LOCAL PROBING OF ELECTRIC AND MAGNETIC ORDER COEXISTENCE IN MANGANITE SYSTEMS

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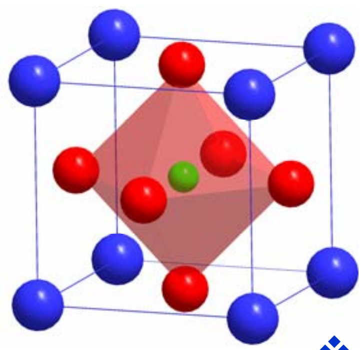
Is390 collaboration

OUTLINE

- Materials
- Experimental results in $Pr_{1-X}Ca_XMnO_3$
- Preliminary results in multiferroic systems
- Conclusions

MANGANITES

Cubic perovskite



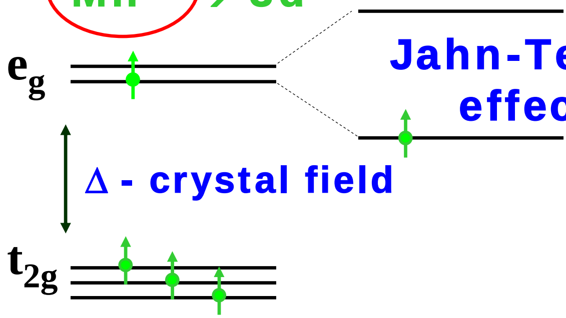
$RMnO_3$

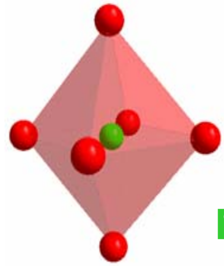
- R
- O
- Mn

↓

❖ **Cation misfit → structure distorts**

Mn^{3+} → $3d^4$





Mn^{3+}
O^{2-}
Pr^{3+}

↓

❖ **Octahedra distortion**

Doping with Divalent ions (Ca, Sr...) → $R^{3+}_{1-x}Ca^{2+}_{x}Mn^{3+}_{1-x}Mn^{4+}_{x}O_3$

↓ **Mn^{3+} / Mn^{4+} MIX-VALENCE**

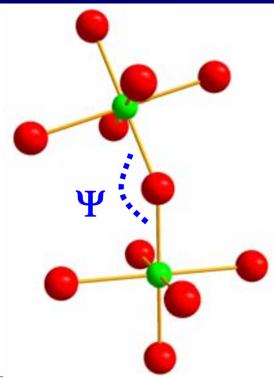
No JT effect

Control

Mn-O distances

Mn-O-Mn angle

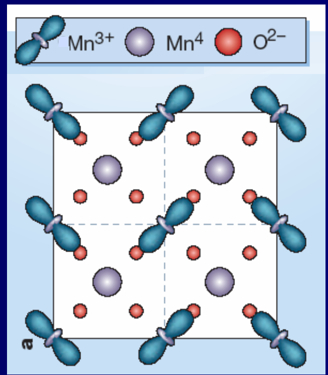
(ψ<180º)



- Overlap between Mn & O orbitals
- Magnetic & electric properties

Strong coupling of **SPIN**, **CHARGE**, **ORBITAL** and **LATTICE**

RICH PHASE DIAGRAM

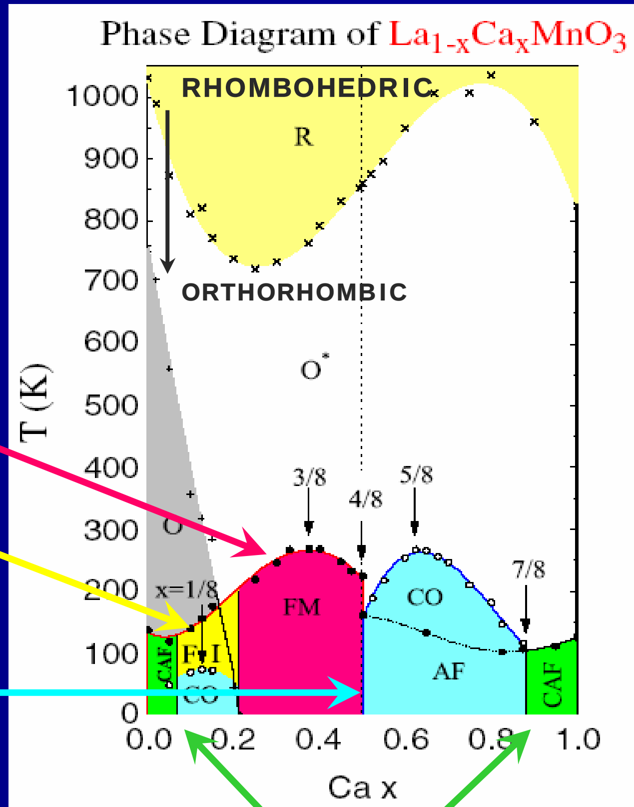


Mn^{3+} / Mn^{4+}
localization in a ordered way

FERROMAGNETIC METALLIC

FERROMAGNETIC INSULATOR

CHARGE ORDER



Cheong et al, Physica B, 318, 39 (2002)

ANTIFERROMAGNETIC

What is the nature of the **CHARGE ORDER** states?

E. Dagotto, *Open questions in CMR manganites...*, New Journal of Physics, 7, 67 (2005)

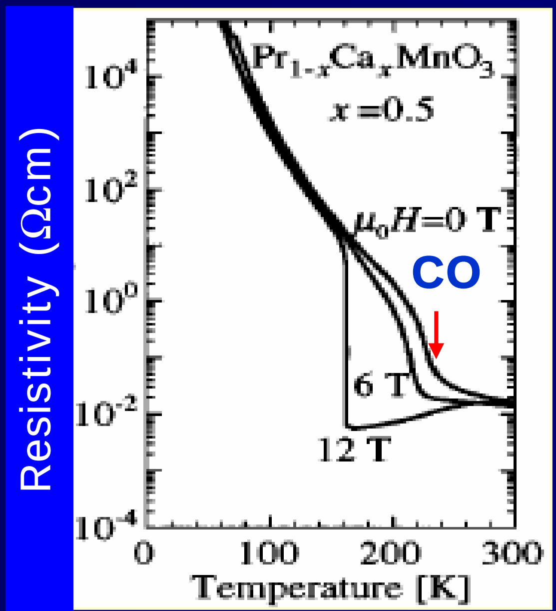
What is hidden behind the **CHARGE ORDER** states?

$Pr_{1-x}Ca_xMnO_3$

Charge Order

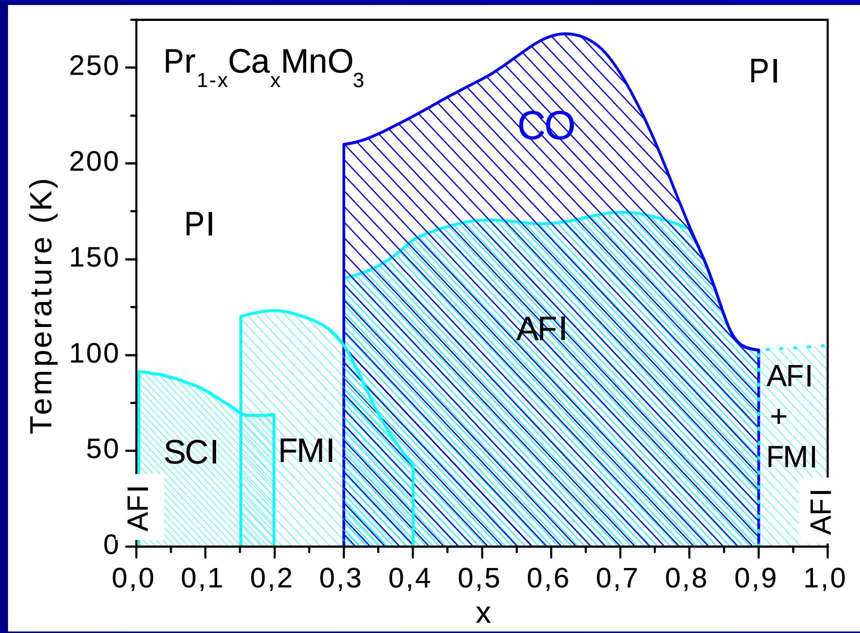
for a large range of compositions

CO/OO signatures



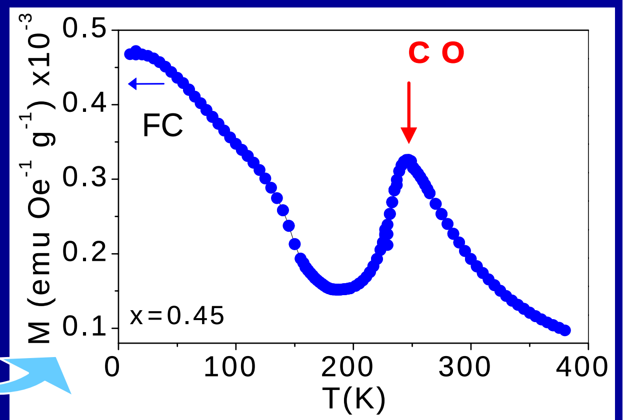
Y. Tokura *et al.*, PRB, 64, (2001) 195133

$Pr_{1-x}Ca_xMnO_3$ mag/elect phase diagram



Sharp resistivity increase

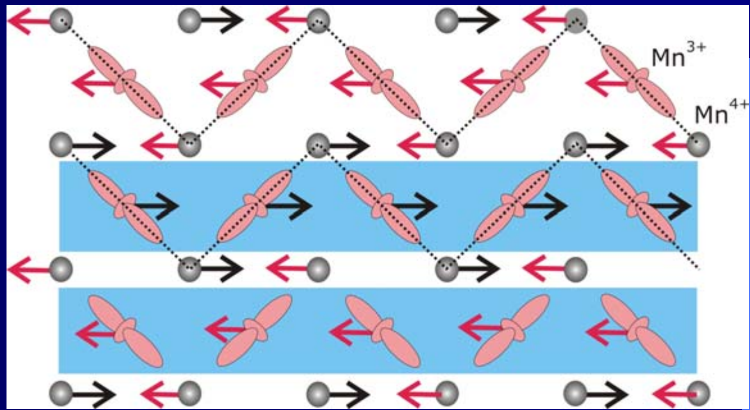
Magnetization decrease



High Magnetic Field -- Melting of CO

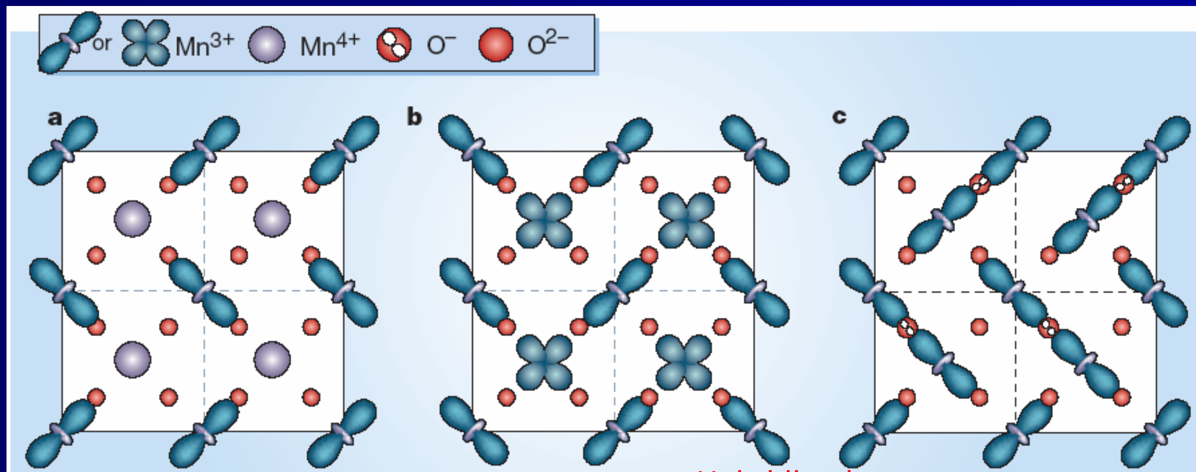
Charge and Orbital Order

Classical picture



Mn^{3+}/ Mn^{4+}
Arrays

FM Zig-Zag
chains
coupled AF



Charge contrast | Small CC | Hybridization | No CC

FM dimers
Mn^{3+}-O-Mn^{3+}
coupled AF
(Zener
polarons)

Adapted
M. Coey, Nature
430,
155 (2004)

P. G. Radaelli et all.
Phys. Rev.B 55, 3015
(1997)

Grenier et al,
Phys Rev. B 69, 134419
(2004)

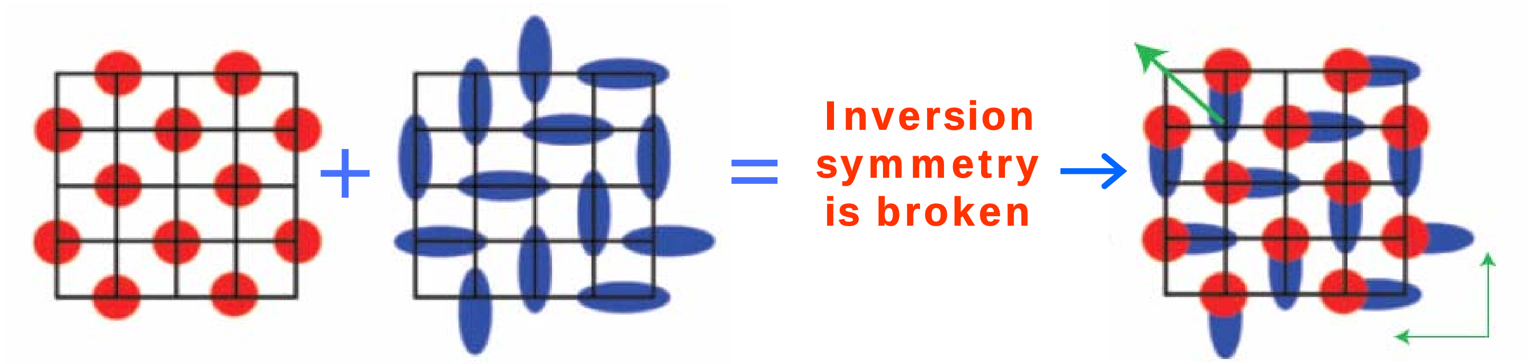
Daoud-Aladine et al,
Phys Rev. Lett 89, 97205
(2002)

New scenario for the Charge Ordered State

Theoretical work predicted the possibility of

local electric dipole moments in CO manganites

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



Wigner crystal
Site centered CO

Zener polaron
bond centered CO

Ferroelectricity

CO state in $Pr_{1-x}Ca_xMnO_3$

New paradigm for ferroelectrics but...

Till now there is no experimental prove that electric polarization exists in CO $Pr_{1-x}Ca_xMnO_3$

Local probe: Perturbed Angular Correlation

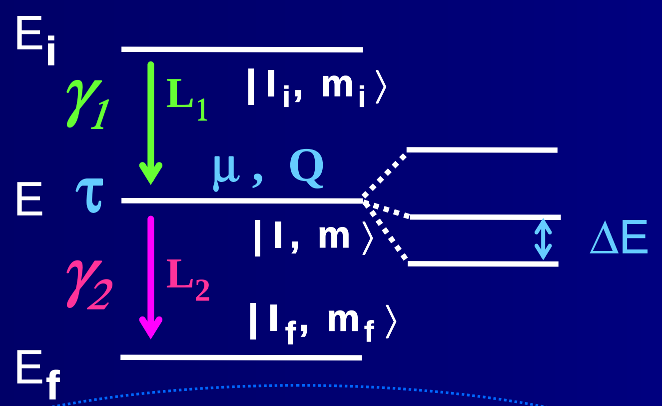
Hyperfine splitting → Source of information

Magnetic hyperfine field / Electric field gradient

Probe nuclear moments

$B_{hf} \cdot \mu$

$\nabla E \otimes Q$



$\Delta E = e.Q.V_{zz}\,(m^2 - m'^2)/4I(2I-1)$

$\eta = (V_{xx} - V_{yy})/V_{zz}$

$\Delta E = \mu\, B_{hf} = h\omega_L (m - m`)$

V_{zz} - EFG principal component

η - Asym

B_{hf} - Mag

Samples implanted

($t_{1/2}$= 85ns, Q=0.83 b, μ=-0.7...)

Cd @ Pr/Ca si

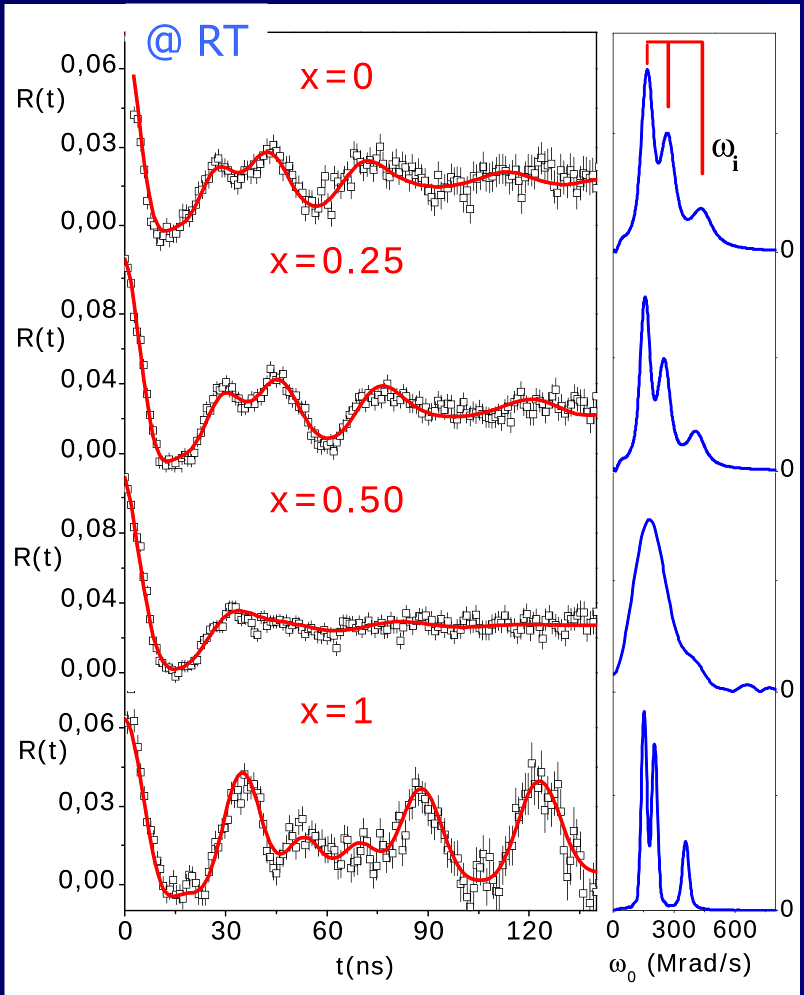
EFG sensitive to small changes in the electronic structure

PAC sensitive tool to probe local electric ordering

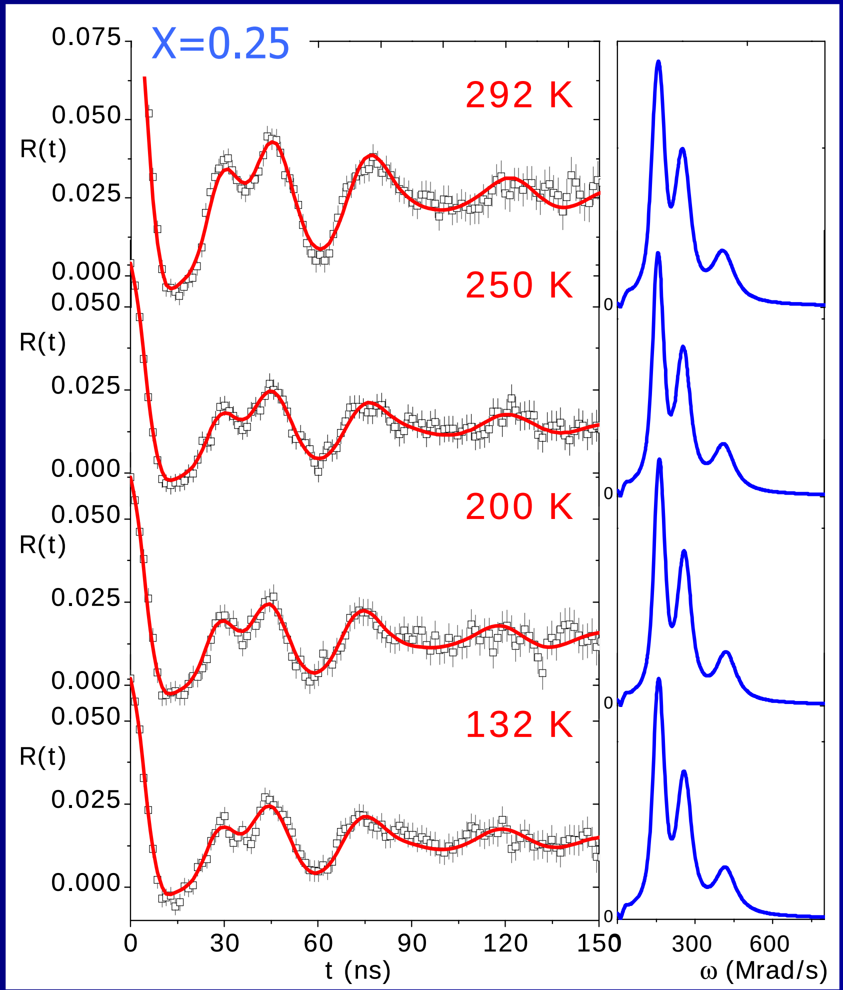
$Pr_{1-x}Ca_xMnO_3$

PAC anisotropy functions

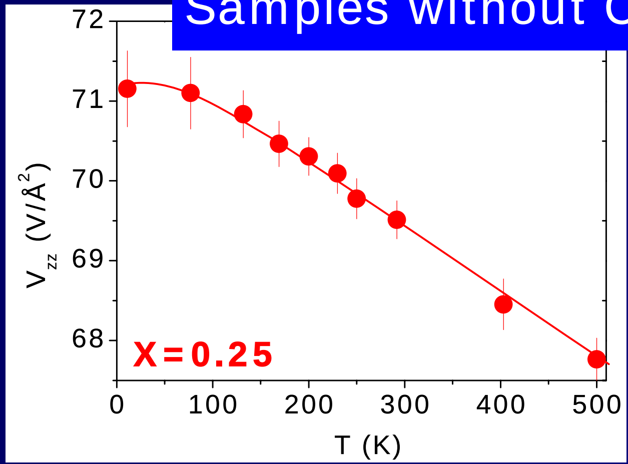
Measured for ≠ Ca (x) content



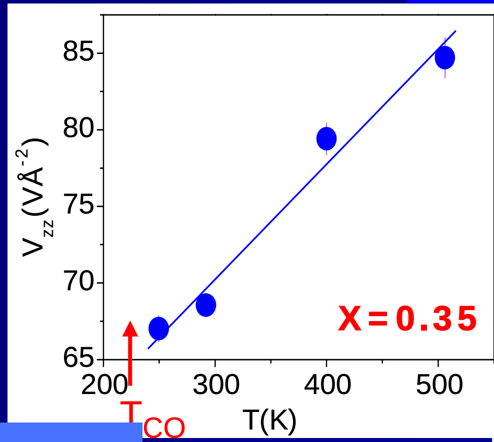
Measured at several temperatures

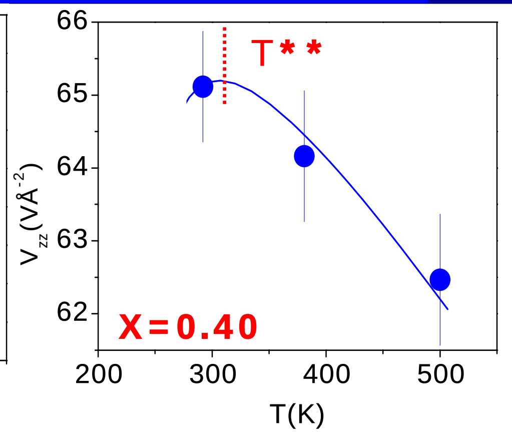


Samples without CO

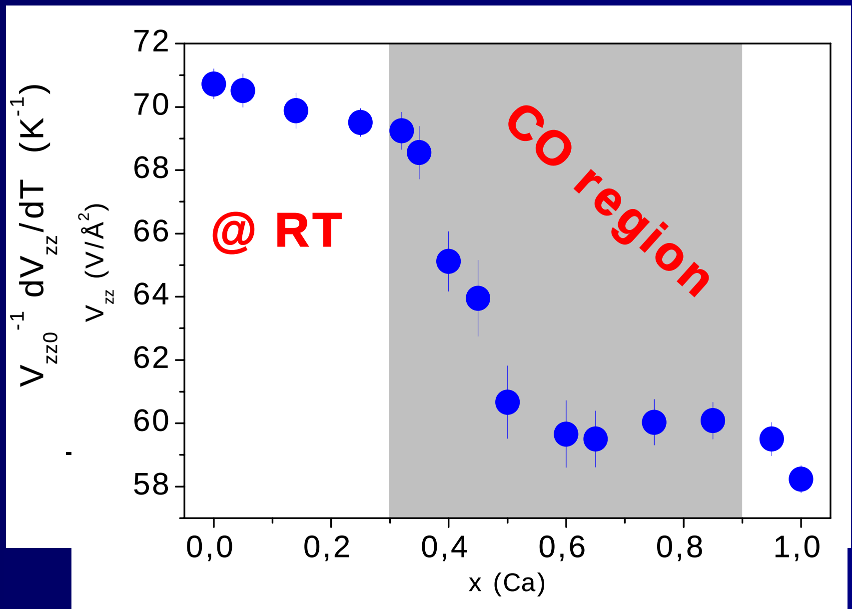


Samples with CO

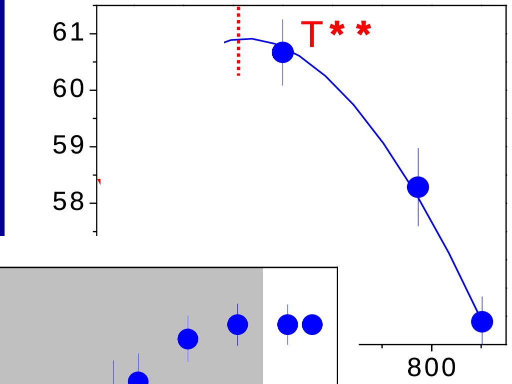


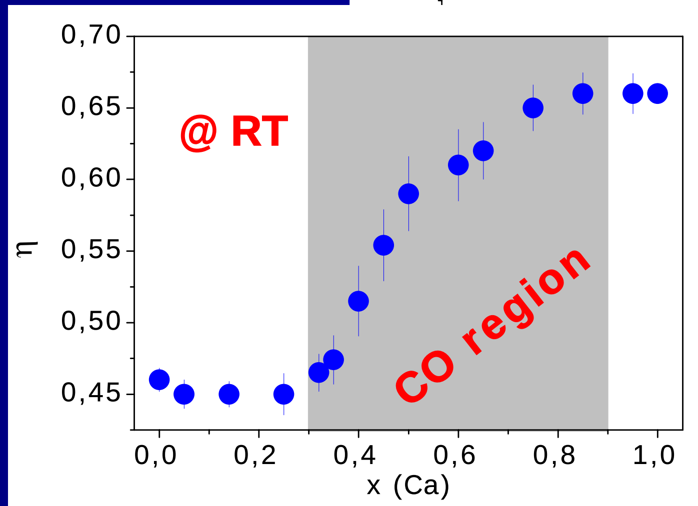


Vzz @ η Room temperature



Anomalous V_{zz} (T) dependence



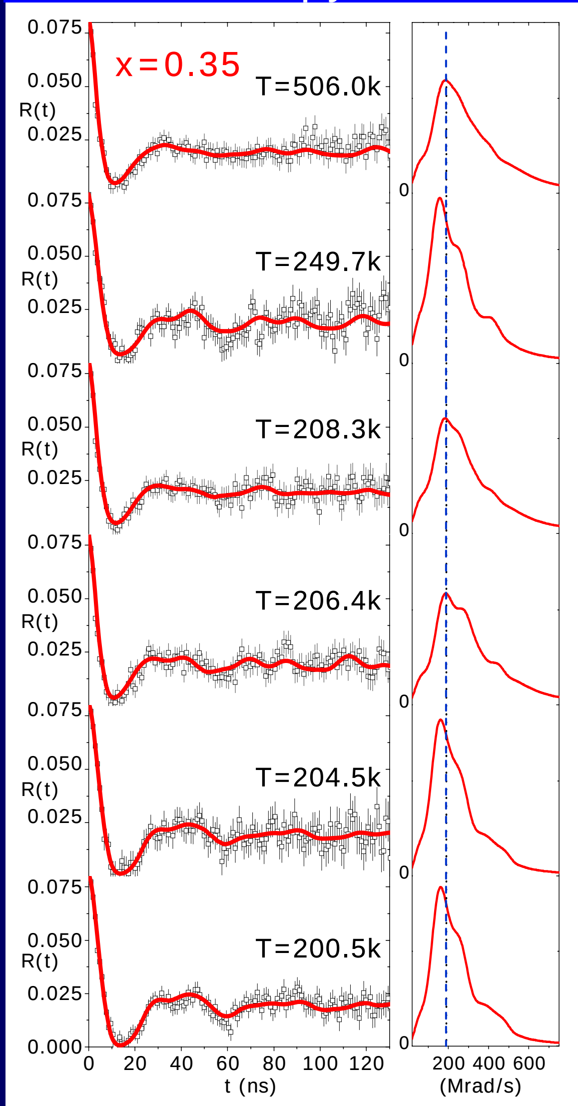


modes

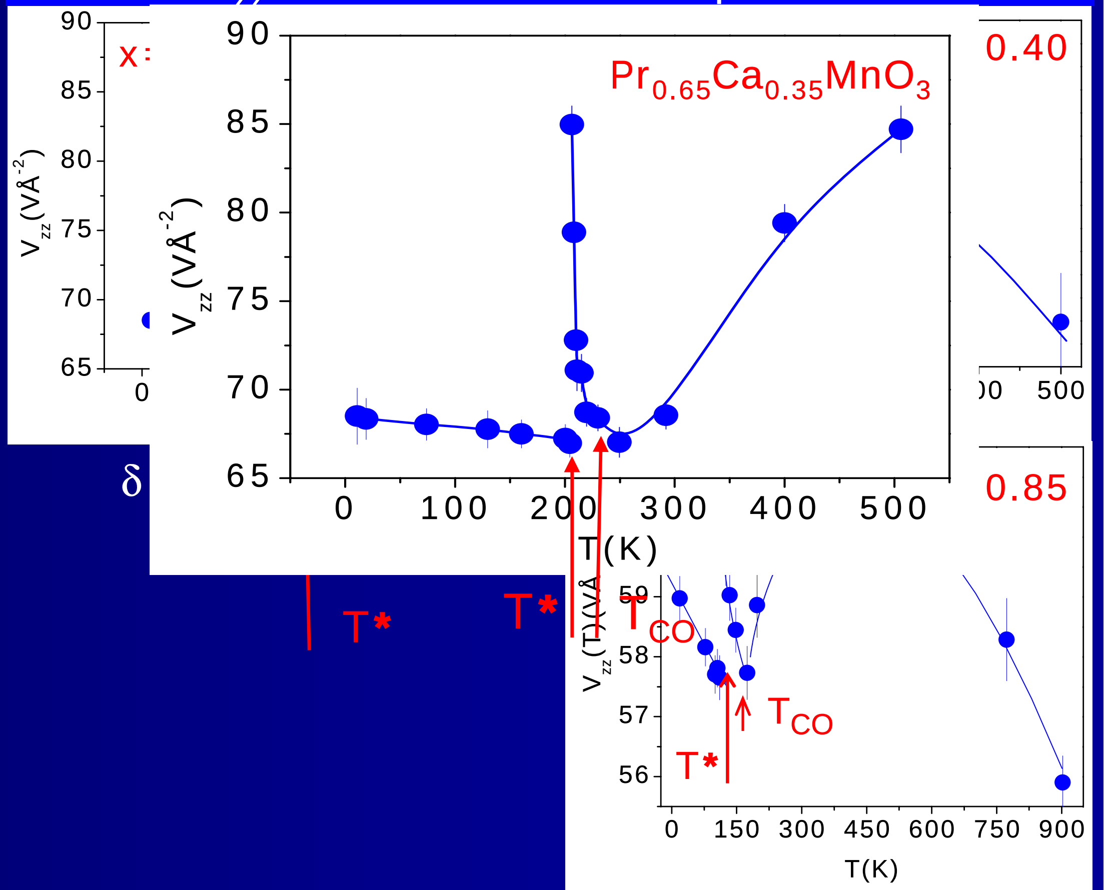
EFG → Sensitive to the lattice dynamics

Charge order region

PAC anisotropy functions

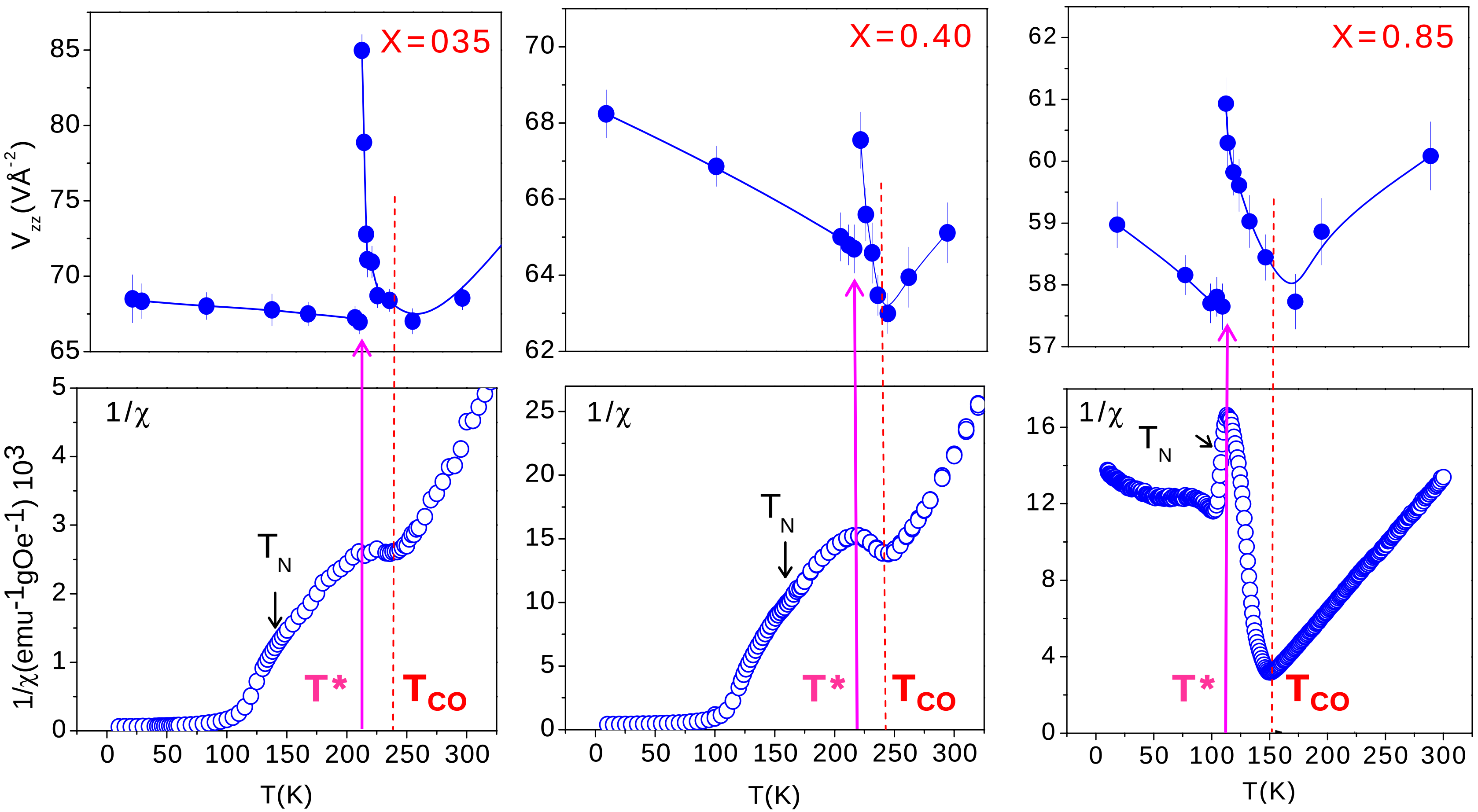


V_{zz} as a function of temperature



- Sharp increase of V_{zz} @ T< T_{CO}
- Dropping at T* from 85 to 67 V_{zz}/Å^{-2} in 2 K

Correlation between EFG and magnetic susceptibility



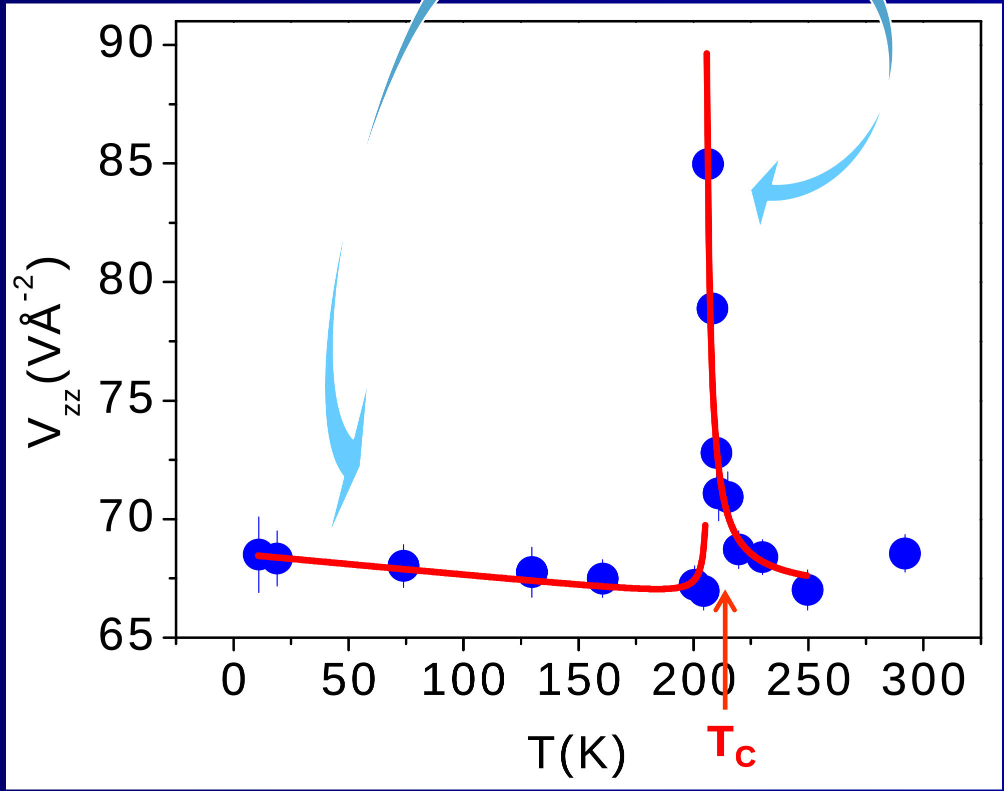
From NMR and PAC studies in Ferroelectrics

EFG → sensitive to local electric dipoles

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

Y. Yeshurun *et al*, J. Phys. & Chem. Solids 40 231 (1979)

Local Spontaneous Polarization



Divergence

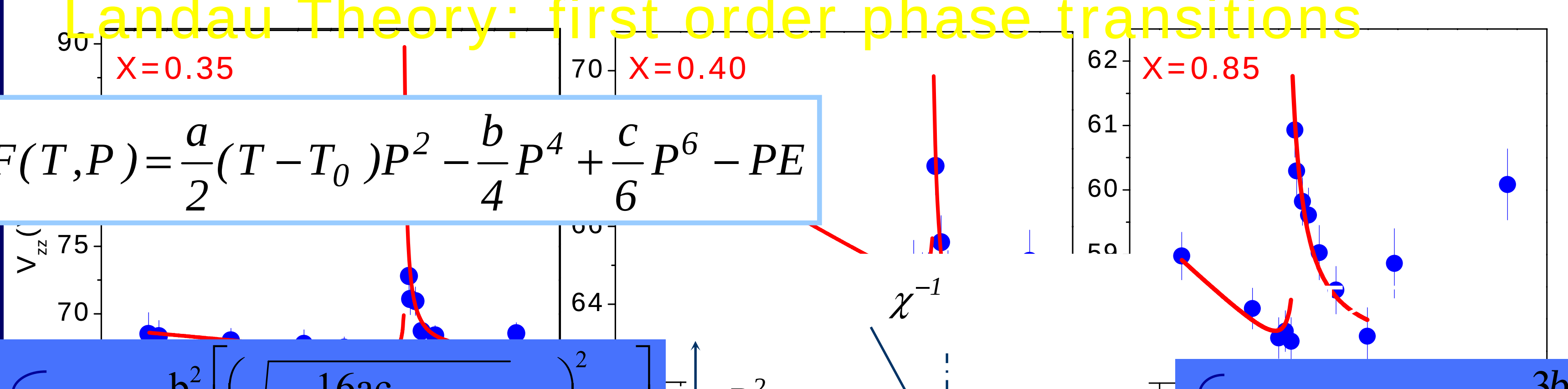
Electric Susceptibility

Fitting the data ...

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

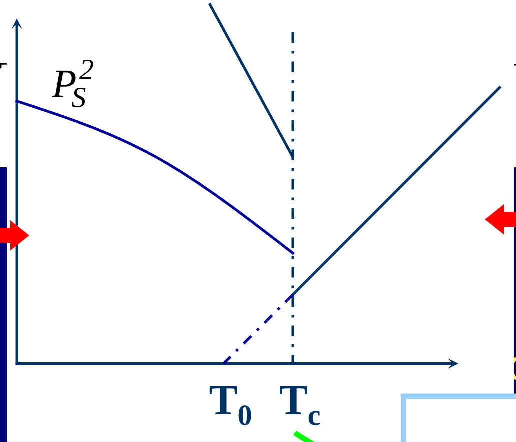
Electric susceptibility / spontaneous polarization below T_C

Landau Theory: first order phase transitions



$$F(T,P)=\frac{a}{2}(T-T_0)P^2-\frac{b}{4}P^4+\frac{c}{6}P^6-PE$$

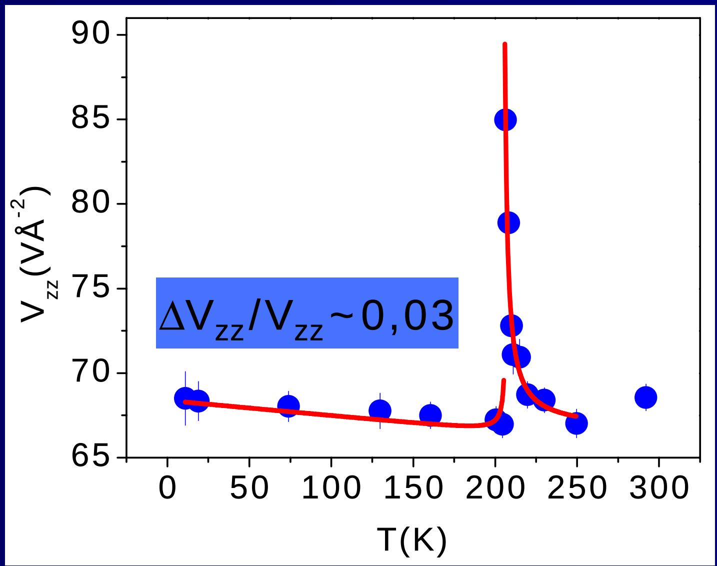
$$\begin{cases}\chi^{-1}(T)=\dfrac{b^2}{4c}\left[\left(\sqrt{1+\dfrac{16ac}{b^2}(T_c-T)}+1\right)^2-1\right]\\ P_S^2=\dfrac{b}{4c}\left[2+\sqrt{1+\dfrac{16ac}{b^2}(T_c-T)}\right]\end{cases}$$

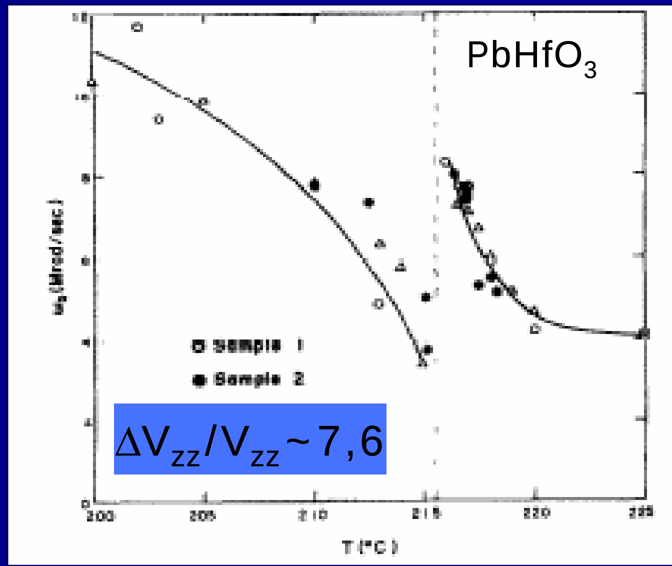


$$\begin{cases}\chi^{-1}(T)=a(T-T_c)+\dfrac{3b^2}{16c}\\ P_S^2=0\end{cases}$$

$$T_c=T_0+\frac{3b^2}{16ac}$$

Spontaneous Polarization





Y. Yeshurun *et al*, J. Phys. & Chem. Solids 40 231 (1979)

P_{Pr}~P_{Hf}/15

P_{Hf}~10mC/m^2

P_{Pr}~0.7mC/m^2

Theoretical prediction

P_{Pr}~1mC/m^2

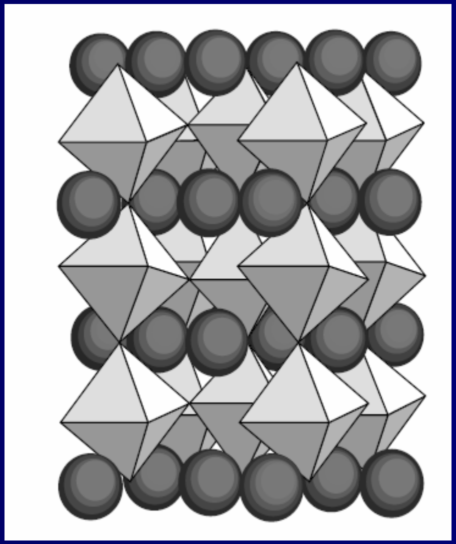
D.Efremov et al, Nature Materials, 3,853 (2004)

Fist observation of polarization in CO Manganites

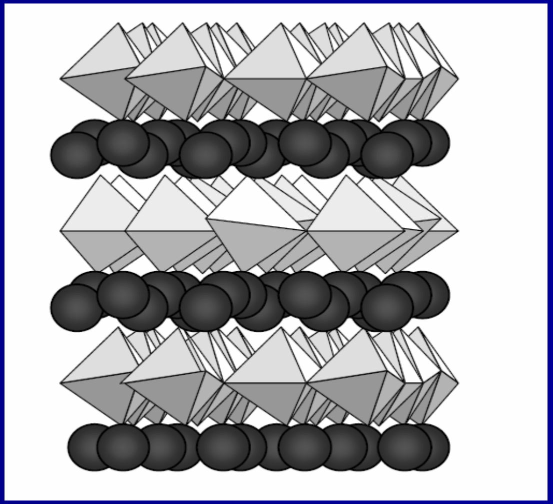
New mechanism for ferroelectricity

MATERIALS WITH SIMULTANEOUS ELECTRIC AND MAGNETIC ORDER

$AMnO_3$ Multiferroic Manganites



Orthorrombic phases
octahedra

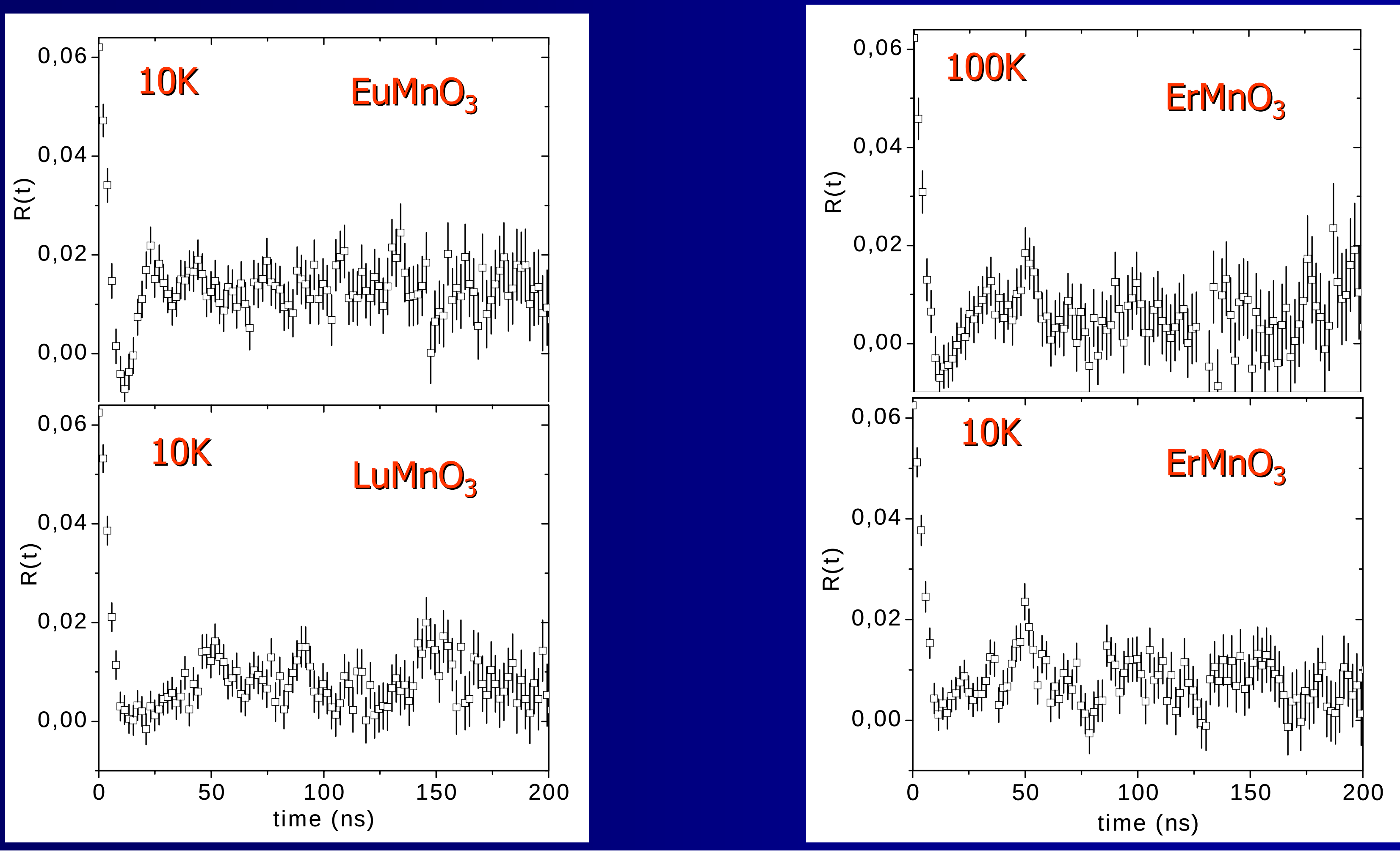


Hexagonal phase
Trigonal bipyramid

Adapted from: Van Aken , thesis univ. Groningen

$AMnO_3$ Multiferroic Manganites

Measurements in $GdMnO_3$, $HoMnO_3$, $YMnO_3$ … at several temperatures



Conclusions

- The charge order transition is driven by the softening of vibration modes
- Experimental evidence for coexistence of electric and magnetic order in charge ordered $Pr_{1-x}Ca_xMnO_3$ system
- The dielectric phase transition is of first-order
- Polar state appears below the charge order temperature
- Promising PAC results in multiferroic $EuMnO_3$, $ErMnO_3$...

Thanks

ISOLDE Collaboration

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