Understanding the insulating phase in CMR manganites: Shortening of the Jahn-Teller long-bond across the phase diagram of $La_{1-x}Ca_xMnO_3$

- *local structural update* -

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LOCAL STRUCTURE FROM DIFFRACTION
MICHIGAN STATE UNIVERSITY

ESRF PDF Powder Diffraction Workshop
Grenoble, October 23, 2007

NIRT STRUCTURE OF NANOCRYSTALS
http://nirt.pa.msu.edu

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Experimental facilities:

NPDF beamline of the MLNSC, LANL
GEM beamline of the ISIS, RAL

Funding in the Billinge group:

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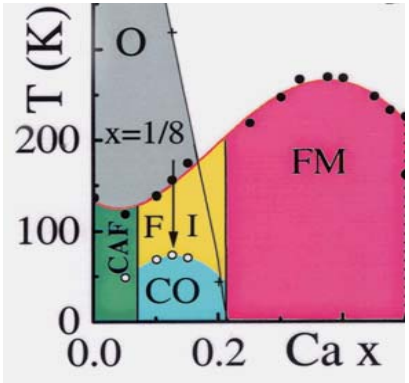
Outline

$La_{1-x}Ca_xMnO_3$ $0 \leq x \leq 0.5$: behavior of the **local** JT long bond

from the atomic pair distribution function (PDF) study

(1) across the Jahn-Teller phase transition line

(2) across the insulator-to-metal phase transition line



Summary: $La_{1-x}Ca_xMnO_3$ ($0.0 \leq x \leq 0.5$)

CANONICAL PICTURE …

(a) local JT long MnO bond does **NOT** shorten w/ doping

is WRONG

(b) local JT distortion disappears in FM phase

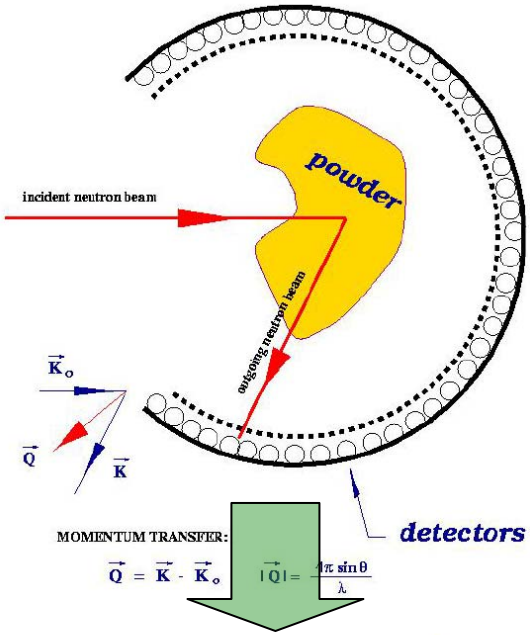
is RIGHT

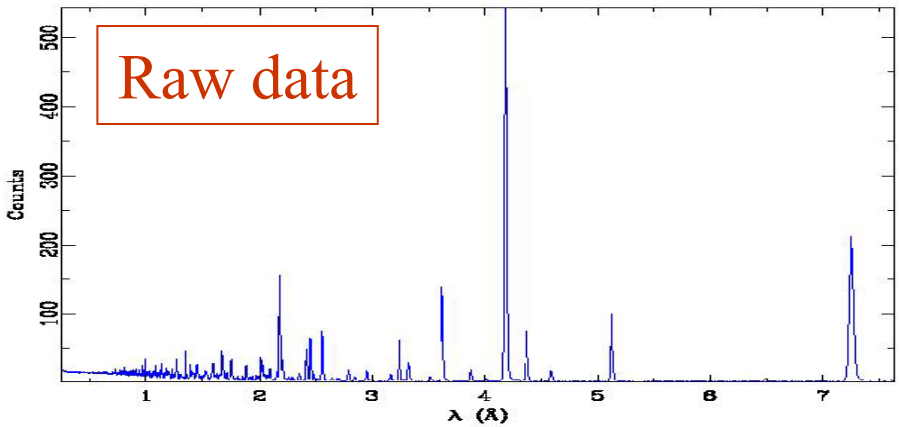
(now better quantified)

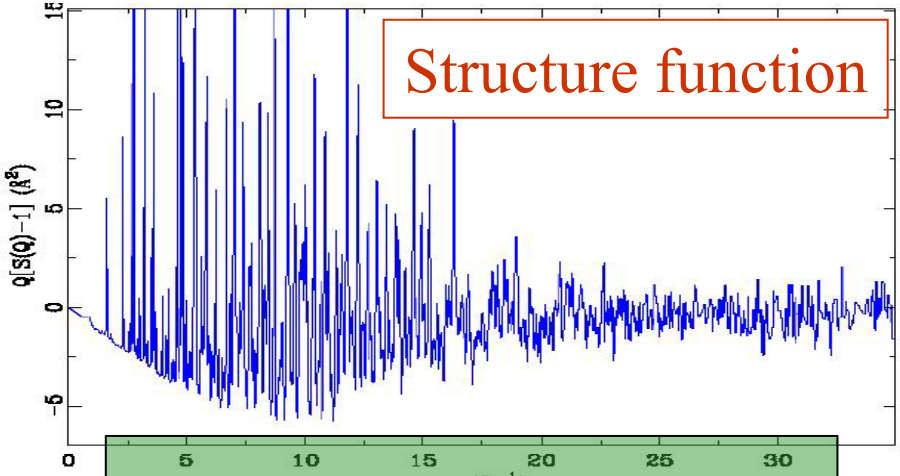
THE IMPLICATION …

charge delocalization **polarons are NOT single site**

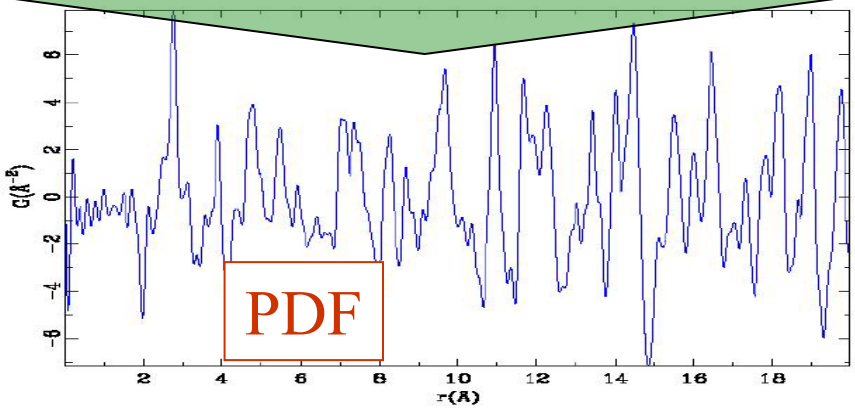
PDF from neutron TOF powder diffraction



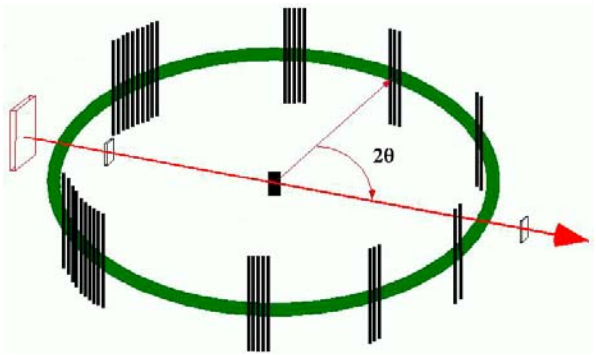




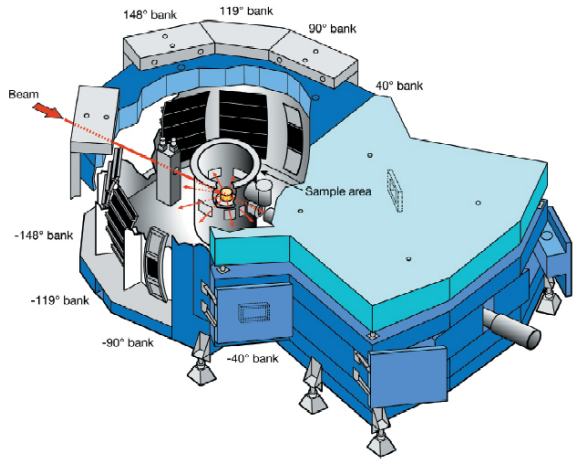
$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin QrdQ$$



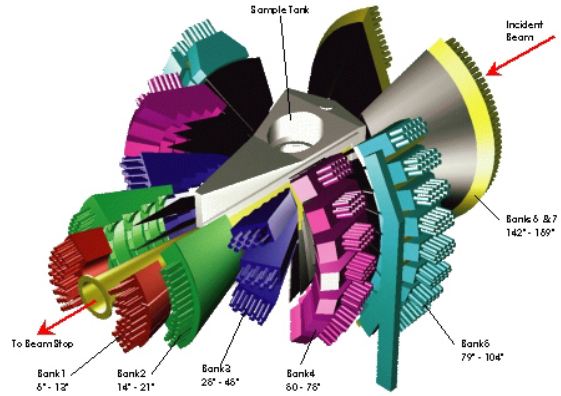
Advances in PDF via advances in the instrumentation and exp. setups



SEPD at IPNS

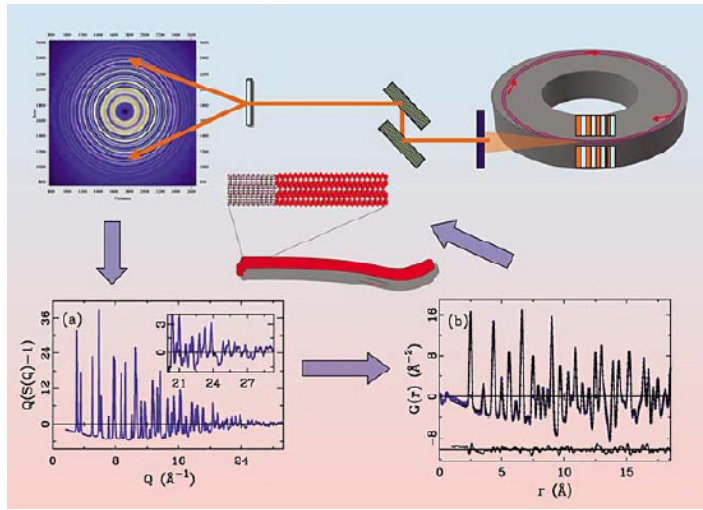


NPDF at LANSCE



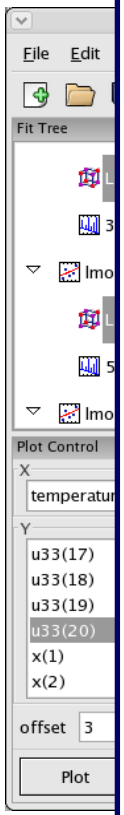
GEM at ISIS

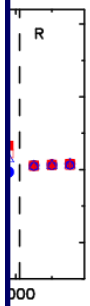
ROUGH COMPARISON	SEPD/IPNS	NPDF/LANSCE	GEM/ISIS
# backscatt. detectors	80	160	6491 elem.
Primary flightpath [m]	14	17	32
Mean current [μA]	15	100	200



RA-PDF setup using synchrotron x-rays

Advancements in PDF modeling software





Advertisement:

1.0 beta of **PDFgui has been released recently!**

- built on new PDFfit2 C++ engine

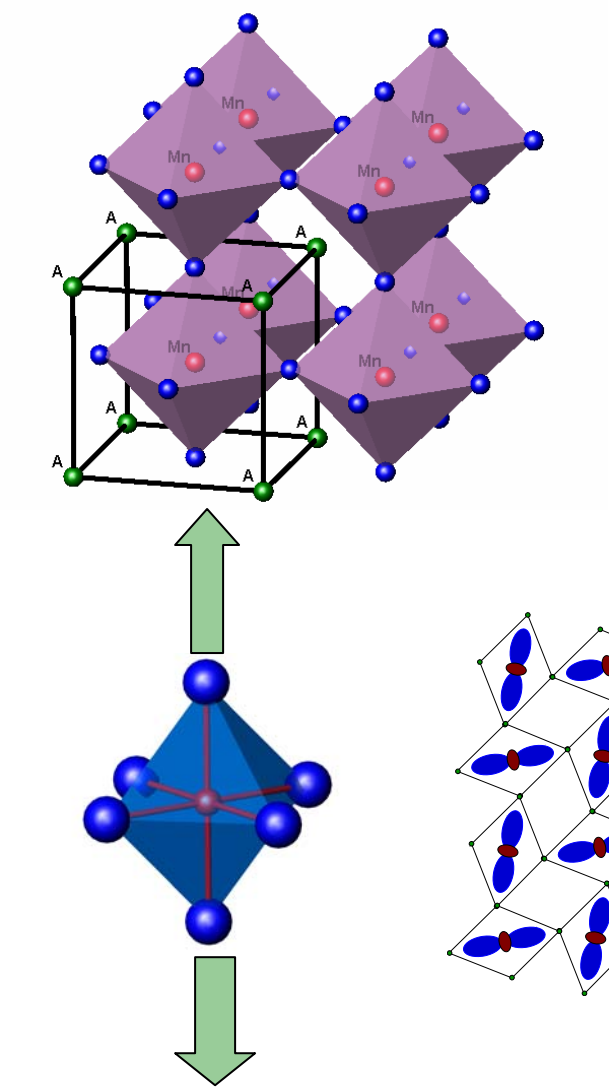
- part of DANSE diffraction project

(**D**istributed Data **A**nalysis for **N**eutron **S**cattering **E**xperiments)

Details and download: www.diffpy.org

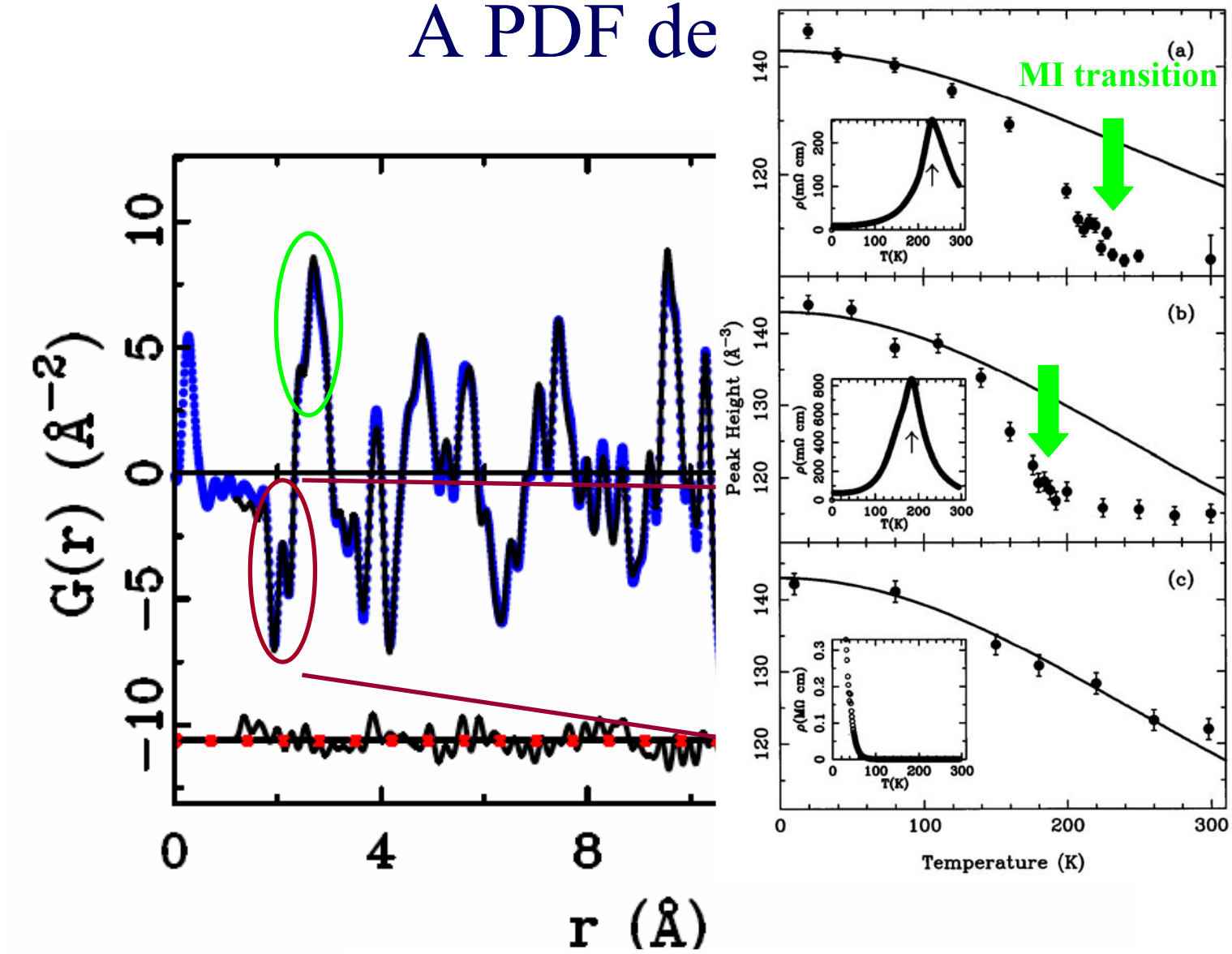
C. L. Farrow, P. Juhas, J. W. Liu, D. Bryndin, E. S. Božin, J. Bloch, Th. Proffen and S. J. L. Billinge, **PDFfit2 and PDFgui: Computer programs for studying nanostructure in crystals**, *J. Phys: Condens. Matter* **19**, 335219 (2007).

MnO_6 octahedra in $LaMnO_3$



- Mn3+: JT distorted octahedra:
  - 4 x ~1.94Å Mn-O bonds
  - 2 x 2.16Å Mn-O bonds
  - R_{LONG}-R_{SHORT} = 0.22Å
  - 8 long and 4 short O-O distances centered around 2.75Å

A PDF de



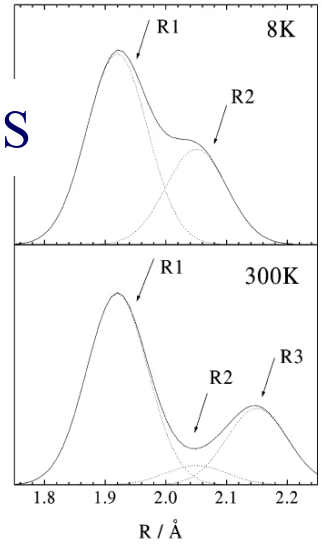
S.J.L. Billinge et al., Phys. Rev. Lett. **77**, 715, (1996).

What happens with doping?

- Phase separation scenario
  - Coexisting *undistorted* metallic regions and *JT-distorted* insulating regions
  - PDF will see short and long-bonds in all samples with the *number* of long-bonds decreasing with doping/metallicity
- Homogeneous scenario
  - Number of long-bonds stays constant, but *length* of the long bond decreases with increasing doping/metallicity

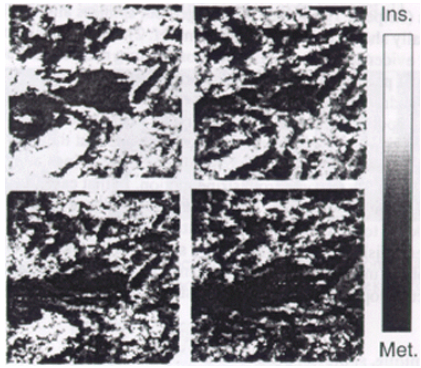
Earlier experimental evidence…

EXAFS



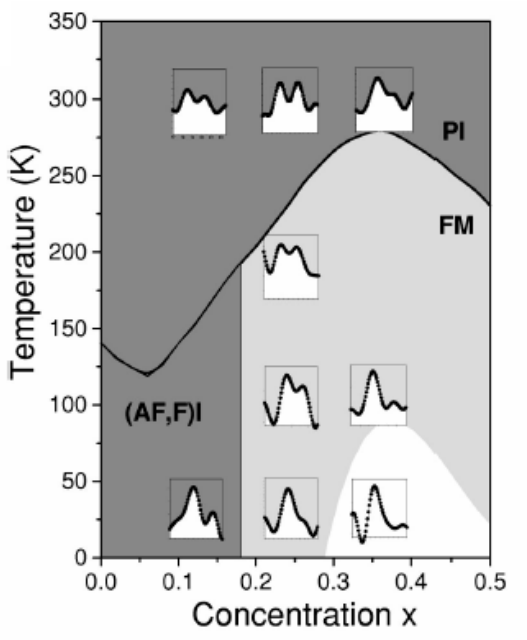
N.E. Massa *et al*., J. of Magn. and Magn. Mater. **233**, 91 (2001).

STS



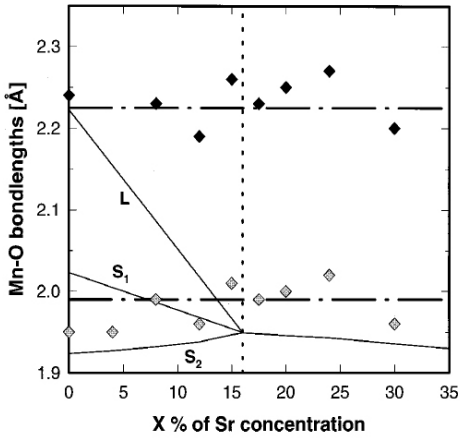
M. Fath *et al*., Science **285**, 1540 (1999).

x-ray PDF



S. Billinge *et al*, Phys. Rev. B **62**, 1203 (2000).

Neutron PDF



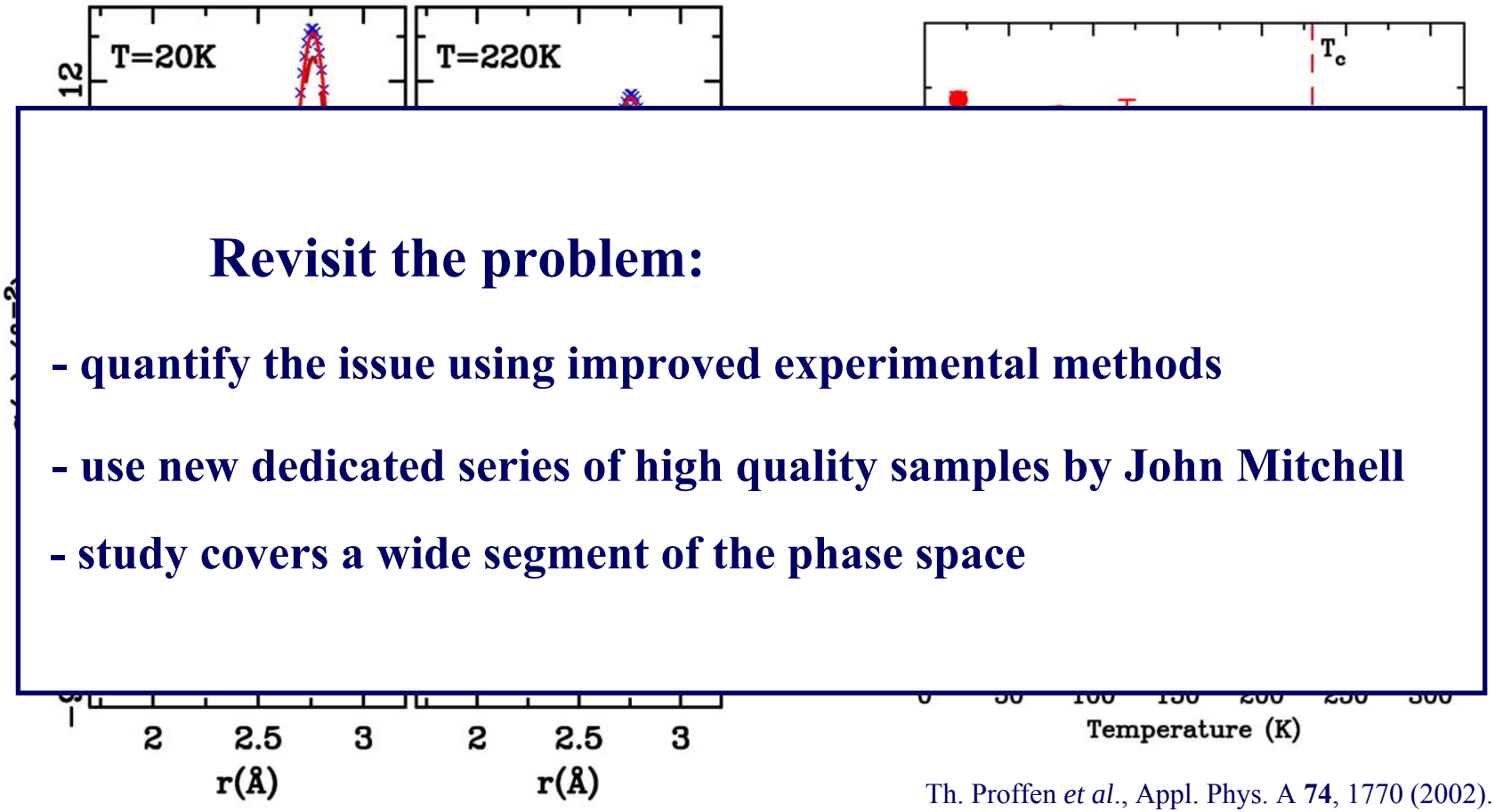
D. Louca *et al*., Phys. Rev. B **56**, R8475 (1997).

…suggested R_{LONG} remains **constant** w/ doping, and that the system is inhomogeneous….

We wanted to quantify the phase separation!

Initial attempts suggested: Strange percolation

- Two phase fitting, LCMO x=0.25
  - Distorted insulating phase
  - Undistorted metallic phase
- Fraction of metallic phase vs T
- 50% metallic above Tc, above the percolation treshold!?



Revisit the problem:

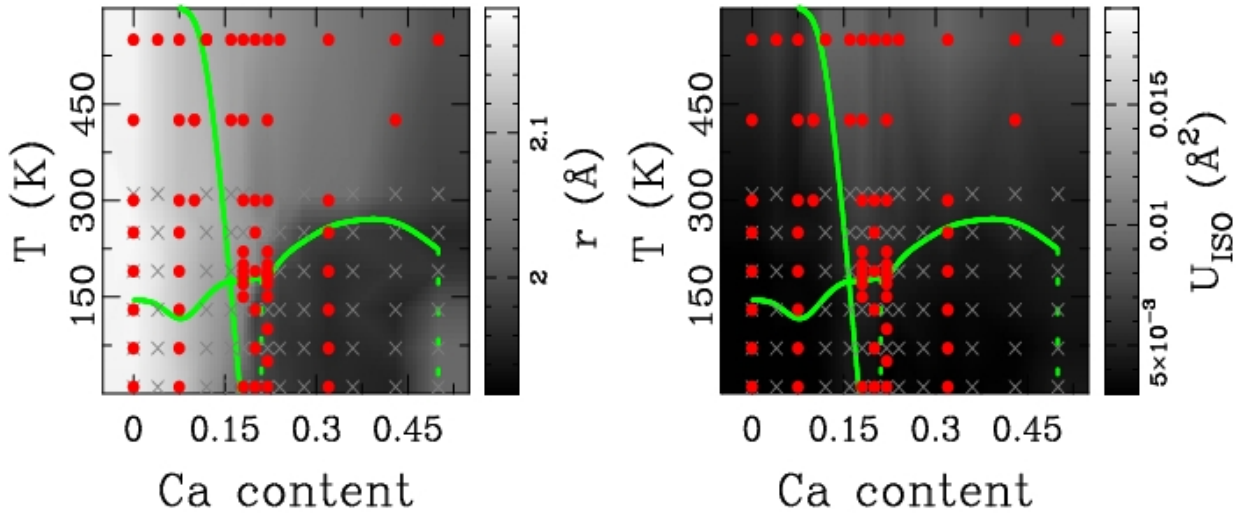
- quantify the issue using improved experimental methods

- use new dedicated series of high quality samples by John Mitchell

- study covers a wide segment of the phase space

Th. Proffen *et al*., Appl. Phys. A **74**, 1770 (2002).

Set to revisit the issue across the phase diagram of $La_{1-x}Ca_xMnO_3$



- To understand colossal magnetoresistance, many data points are needed throughout the phase diagram.
- High throughput local structural studies at GEM (ISIS) and NPDF (LANSCE)

Unexpected result emerges from the new data: length of local JT R_{LONG}(MnO) shortens w/ doping

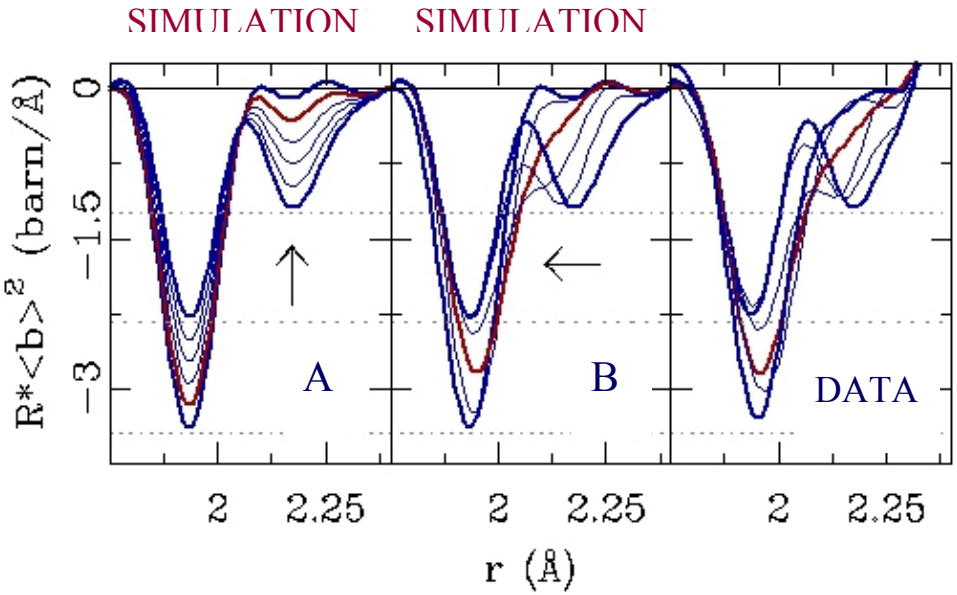
Two extreme doping dependencies for the insulating phase

A Complete localization: Doped charges localized as single site polarons

xMn^{4+} sites	octahedra undistorted	($CaMnO_3$ like)
(1-x)Mn^{3+} sites	octahedra fully distorted	($LaMnO_3$ like)

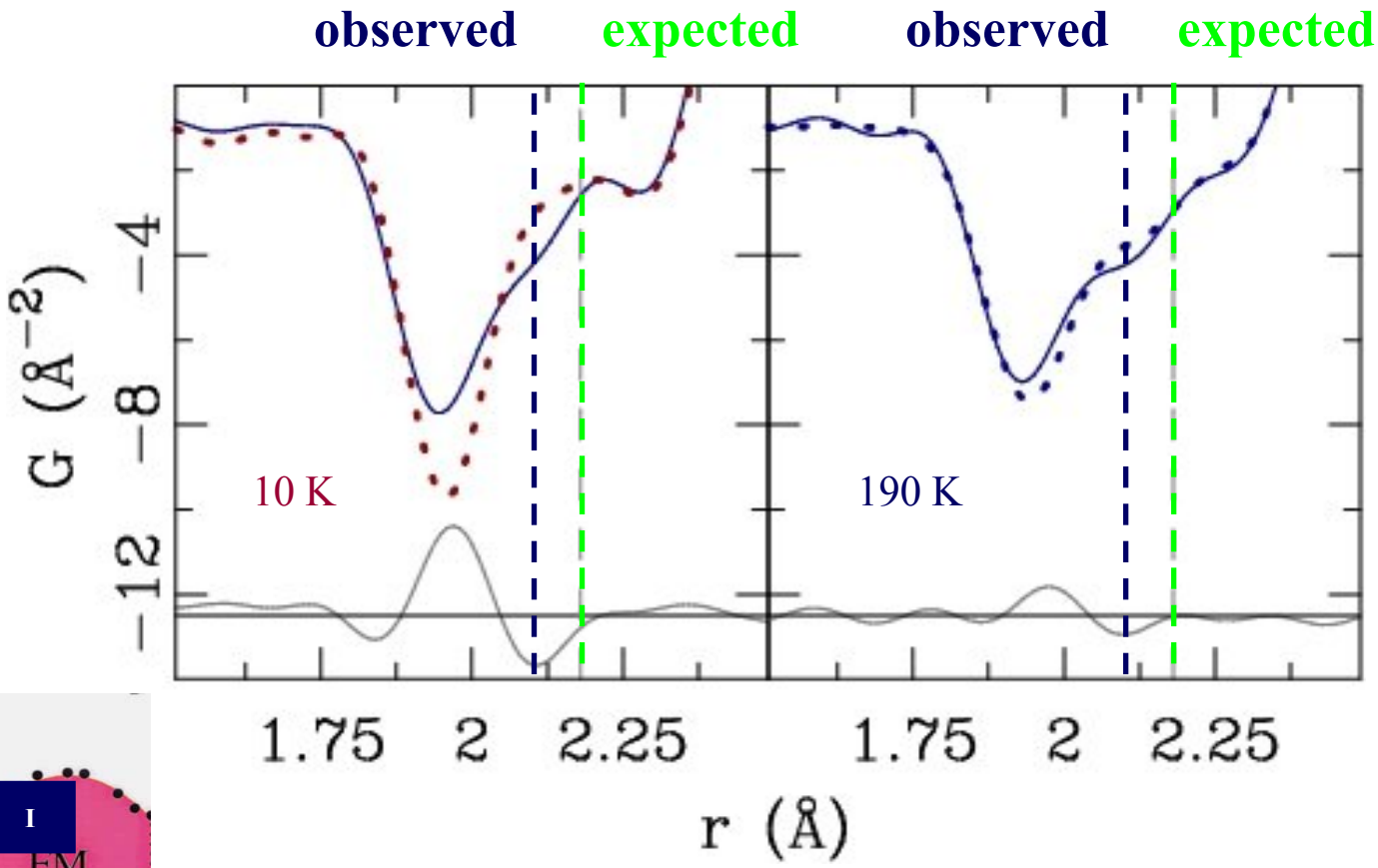
B Complete delocalization: Doped charges delocalized through the lattice

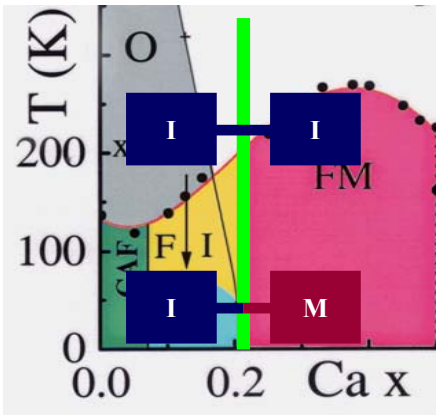
all sites Mn$^{(3+x)+}$	octahedral distortion reduced in size



Crossing the IM transition line at constant T

high resolution NPDF data of x=0.18 (insulating) and x=0.22 (metallic)





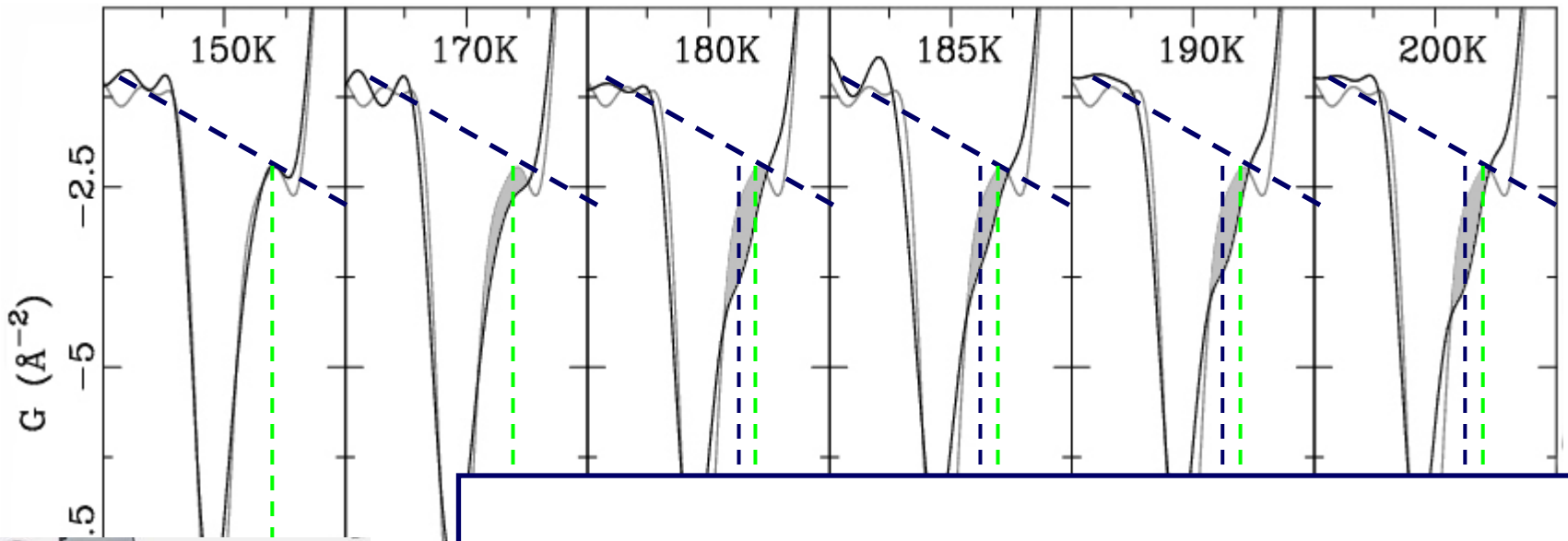
data vs data: *x=0.18 (solid) vs x=0.22 (dotted)*

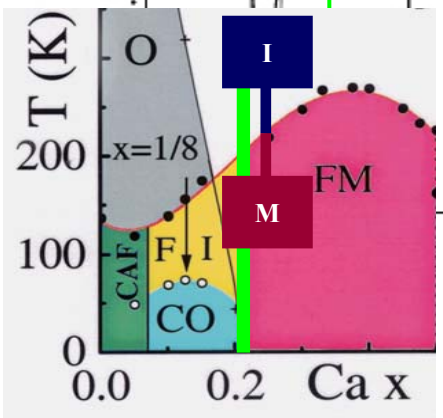
metallic insulating

Driving it insulating at constant x

high resolution NPDF data of x=0.22 (metallic) sample

$T_{MI} \approx 180K$

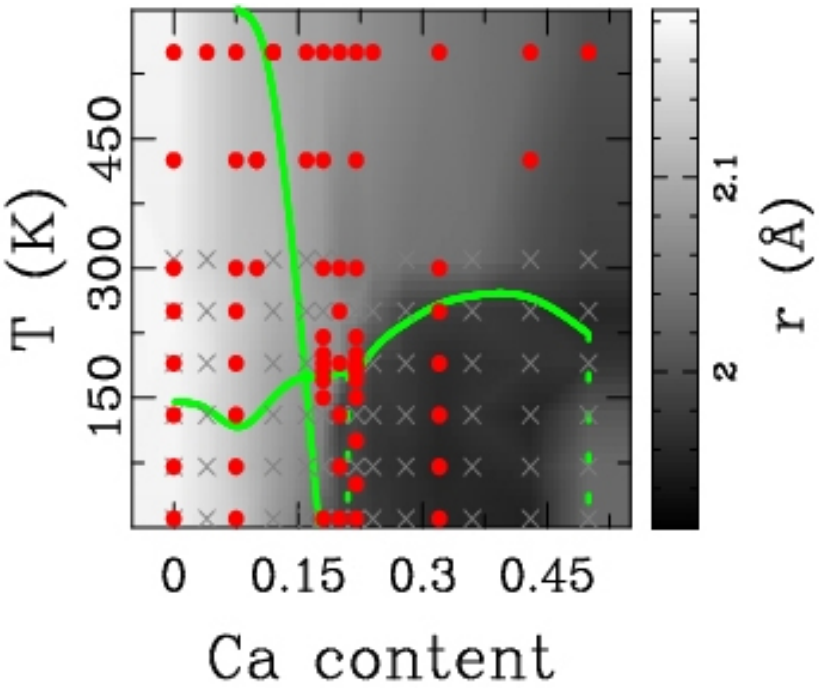


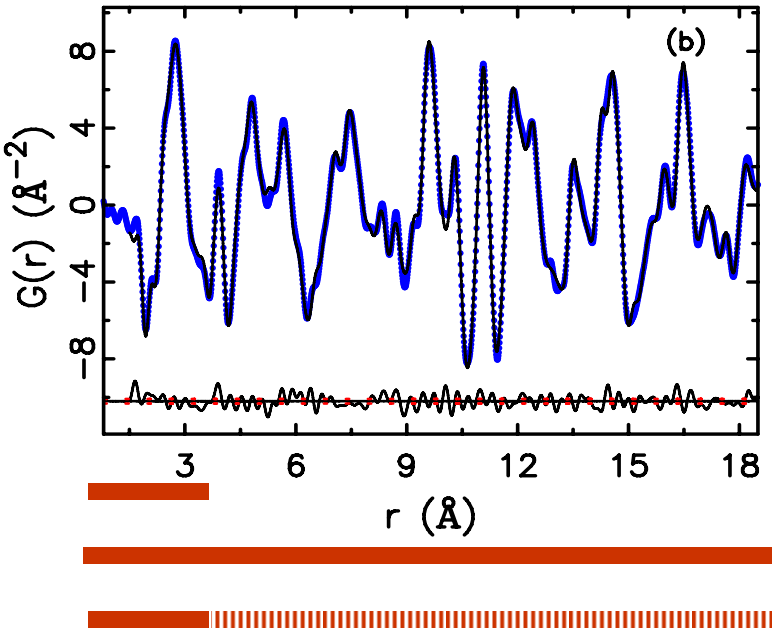


Rebaseline the goal:

quantify the long JT bond across the phase diagram

Scanning the (x,T) phase diagram of LCMO





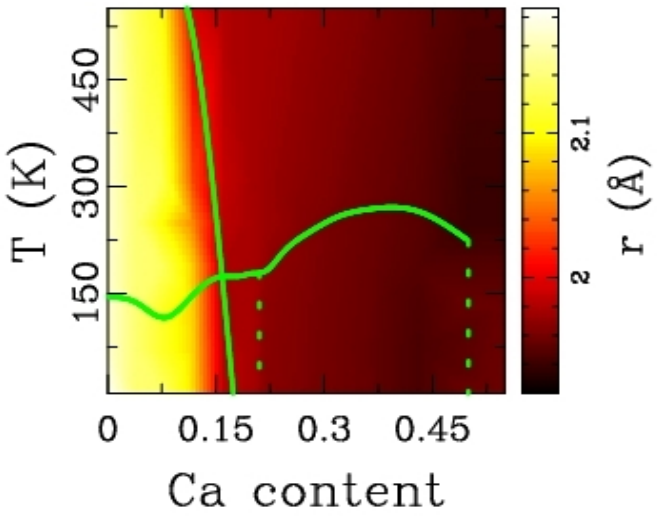
Structural modeling:	Rietveld and PDF (over 20 Å and 6 Å)
Space group:	P b n m
Total datasets:	around 100

(x,T) results: Rietveld vs PDF in P b n m setting

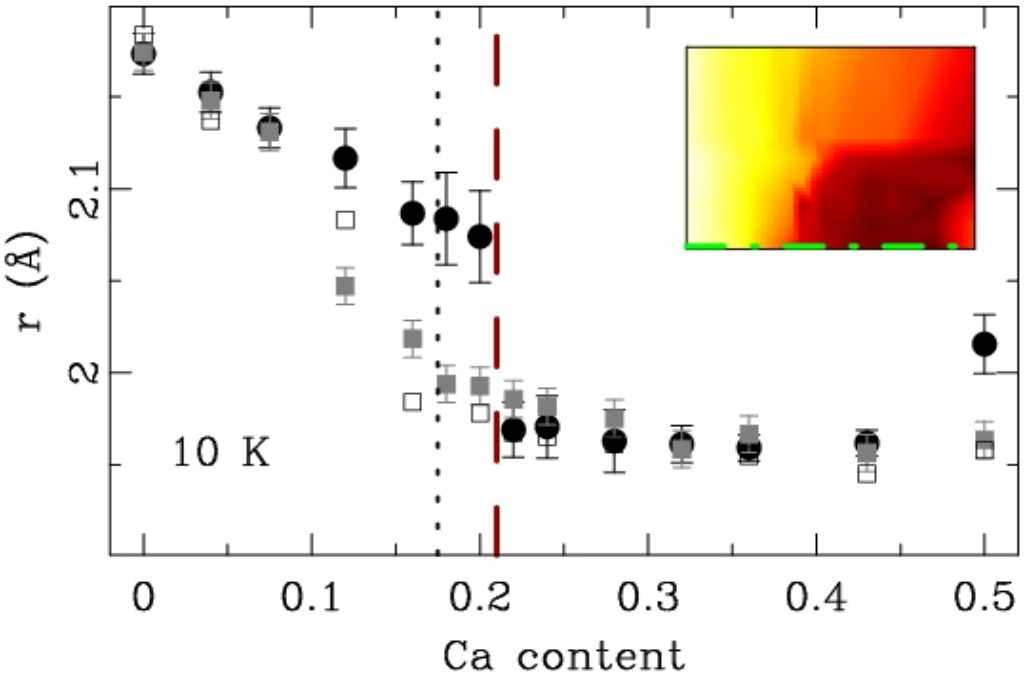
AVERAGE

LOCAL

Long MnO bond



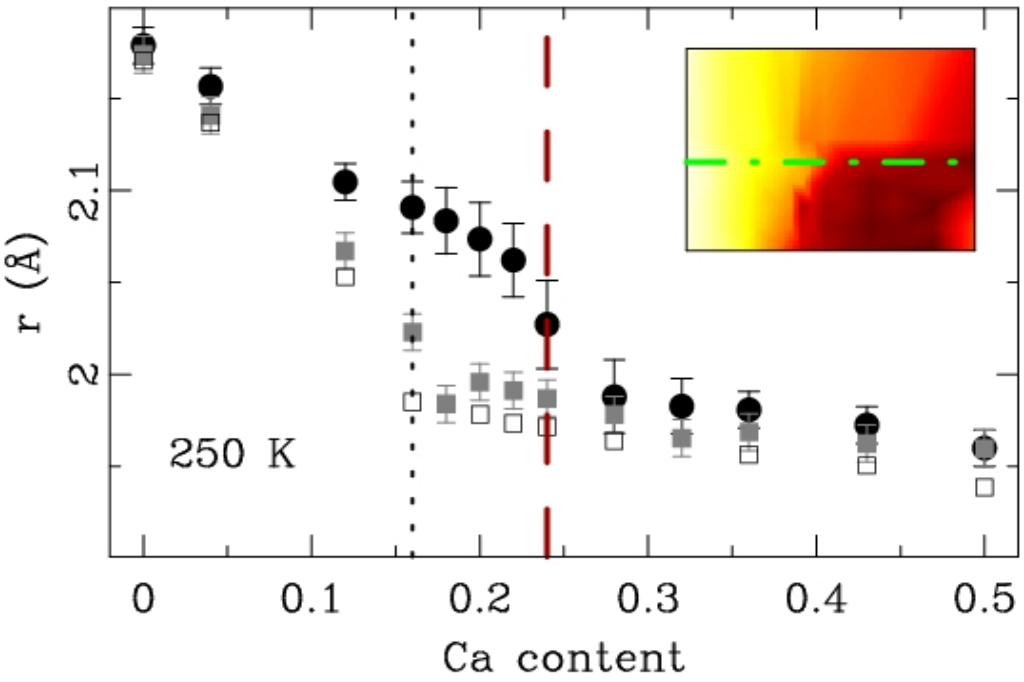
Constant T-cuts: 10 K



Open squares: Rietveld
Solid squares: PDF over 20 Å
Solid circles: PDF over 6 Å

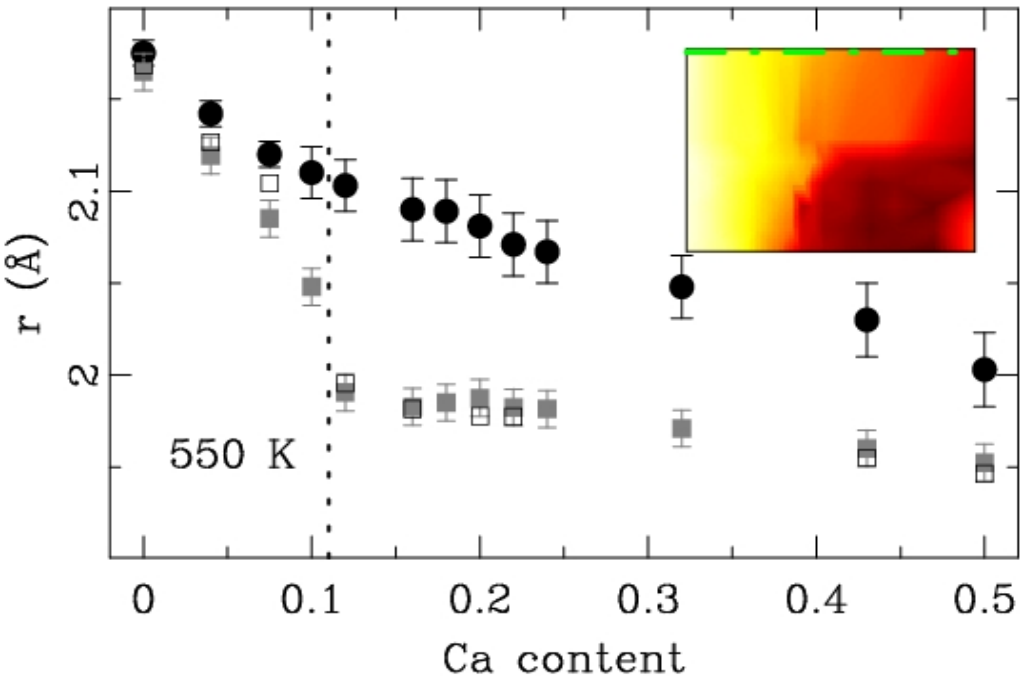
local JT disappears ABRUPTLY in the metallic phase

Constant T-cuts: 250 K



Open squares: Rietveld
Solid squares: PDF over 20 Å
Solid circles: PDF over 6 Å

Constant T-cuts: 550 K



Open squares: Rietveld
Solid squares: PDF over 20 Å
Solid circles: PDF over 6 Å

Long JT bond in the insulating phase

(a) crystallography

- long bond disappears in pseudocubic phase

(b) local structure

- long bond persists in pseudocubic phase
- long bond shortens with increasing doping
- long bond disappears abruptly at IM transition

Possible scenarios for insulating phase

~~A Complete localization: Doped charges localized as single site polarons~~
~~long JT bond stays long~~

B Complete delocalization: Homogeneous doping
- long bond shortens continuously with doping

C Partial delocalization: Multi-site polarons
- intermediate behavior: shortens less quickly with doping

Summary: $La_{1-x}Ca_xMnO_3$ ($0.0 \leq x \leq 0.5$)

CANONICAL PICTURE …

(a) local JT long MnO bond does **NOT** shorten w/ doping **is WRONG**

(b) local JT distortion disappears in FM phase **is RIGHT (better quantified)**

local JT ABRUPTLY disappears at IM transition

THE IMPLICATION …

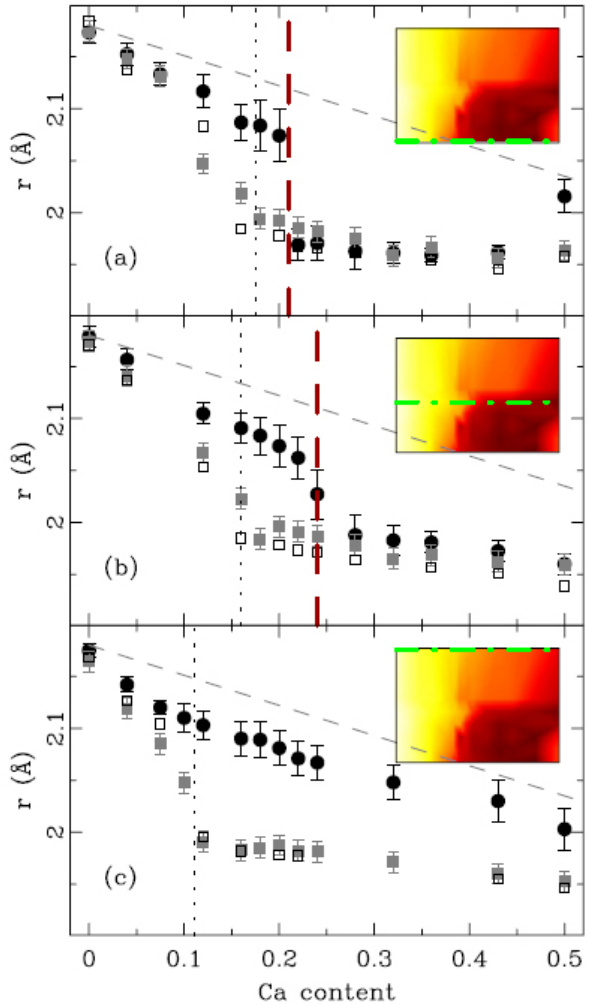
charge delocalization **polarons are NOT single site**

Systematic local structural studies across the phase diagram are important!

E.S. Božin *et al*., Phys. Rev. Lett. **98**, 137203, (2007).

Extras

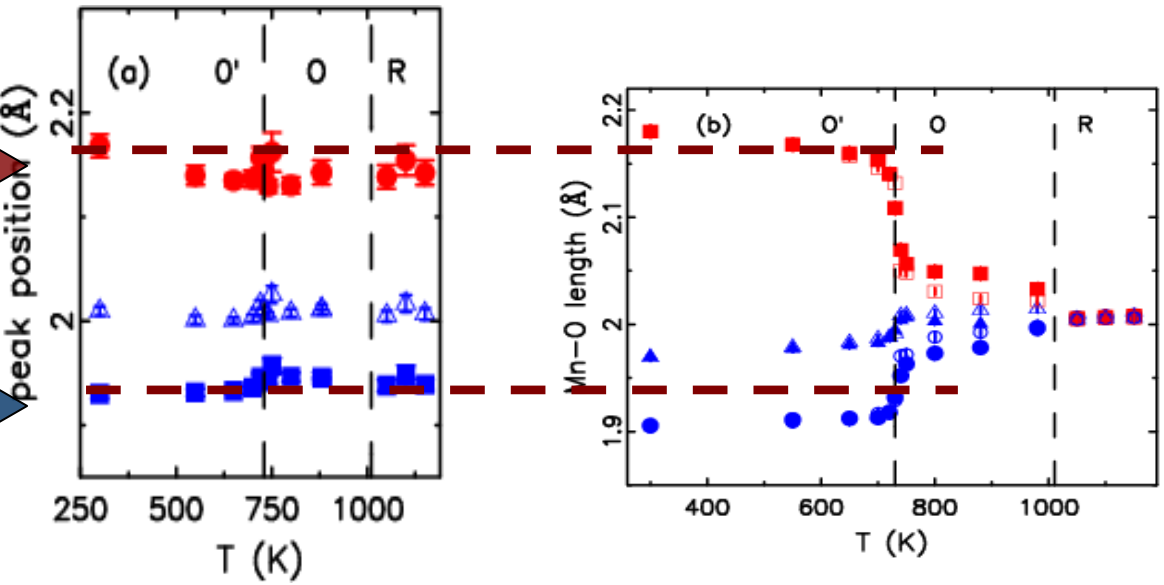
Strain



T-dependence of Mn-O bond distribution

Long-bonds

Short-bonds



Local structure

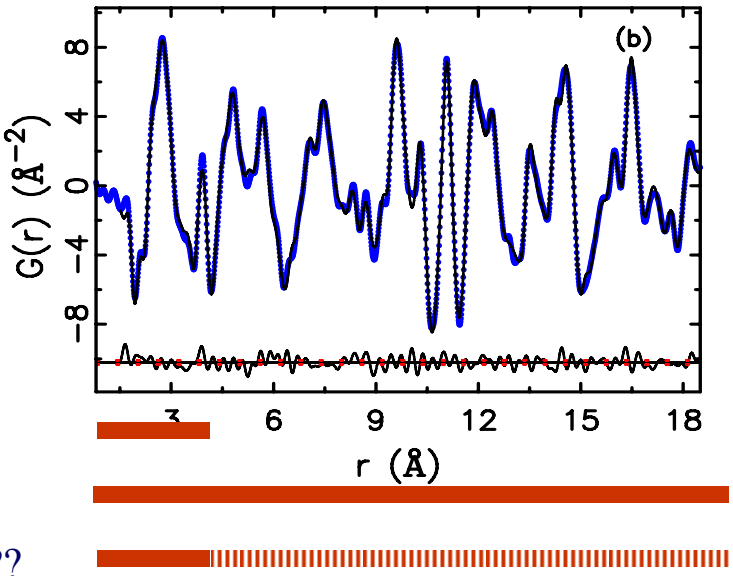
Average structure

- Mn-O bond lengths are invariant with temperature, right up into the R-phase

JT distortions persist locally in the pseudocubic and rhombohedral phases

Agrees with XAFS result: M.C. Sánchez *et al.*, Phys. Rev. Lett. **90**, 045503, (2003).

Crossover from local to average structure

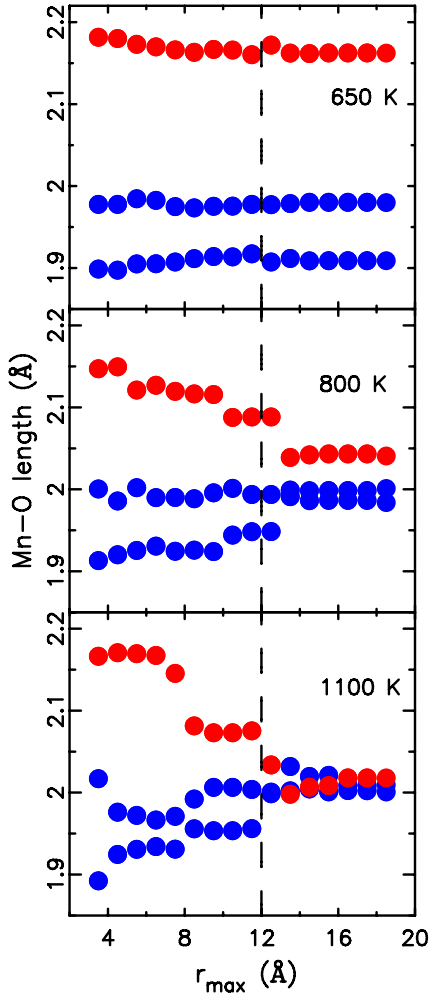


Local

Average

Intermediate???

- Varying range refinement
  - Fix r_{min}
  - Vary r_{max}
  - x axis is r_{max}

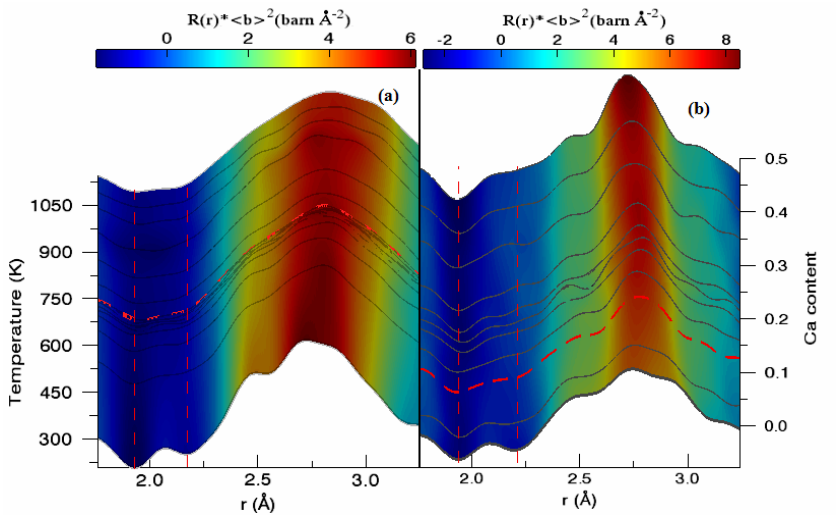


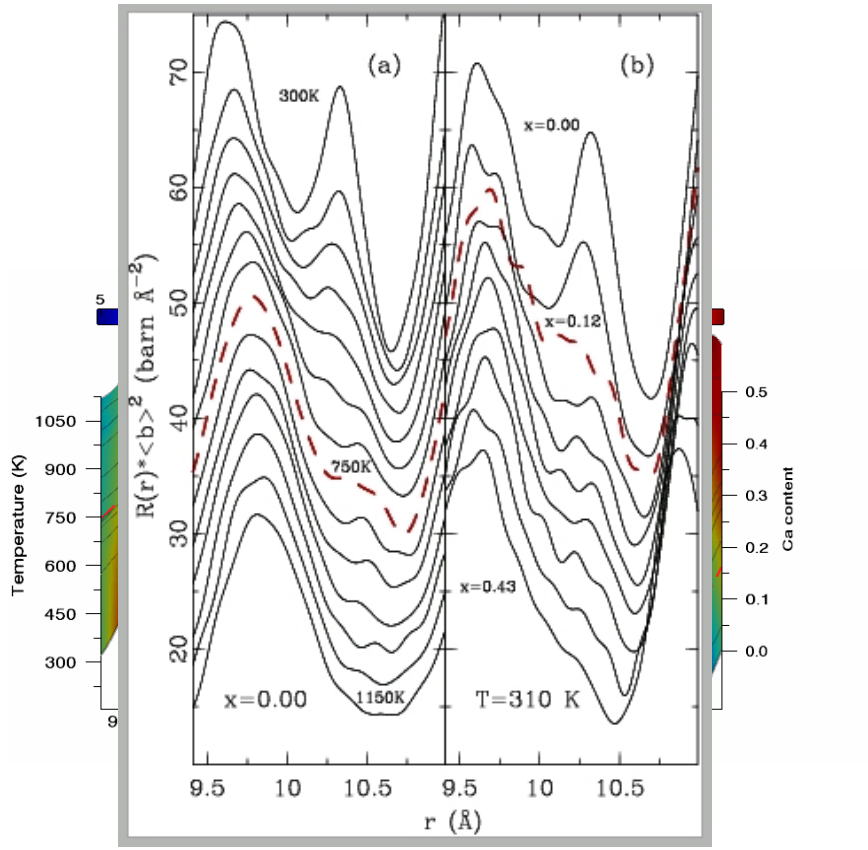
X. Qiu et al., Phys. Rev. Lett. **94**, 177203, (2005).

Nature of the O to O' phase transformation

Upon crossing the O-O' phase boundary, both along T and along x :

- JT-distortions persist locally (PDF features at ~2Å)
- PDF peaks sensitive to oxygen rotations change abruptly (features at ~10.3Å)





E.S. Božin *et al.*, Physica B, **385**, 110 (2006).