New **magnetic structures** in **novel** and **conventional Manganites**

Aziz Daoud-Aladine

ISIS facility, STFC Rutheford Appleton Laboratories, Didcot, UK

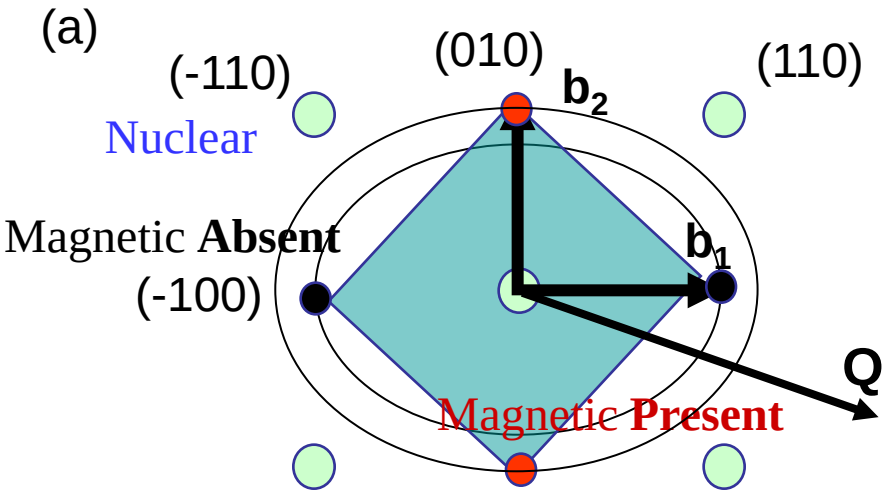
Science & Technology Facilities Council
ISIS

Problematic

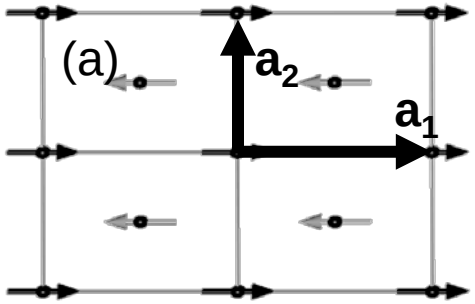
Magnetic structure determination from Powder diffraction:

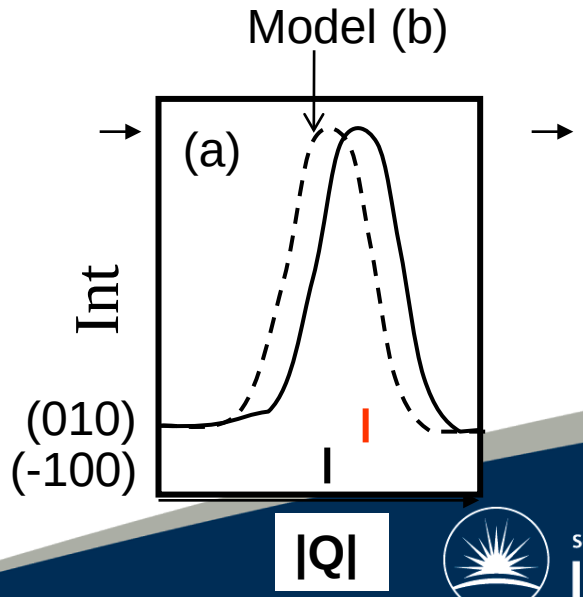
Low symmetry lattices generally OK

Reciprocal space



AF order on a **ortho-lattice**





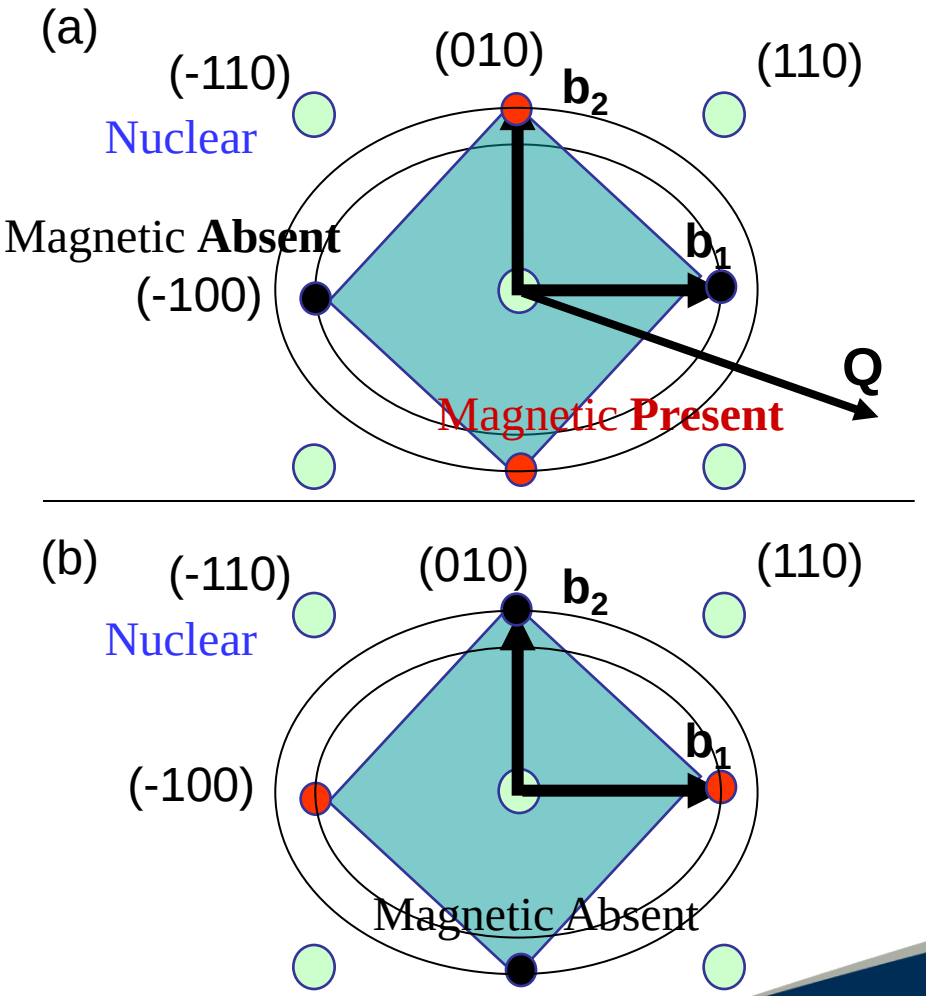
Science & Technology Facilities Council
ISIS

Problematic

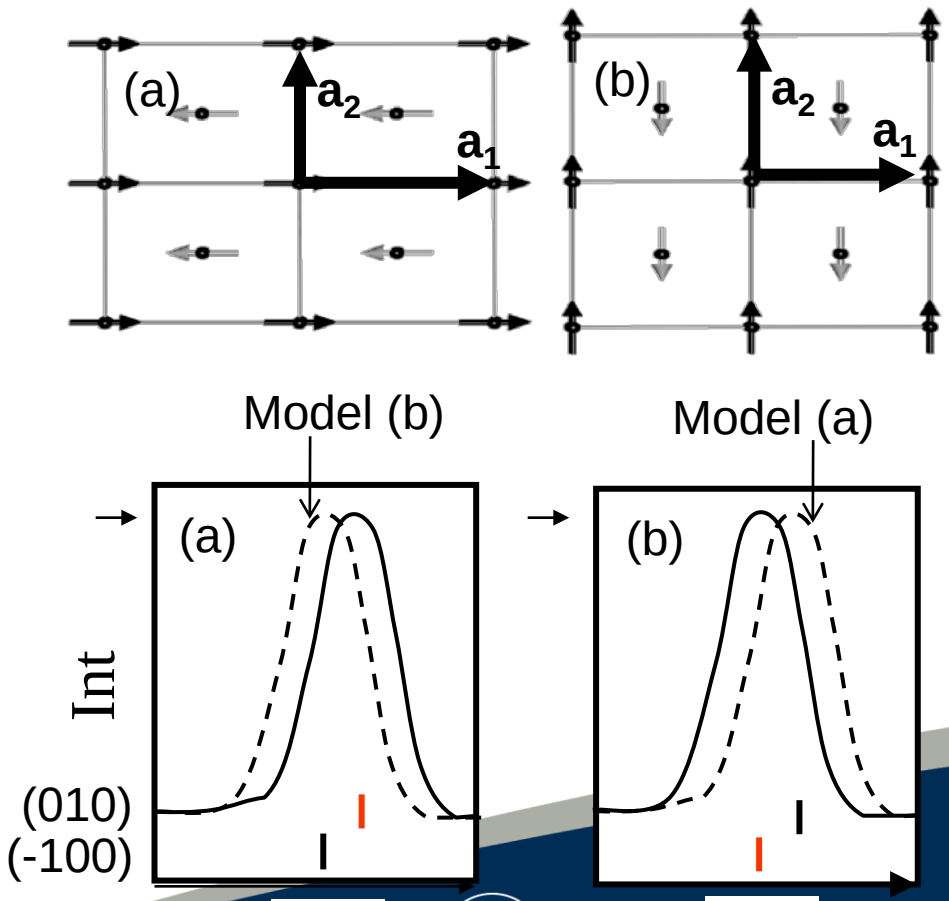
Magnetic structure determination form Powder diffraction:

Low symmetry lattices generally OK

Reciprocal space



AF order on a **ortho-lattice**

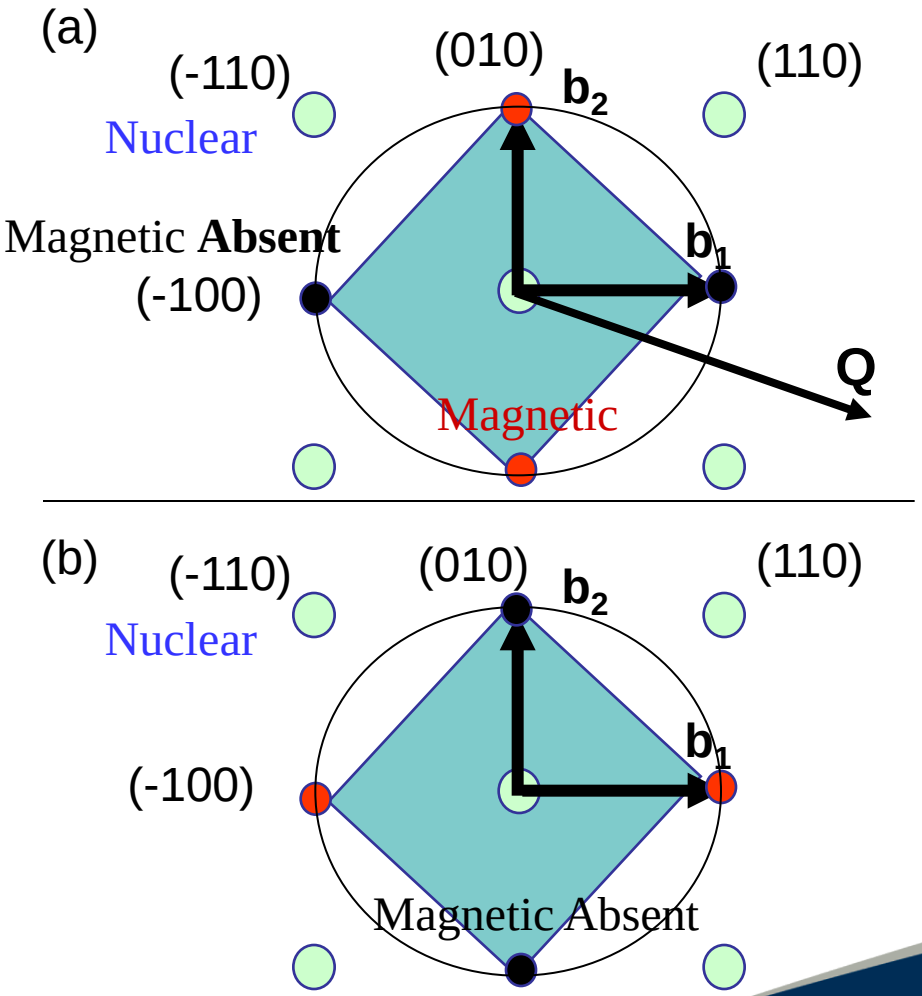


Problematic

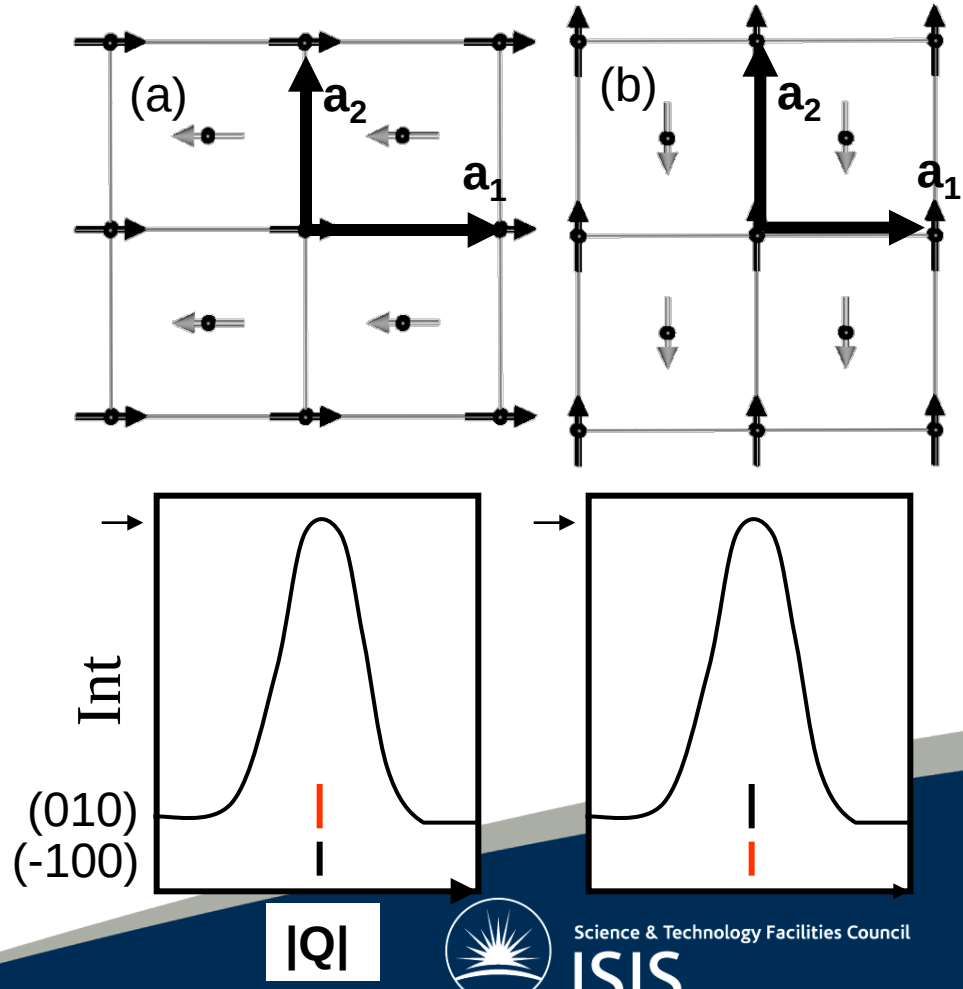
Magnetic structure determination form Powder diffraction:

High symmetry lattices => accidental Peak overlap **=> MODEL DEGENERACY**

Reciprocal space

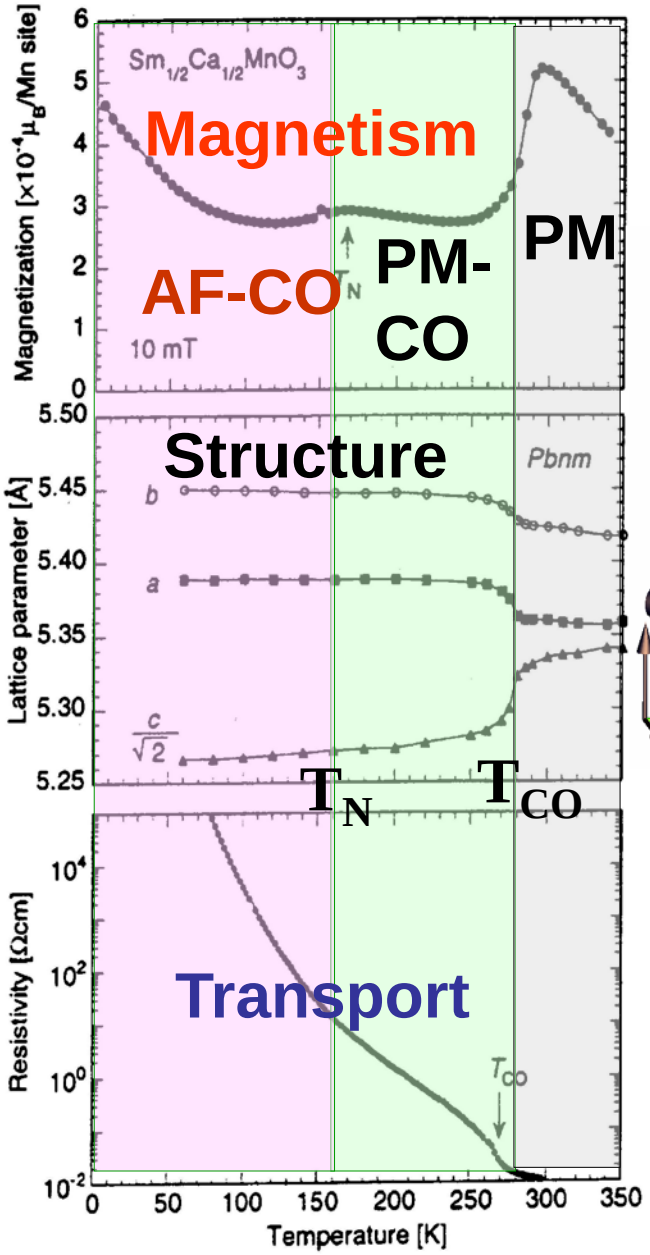


AF order on a **CUBIC lattice**

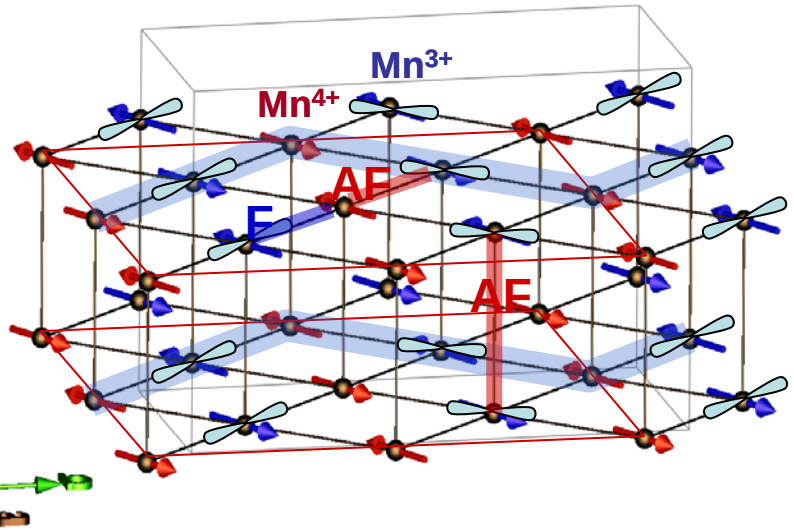


Science & Technology Facilities Council
ISIS

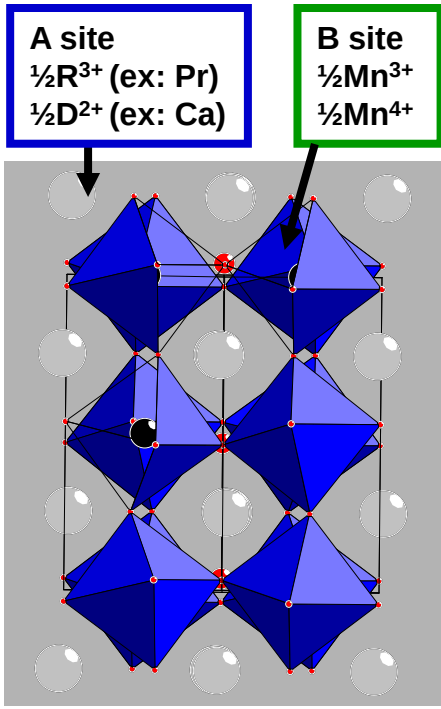
Problematic



Pseudo-cubic manganites:
The MODEL DEGENERACY
Can be pathological!…..



$R_{1/2}D_{1/2}MnO_3$



X=1/2 : the CE-type magnetic structure

Pbnm

T_{CO} =240K

T_N=170K

SX- Powder Neutron diffraction studies questioning…

Study of alternative charge ordered materials : $YBaMn_2O_6$
(with L. Pinsard-Gaudart (LPCES, Orsay University, Paris) and J. Rodriguez Carvajal (ILL, Grenoble France)):

- Instrument : ***Medium resolution*** **Constant Wavelength Neutron Powder Diffraction (NPD)**
- Sample : ~5g of **$YBaMn_2O_6$ POWDER**

Validity of the CE- type structure*?*
(Toby PERRING, at the ISIS facility)

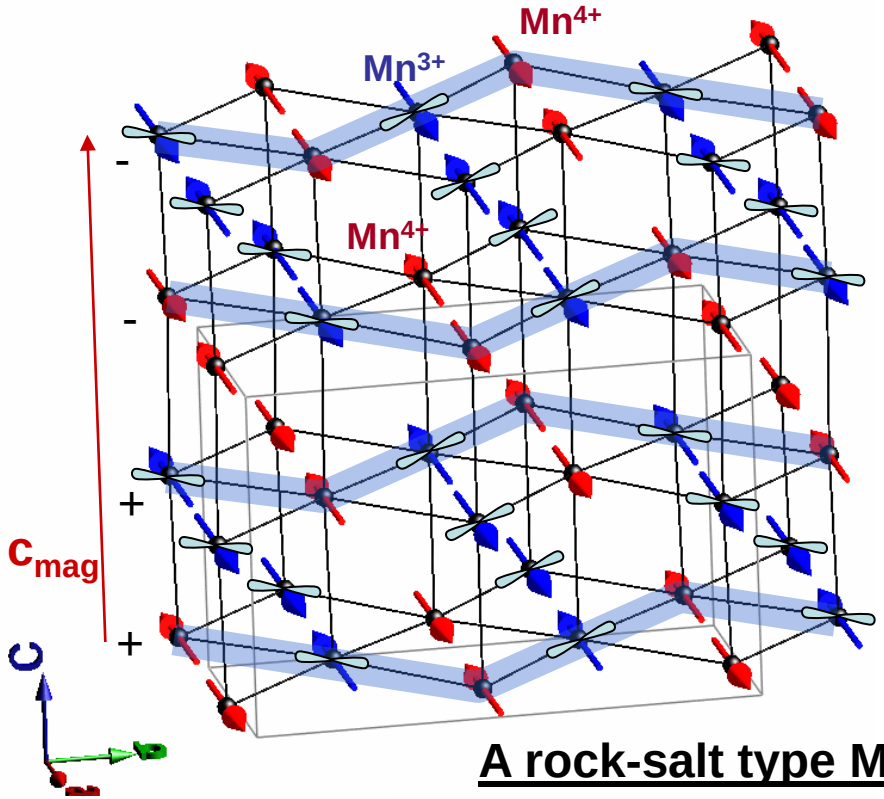
- Instrument**: 4-circle Diffractometer (**D10 4-circle at ILL, Grenoble, France)
- Sample**: ~60mm³ SINGLE-CRYSTAL**, of the **conventional $Pr_{1/2}Ca_{1/2}MnO_3$**

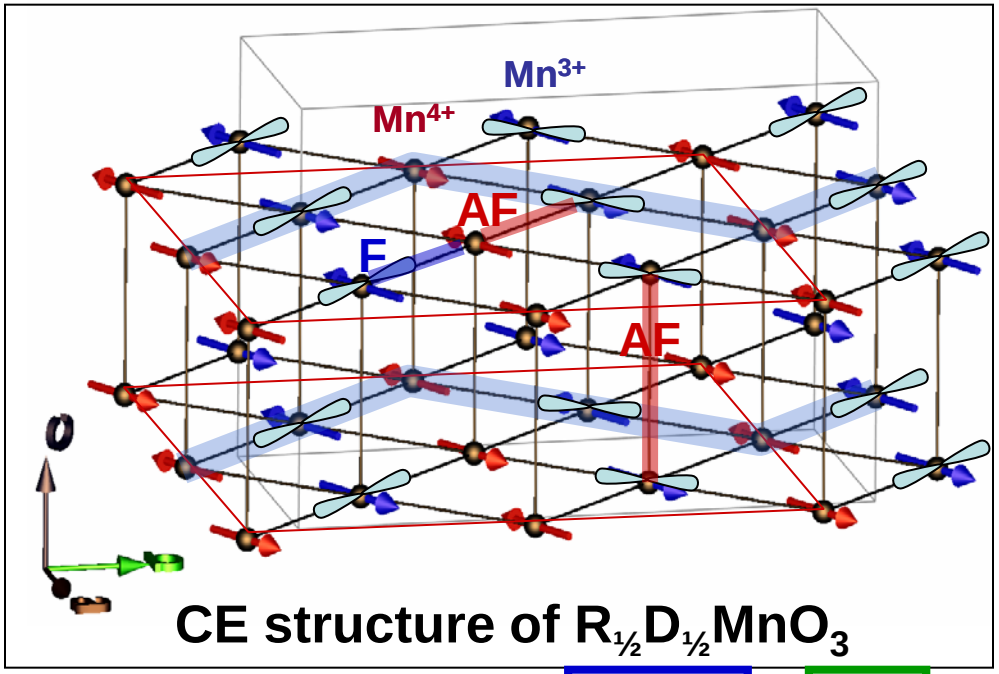
What happens off half- doping:

- Instrument: ***High resolution*** **TOF- NPD (**HRPD, at ISIS, UK)
- Sample : ~3g of **POWDER** of the **conventional $Pr_{0.625}Ca_{0.375}MnO_3$**

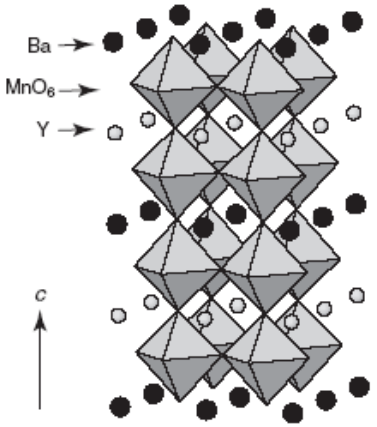
Science & Technology Facilities Council
ISIS

$YBaMn_2O_6$





CE structure of $R_{½}D_{½}MnO_3$



A rock-salt type Mn^{3+}/Mn^{4+} charge order "polymorph" (structure from NPD):

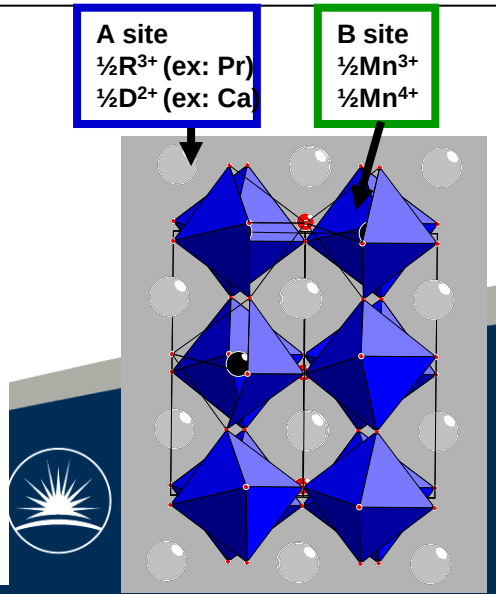
A. J. Williams and J. P. Attfield,

Phys. Rev. B **66**, 220405 (2002)

A variant of the CE-type structure (Magnetic structure from NPD) :

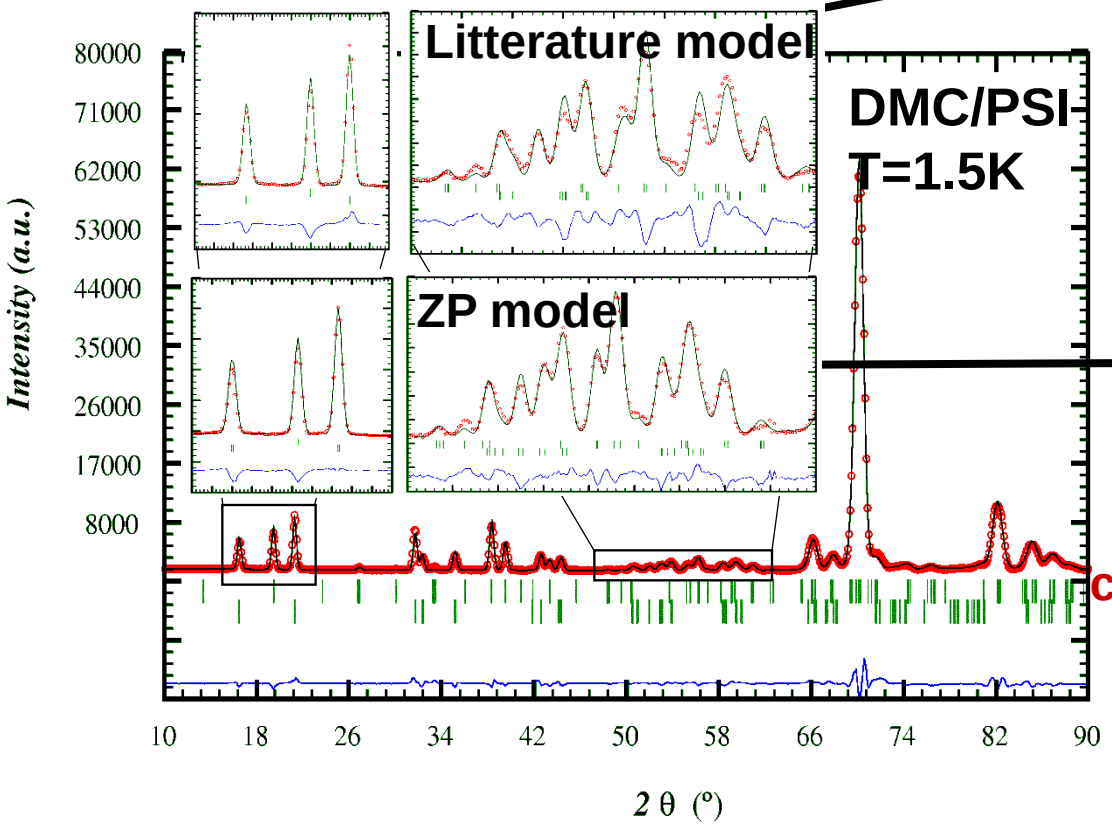
T. Arima, et al.

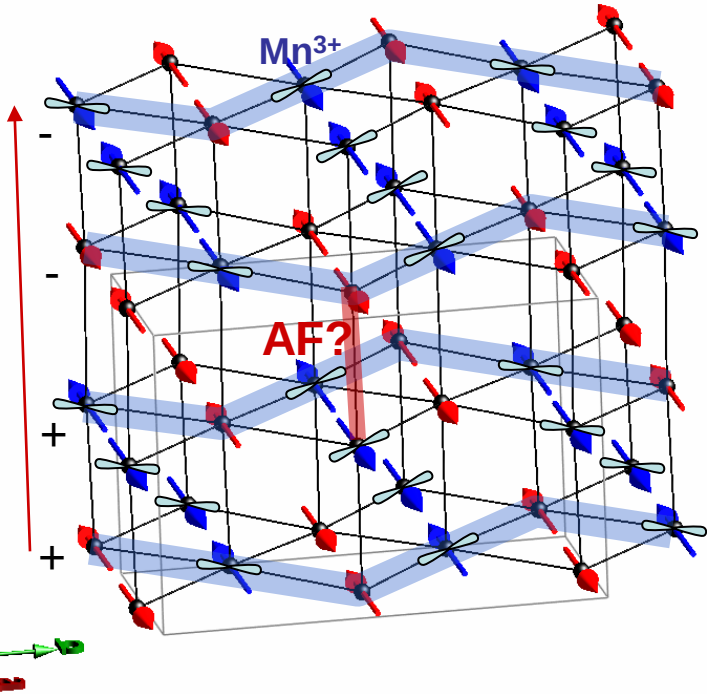
Phys. Rev. B **66**, 140408 (2002)

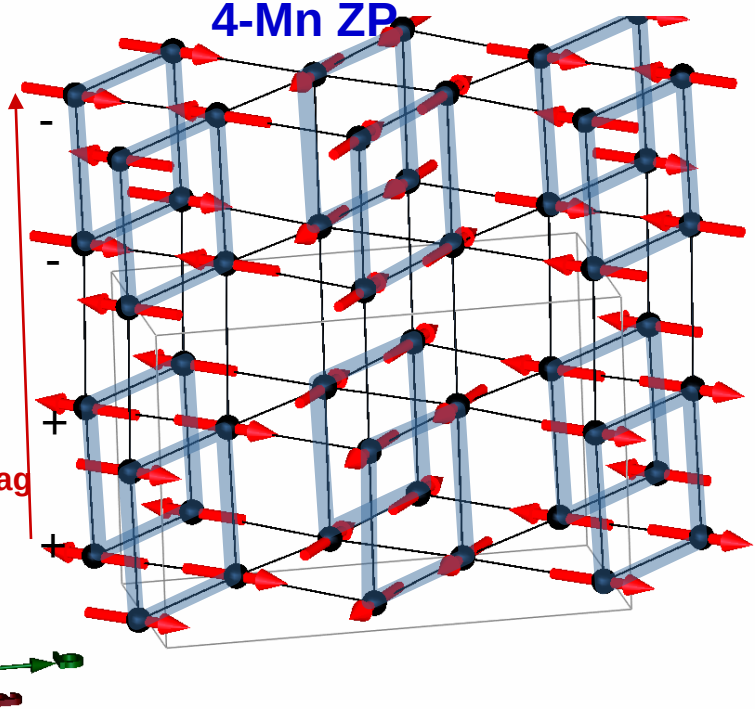


$YBaMn_2O_6$

- Resolution limited magnetic Bragg peaks
- This time, a **better solution can be obtained using structure solution methods** (simulated annealing)
- Evidences **"Zener Polarons"** of 4-Mn atoms



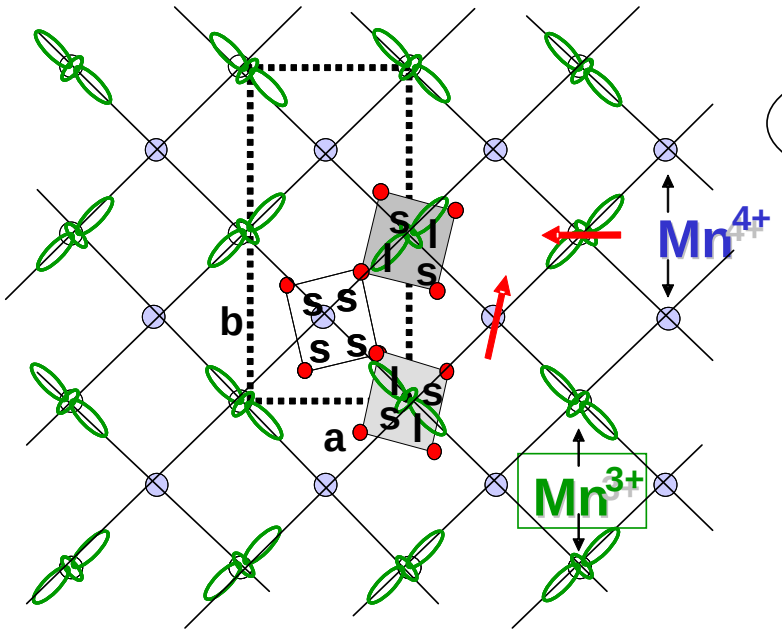




$YBaMn_2O_6$

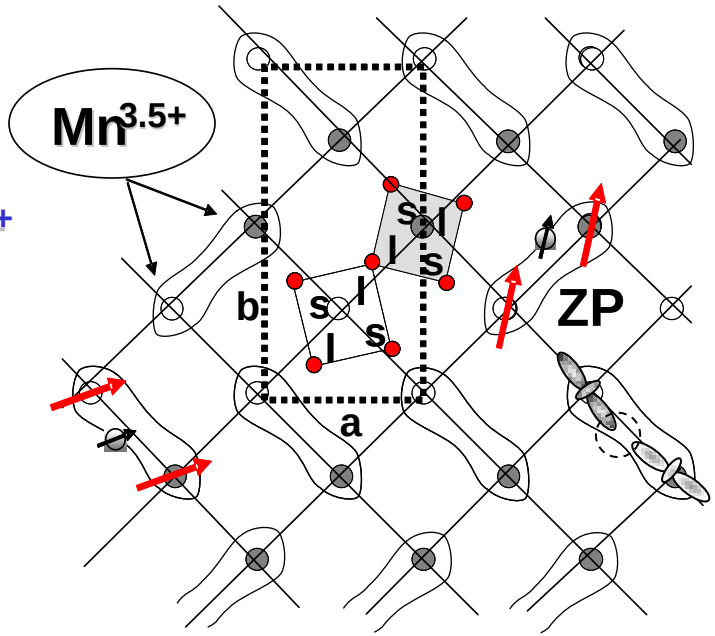
Neutron Diffraction study of the $Pr_{0.60}Ca_{0.40}MnO_3$ charge ordered superstructure from twinned *single crystal* :

A. Daoud-Aladine, et al. ***Phys. Rev. Lett.,*** vol. **89** pp. 097205 (2002)



Ionic ordering

site centered CO



Zener polaron ordering

bond centered CO

oxygen hole ordering

- **Van der Brink, Nature Mat 2004 (doubly degenerate DE model)**
- **Zheng, PRB 2003 (Hartree Fock)**
  de Graaf, PRB 2004 (Large cluster Quantum chemical calculations)

SX- Powder Neutron diffraction studies questioning…

Study of alternative charge ordered materials
(with L. Pinsard-Gaudart (LPCES, Orsay University, Paris) and J. Rodriguez Carvajal (ILL, Grenoble France)):

- Essentially Discards the **original** "CE-type variants" & **corroborates** "Zener Polarons ordering"-
- *Result published in A. Daoud-aladine et. al Phys. Rev. Lett. 101, 166404 (2008)*

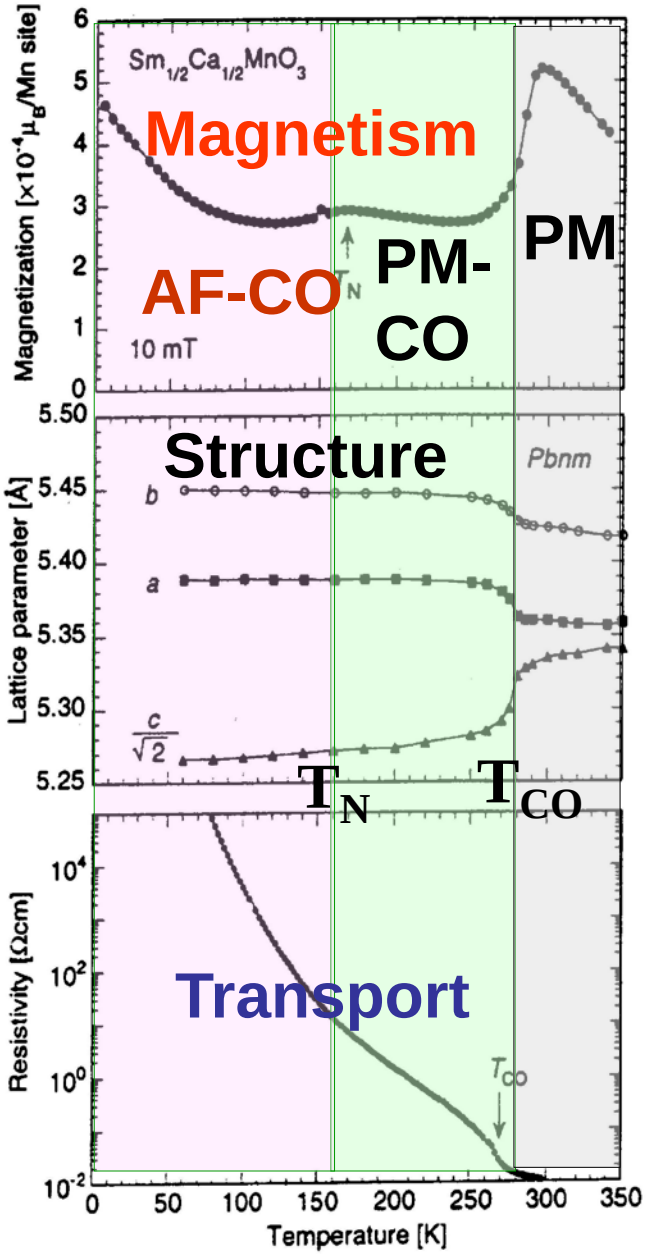
Validity of the CE- type structure*?*
(With Toby PERRING, ISIS facility)

- Instrument**:** the D10 4-circle **SINGLE-CRYSTAL machine** at ILL, France
- Sample**: ~60mm³ SINGLE-CRYSTAL**, of the **conventional $Pr_{1/2}Ca_{1/2}MnO_3$**

What happens off half- doping:
- Instrument: **High resolution TOF- NPD (**instrument HRPD, at ISIS, UK)
- Sample : ~3g of **POWDER** of the **conventional *$Pr_{0.625}Ca_{0.375}MnO_3$***

Science & Technology Facilities Council
ISIS

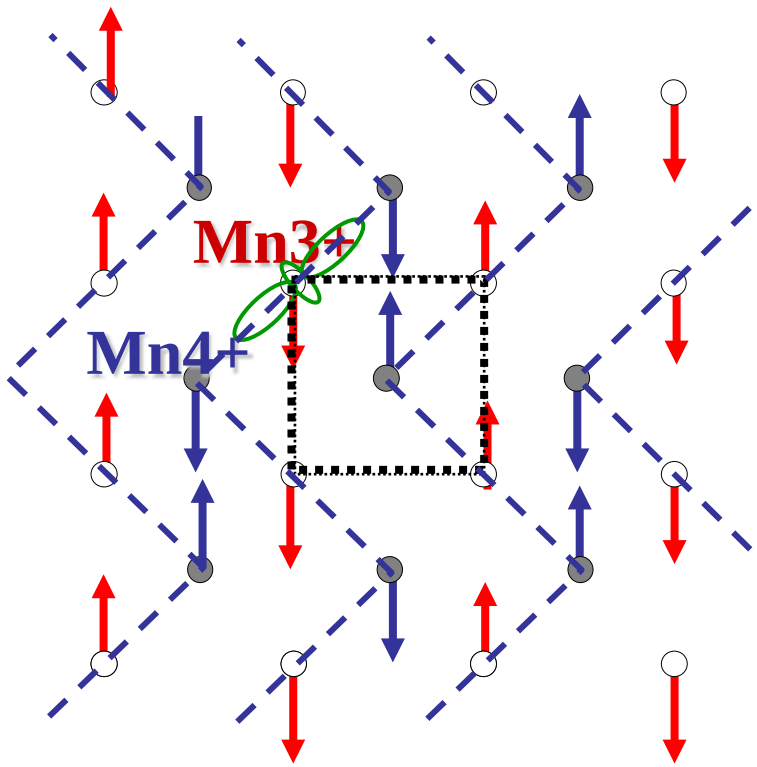
$Pr_{1/2}Ca_{1/2}MnO_3$



$H_{mag}=H+k$

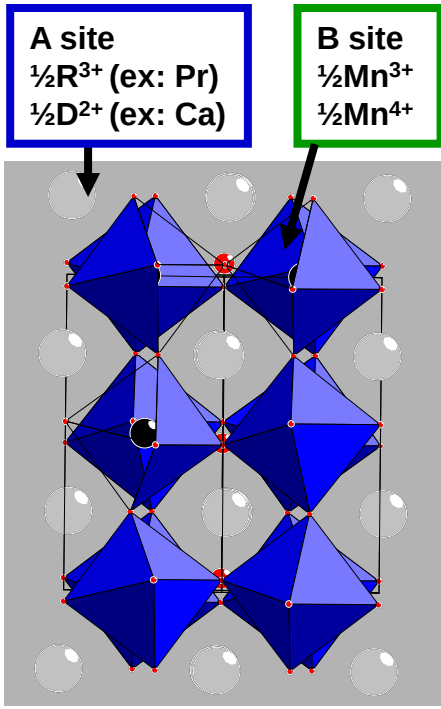
$k_1=(1/2\ 0\ 0)$

$k_2=(1/2\ 1/2\ 0)$



X=1/2 : the CE-type magnetic structure

$R_{1/2}D_{1/2}MnO_3$



Pbnm

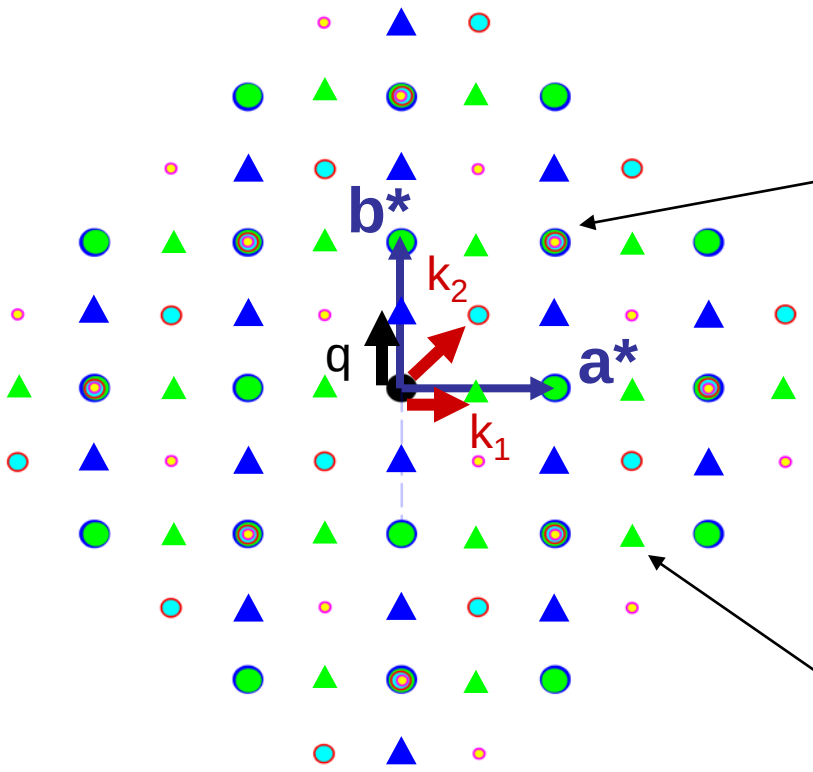
T_{CO} =240K

T_N=170K

$Pr_{1/2}Ca_{1/2}MnO_3$

Twinned Crystal

$T<T_N$ (AF-CO phase)



Possibly up to 6 domain contributions

Circles

(0 0 -4)$_6$+ Strong Nuc
(0 0 -4)$_5$+ Strong Nuc
(-2 2 0)$_4$+ Strong Nuc
(-2 -2 0)$_3$+ Strong Nuc
(2 2 0)$_2$+ Strong Nuc
(-2 2 0)$_1$ Strong Nuc

(1/2 - 1/2 1)$_6$ + CE-k2
(1/2 1/2 1)$_5$ + CE-k2
(0 -1 0)$_4$ + Negligible or strong Nuc
(1 0 0)$_3$ + Negligible or strong Nuc
(-1/2 -1/2 1)$_2$ + CE-k2
(1/2 -1/2 1)$_1$ CE-k2

Triangles

(0 -1/2 -1)$_6$+ “negligible” SurStruct
(1/2 0 -1)$_5$ intense CE-k1

(2 1/2 0)$_2$ + “intense” SS
(-1/2 2 0)$_1$ negligible pCE-k1

Basic structure peaks of different orthorhombic domains overlap (circles)

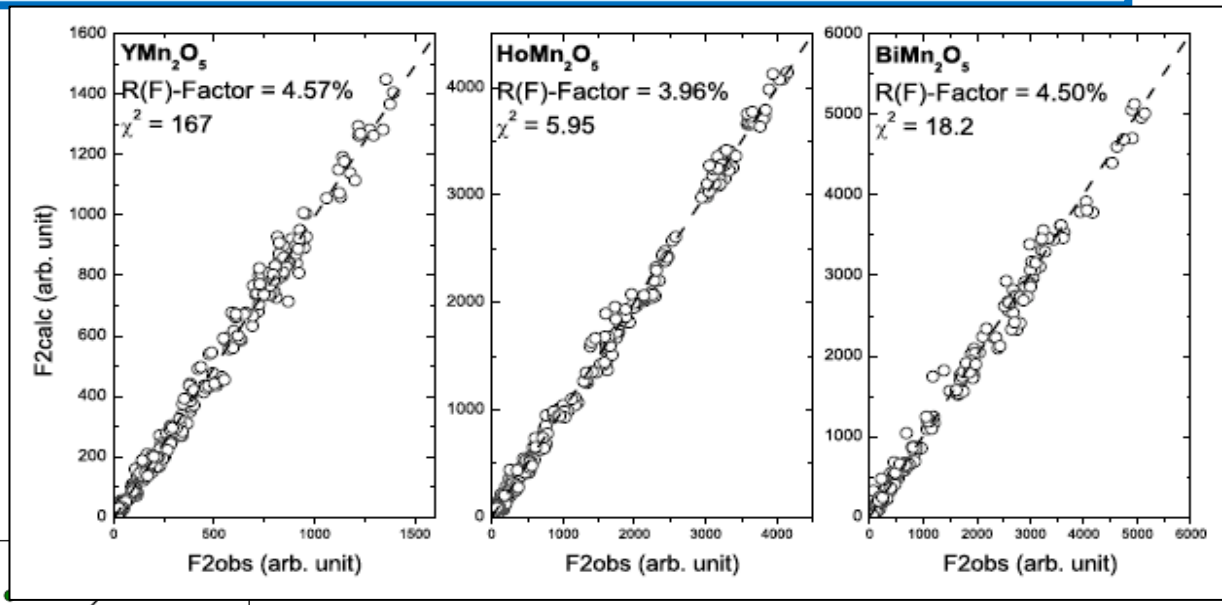
Superlattice (triangles) **Magnetic peaks**

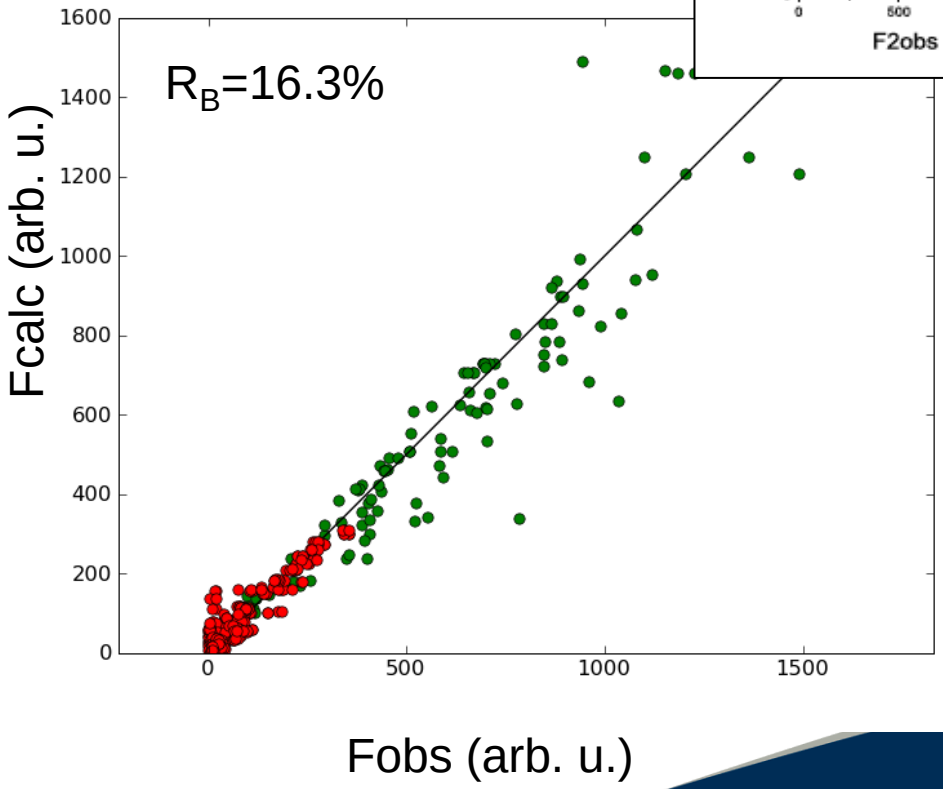
$Pr_{1/2}Ca_{1/2}MnO_3$

Comparison with the
1-2-5 Multiferroics manganites

Vecchini, Chapon et al
Phys. Rev. B **77**, 134434 (2008)

- Data from the *same instrument*
-similar sample size (*similar stats, a priori…*)
- But… crystals **untwinned**





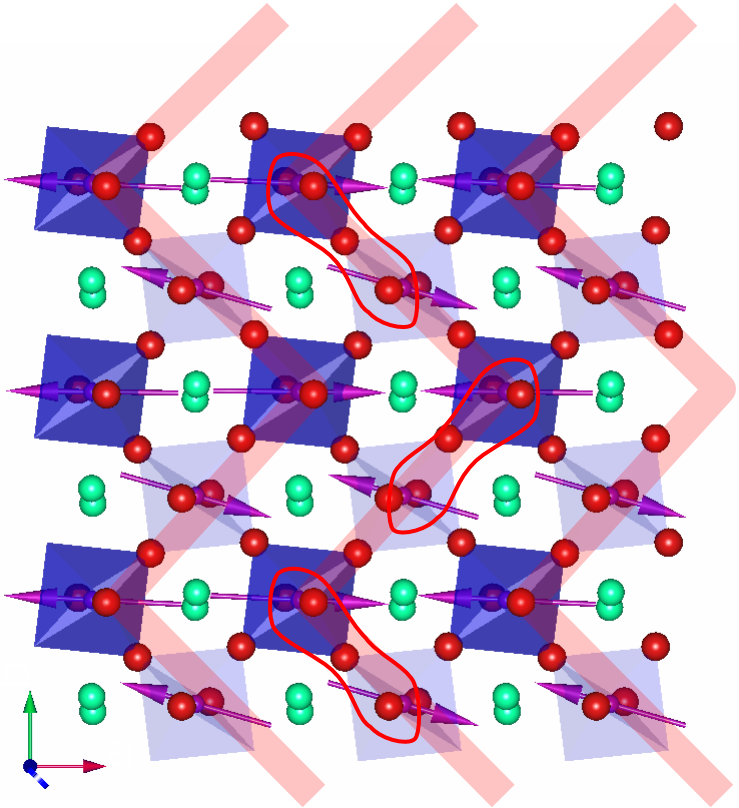
(1/2 - 1/2 1)$_6$ + CE-k2
(1/2 1/2 1)$_5$ + CE-k2
(0 -1 0)$_4$ + Negligible or strong Nuc
(1 0 0)$_3$ + Negligible or strong Nuc
(-1/2 -1/2 1)$_2$ + CE-k2
(1/2 -1/2 1)$_1$ CE-k2

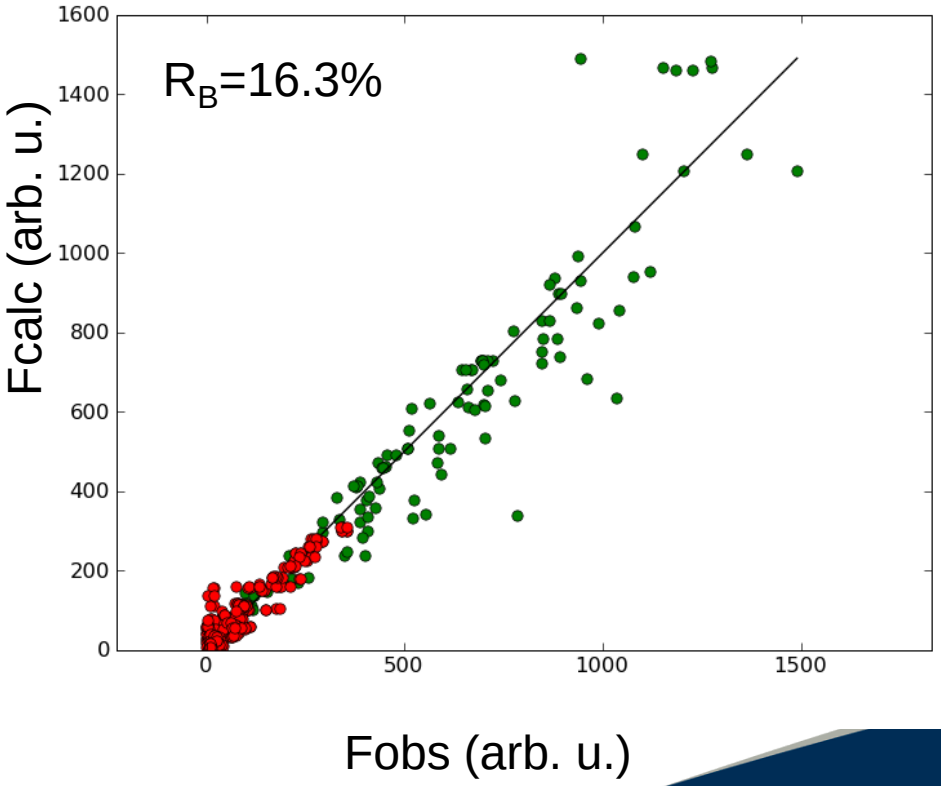
(0 -1/2 -1)$_6$+ “negligible” SurStruct
(1/2 0 -1)$_5$ intense CE-k1

Science & Technology Facilities Council
ISIS

$Pr_{1/2}Ca_{1/2}MnO_3$

Result : **Collinear** CE-type **structure**
=>
compatible with both **Ionic** and **ZP ordering** models…





Science & Technology Facilities Council
ISIS

SX- Powder Neutron diffraction studies questioning…

Study of alternative charge ordered materials
(with L. Pinsard-Gaudart (LPCES, Orsay University, Paris) and J. Rodriguez Carvajal (ILL, Grenoble France)):

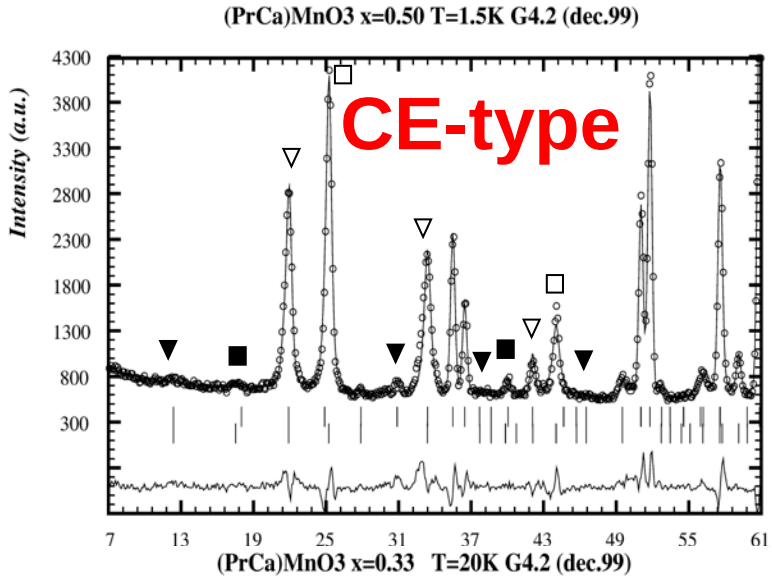
- Essentially Discards the **original** "CE-type variants" & **corroborates** "Zener Polarons ordering"-
- *Result published in A. Daoud-aladine et. al Phys. Rev. Lett. 101, 166404 (2008)*

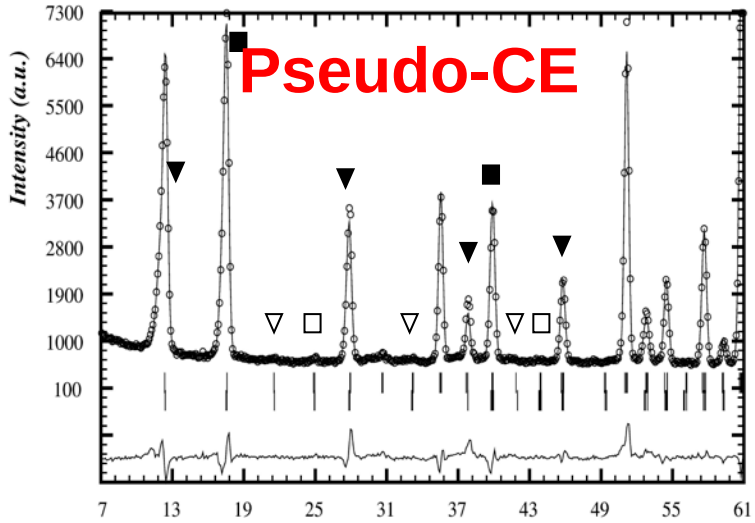
Validity of the CE- type structure*?*
(With Toby PERRING, ISIS facility)

-- Interpretation**:** Collinear structure **compatible** with both **Ionic and ZP ordering models**…
- data analysis tricky, not 100% satisfactory (twinning etc…)

What happens off half- doping:
- Instrument: **High resolution TOF- NPD (**instrument HRPD, at ISIS, UK)
- Sample : ~3g of **POWDER** of the **conventional** $Pr_{0.625}Ca_{0.375}MnO_3$

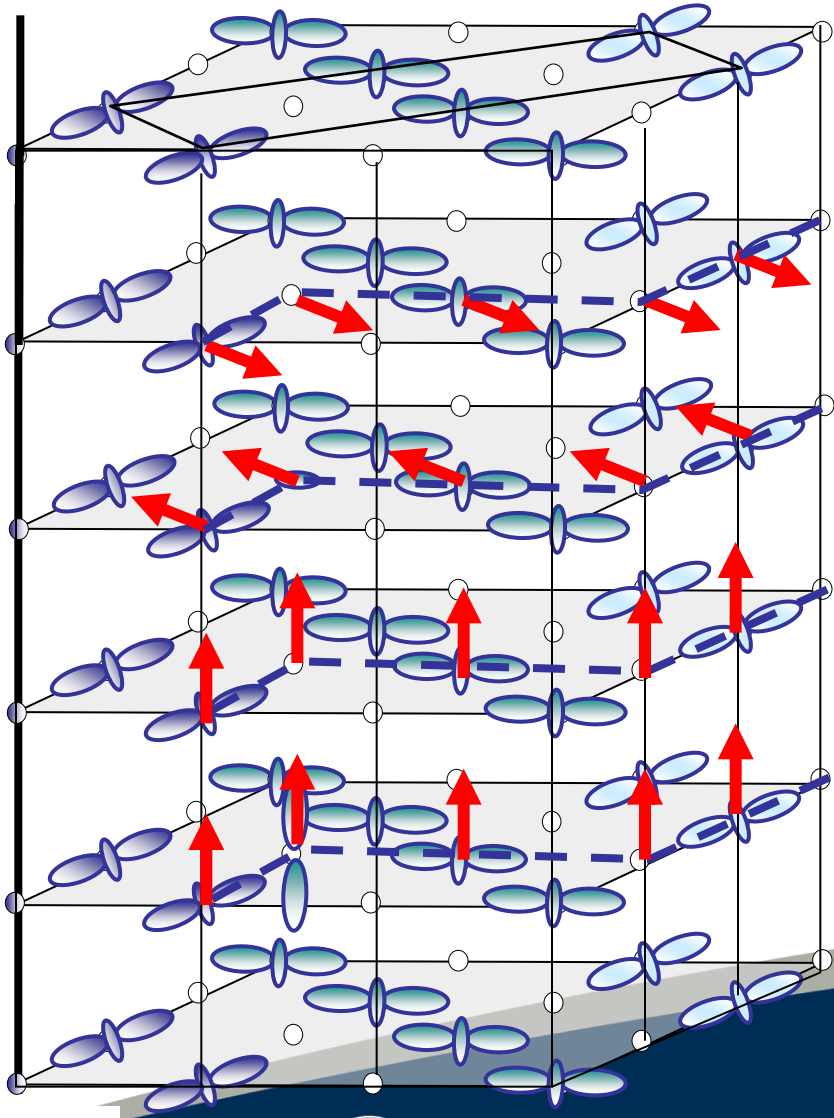
$Pr_{1-x}Ca_xMnO_3$ (x<1/2)





x=0.5

x=0.33



Z. Jirak
J.Mag. Mat. Mat **53,** 153 (1985)

D. E. Cox, et al
Phys. Rev. B **57**, 3305 (1998)

Science & Technology Facilities Council
ISIS

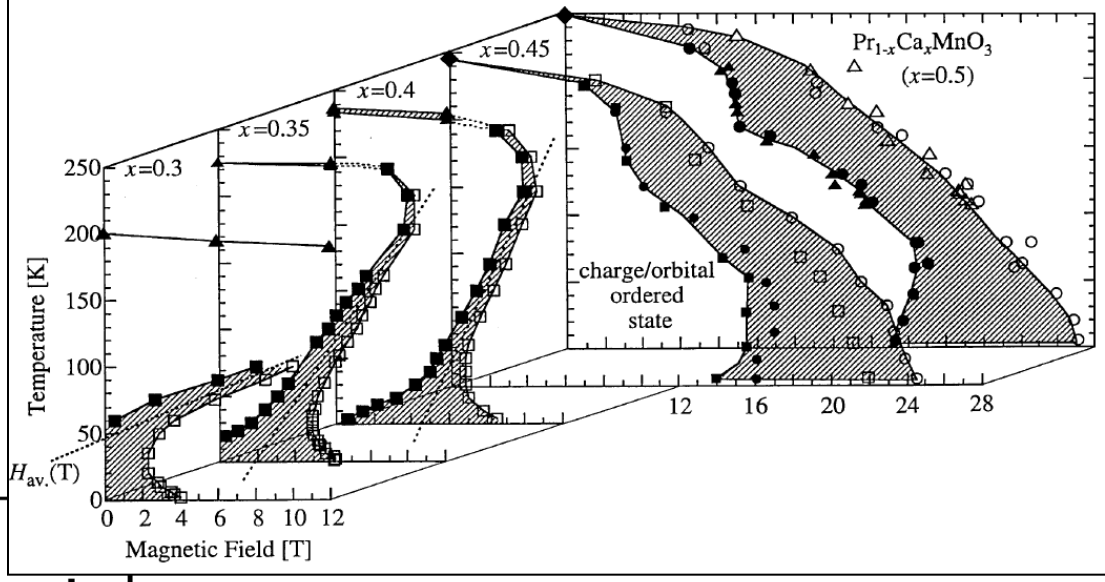
$Pr_{1-x}Ca_xMnO_3$ (x<1/2)

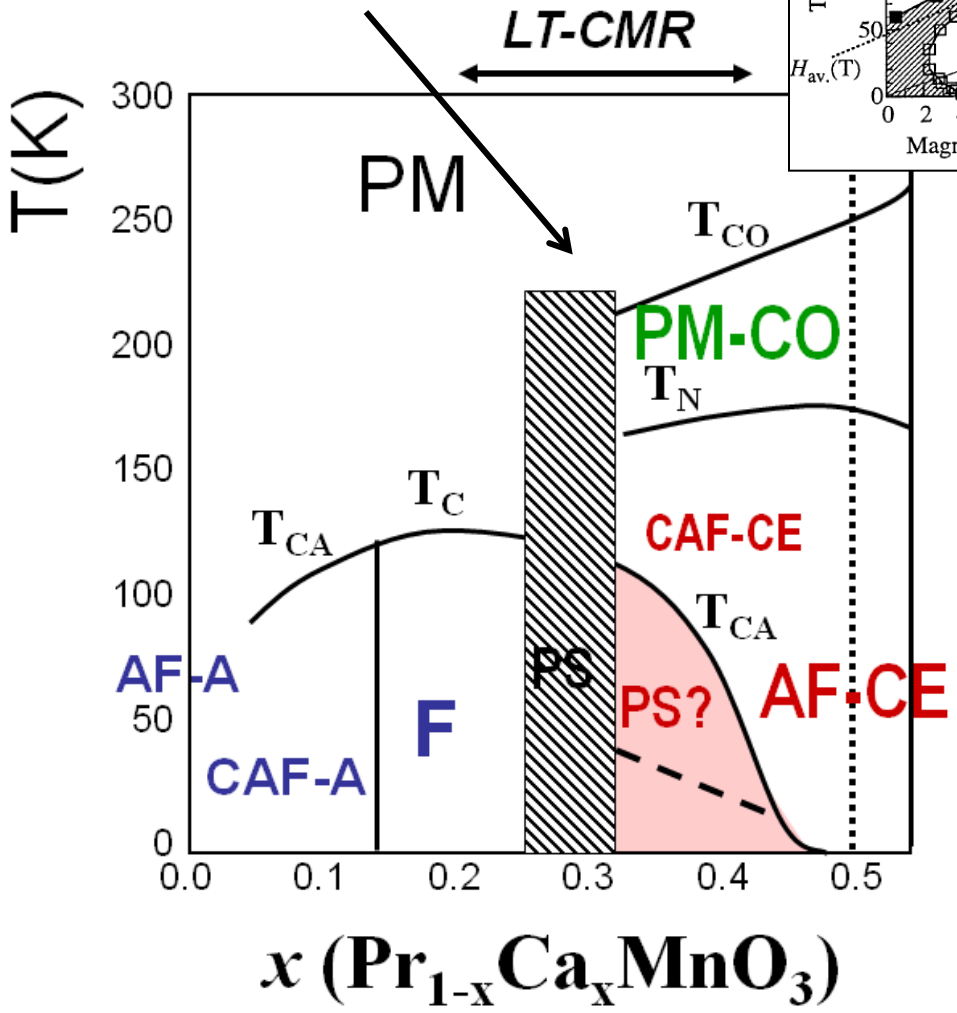
x=0.3 ISIS-HRPD data

P. Radaelli, et al

Rev. B 6317, 2419 (2001)

macroscopic Ferro- AF- PS (Micrometer scale)
+ mesoscopic PS (Nanometer scale)





Science & Technology Facilities Council
ISIS

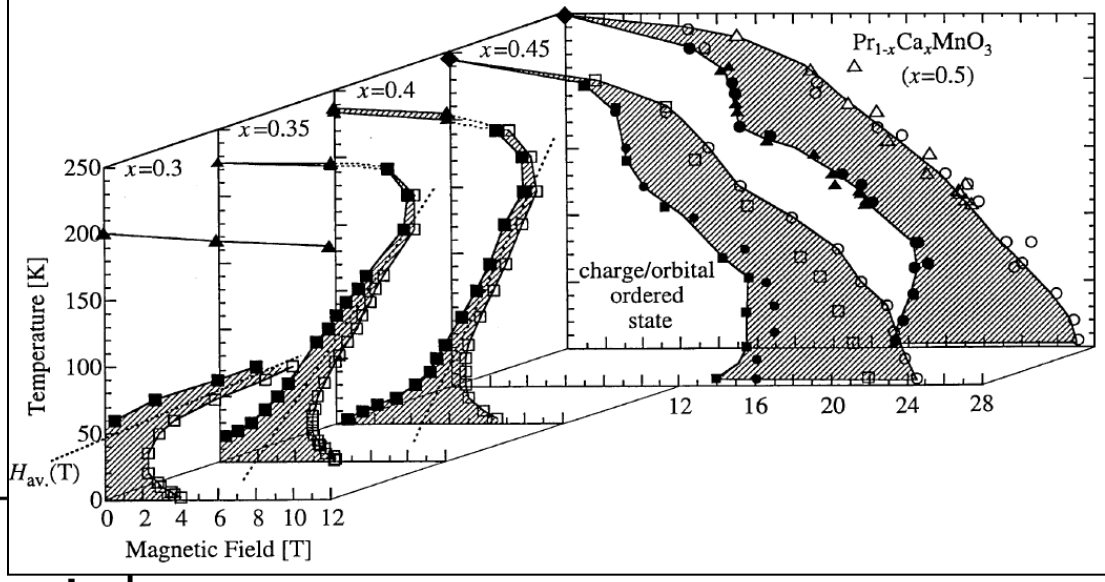
$Pr_{1-x}Ca_xMnO_3$ (x<1/2)

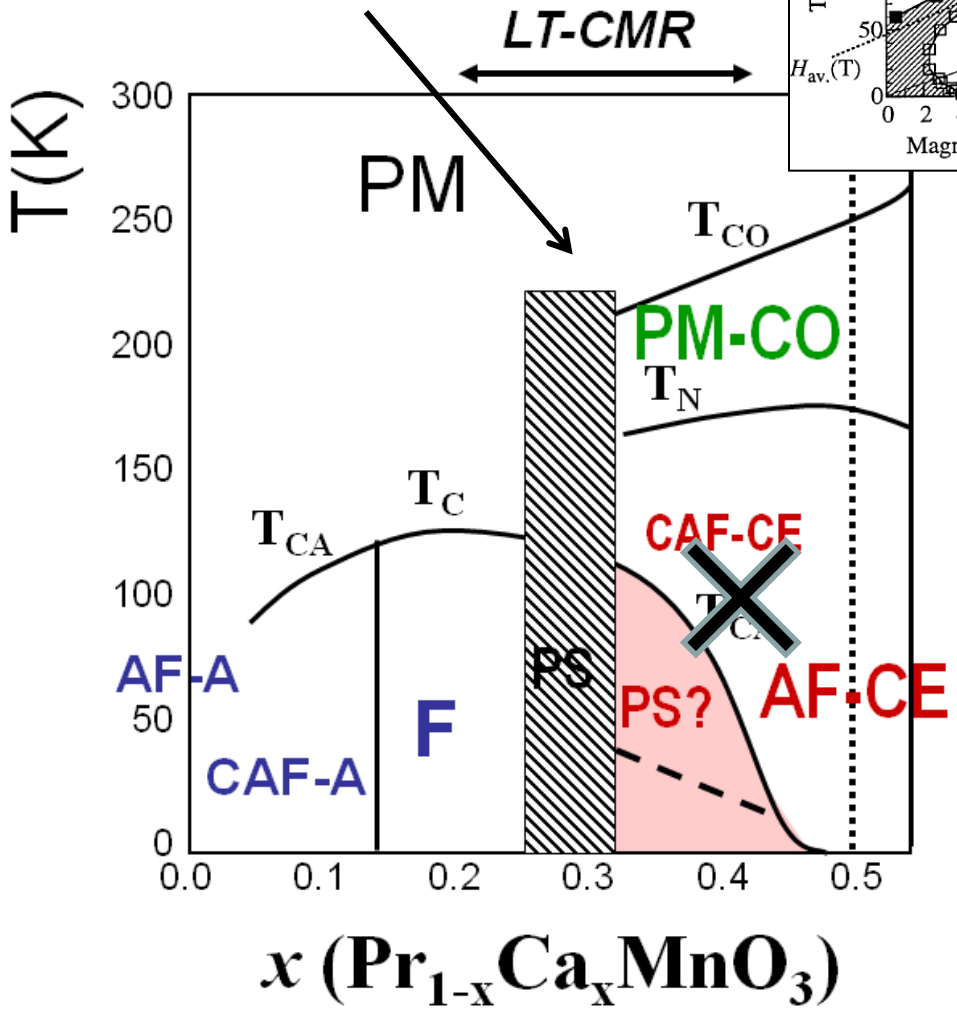
x=0.3 ISIS-HRPD data

P. Radaelli, et al

Rev. B 6317, 2419 (2001)

macroscopic Ferro- AF- PS (Micrometer scale)
+ mesoscopic PS (Nanometer scale)





Our NPD at x=0.33, x=0.375

No **macroscopic** F/AF PS around T~110K

(clear at x=0.375 from Small Angle Neutron Scattering studies, where PS ***is*** seen at x=0.33
Ch. Simon et al PRL **89**, 207202 (2002))

Science & Technology Facilities Council
ISIS

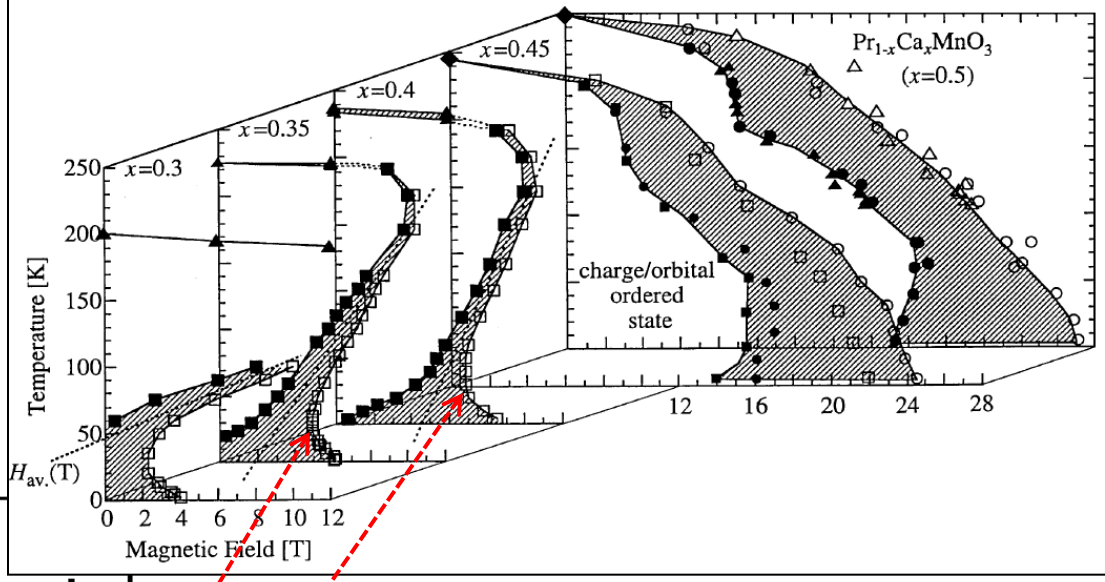
$Pr_{1-x}Ca_xMnO_3$ (x<1/2)

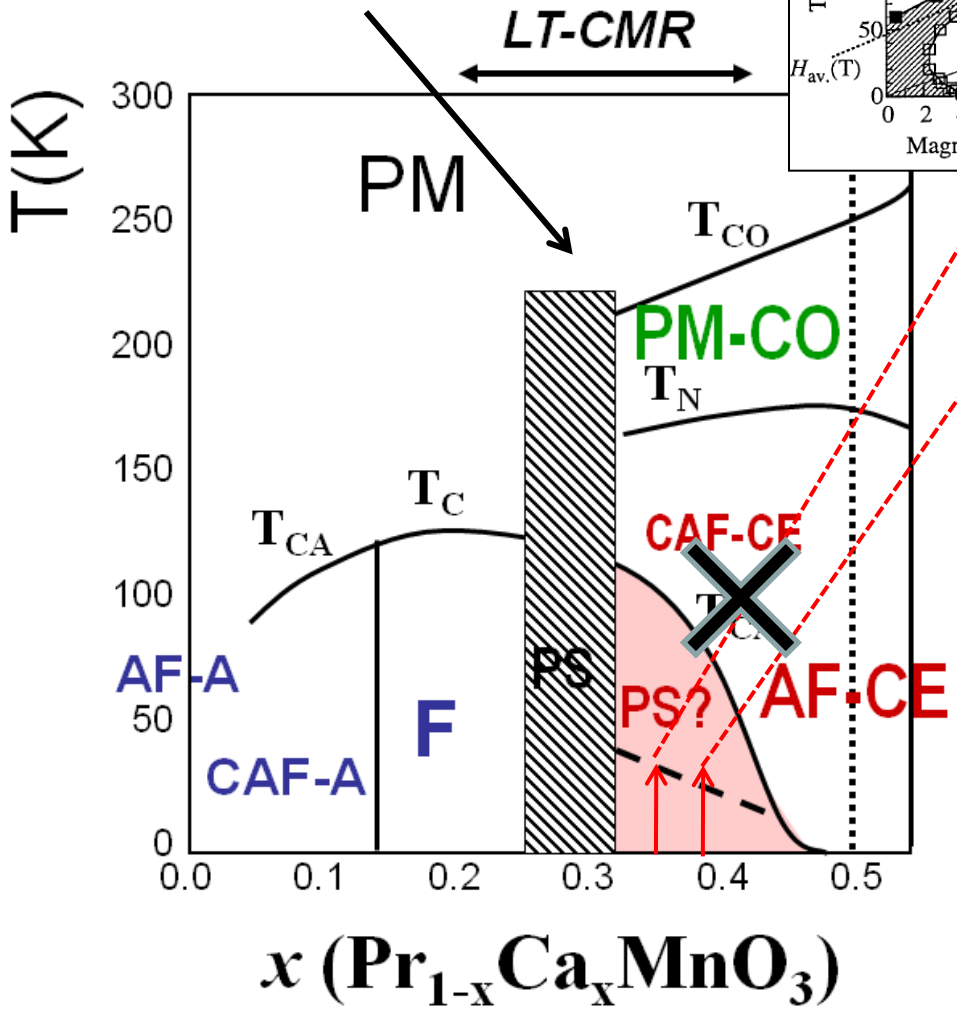
x=0.3 ISIS-HRPD data

P. Radaelli, et al

Rev. B 6317, 2419 (2001)

macroscopic Ferro- AF- PS (Micrometer scale)
+ mesoscopic PS (Nanometer scale)





Our NPD at x=0.33, x=0.375

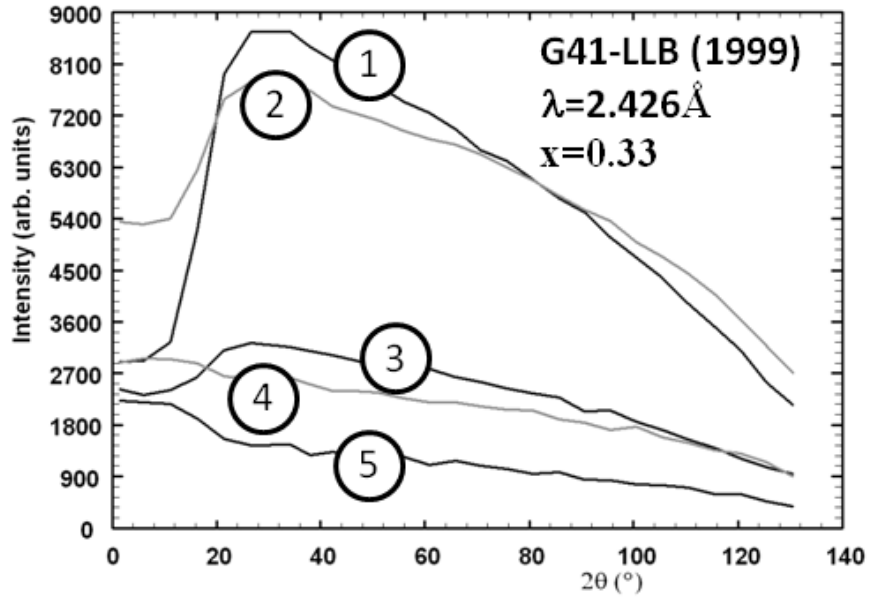
No **macroscopic** F/AF PS around T~110K

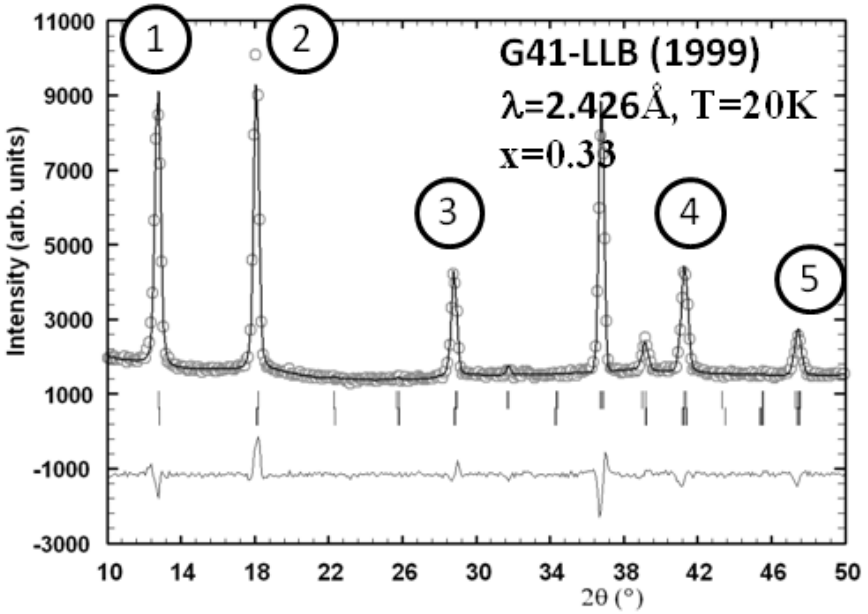
(clear at x=0.375 from Small Angle Neutron Scattering studies, where PS ***is*** seen at x=0.33
Ch. Simon et al PRL **89**, 207202 (2002))

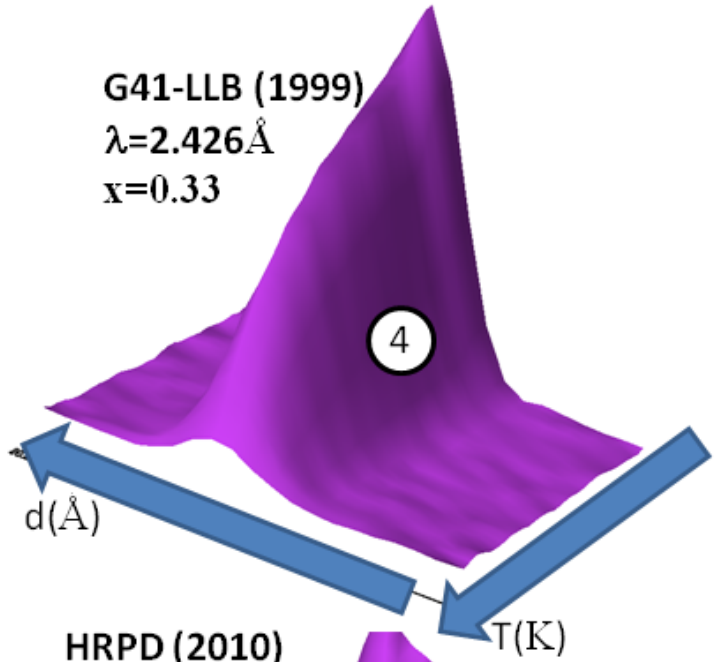
We evidence a LT magnetic transition
At a temperature ~25K
matching the inflexion
point of the **Magnetic field induced Insulator to Metal transition** line

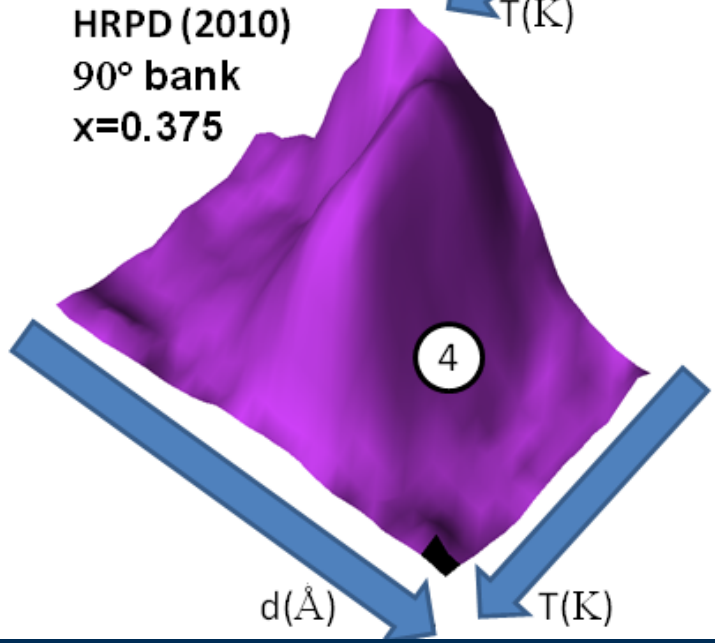
Science & Technology Facilities Council
ISIS

$Pr_{1-x}Ca_xMnO_3$ (x<1/2)









Conclusions

- Technique : **Medium resolution NPD** enough to determine the magnetic structure **(a very RARE case,** helped by the low cell symmetry of $YBaMn_2O_6$**!!!)**

- Interpretation: This essentially **discards** the **originally proposed** "CE-type ionic Charge ordering variants" BUT **corroborates** "Zener Polarons ordering" scenarios
- *Results published in A. Daoud-aladine et. al Phys. Rev. Lett. 101, 166404 (2008)*

- Technique **: First and unique Single Crystal Neutron diffraction on prototype** $\mathbf{Pr_{1/2}Ca_{1/2}MnO_3}$

- Interpretation**:** Collinear structure **compatible** with both **Ionic and ZP ordering models**…
- data analysis tricky, not 100% satisfactory (twinning etc…)

- Technique : Using **much higher resolution on TOF instruments**…

- *$Pr_{0.625}Ca_{0.375}MnO_3$ appears to be markedly different to $Pr_{0.7}Ca_{0.3}MnO_3$*
- It is **SINGLE-PHASE** and show no macroscopic F-component
- It shows instead an (almost) unreported AF spin re-orientation below T_{N2}=25K
- The phenomenon seems **intimately related to the LT- CMR properties**