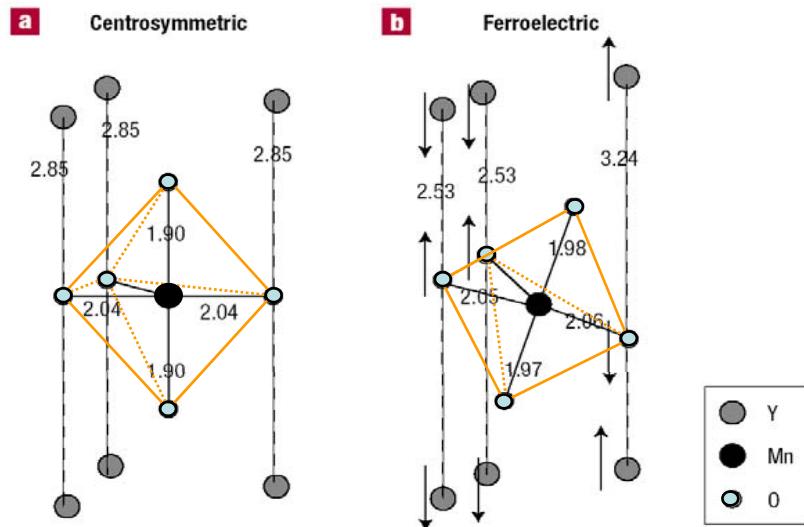
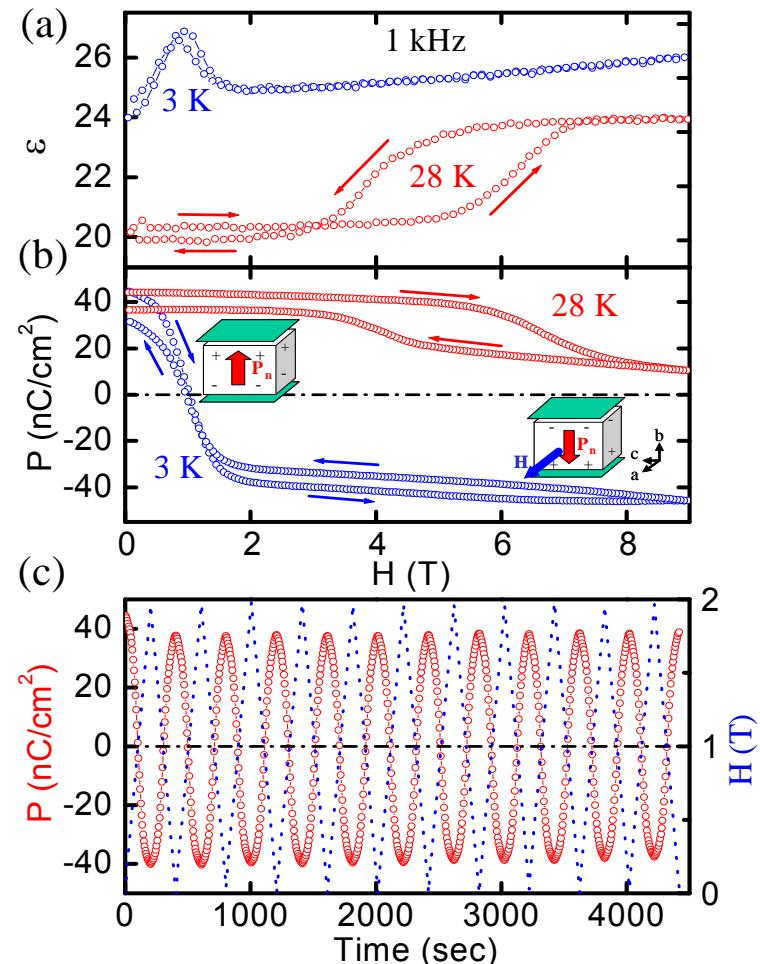


Figure 3 Schematic of a MnO_5 polyhedron with Y layers above and below.

a,b, The calculated atomic positions of the centrosymmetric (a) and ferroelectric structures (b). The numbers give the bond lengths in Å. The arrows indicate atomic displacements with respect to the centrosymmetric structure.

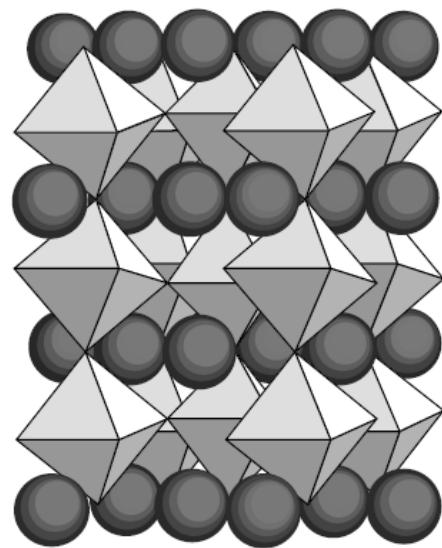
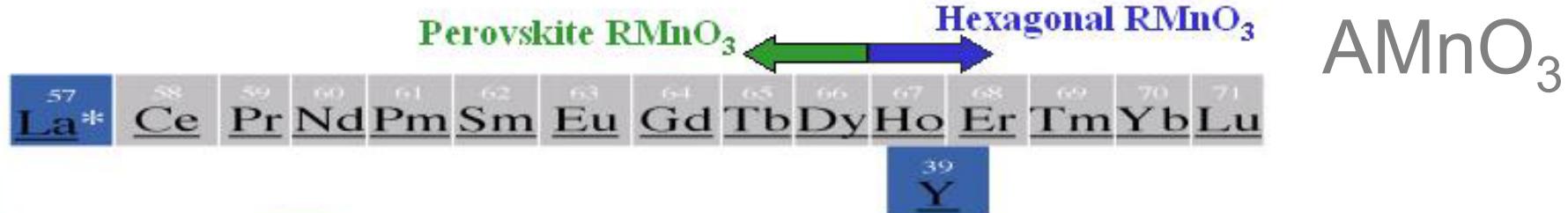
Tb/YMn₂O₅ Nature, 429, 392 (2004)

Nature Materials 3, 164, (2004)

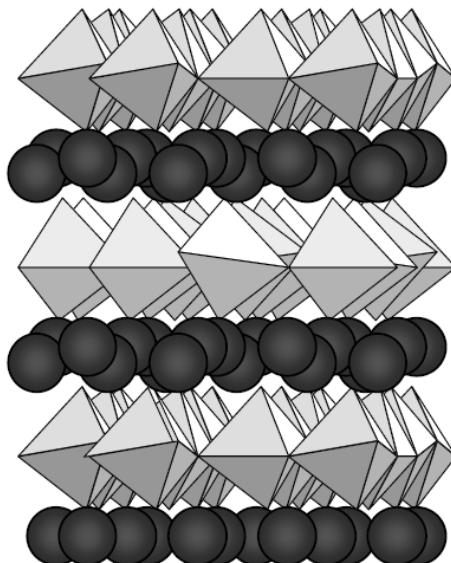


Magnetic field induces a sign reversal of the electric polarization

Multiferroic manganites



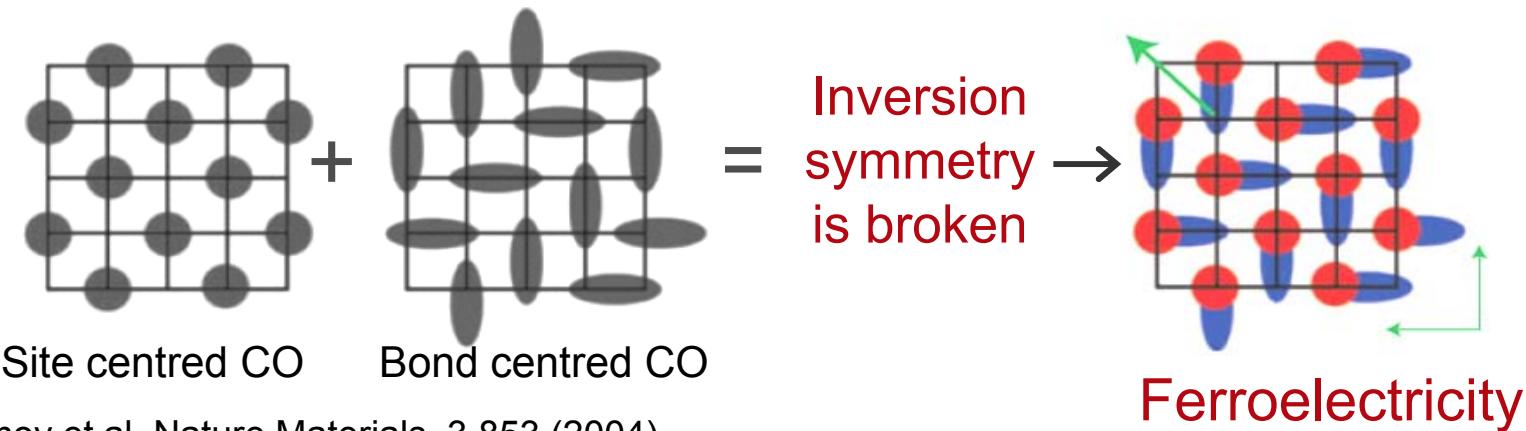
Perovskite phases
octahedra



Hexagonal phase
Trigonal bipyramidal

New scenario for the Charge Ordered State

Theoretical work predicts the possibility of local electric dipole moments in CO manganites



D.Efremov et al, Nature Materials, 3,853 (2004)

J. Van den Brink, D.I. Khomskii, J. Phys. Cond. Matt 20, 434217 (2008)

Ferroelectricity due to Charge Ordering in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$

New paradigm for ferroelectrics, but it has been hard to prove experimentally that electric polarization exists in CO $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ (due to finite conductivity)

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Two-Photon PERTURBED ANGULAR CORRELATION

Hyperfine splitting → Electric field gradient / Magnetic hyperfine field

Probe nucleus:

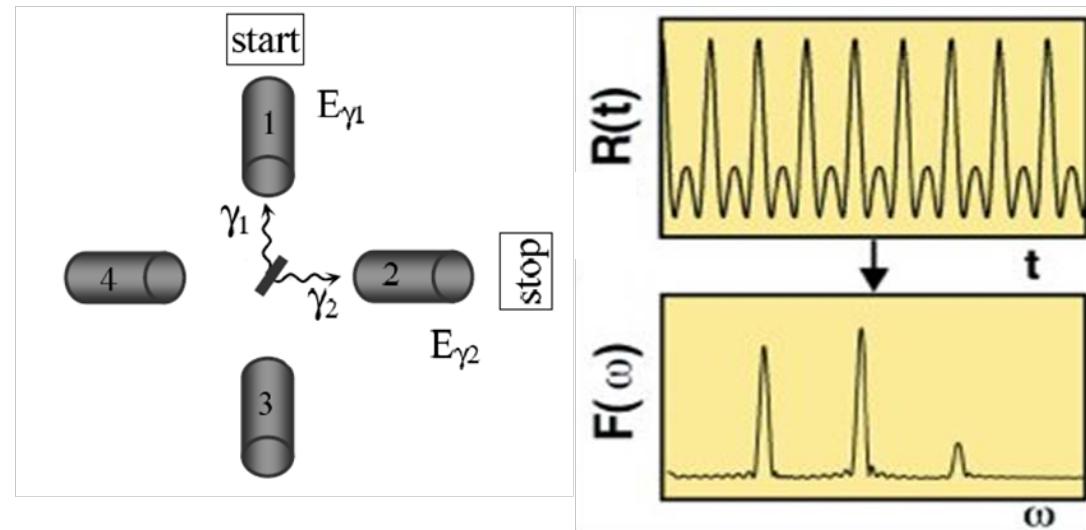
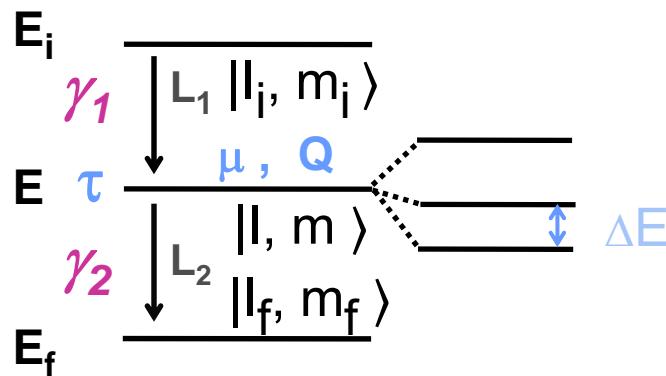
Q – quadrupolar moment

μ - magnetic moment

V_{zz} - EFG principal component

η - Asymmetry parameter

B_{hf} - Magnetic hyperfine field



Time dependence gives access to splitting of hyperfine levels

Two-Photon PERTURBED ANGULAR CORRELATION

Samples implanted with radioactive ^{111m}Cd @ ISOLDE/CERN

E=60 keV, Dose < 10^{12} at/cm²

^{111m}Cd : I=5/2 and $t_{1/2} = 85$ ns

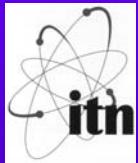
Q=0.83 b and $\mu = -0.766 \mu_n$

Cd @ Pr/Ca site

Samples annealed @ T=700 °C in air



Universidade
de Aveiro



PROPOSAL TO THE ISOLDE COMMITTEE – INTC/P132 Add1

IS390-Studies of Colossal Magnetoresistive Oxides with Radioactive Isotopes

Aveiro¹, Dublin², Leuven³, Lisboa⁴,
Moscow⁵, Orsay⁶, Porto⁷, Sacavém⁸,
Stuttgart⁹, Tokyo¹⁰, Tsukuba¹¹ Vila Real¹²
and the ISOLDE/CERN¹³ Collaboration

Spokesman: V. S. Amaral

Contact person: J.G. Correia

E. Alves⁸, T. Agne¹³, J.S. Amaral¹, V.S. Amaral¹, J.P. Araújo⁷, J. M. D. Coey², N. A. Babushkina⁵, J.G. Correia^{8,13}, H.-U. Habermeier⁹, A. L. Lopes¹, A.A. Lourenço¹, J.G. Marques^{4,8}, T. M. Mendonça⁷, M. S. Reis¹, E. Rita⁸, J.C. Soares⁴, J.B. Sousa⁷, R. Suryanarayanan⁶, P.B. Tavares¹², Y. Tokura^{10,11}, Y. Tomioka¹¹, A. Vantomme³, J.M. Vieira¹ and U. Wahl⁸.

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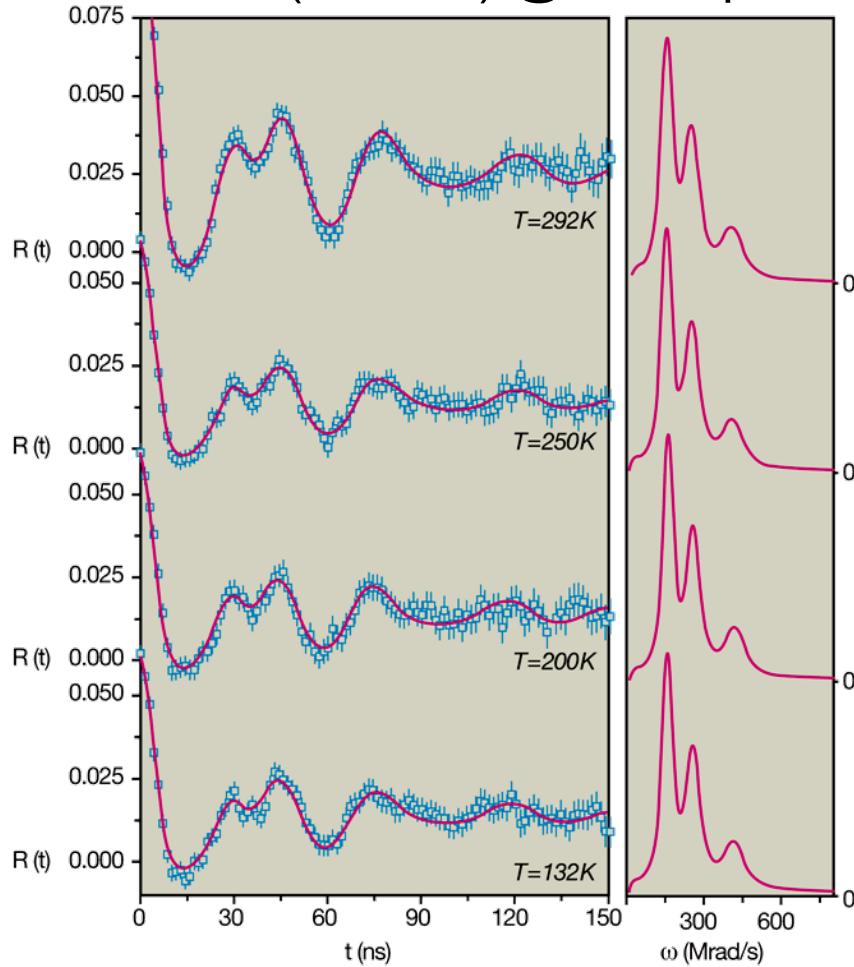
Other oxide systems

Perspectives

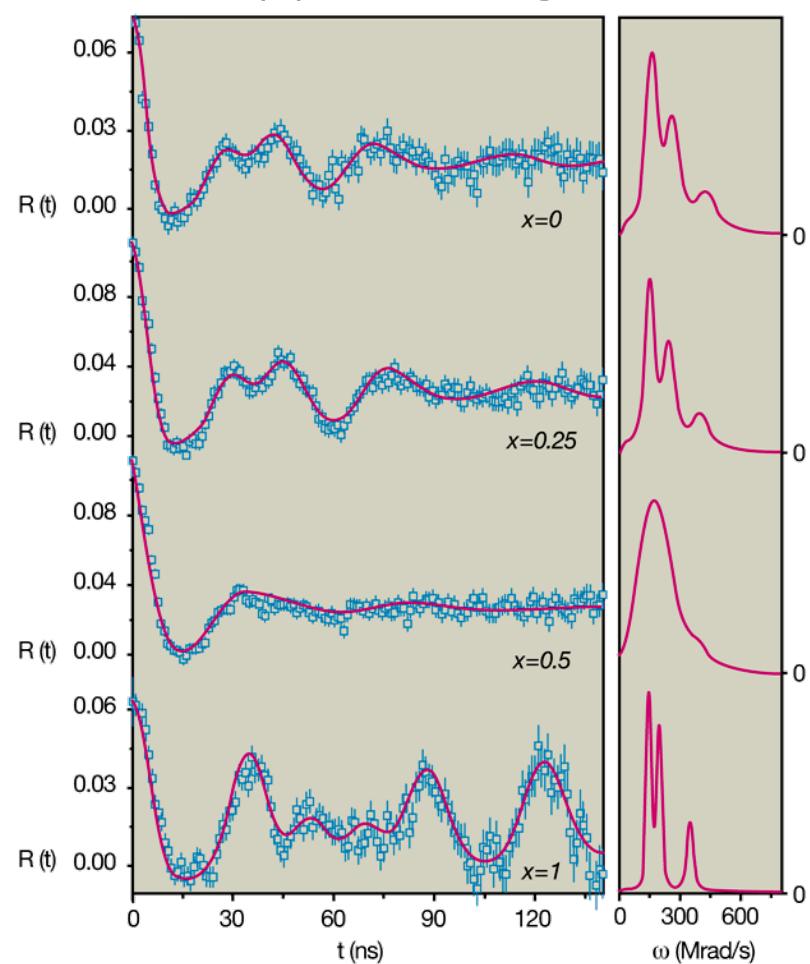
EXPERIMENTAL RESULTS

$\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ PAC Anisotropy Functions

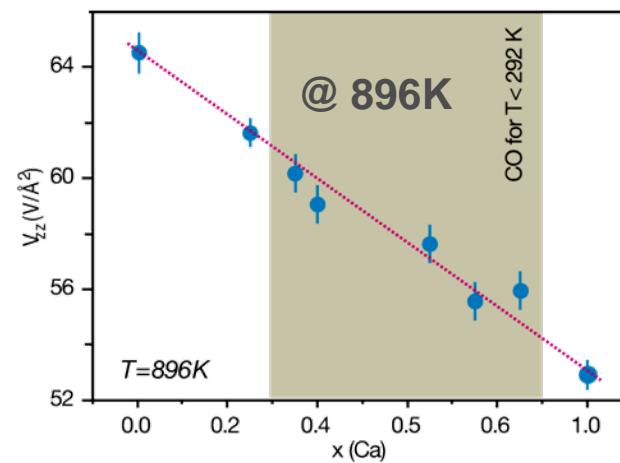
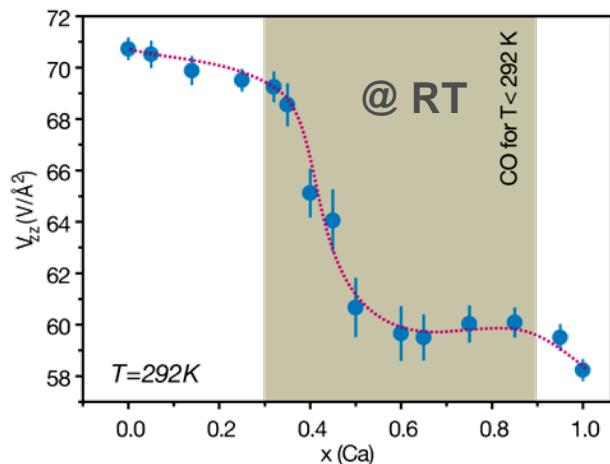
$x=0.25$ (NO CO) @ \neq Temperature



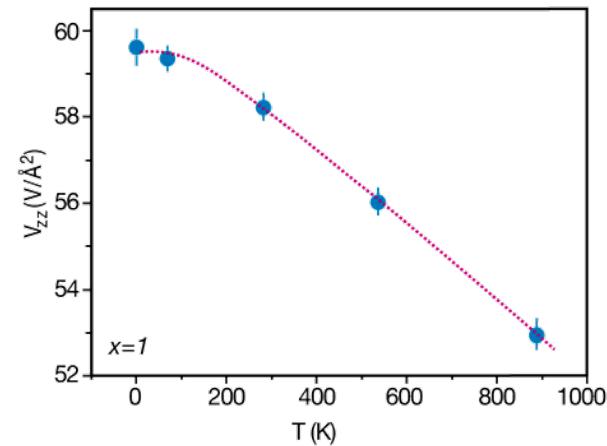
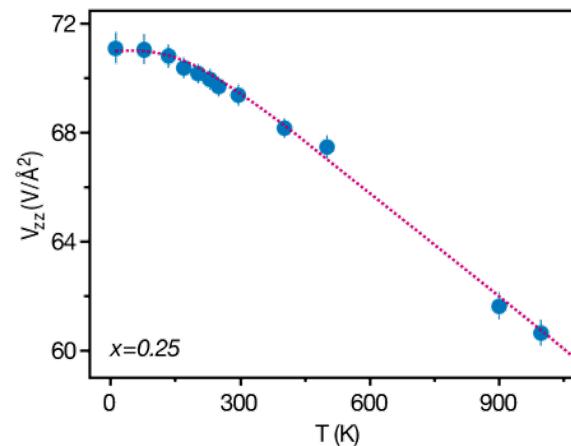
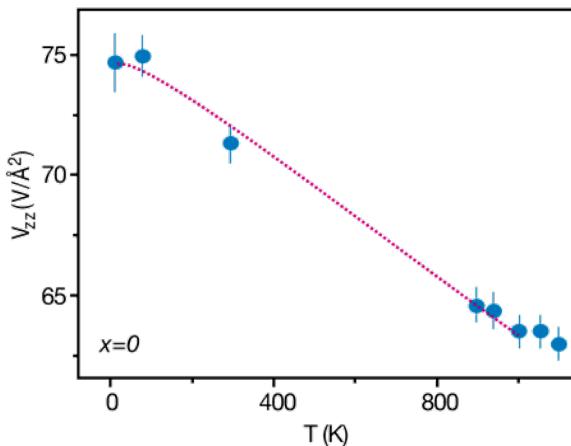
\neq Ca (x) content @ RT



EFG principal component V_{zz}



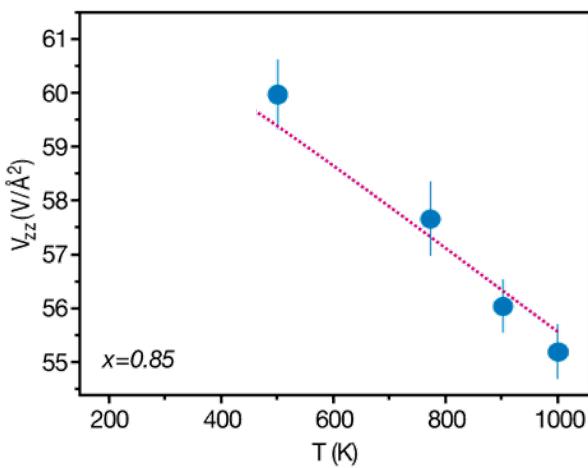
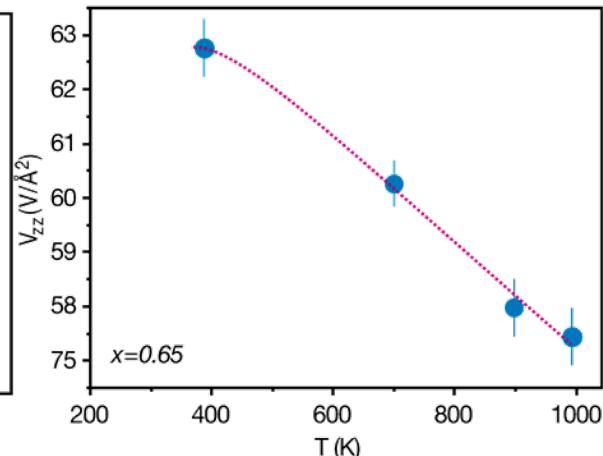
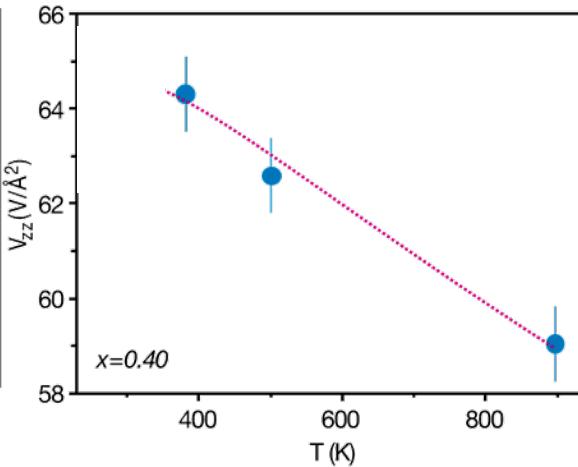
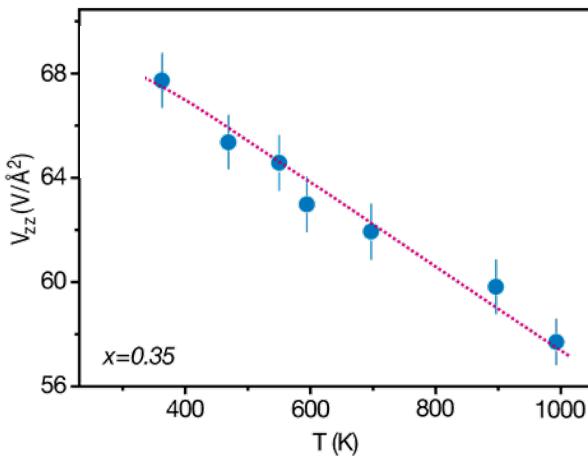
Temperature dependence for samples outside CO region



V_{zz} increases with decreasing T due to atomic vibrations (rms displacements)

High temperature linear slope $\sim -1.5(1) \times 10^{-4} \text{ K}^{-1}$

Samples within CO region



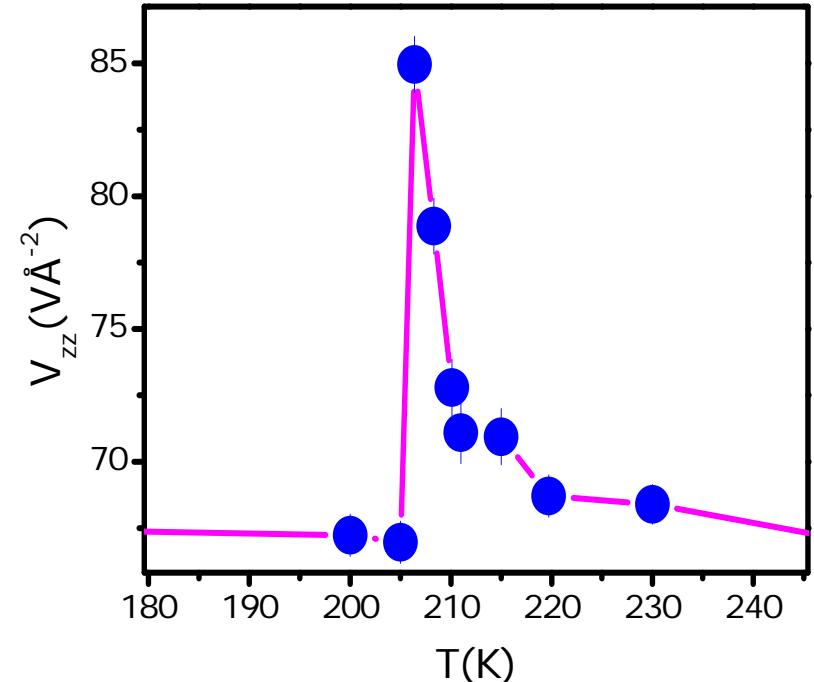
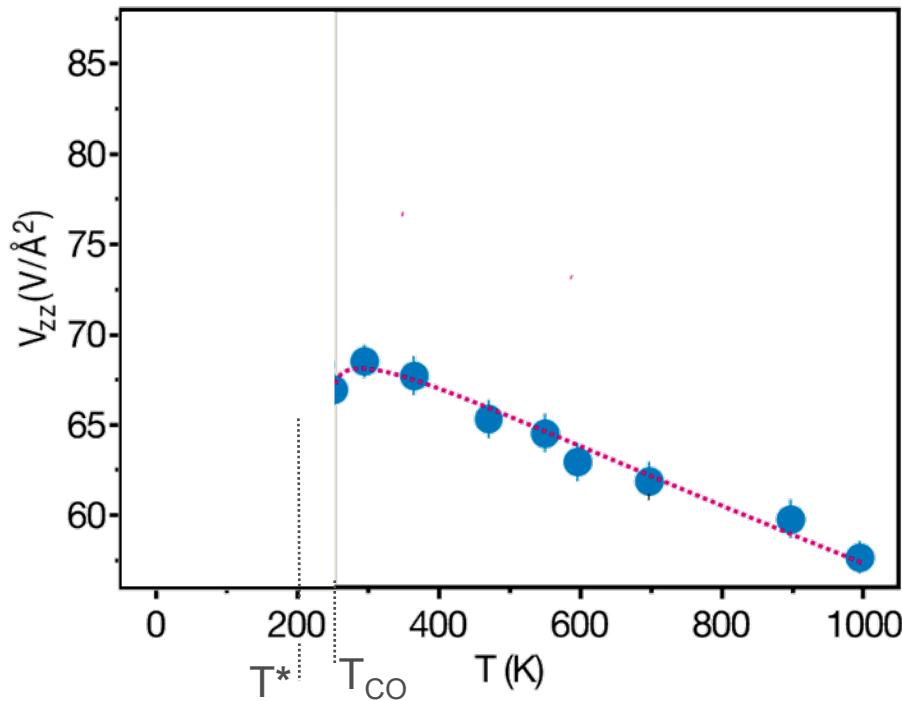
Same high temperature linear slope
 $\sim -1.5(2) \times 10^{-4} \text{ K}^{-1}$

**Anomalous $V_{zz}(T)$ dependence
 approaching CO transition**

Softening of vibration modes?

Charge order driven by the softening of a vibration mode?

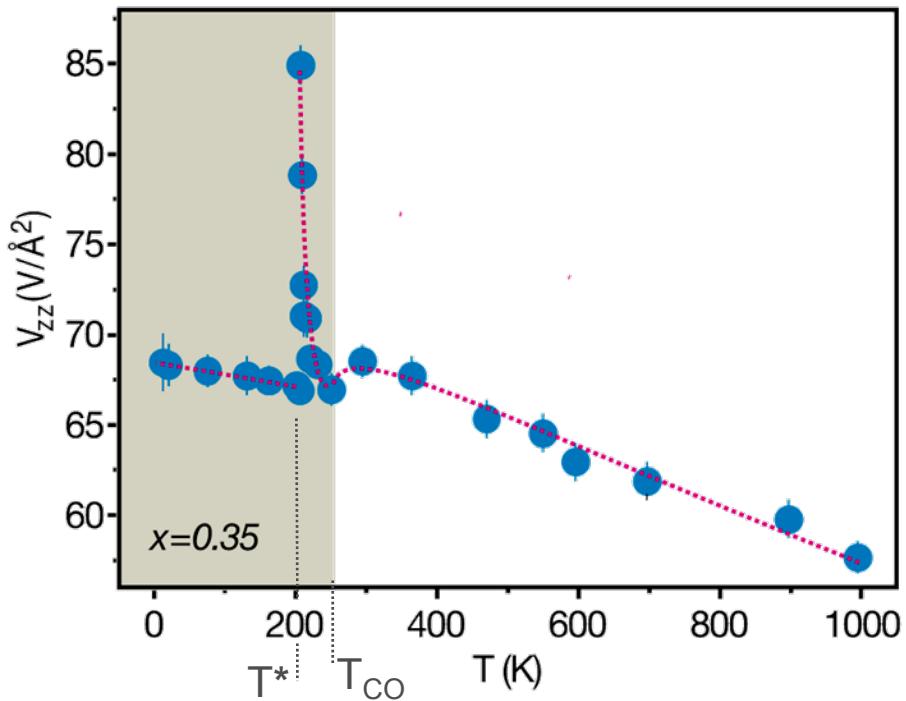
CO region, V_{zz} vs Temperature



Sharp increase of V_{zz} @ $T < T_{CO}$

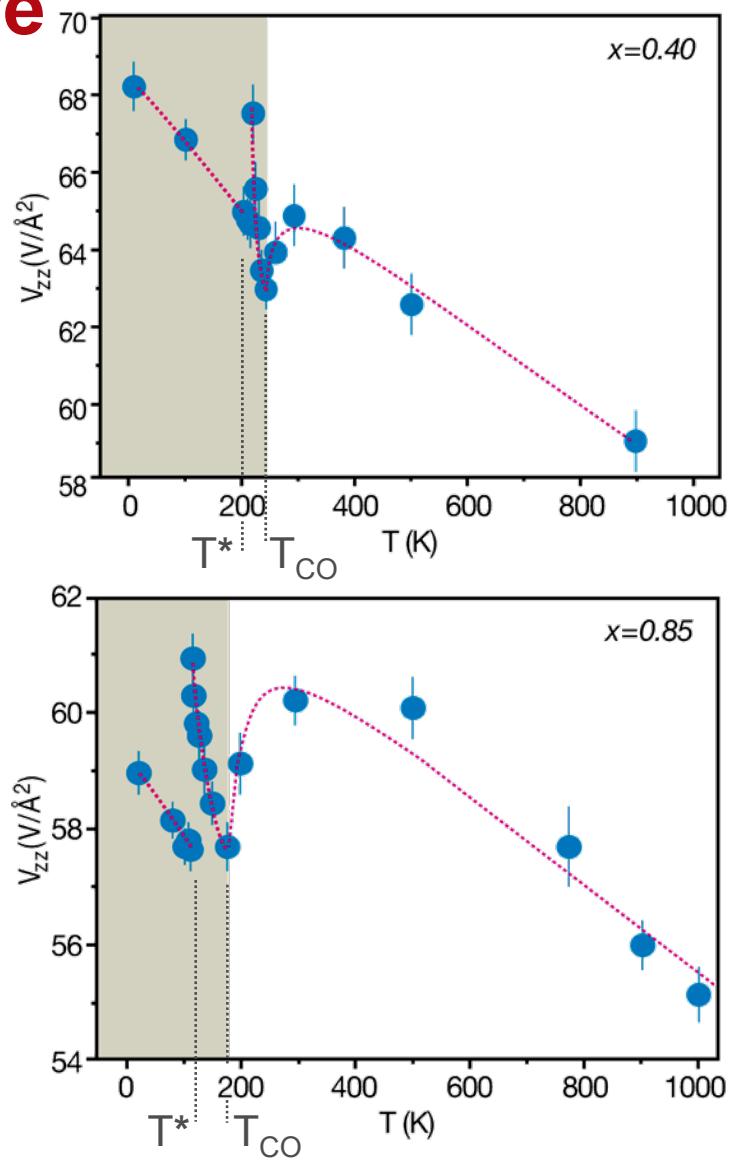
Dropping @ T^* (85 to 67 $V_{zz}/\text{\AA}^{-2}$ in 2K)

CO region, V_{zz} vs Temperature

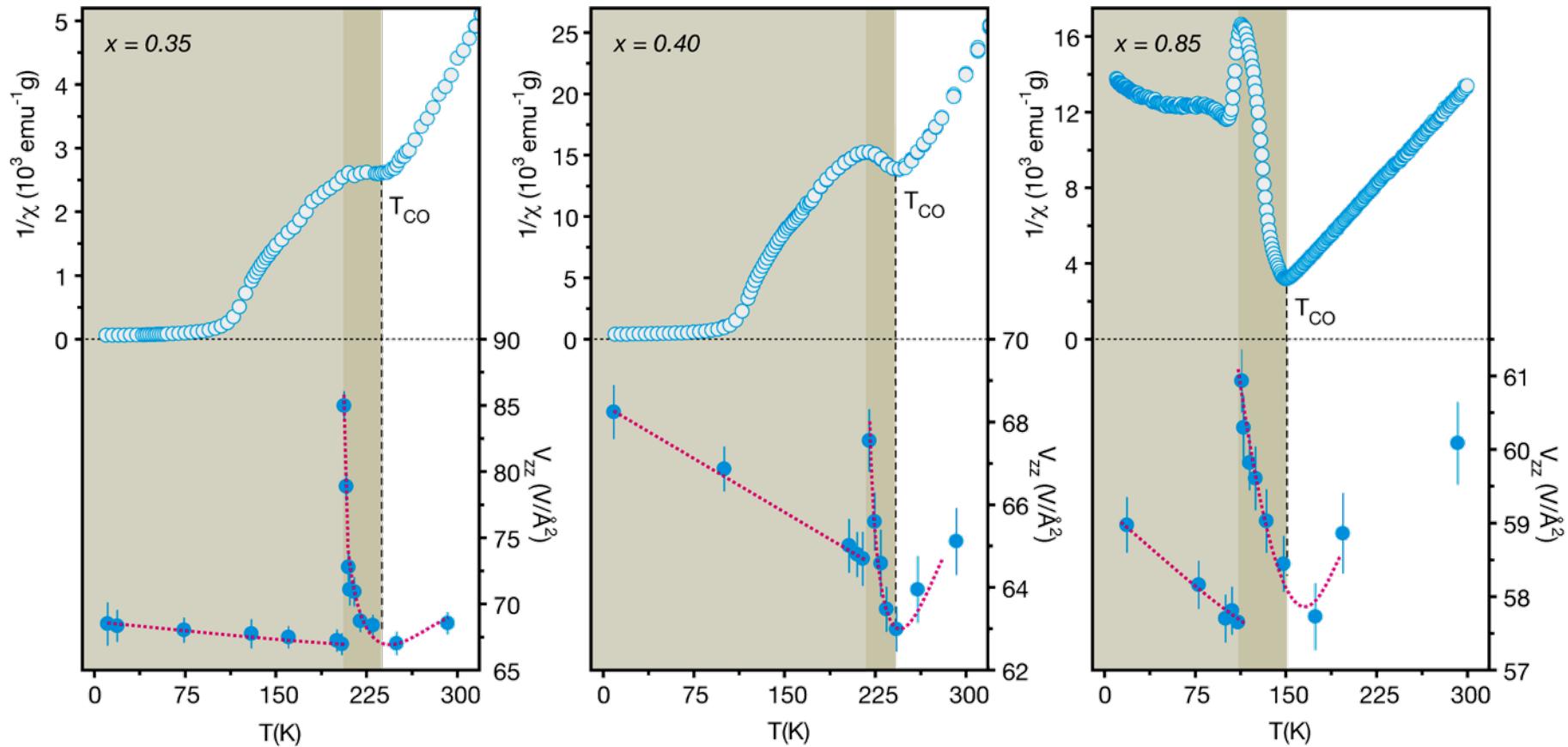


Sharp increase of V_{zz} @ $T < T_{CO}$

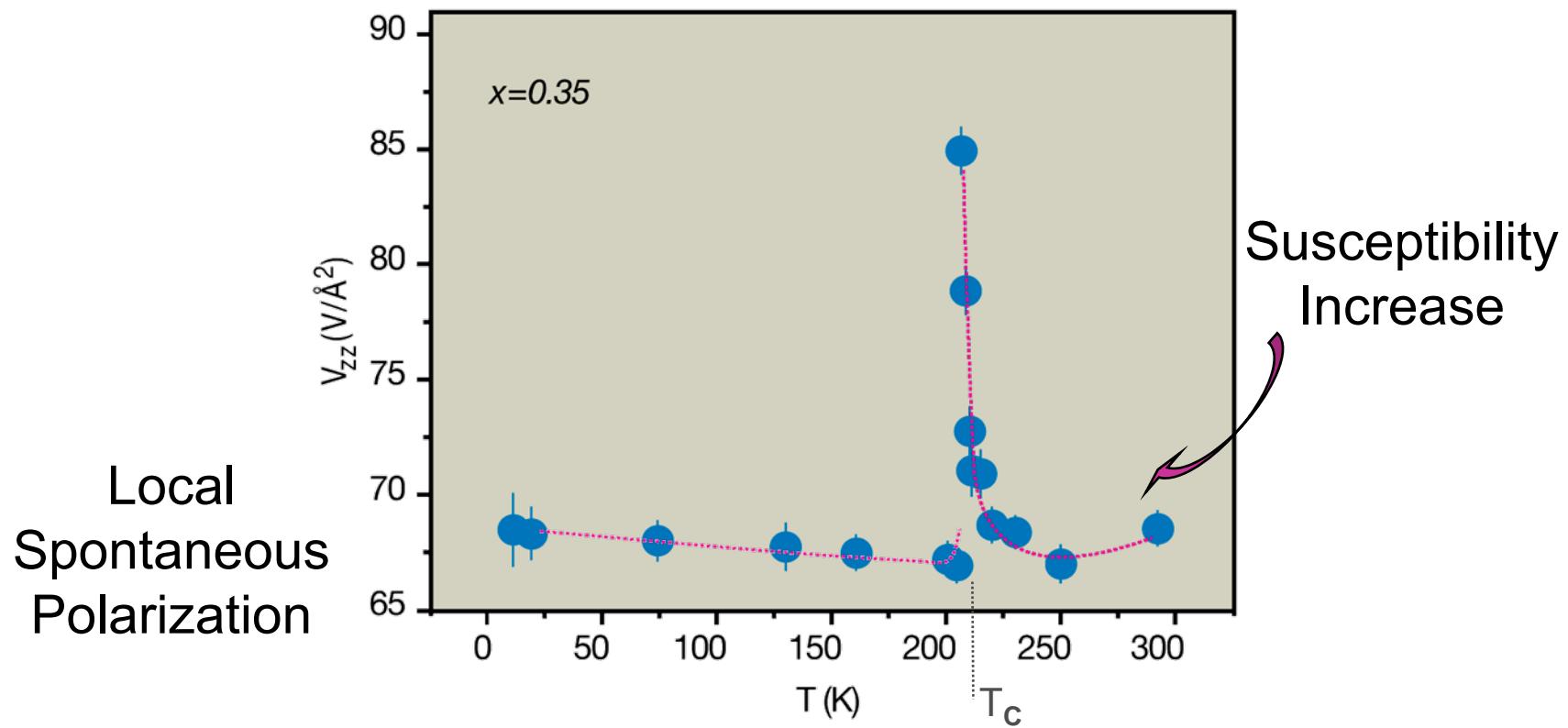
Dropping @ T^*



EFG and magnetic susceptibility



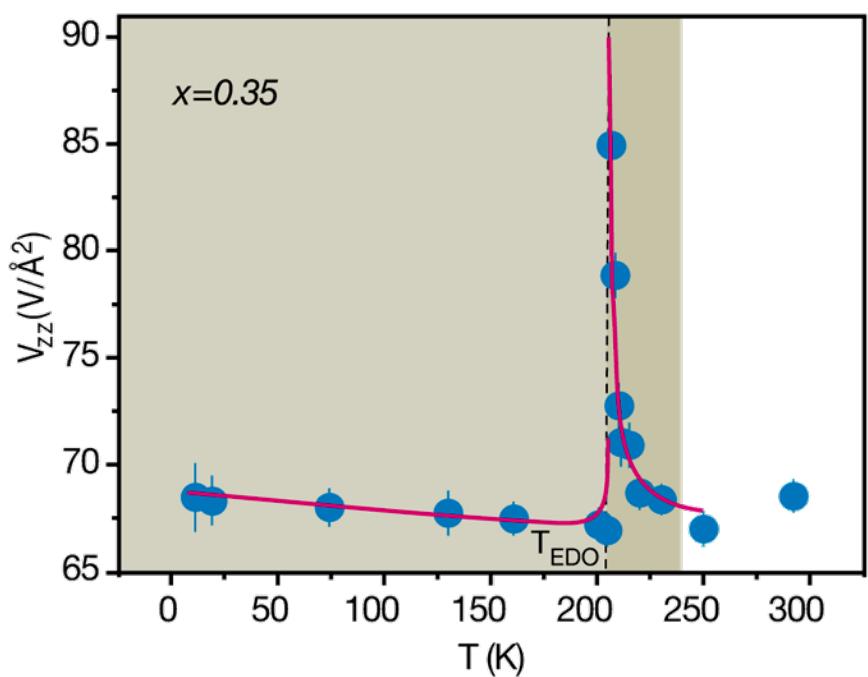
EFG sensitive to atomic vibrations and critical fluctuations



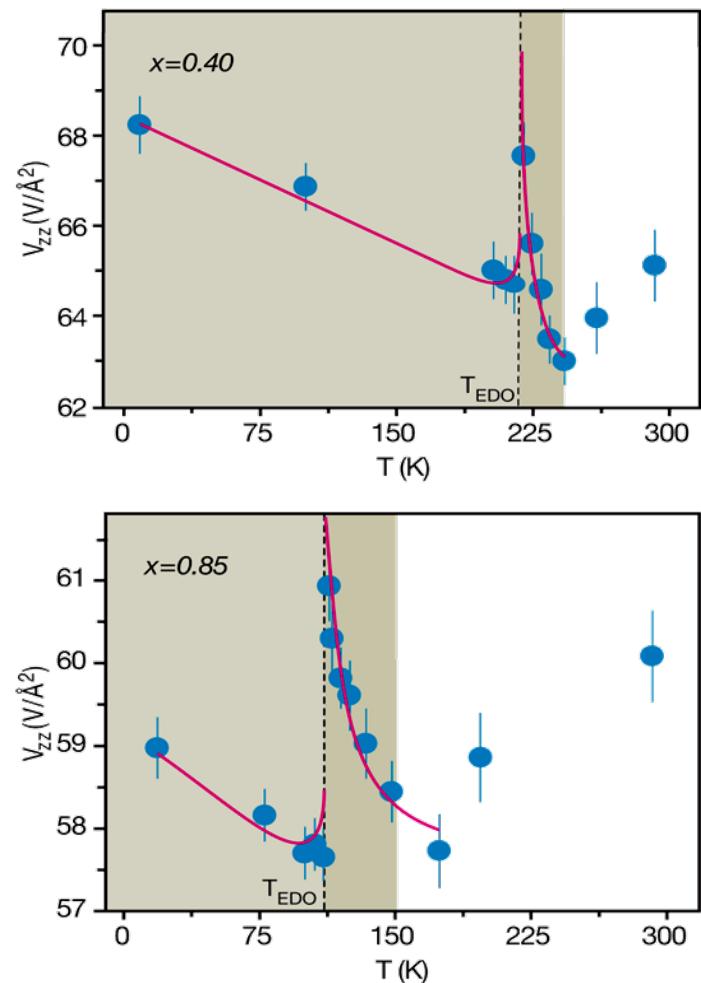
From NMR and PAC studies in Ferroelectrics

$$V_{zz} = V_{zz}^0 + \alpha P_s^2 + \beta T \chi_{el}$$

Results Electric susceptibility / spontaneous polarization below T_C



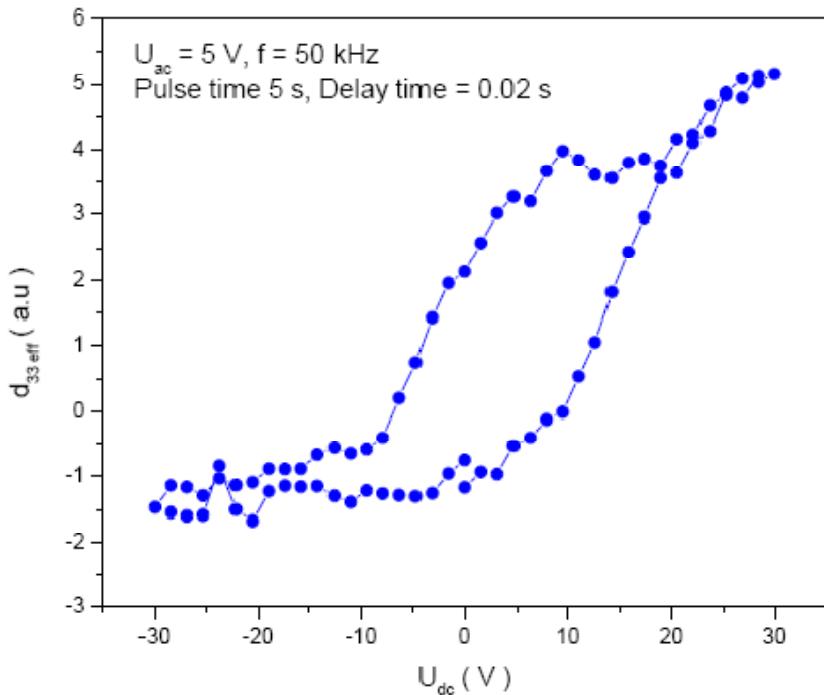
$x=0.35 \rightarrow T_{EDO}=206$ K, $x=0.4 \rightarrow T_{EDO}=218$ K,
 $x=0.85 \rightarrow T_{EDO}=112$ K



compatible with first-order dielectric phase transition below T_{co}

A.M.L. Lopes et al., Phys. Rev. Lett. 100, 155702 (2008)

Local Ferroelectric response in $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ single crystal



Piezoresponse Force Microscopy-hysteresis loop at room temperature:

The piezoelectric contrast points to the existence of a local polar state

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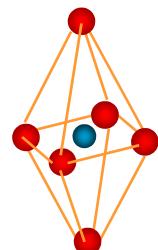
Other oxide systems

Perspectives



Only Mn³⁺ \Rightarrow collective JT distortion

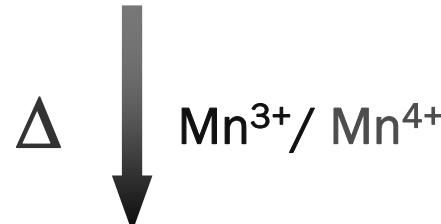
Doping Mn³⁺_{1-2Δ} / Mn⁴⁺_{2Δ} MIX-VALENCE



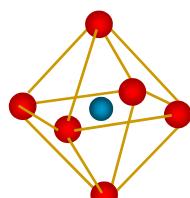
Orthorhombic (O')

Strong JT distortion

Antiferromagnetic



Mn³⁺/ Mn⁴⁺ MIX-VALENCE



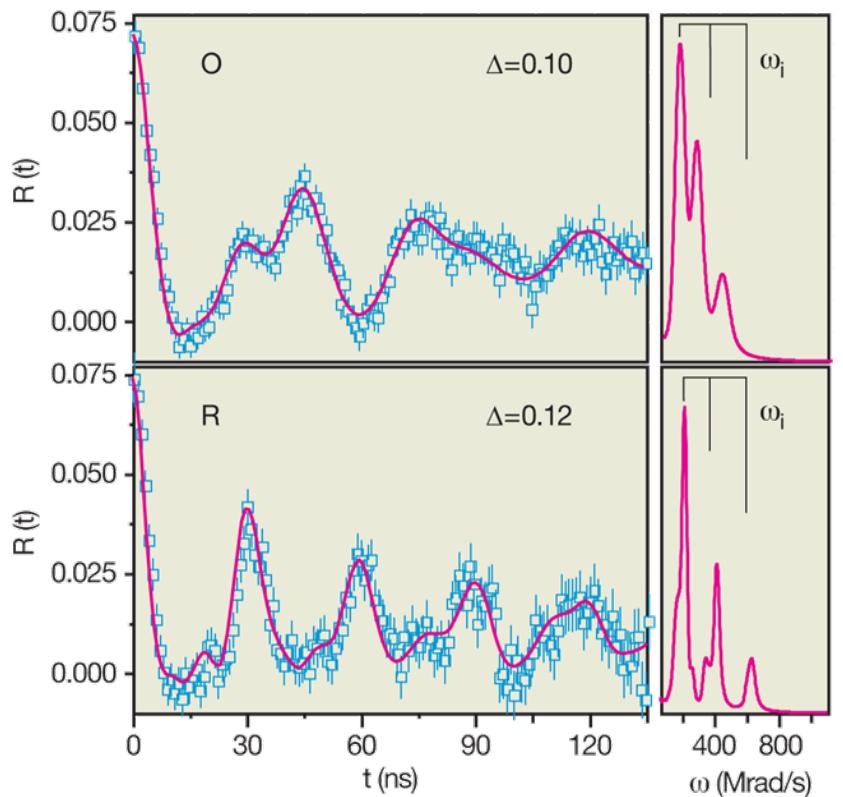
Rhombohedral (R)

No collective JT distortion

Ferromagnetic

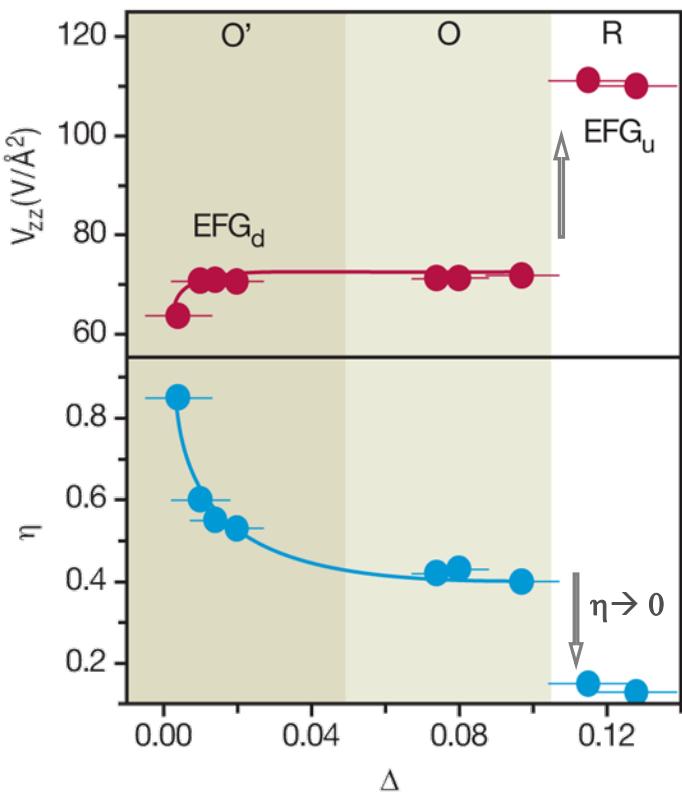
$\text{LaMnO}_{3+\Delta}$

PAC anisotropy functions
@ RT



Orthorhombic \rightarrow Rhombohedral

η and V_{zz} as a function
of Δ



LaMnO_{3.12}

Ferromagnetic Insulator state @ $T < T_c$

Rhombohedral \rightarrow Orthorhombic phase transition $\sim RT$

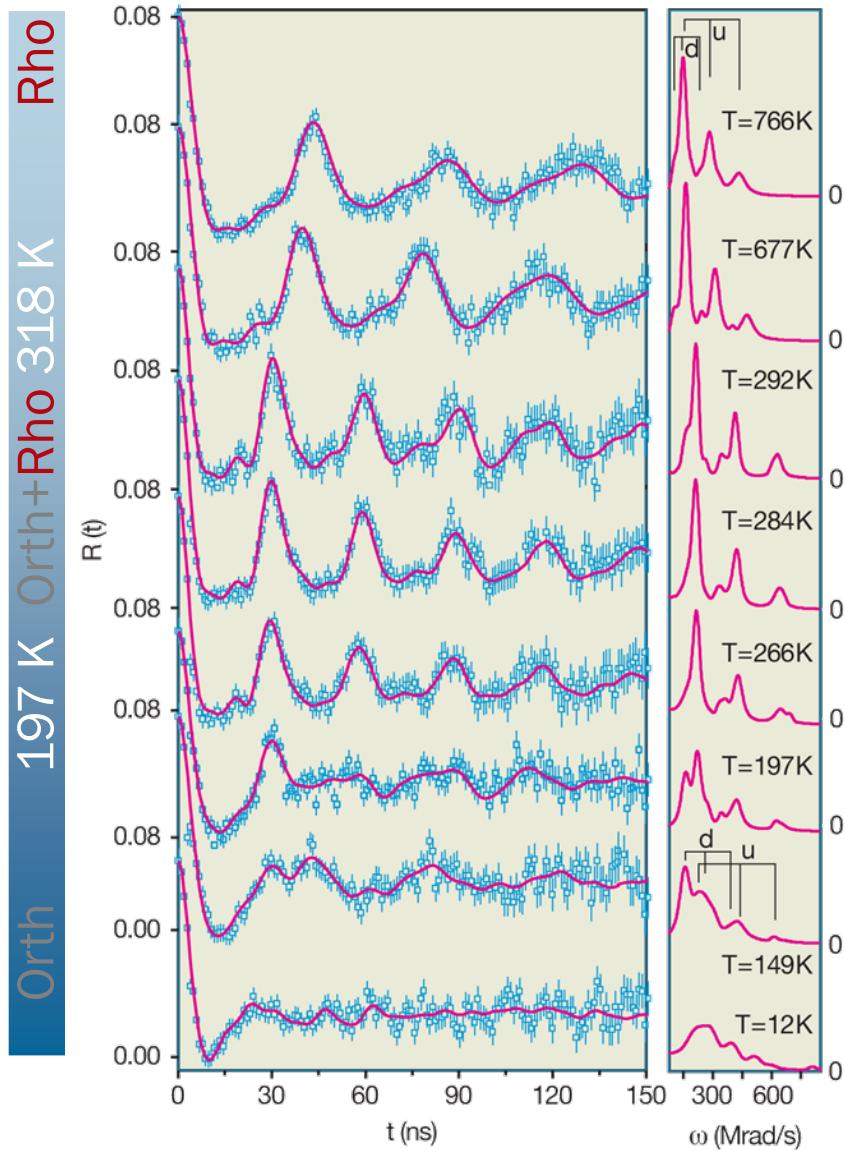
Phase coexistence in a broad range of T

Polarons ?

Polaron nature and evolution?

Polarons responsible for FM INSULATOR state?

PAC anisotropy functions @ $\neq T$



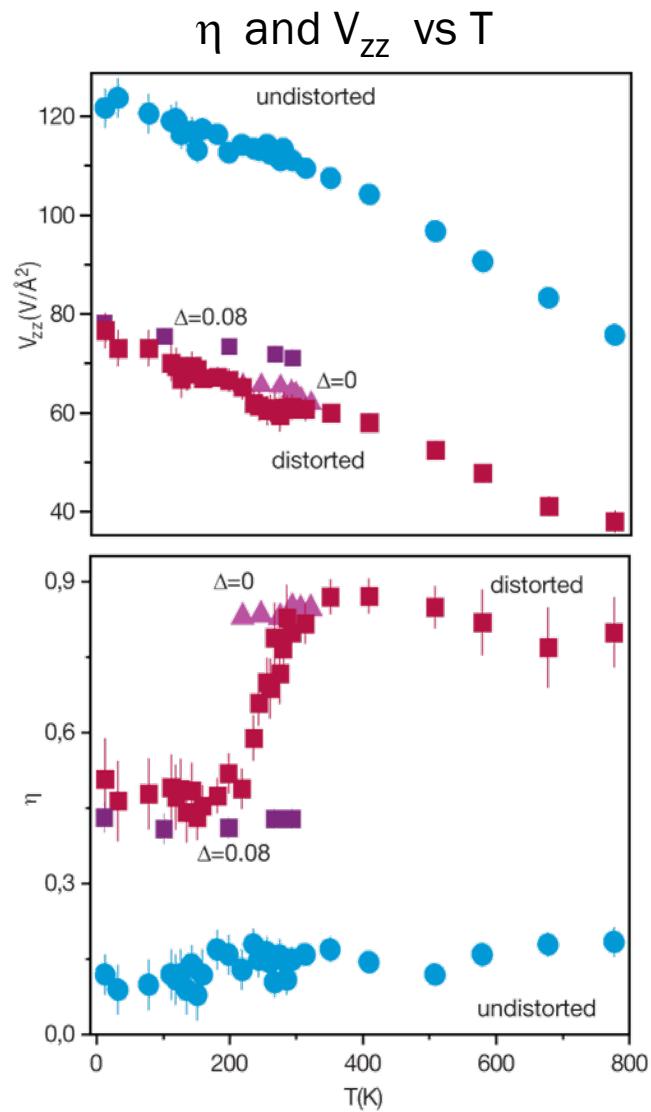
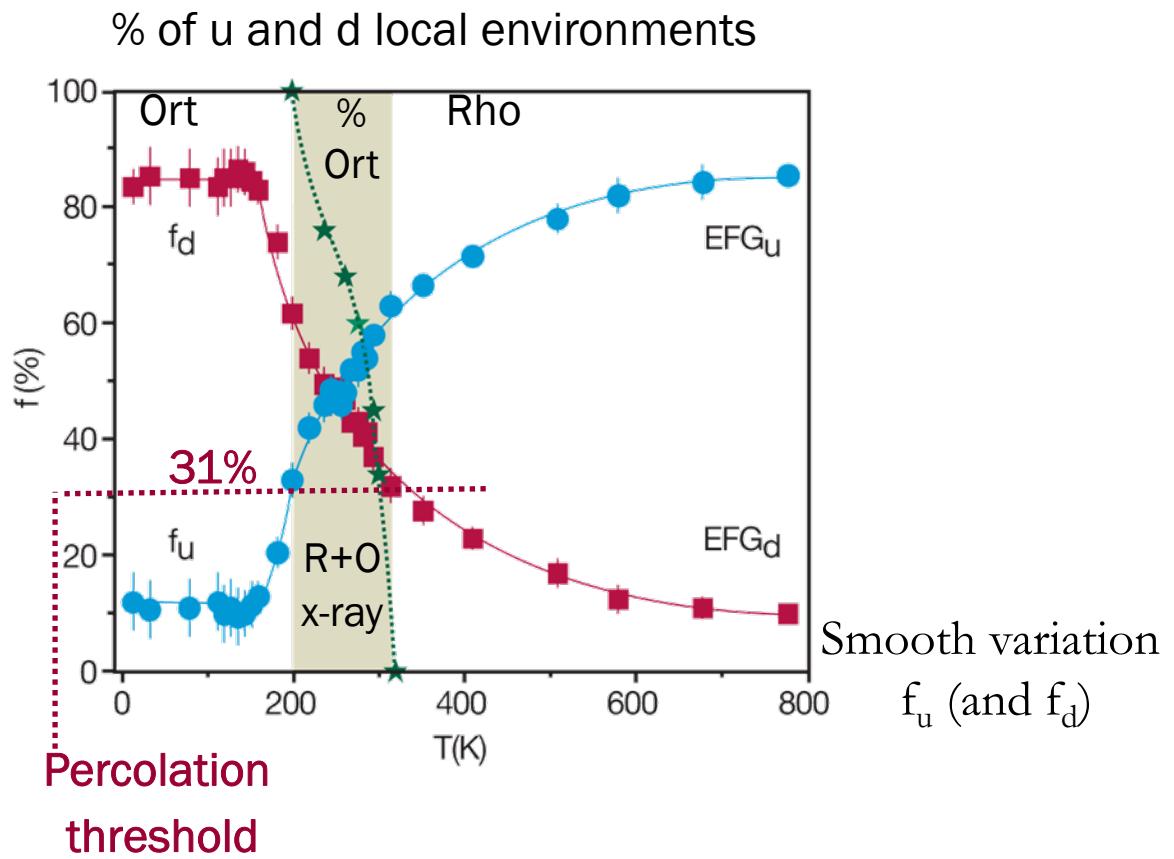
Coexistence of two local environments for all T

Rho crystallographic phase
(x-ray)

Macroscopic Rho + Orth phase coexistence (x-ray)

Orth crystallographic Phase (x-ray)

MHF for $T < T_c$ ($T_c = 145$ K)

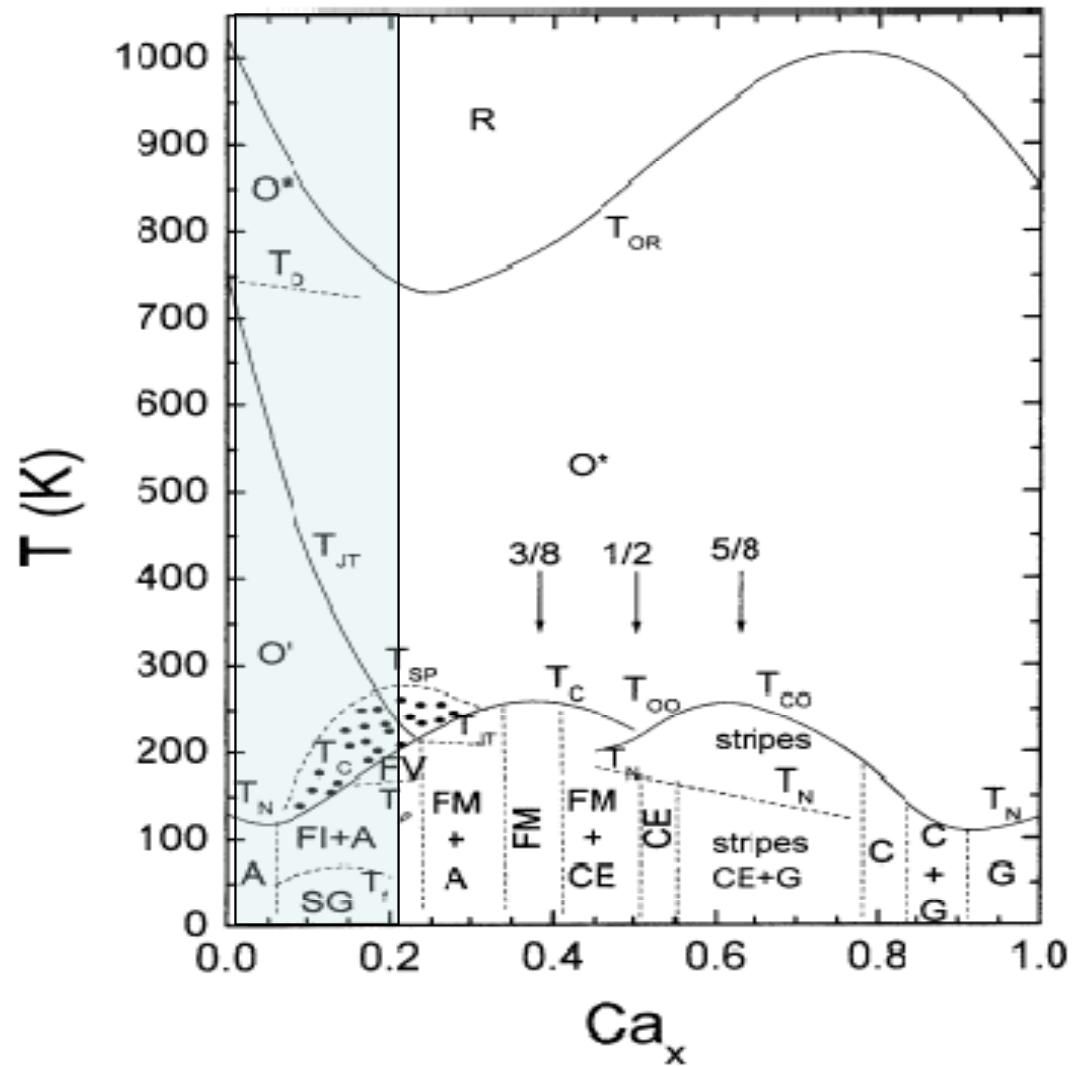


Lightly doped La-Ca manganite

The same physics?

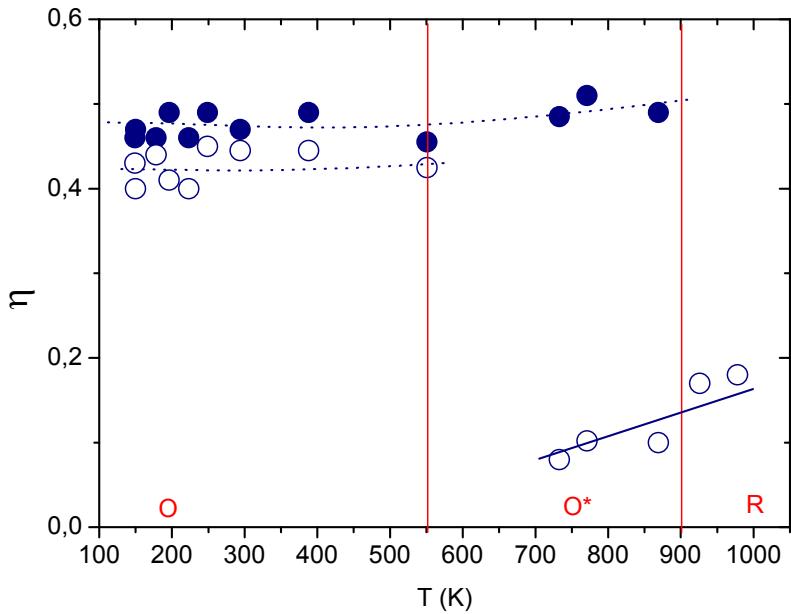
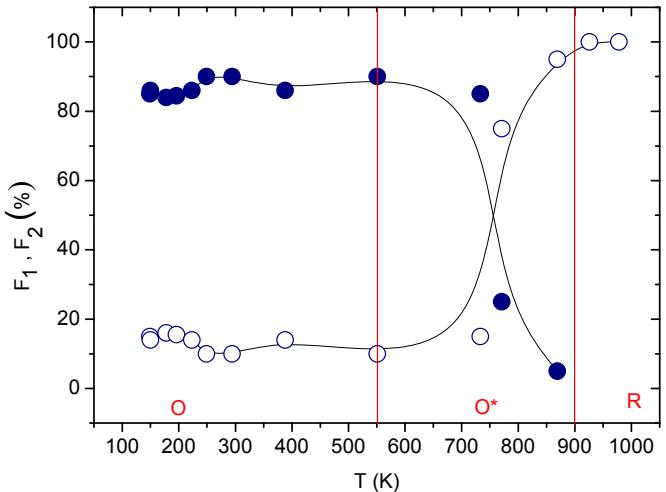
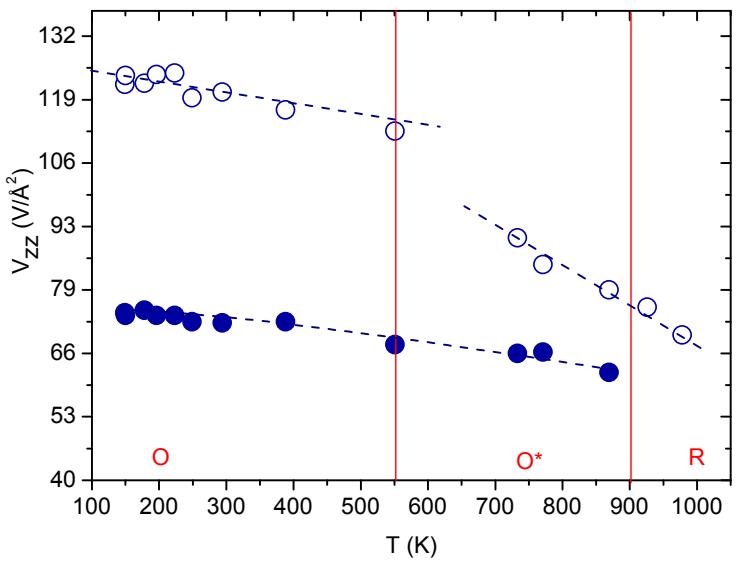
R to O* transitions
on cooling

Intermediate JT-
orbital ordering
transition to O
structure



J. B. Goodenough, 2003

$\text{La}_{0.95}\text{Ca}_{0.05}\text{MnO}_3$



$T > 900\text{K}$ One fraction; low η

$T = 900\text{K}$ R to O* transition

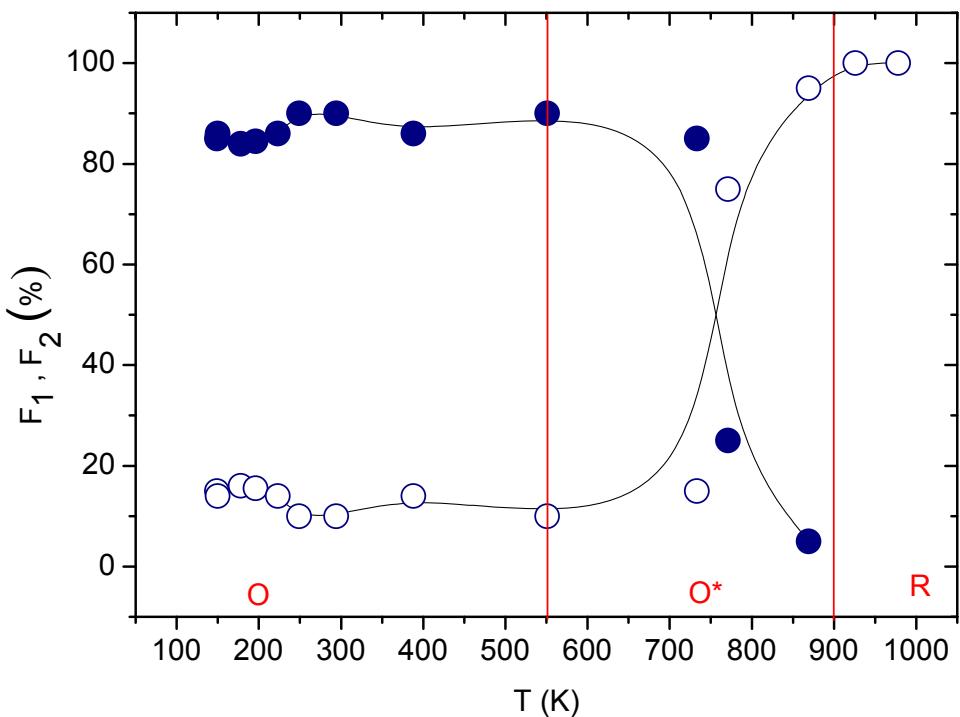
$T < 900\text{K}$

Two fractions: high/low V_{zz}

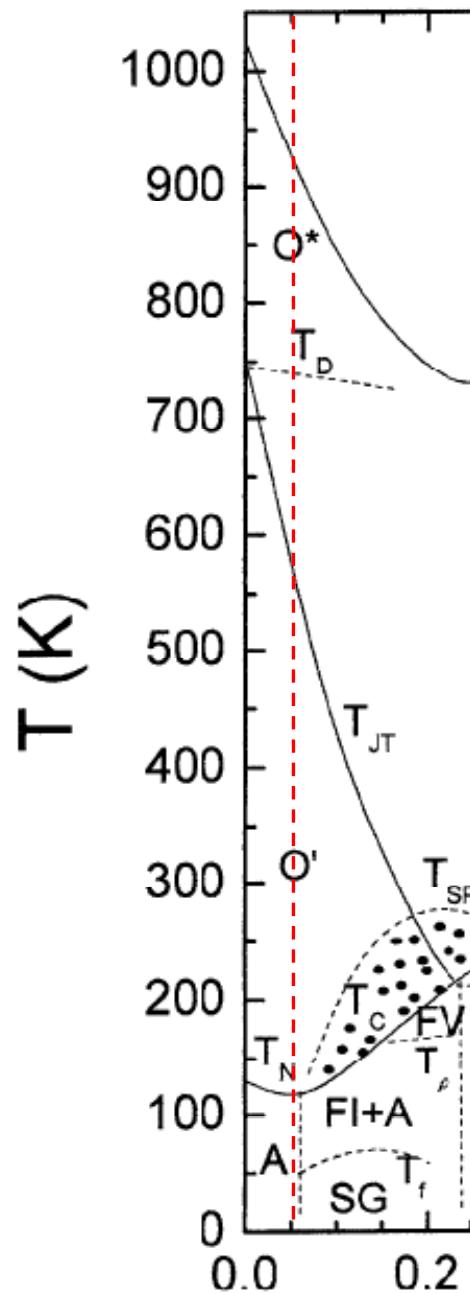
Change ratio at $T \sim 750\text{K}$

Only minority fraction sensitive to JT transition

$\text{La}_{0.95}\text{Ca}_{0.05}\text{MnO}_3$



PAC very sensitive to charge distribution changes:
Disproportionation?



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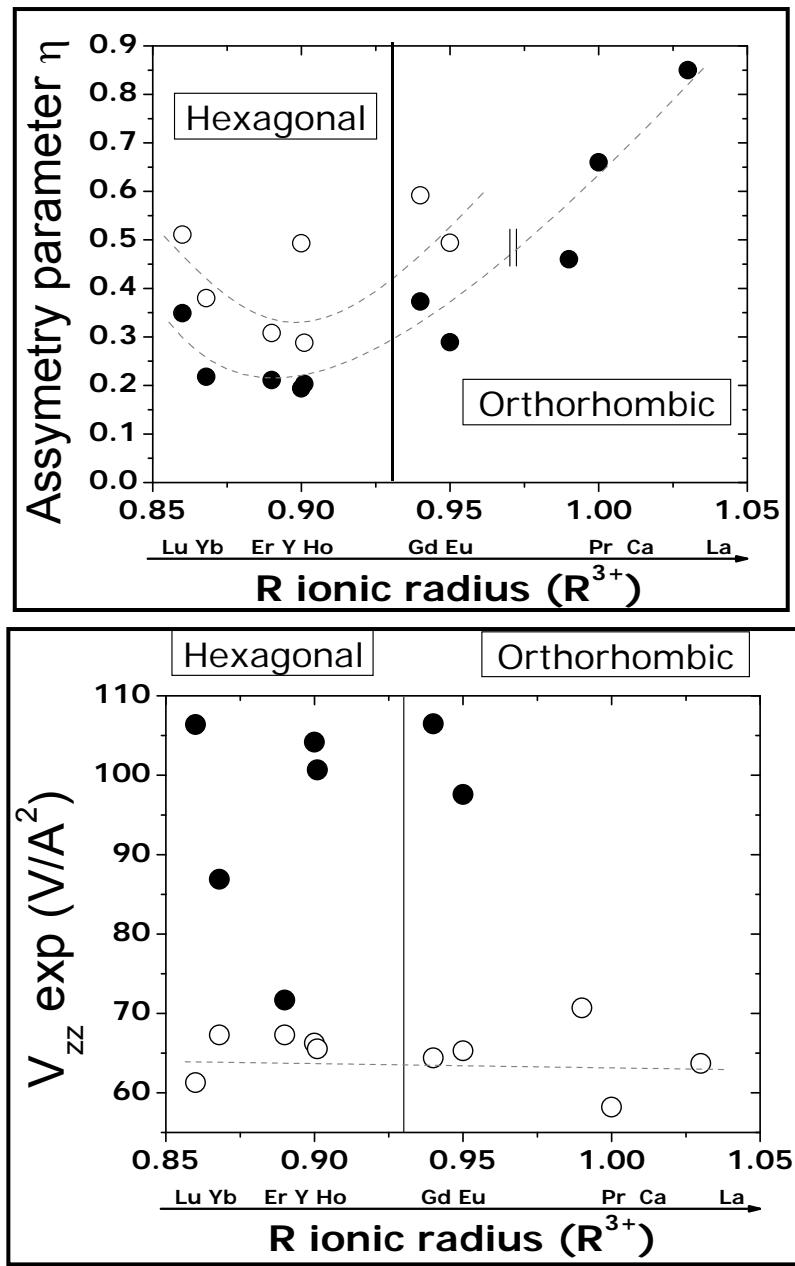
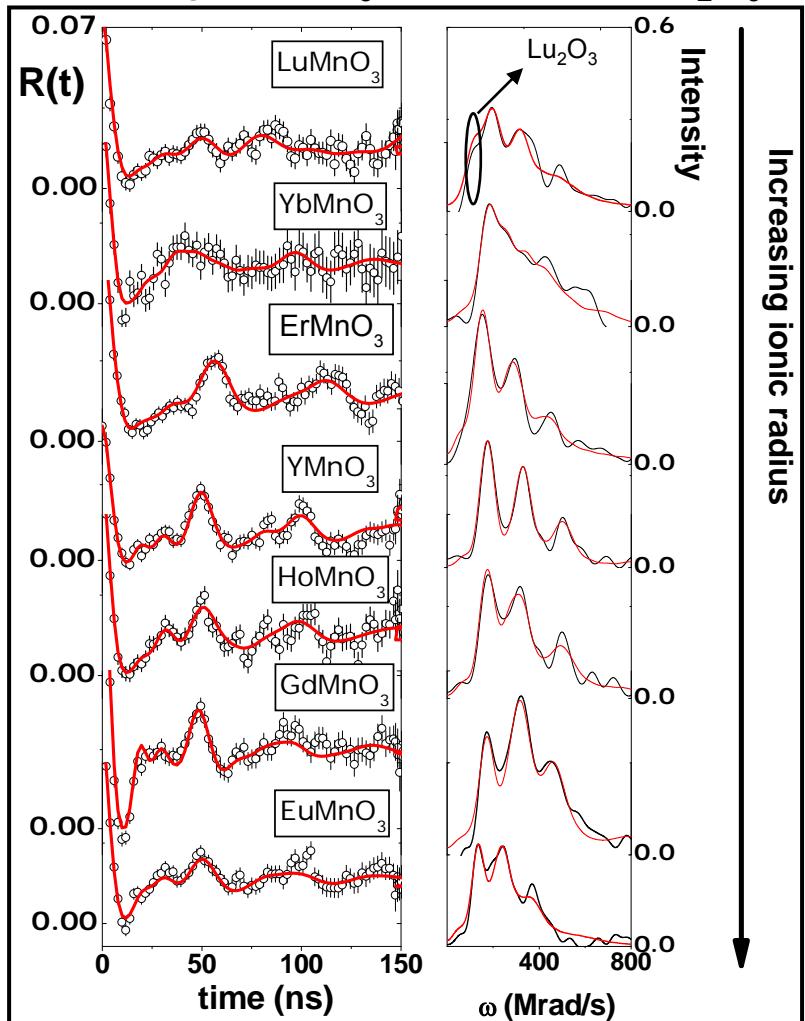
Multiferroics: RMnO_3

Other oxide systems

Perspectives

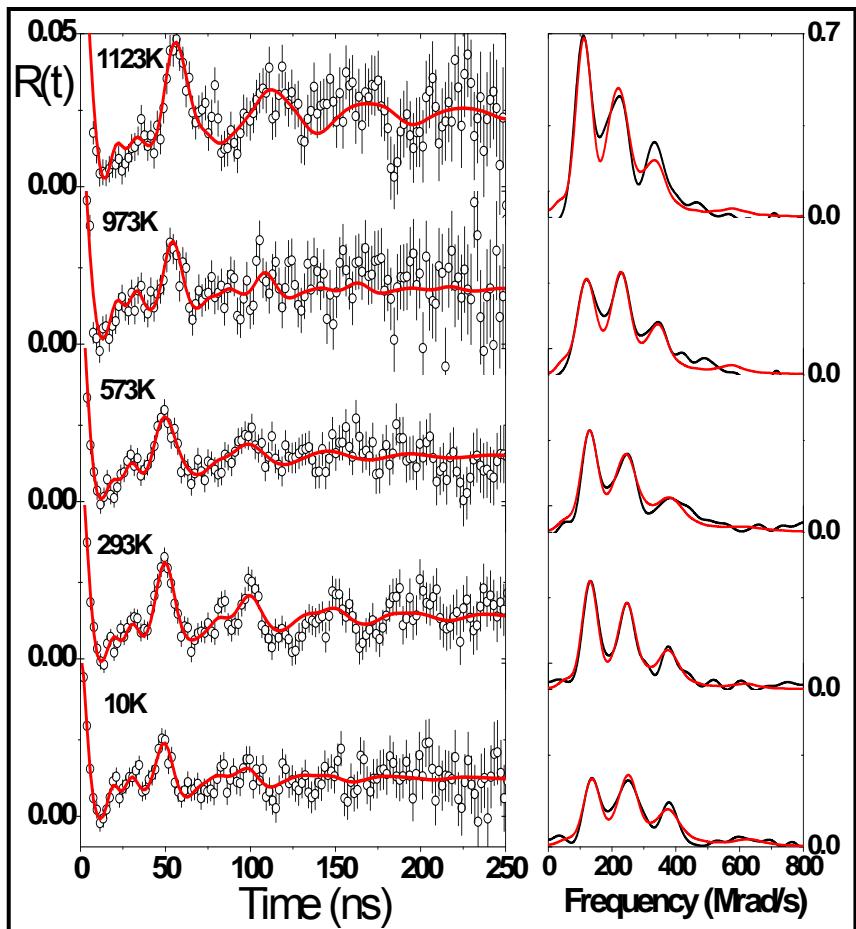
RMnO_3 vs. R ionic radius

Single phase RMnO_3 samples
(excepting LuMnO_3 with traces of Lu_2O_3)



YMnO₃ vs. Temperature

Hexagonal structure



Two EFG's present in YMnO₃ samples

EFG1

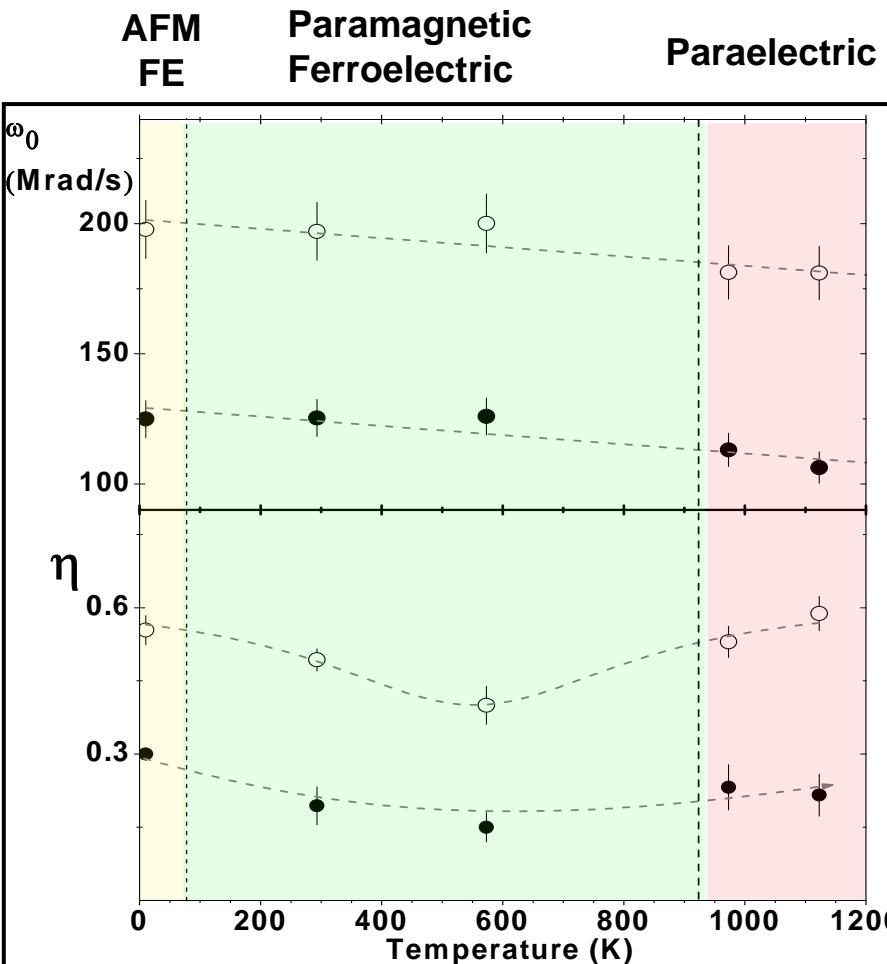
$f_1 \sim 70\%$

$\omega_0 \sim 120$ Mrad/s

EFG2

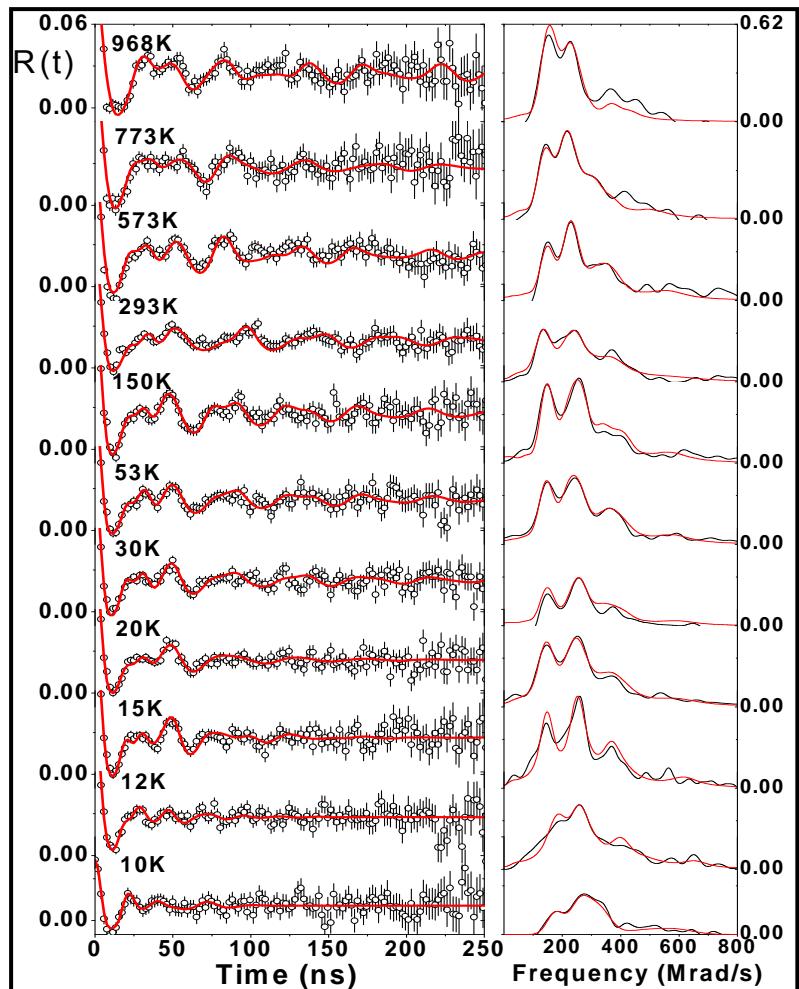
$f_2 \sim 30\%$

$\omega_0 \sim 180$ Mrad/s



EuMnO_3 vs. Temperature

Orthorhombic structure



Two EFG's present in EuMnO_3 samples

EFG1

$f_1 \sim 35\text{-}40\%$

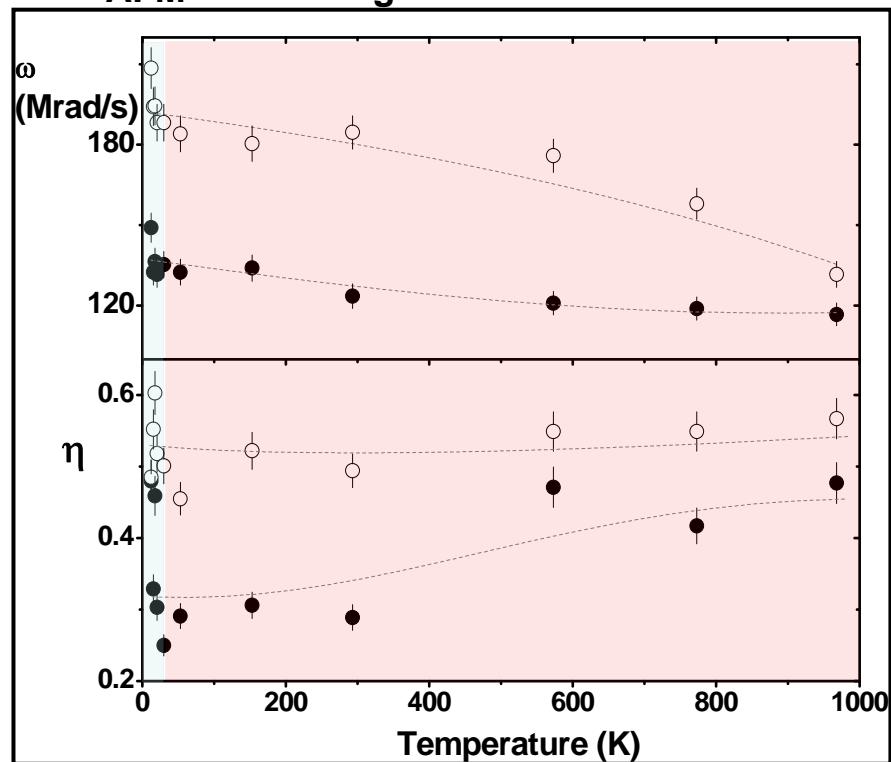
$w_0 \sim 120 \text{ Mrad/s}$

EFG2

$f_2 \sim 60\text{-}65\%$

$w_0 \sim 180 \text{ Mrad/s}$

AFM Paramagnetic and Paraelectric



Inversion of the main EFG below 20K

OUTLINE

Manganites and intrinsic complexity

Charge-ordering scenarios, phase separation
Multiferroic systems

Local Probe Studies

Hyperfine technique: Perturbed Angular Correlations

Probing electric fields in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ system

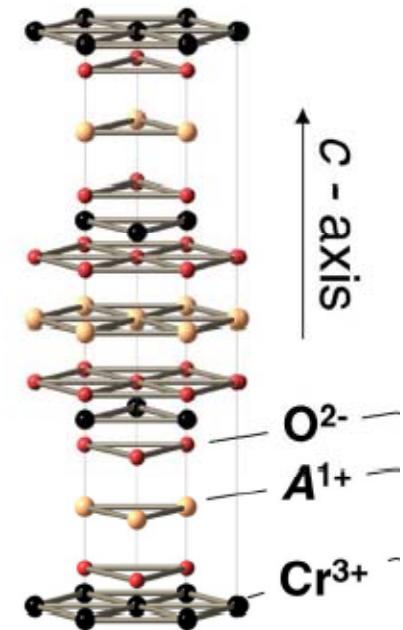
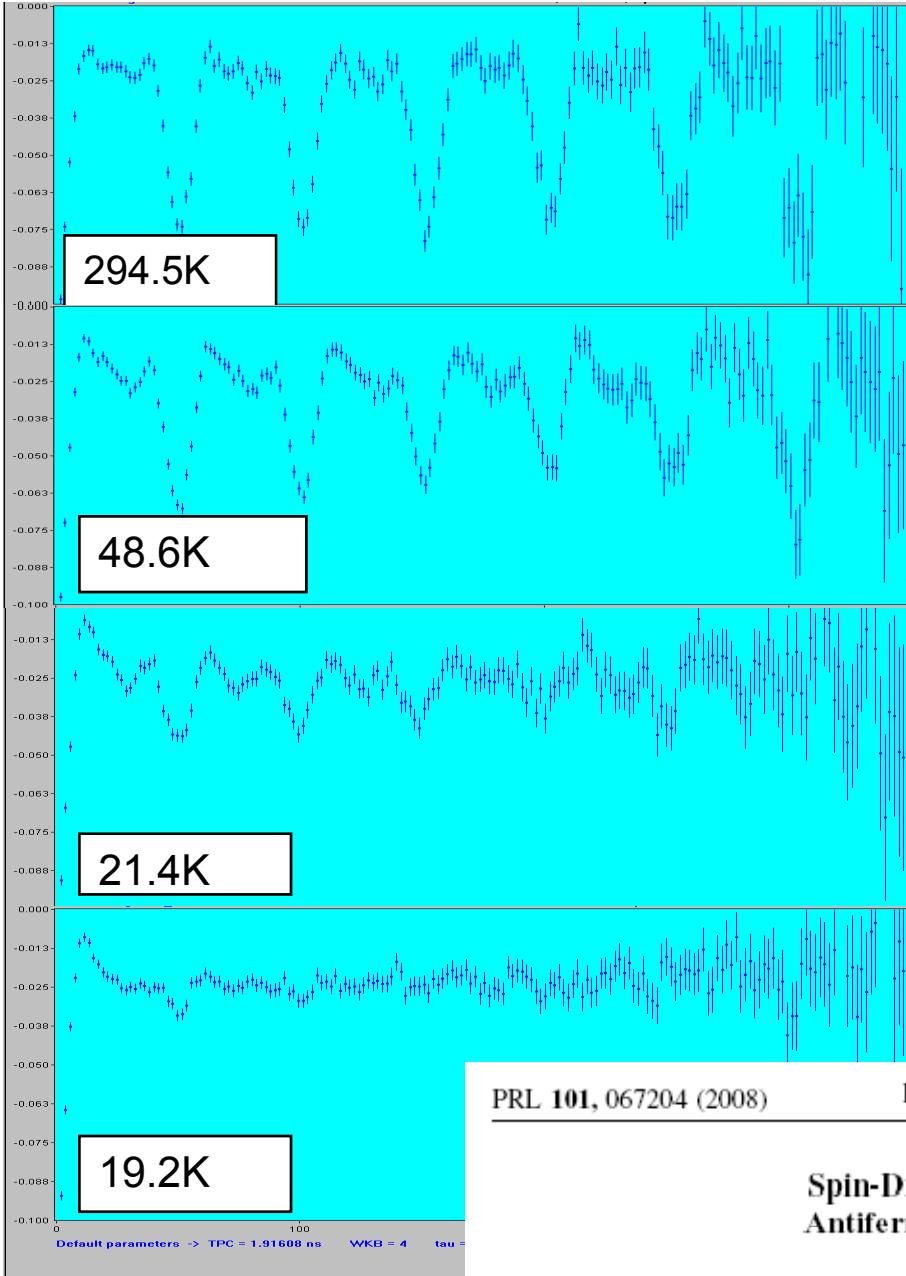
Phase separation, polaron dynamics in $\text{LaMnO}_{3+\delta}$ and $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$

Multiferroics: RMnO_3

Other oxide systems

Perspectives

AgCrO_2 (^{111}In probe): a new multiferroic

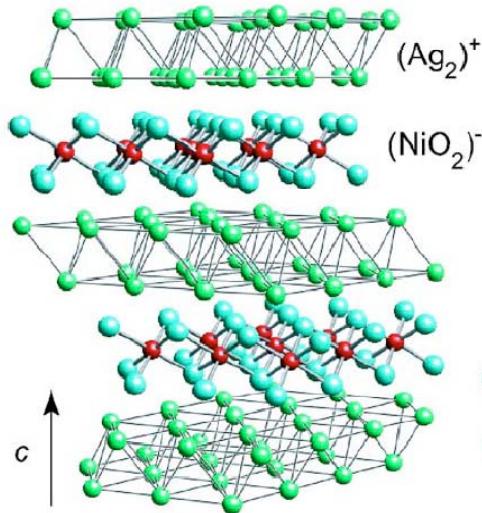


Spin-Driven Ferroelectricity in Triangular Lattice
Antiferromagnets ACrO_2 ($\text{A} = \text{Cu, Ag, Li, or Na}$)

S. Seki,¹ Y. Onose,^{1,2} and Y. Tokura^{1,2,3}

week ending
8 AUGUST 2008

Ag_2NiO_2 and analogous: Orbital physics vs Charge Order



Valence(charge) changes in Ag and Ni avoiding Jahn-Teller distortion

PRL 99, 157204 (2007)

PHYSICAL REVIEW LETTERS

week ending
12 OCTOBER 2007

Orbital Degeneracy Removed by Charge Order in Triangular Antiferromagnet AgNiO_2

PRL 98, 176406 (2007)

PHYSICAL REVIEW LETTERS

week ending
27 APRIL 2007

Charge Ordering as Alternative to Jahn-Teller Distortion

I. I. Mazin,^{1,2} D. I. Khomskii,^{2,*} R. Lengsdorf,² J. A. Alonso,³ W. G. Marshall,⁴ R. M. Ibberson,⁴ A. Podlesnyak,⁵ M. J. Martínez-Lope,³ and M. M. Abd-Elmeguid²

**Like AgCrO_2 , ^{111}Ag and $^{111}\text{Cd}/\text{In}$ probes for the 2 sites:
more complete mapping of charge distributions**

CONCLUSIONS

- Combined with other techniques and theoretical modeling, PAC brings new insights on current cutting edge research on solid state physics: correlated electrons systems.
- The availability of different probes at Isolde allows tackling different situations: chemical compatibility and environments.