Local Probe Studies on Highly Distorted Rare-Earth Manganites (IS390)

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Outline

→ The Rare Earth's + MnO_3 ($RMnO_3$) family and their questions

Ferroelectricity + Ferromagnetism (and Ferroelasticity)

→ Experimental method

Sample preparation and macroscopic characterization

^{111m}Cd Perturbed Angular Correlation (PAC):

nanoscopic scale information ⇨ probing of local phenomena

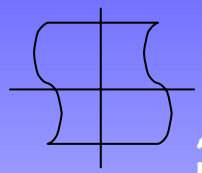
→ PAC preliminary results

→ Summary

Multiferroics: Materials showing Ferroelectricity, Ferromagnetism (and Ferroelasticity)

Ferroelectric Devices

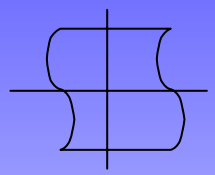
Polarization (P)



Applied Electric field (E)

Ferromagnetic Devices

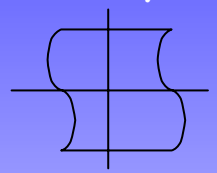
Magnetization (M)



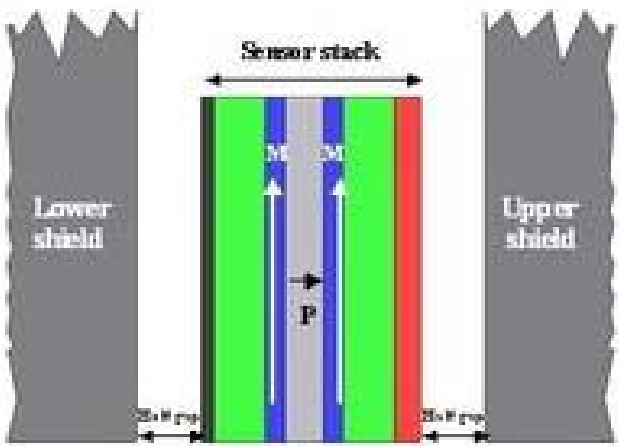
Applied Magnetic Field (H)

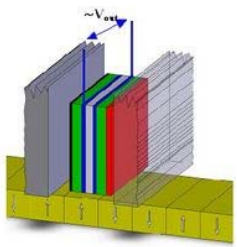
Multiferroic Magnetoelectrics

P, M



E, H



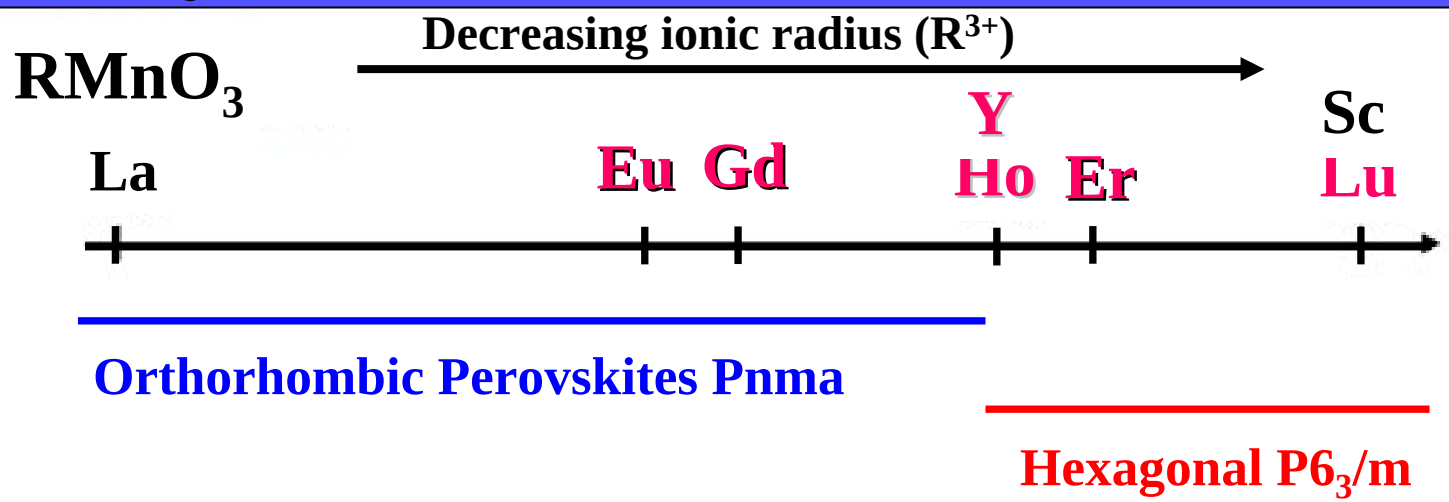


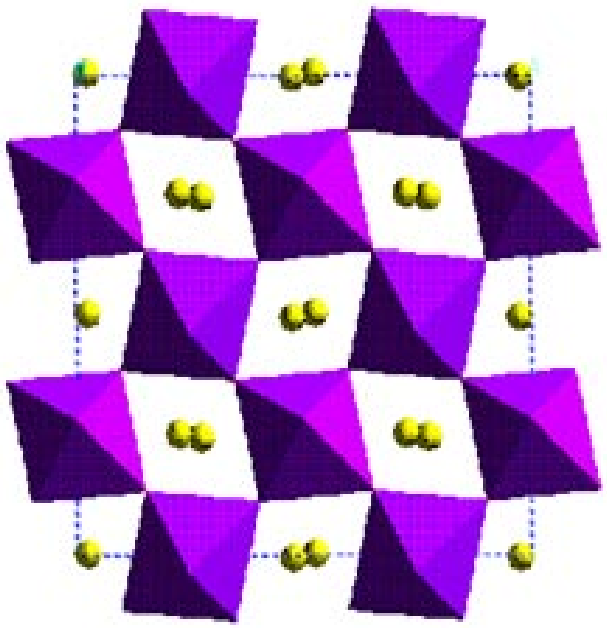
- Shield
- Seed layer
- AntiFerromagnet
- Ferromagnet
- Ferroelectric
- CAO layer

Antiferromagnetic	T_N (K)
Cr_2O_3 (Cr^{3+})	307
$LiMnPO_4$ (Mn^{3+})	35
$LiFePo_4$ (Fe^{2+})	50
$LiCoPO_4$ (Co^{2+})	23
$EuTiO_3$ (Ti^{3+})	5.5
$RTiO_3$ (Rare Earth^{3+})	?
$YMnO_3$ (Mn^{3+})	71
$Lu(Sc)MnO_3$ (Mn^{3+})	90 (130)
Weak Ferromagnetic	**T_C (K)**
$TbFeO_3$ (Tb^{3+})	3
$Ni_3B_7O_{11}$ (Ni^{2+})	64
Ferrimagnetic	**T_C (K)**
$Y_3Fe_5O_{12}$ (Fe^{3+})	~463
$Gd_3Fe_5O_{12}$ (Gd^{3+}, Fe^{3+})	~463
Ferromagnetic multiferroic	**T_C (K)**
$BiMnO_3$ (Mn^{3+})	48

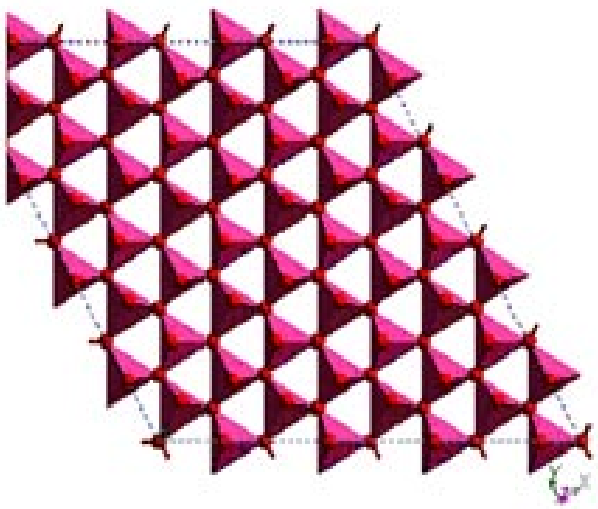
M. Vopsaroiu et al., Journ. Phys. D: Appl. Phys. 40 (2007) 5027
N. Hill et al., Phys. Rev. B 59 (1998), 8759

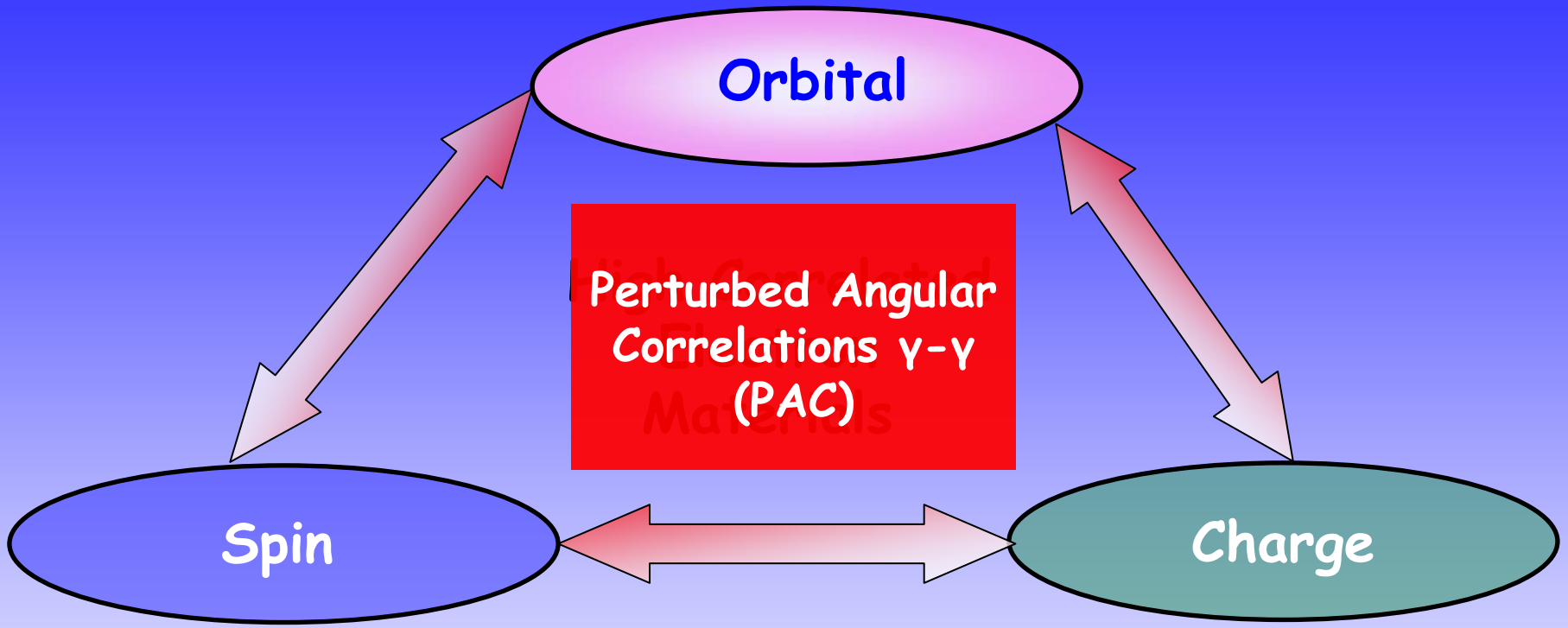
Rare Earth Manganites family
$RMnO_3$ (R= Lu, Er, Y, Ho, Gd, Eu)





Hexagonal $RMnO_3$ can be stabilized as orthorhombic, with synthesis under pressure



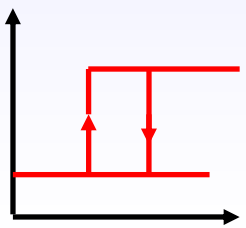


Structural Studies

- X-ray Diffraction (XRD)
- Neutron Diffraction (NPD)
- Scanning Electron Microscopy (SEM/EDX)
- Raman Spectroscopy

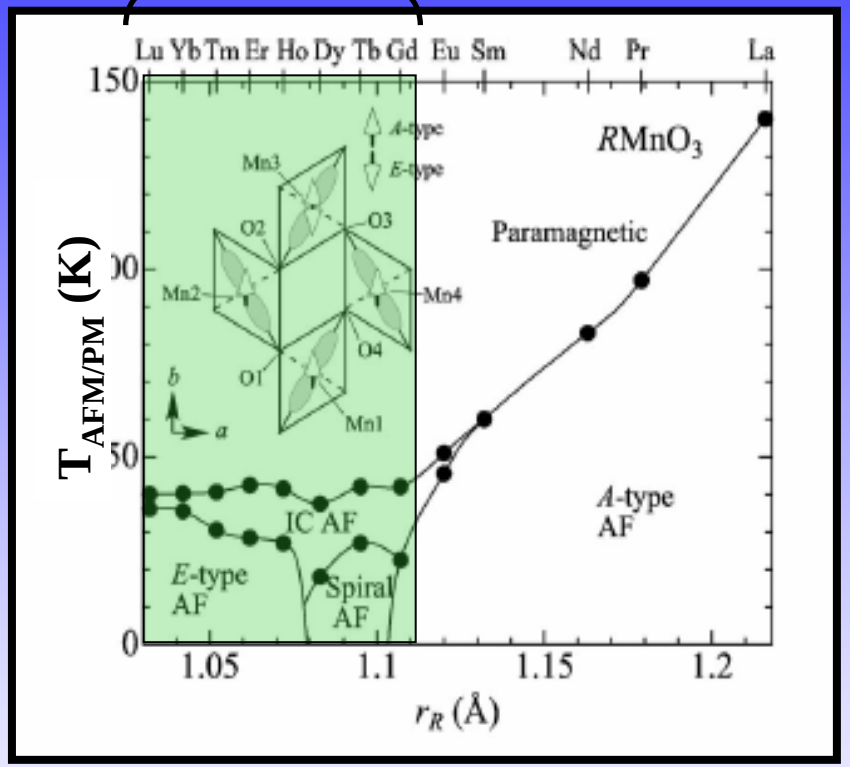
Magnetic / Electric Studies

- Magnetic Measurements (SQUID)
- Electric Measurements (Resistivity, Dielectric Response,..)



$RMnO_3$ versus ionic radius

FE compounds



Magnetic Phase Diagram for $RMnO_3$ for Orthorhombic structures

M. Tachibana et a.,Phys. Rev. B 75 (2007) 144425

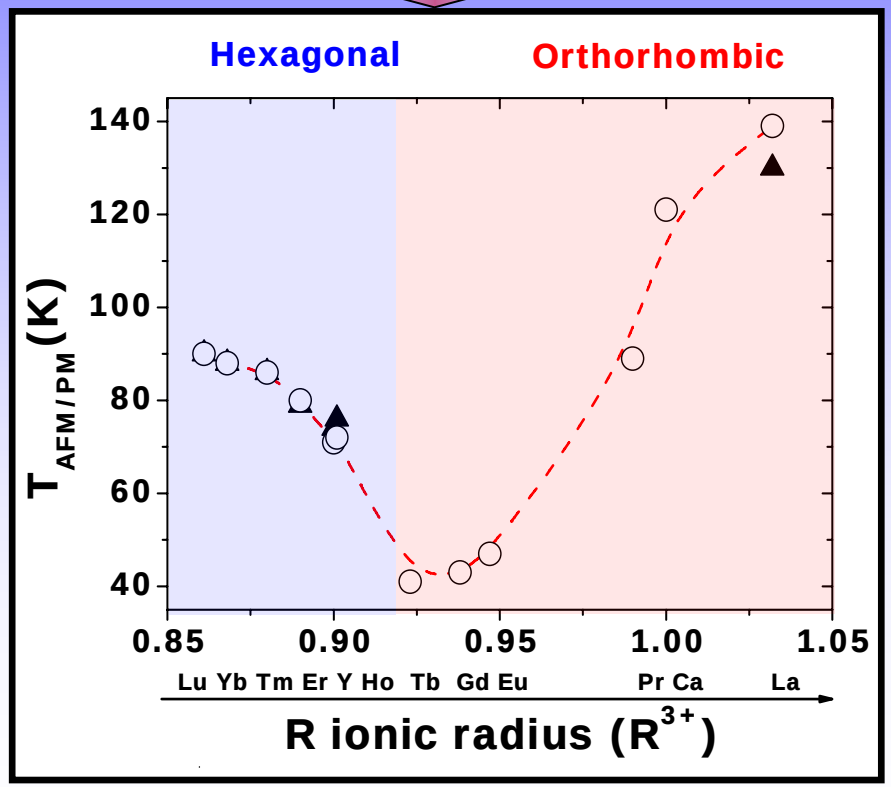
Influence of ionic radius on macroscopic properties

What happens at atomic scale?

Simple dependence on T_N

Orthorhombic: increase with R_i

Hexagonal: decrease with R_i



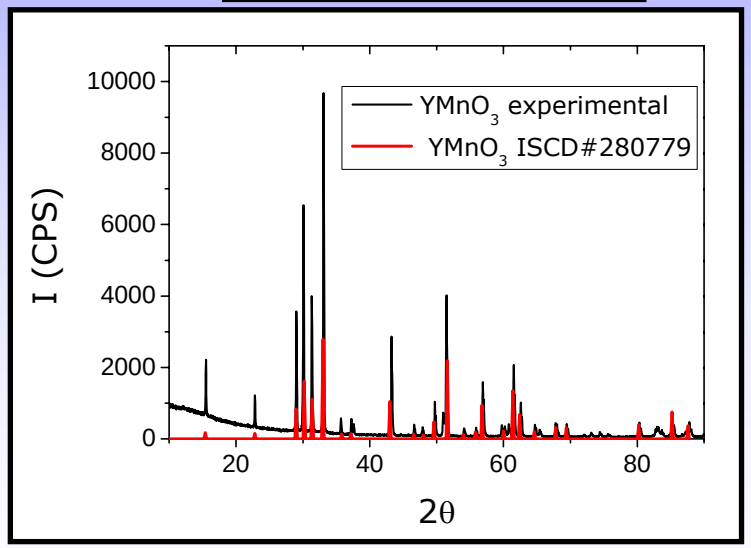
Studied Compounds

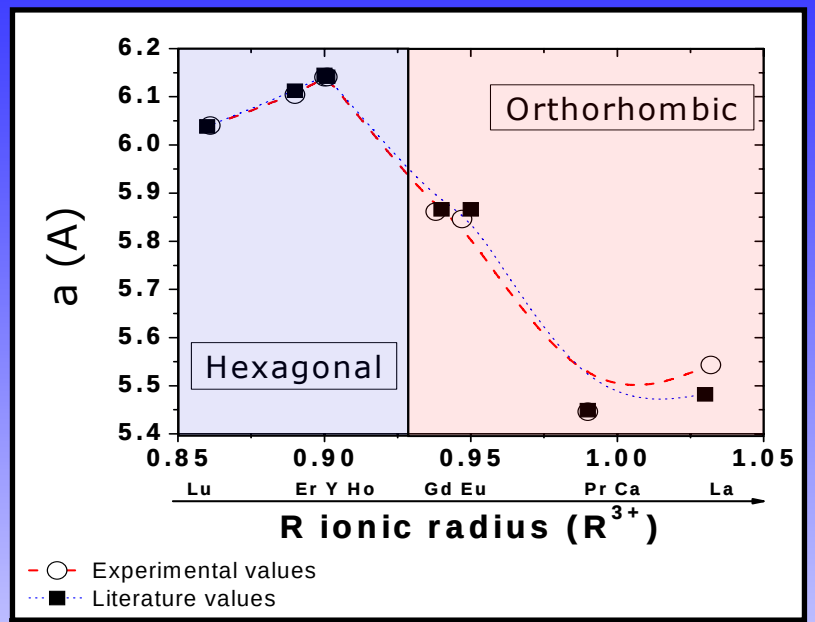
Compound	Structure	$T_{AFM/PM}$ (K)	T_{FE} (K)	$Z_{Relement}$	Ionic radius $R_{element}$ (R^{3+}) (nm)
$LuMnO_3$	Hexagonal (S.G. $P6_3cm$)	90	>750	71	0.860
$ErMnO_3$	Hexagonal (S.G.: $P6_3cm$)	80	833	68	0.890
$YMnO_3$	Hexagonal (S.G.: $P6_3cm$)	71	920	39	0.900
$HoMnO_3$	Hexagonal (S.G.: $P6_3cm$)	76	873	67	0.901
$GdMnO_3$	Orthorhombic (S.G.: *Pnma*)	42	<13	64	0.940
$EuMnO_3$	Orthorhombic (S.G.: *Pnma*)	47	-	63	0.960

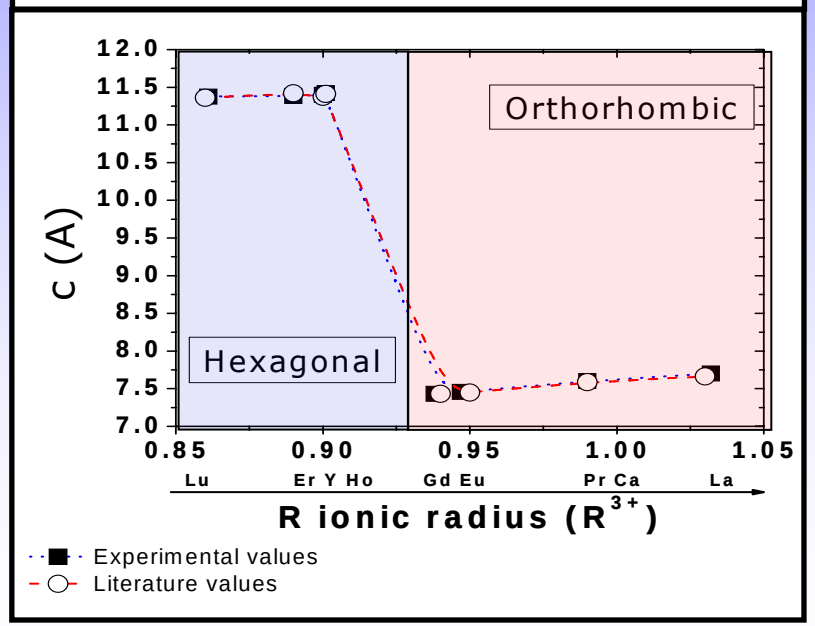
Th. Lonkai et al., Phys. Rev. B 69 (2004), 134108

Sample preparation and structural characterization

Sol-Gel: Urea combustion Method







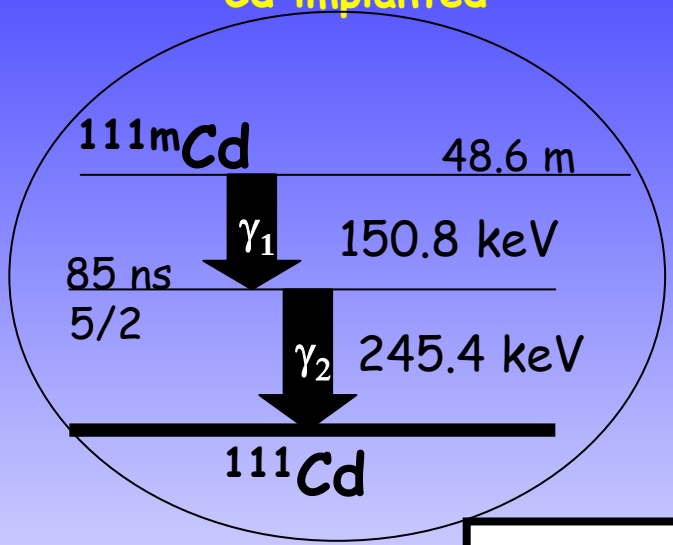
High quality bulk samples

J.-S. Zhou et al., Phys. Rev. B 74 (2006), 014422
T. Mori et al., Materials Lett. 54 (2002), 238

Perturbed Angular Correlations PAC

Probe doping at ISOLDE/CERN

^{111m}Cd implanted

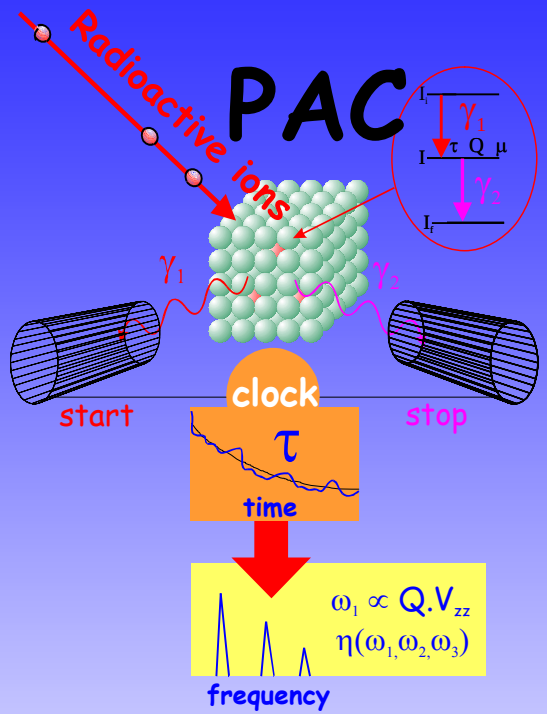


Electric Field Gradient (EFG)

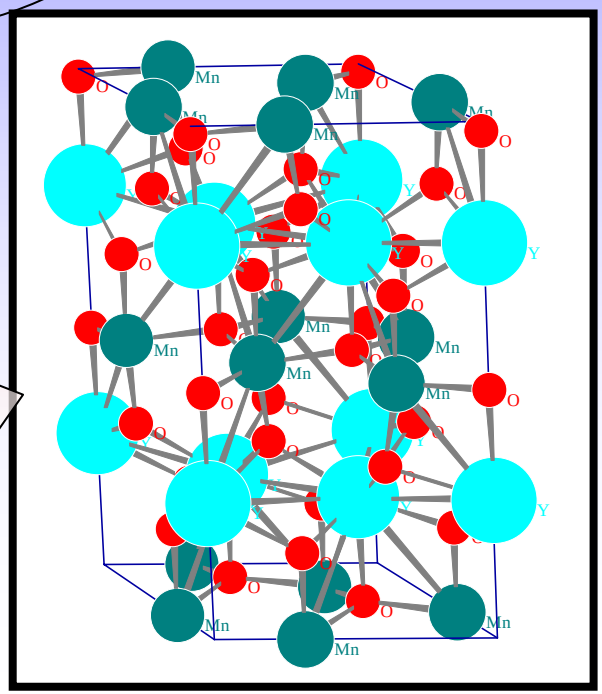
V_{zz},

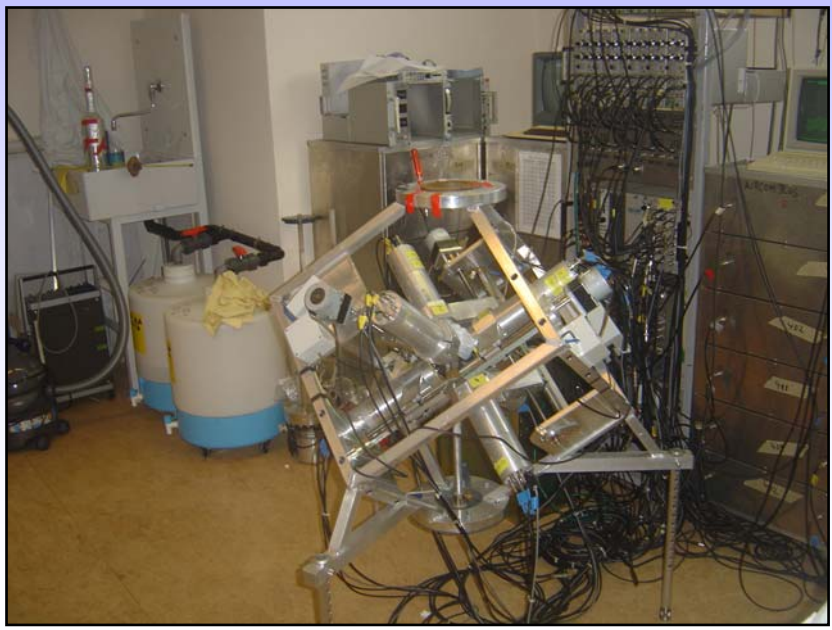
$\eta=(V_{xx}-V_{yy})/V_{zz}$

Magnetic Hyperfine Field (MHF)

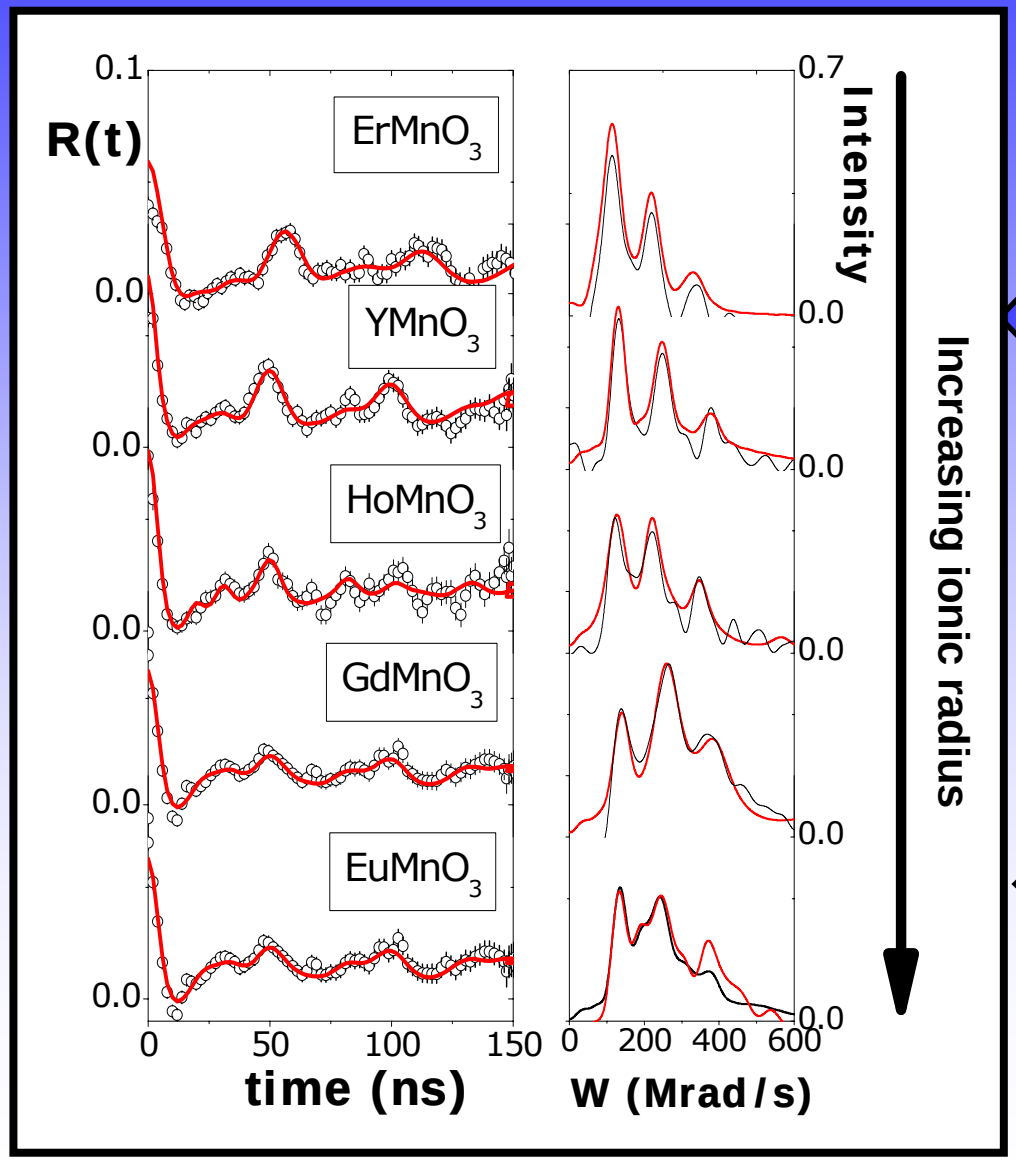


- No changes in element during measurement
- Cd occupies RE position





Room Temperature Results



Hexagonal $RMnO_3$

EFG_1~70%

W_1~130 Mrad/s

η_1~0.19

EFG_2~30%

W_2~200 Mrad/s

η_2~0.4

Orthorhombic $RMnO_3$

EFG_1~70%

W_1~125 Mrad/s

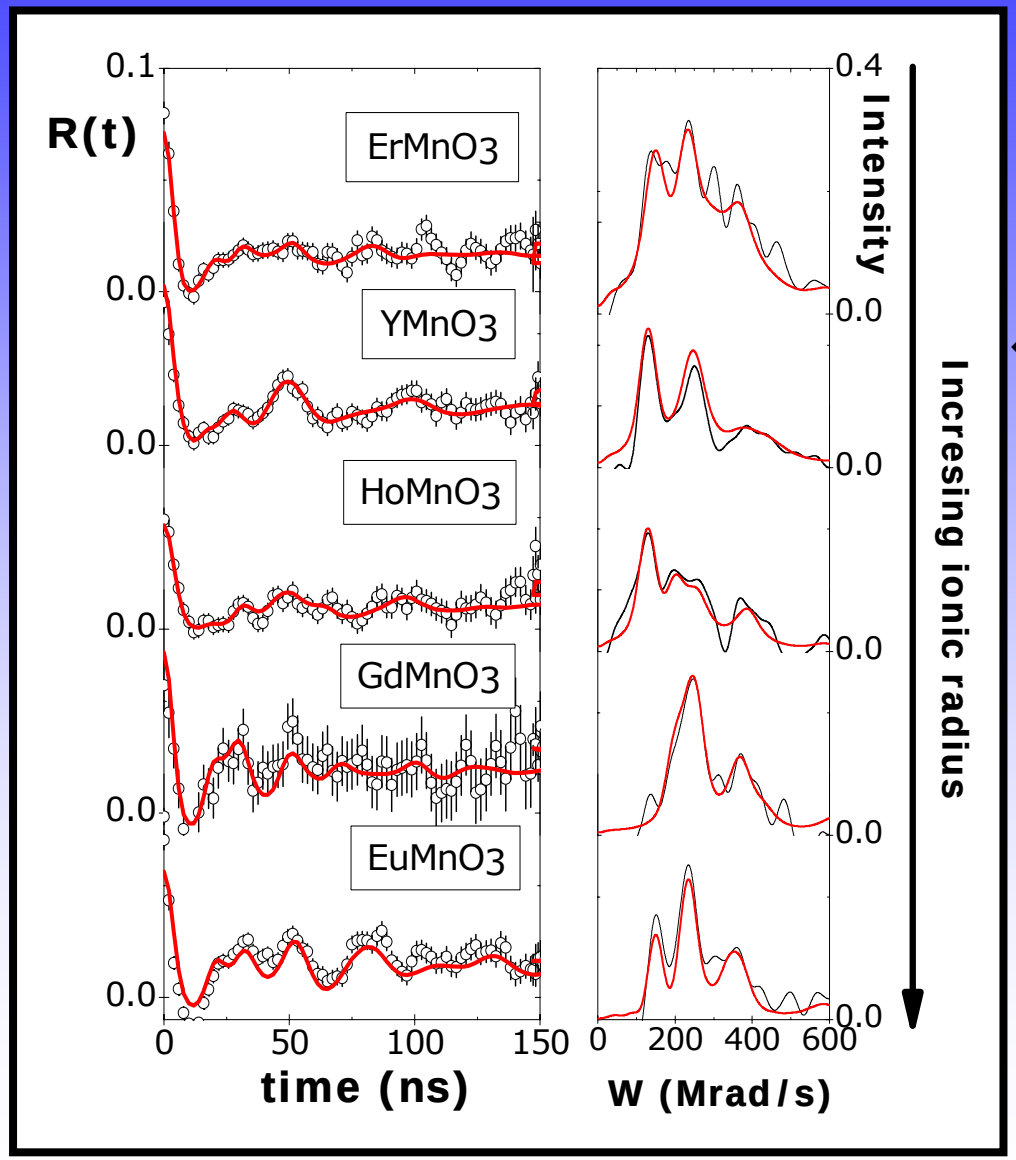
η_1~0.45

EFG_2~30%

W_2~180 Mrad/s

η_2~0.5

573 K Preliminary Results



Hexagonal $RMnO_3$

EFG_1~70%

W_1~135 Mrad/s

η_1~0.2

EFG_2~30%

W_2~200 Mrad/s

η_2~0.3

Orthorhombic $RMnO_3$

EFG_1~60%

W_1~120 Mrad/s

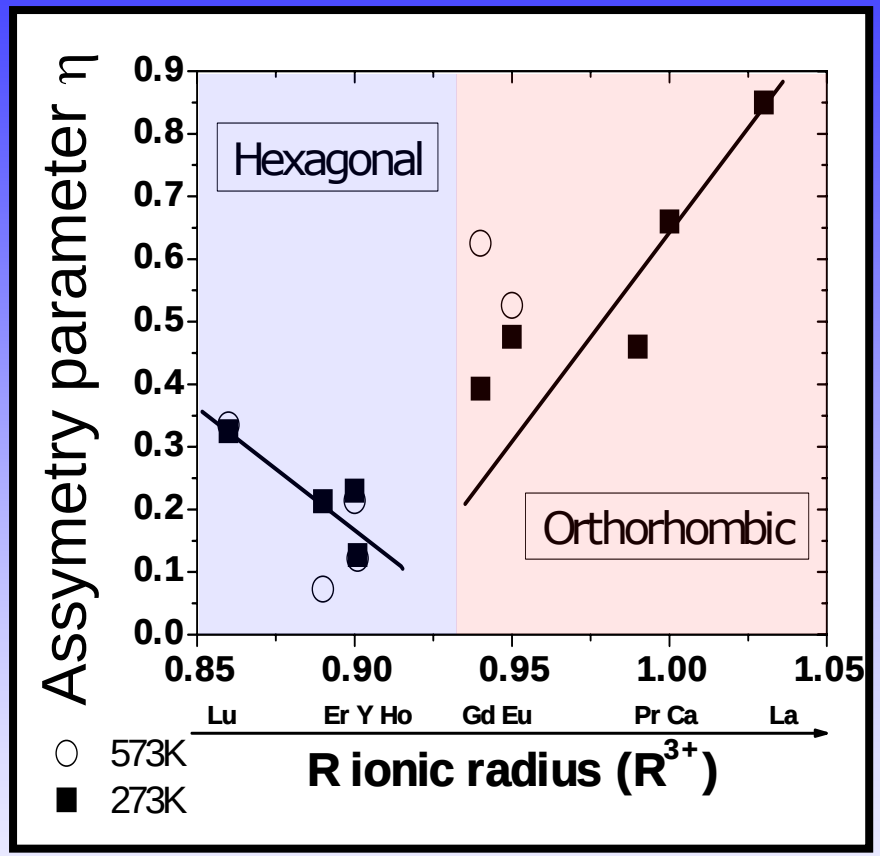
η_1~0.5

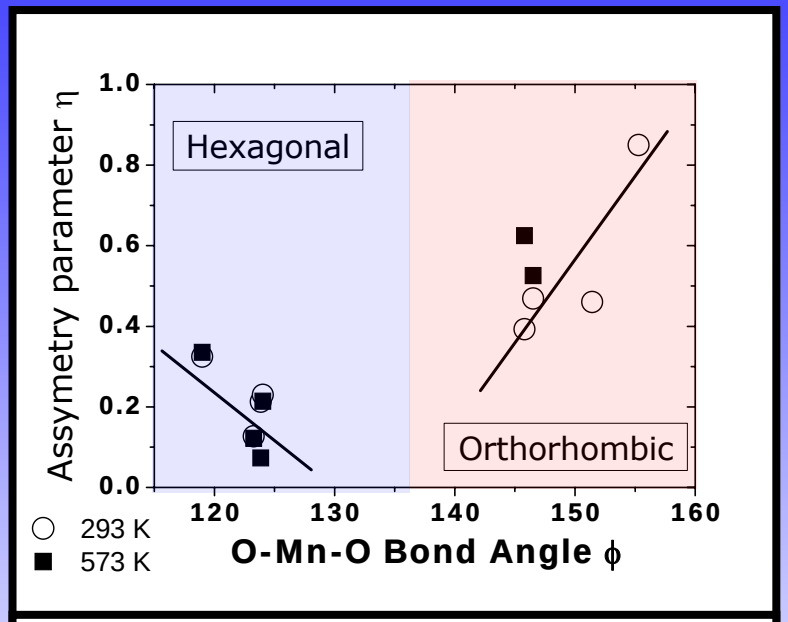
EFG_2~40%

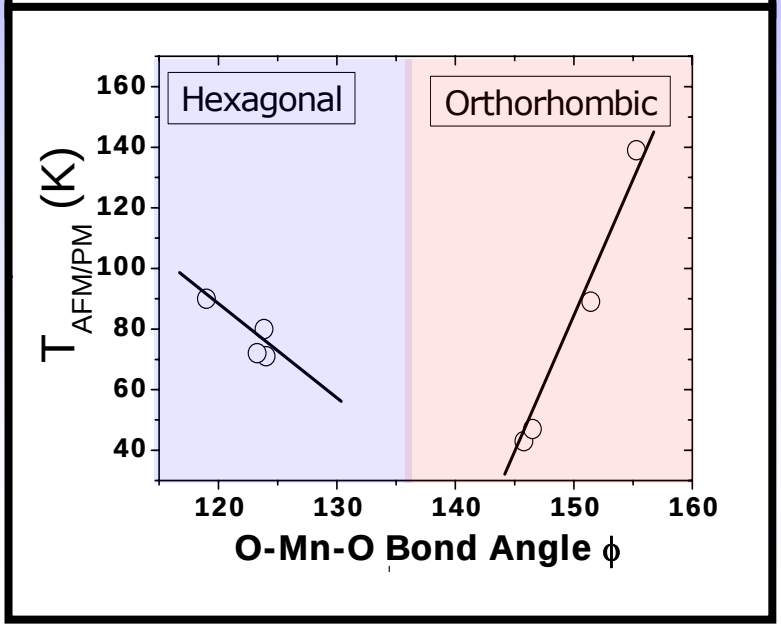
W_2~180 Mrad/s

η_2~0.6

Assymetry parameter vs temperature: EFG_1





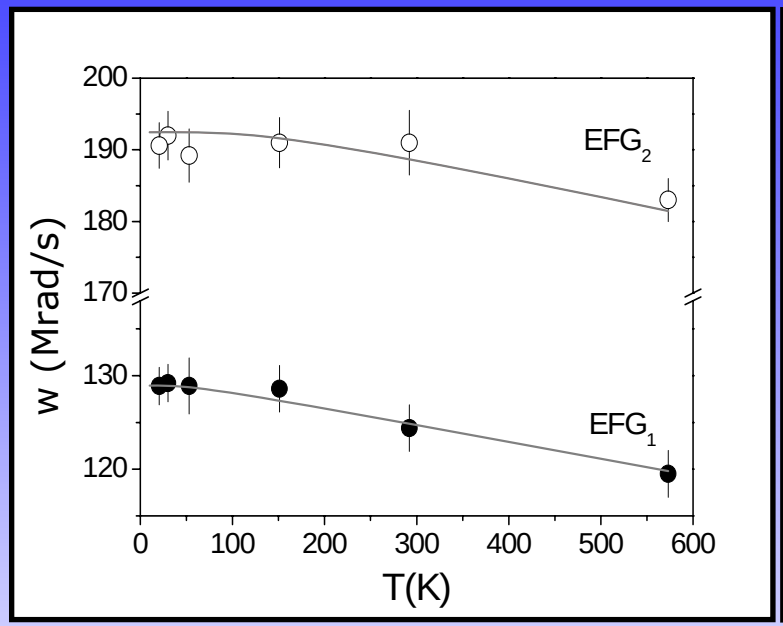


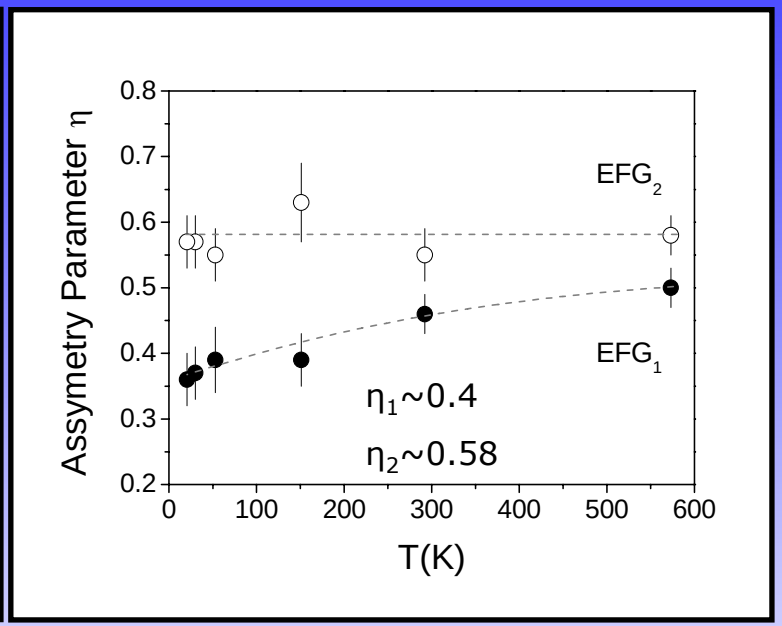
For the main EFG component (EFG_1):

Hexagonal $RMnO_3$ – η decreases with R ionic size

Orthorhombic $RMnO_3$ – η increases with R ionic radius

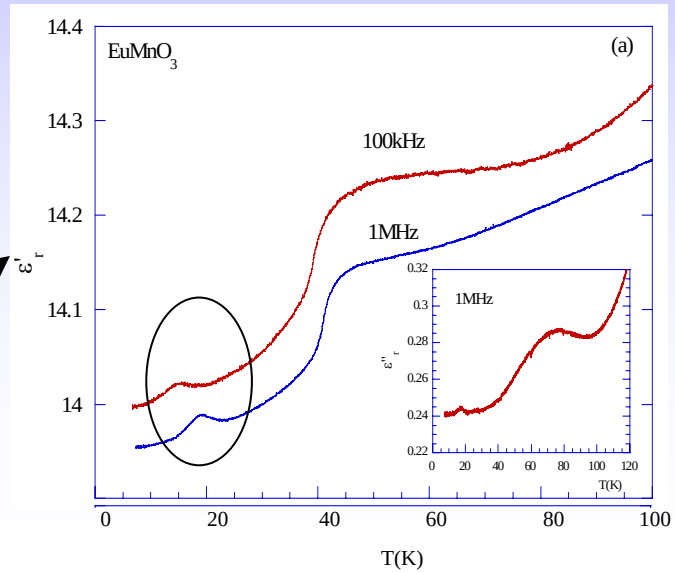
$EuMnO_3$: behavior as function of temperature





Decrease of W with temperature due to an increase of atomic vibrations (typical in other Perovskites)

Measurement@10K: R(t) spectrum different from other temperatures. Hints changes between 10k and 20K. Dielectric constant measurements show a peak below 20K.



Summary

Hexagonal Manganites (R= Lu, Er, Y, Ho)

Main EFG (EFG_1) with assymetry parameter decreasing with bigger R ionic radius which seems independent from temperature.

Orthorhombic Manganites (R= Gd and Eu)

Two EFG's: main EFG (EFG_1) with assymetry parameter increasing with R ionic radius.

The assymetry parameter evolution as function of the bond angle present the same behavior as $T_{AFM/PM}$: correlation between macroscopic and microscopic properties.

$EuMnO_3$: Behavior as function of temperature

Highly distorted environments (η~0.5) for all range of temperatures. Frequency evolution following the trend found in other perovskites. Below 20K, changes in R(t) spectra hints an unknown transition (observed as a peak in dielectric measurements). Measurements on temperature in this range are needed.

Thanks for your attention!

Future Perspectives

Measurements on temperature for all compounds of this series.

Use of 3+ isotopes (e.g. $^{117}Ag/^{117}In/^{117}Cd$) allowing the measurement of the same sample at different temperatures.

Synthesis of new multiferroic/magnetoelectric systems ($BiMnO_3$, $InMnO_3$, $PrCdMnO_3$)