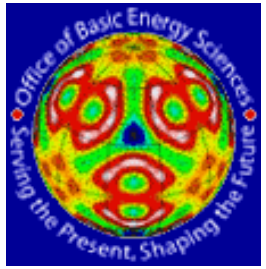
Search for hidden *LOCAL* broken symmetry states in correlated electron systems

S.J.L. Billinge

Department of Applied Physics and Applied Mathematics

Columbia University,

CMPMS, Brookhaven National Laboratory



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I will address the following questions:

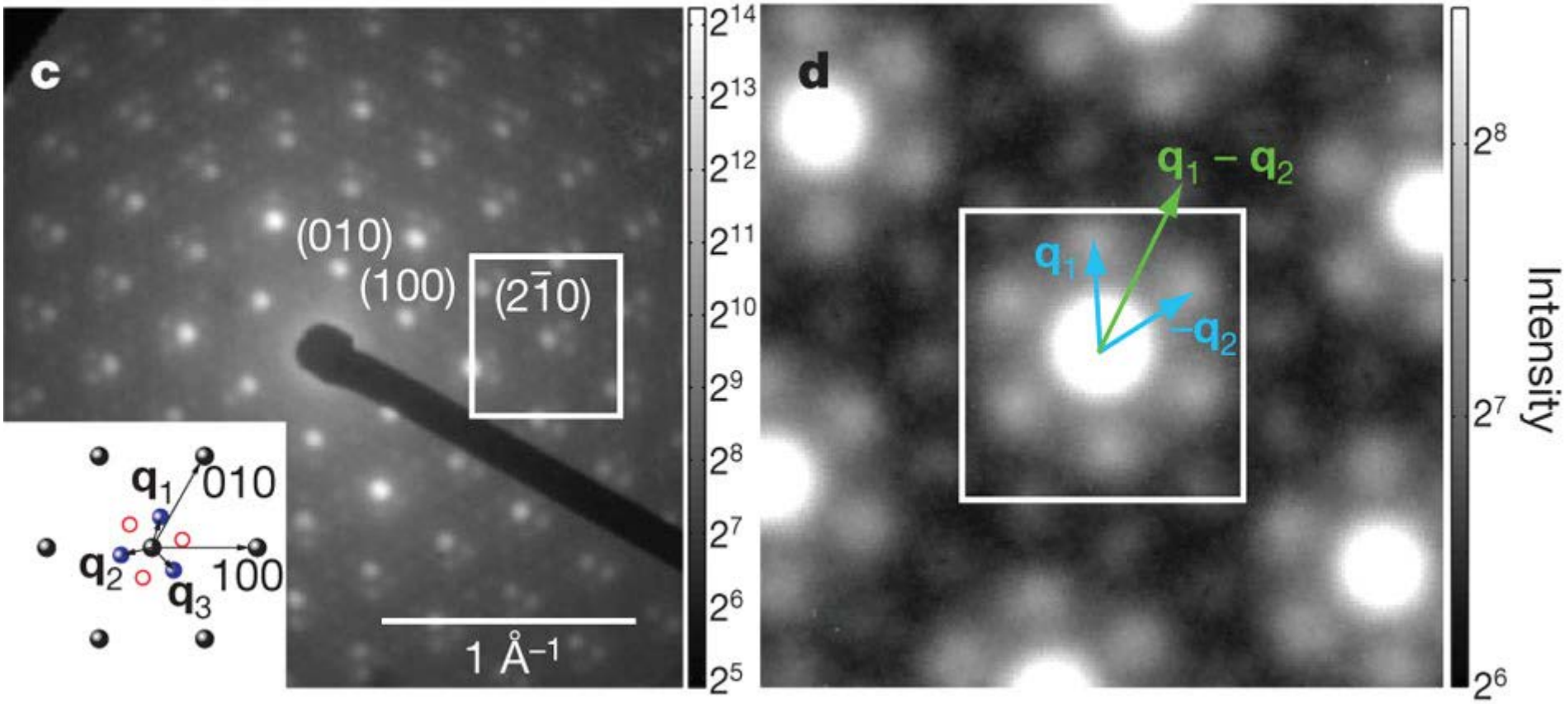
1. How can we detect and measure *LOCAL* broken symmetry electronic states in materials?

2. How ubiquitous are they?

3. How important are they?

How do we detect a global broken symmetry state?

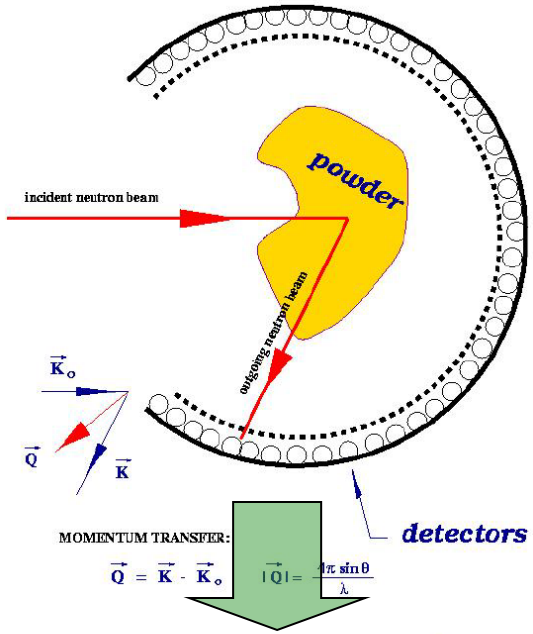
- New Bragg Peaks! E.g., CDW in 1T-TaS_2
- Eichberger etal Nature **468**, 799–802 (2010) doi:10.1038/nature09539
- Accompanying changes in transport/susceptibility/spectroscopy

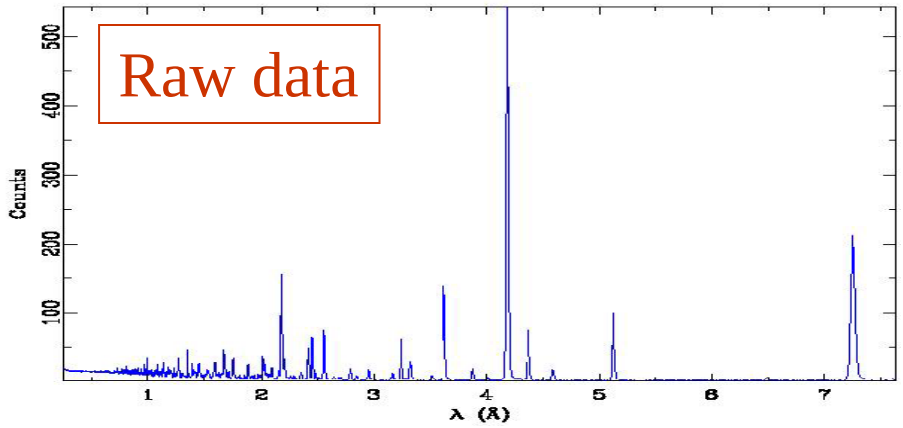


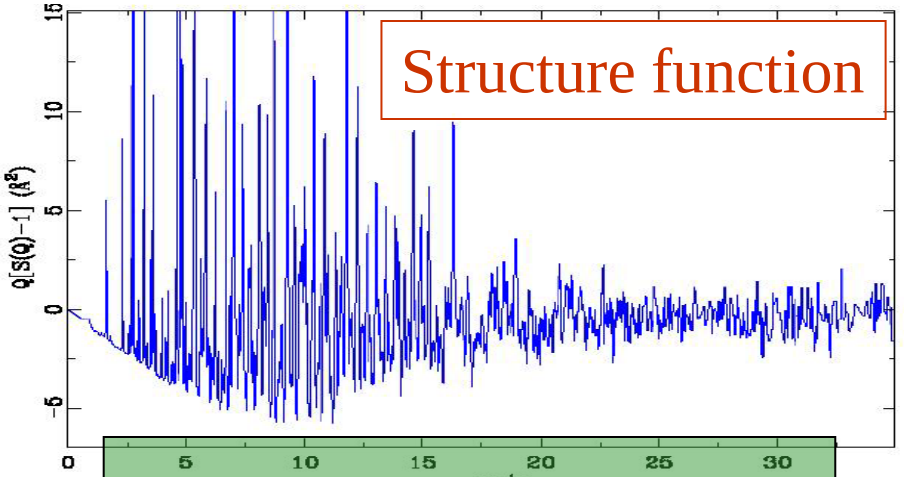
What happens if the broken symmetry state is only *short-range ordered*?

- Signal from the broken symmetry state is becomes diffuse
- Need a probe of local correlations
- Need to look for signals in measures of disorder in the material

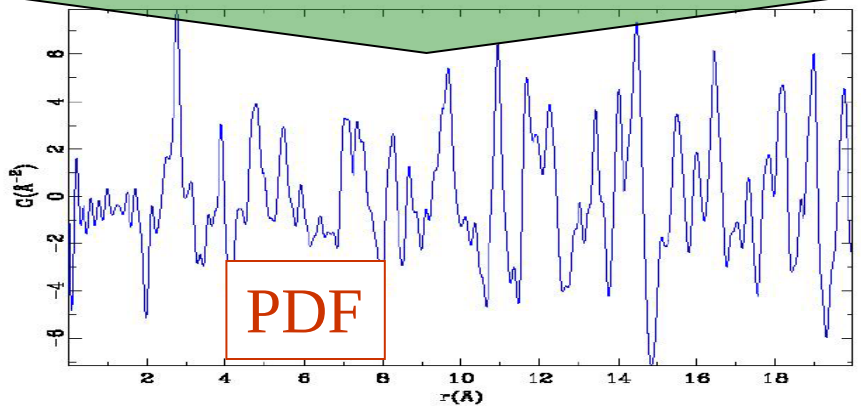
Obtaining the PDF



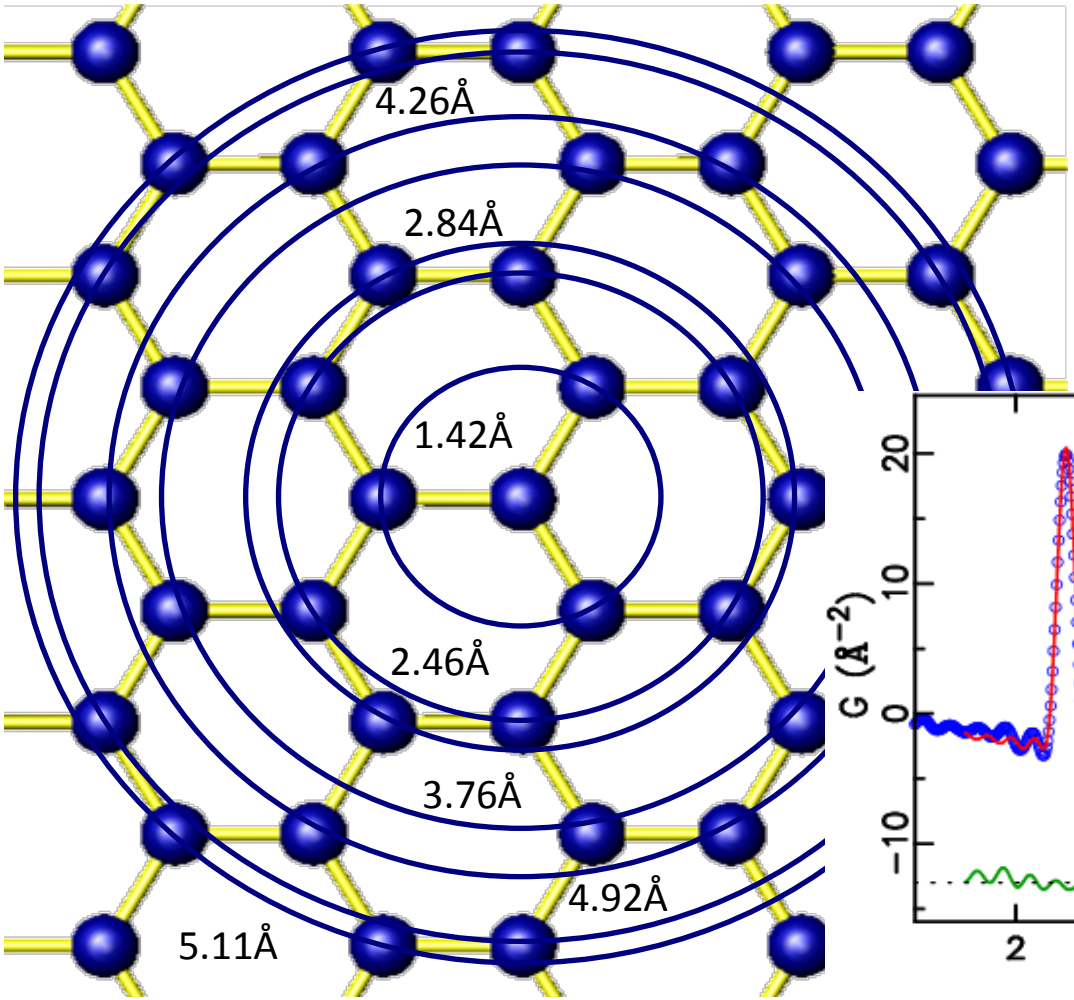




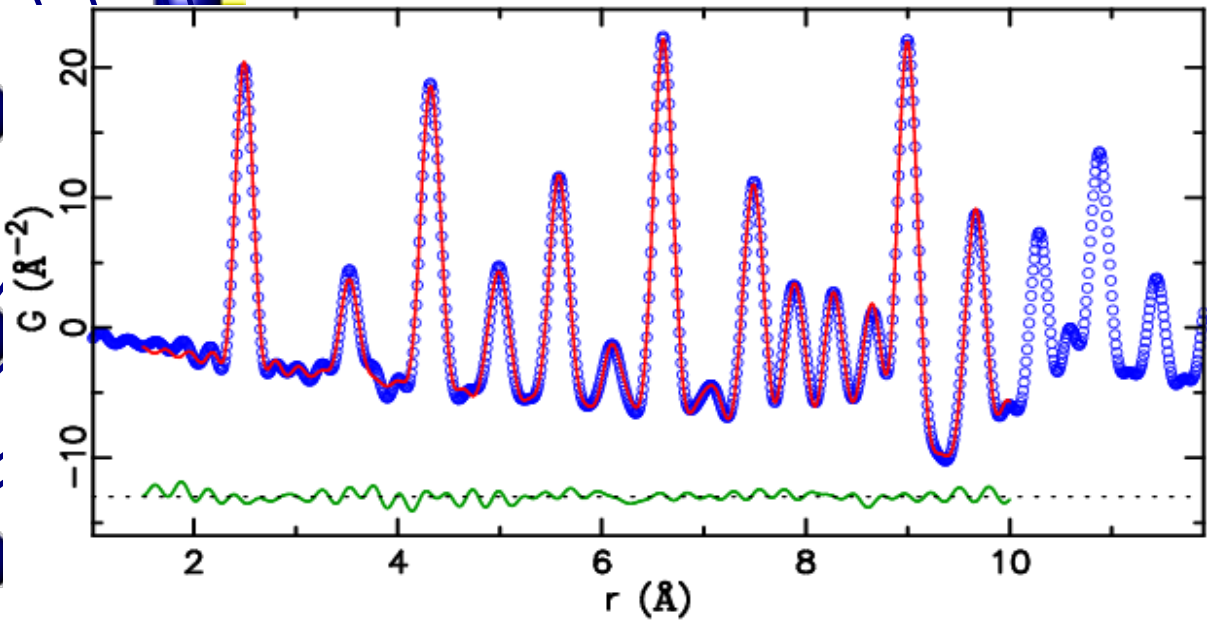
$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin QrdQ$$



Nanostructure refinement



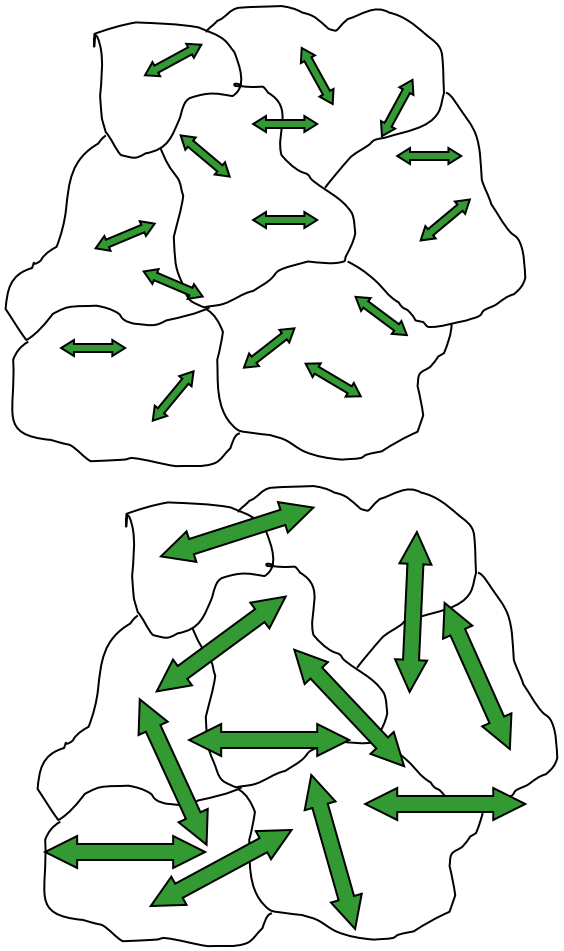
Pair distribution function (PDF) gives the probability of finding an atom at a distance “r” from a given atom.

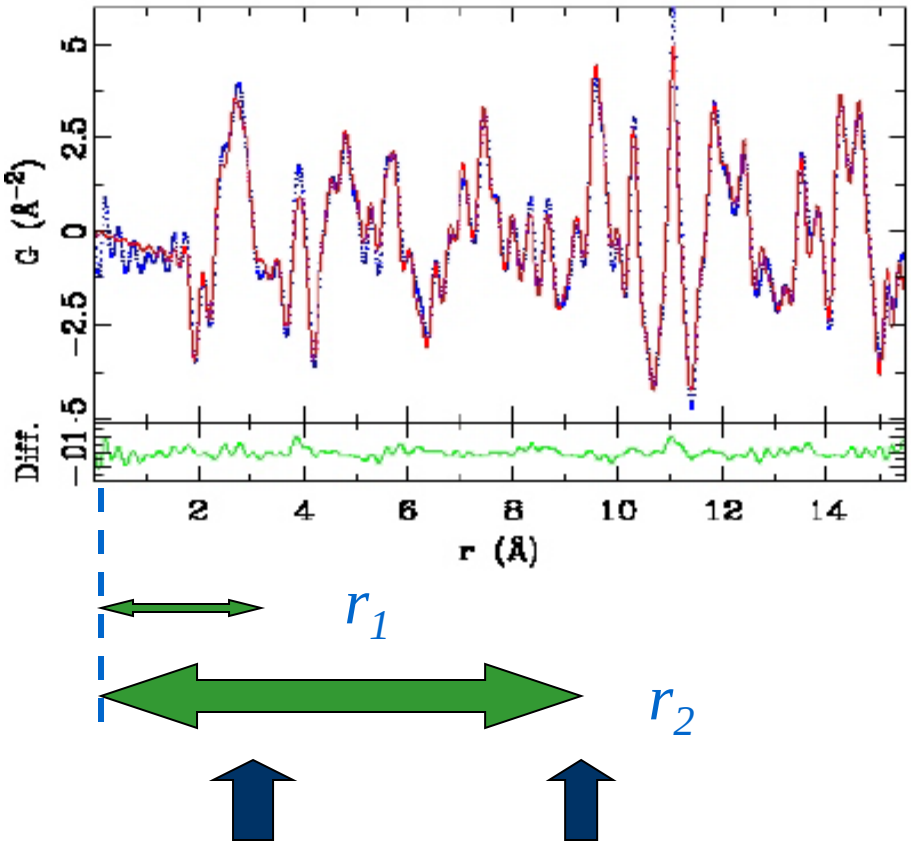


Observing Nanodomains in the PDF

$r_1 << \xi$

$r_2 \sim \xi/2$

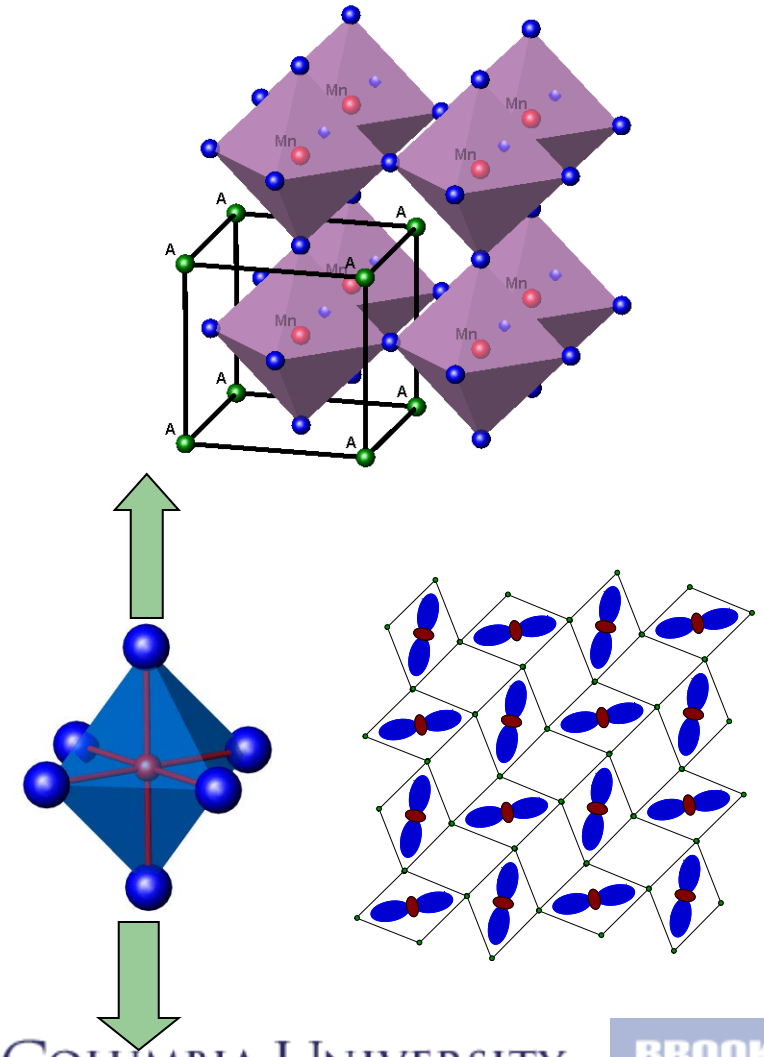




Intra-domain structure

Inter-domain structure

How is PDF sensitive to MI transition?

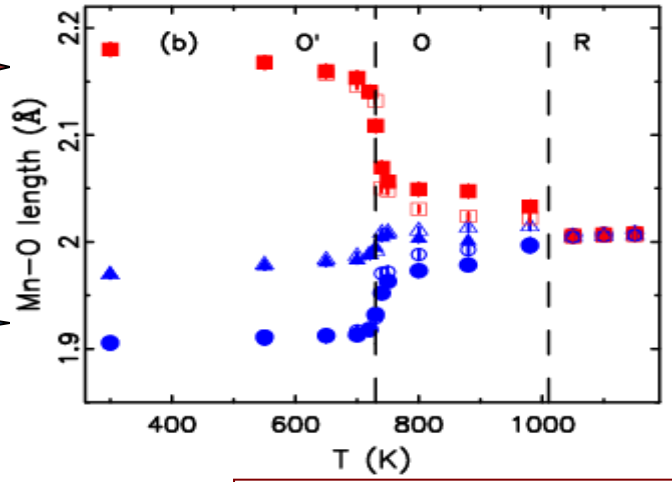


- Mn^{3+}: JT distorted octahedra:
  - 4 x ~1.94 A Mn-O bonds
  - 2 x 2.17 A Mn-O bonds
  - R_{long}-R_{short} = 0.23A
  - 8 long and 4 short O-O distances centered around 2.75A
- Mn^{4+}: undistorted octahedra:
  - 6 x ~1.94 A Mn-O bonds
- Delocalized holes: undistorted octahedra:
  - 6 x ~1.94 A Mn-O bonds

T-depence of Mn-O bond distribution

Long-bonds

Short-bonds



Average structure

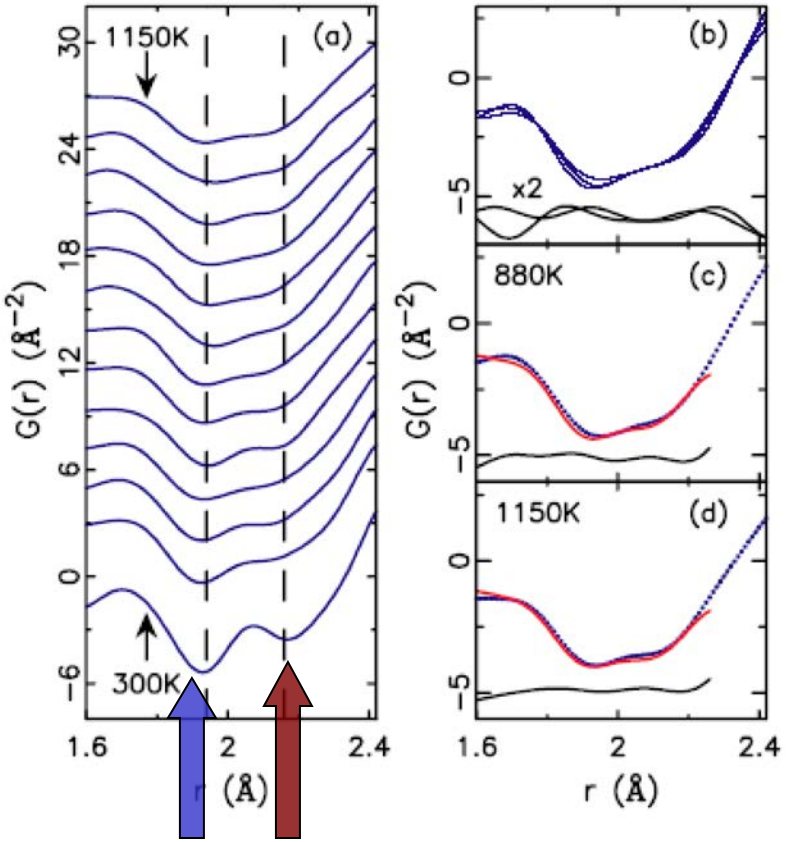
- Mn-O bond lengths are invariant with temperature, right up into the R-phase

JT distortions persist locally in the pseudocubic phase

Xiangyun Qiu, Th. Proffen, J. F. Mitchell and S. J. L. Billinge, *Phys. Rev. Lett.* **94**, 177203 (2005).

Agrees with XAFS result: M. C. Sanchez et al., PRL (2003).

Example: orbitally disordered phase in $La_{1-x}Ca_xMnO_3$



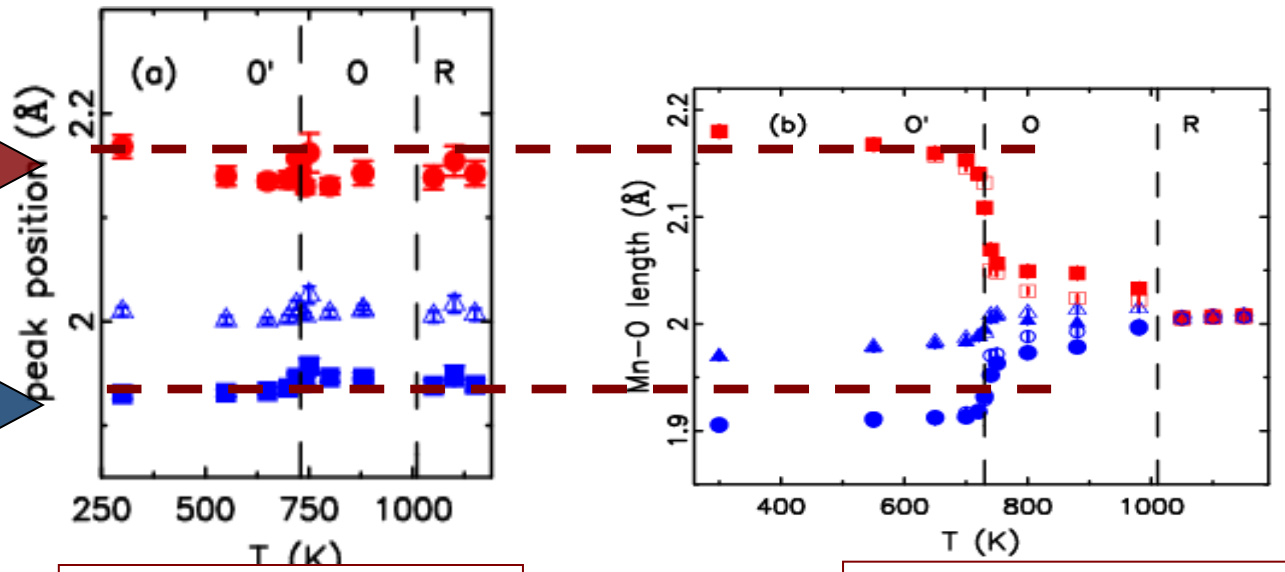
Local structure: JT distorted
Average structure: no JT distortion
=> Domains of local JT order

From Qui X., Proffen Th., Mitchell J. and Billinge S.J.L.
PRL, 94, 177203 (2005).

T-depence of Mn-O bond distribution

Long-bonds

Short-bonds



Local structure

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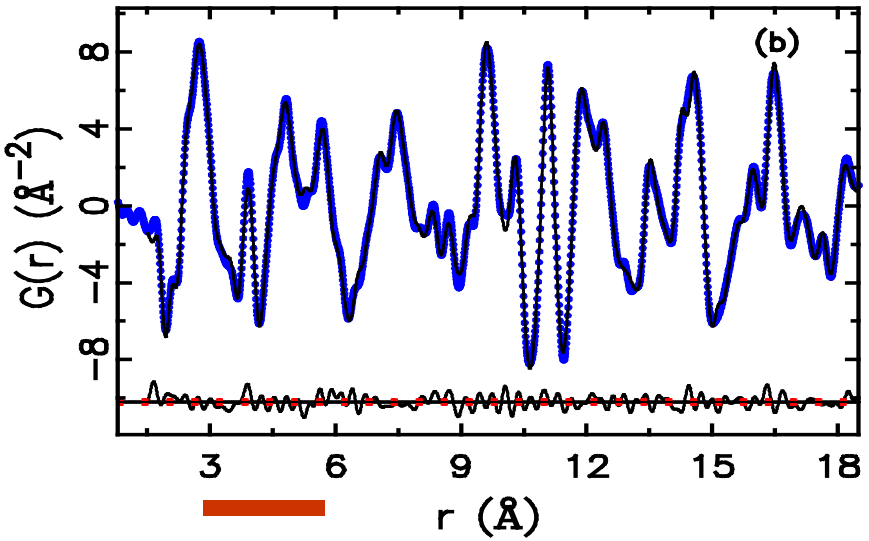
Crossover from local to average structure

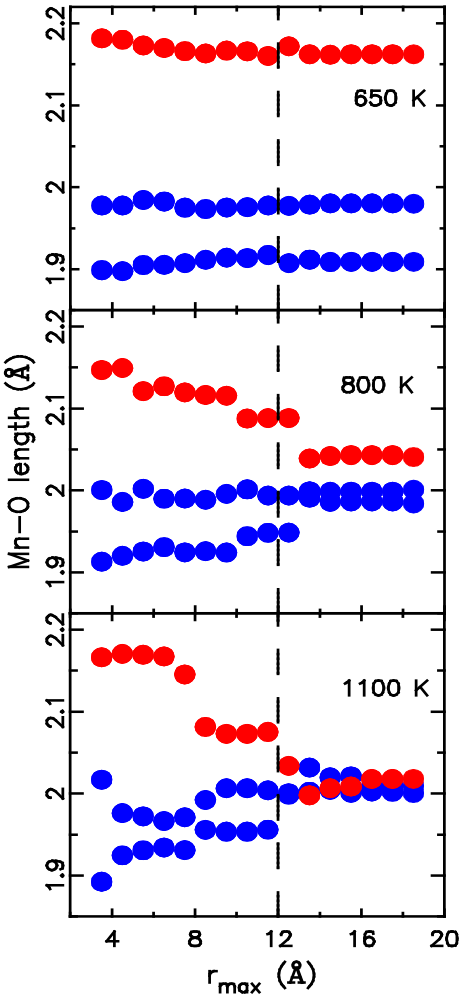


Local

Average

Intermediate???

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

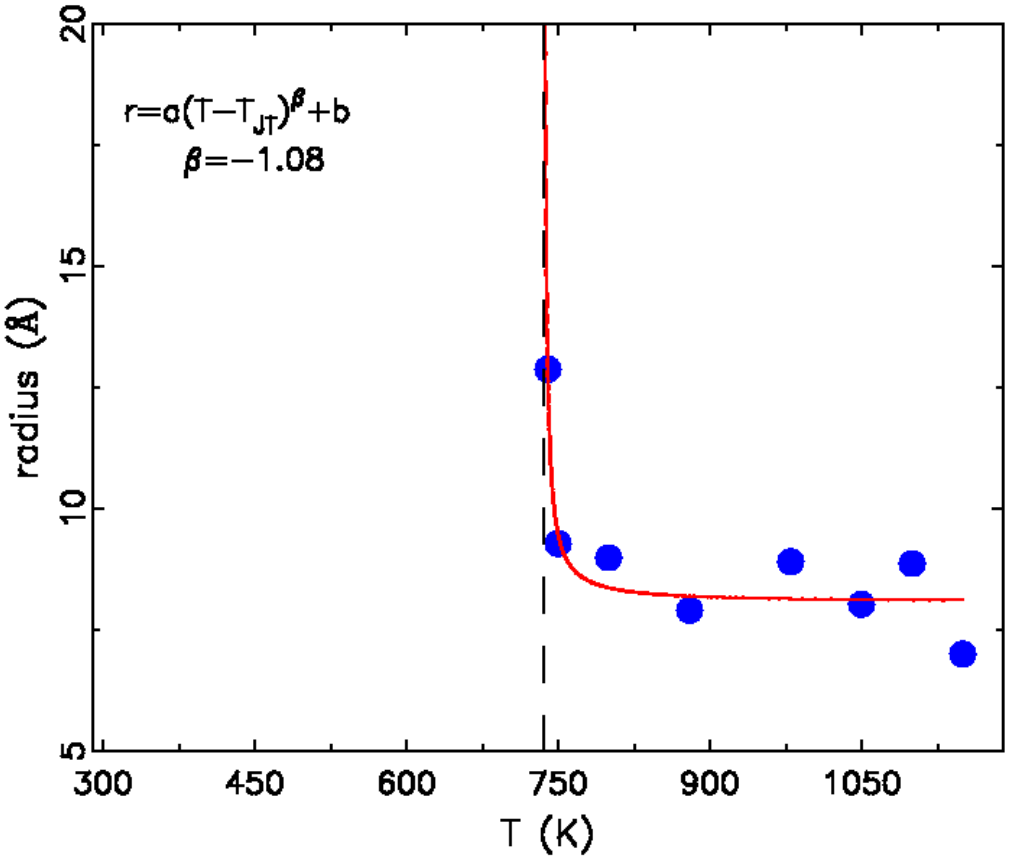


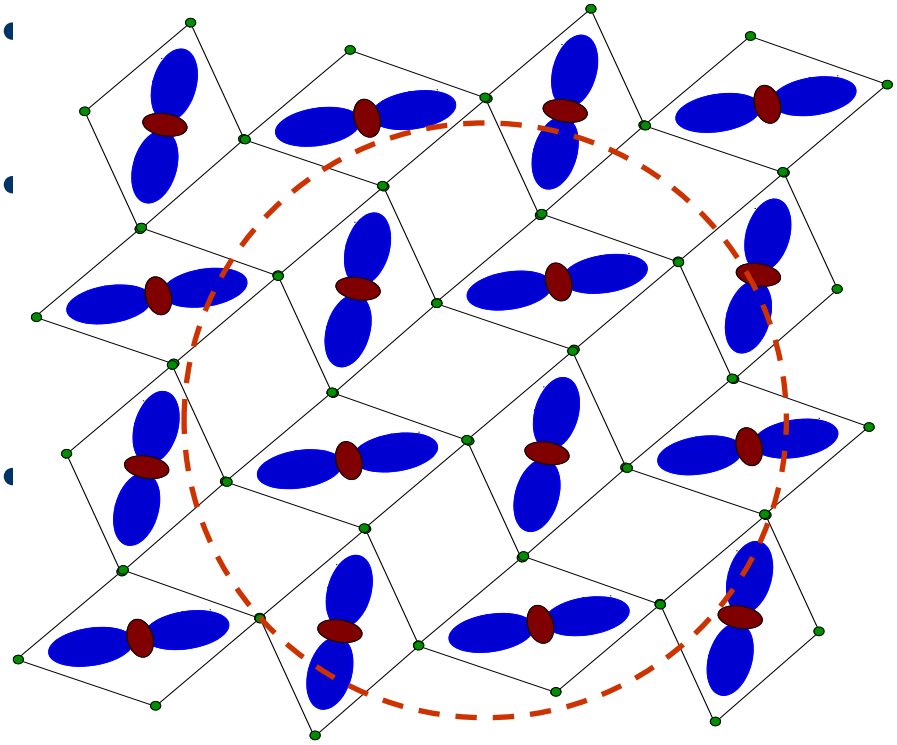
O

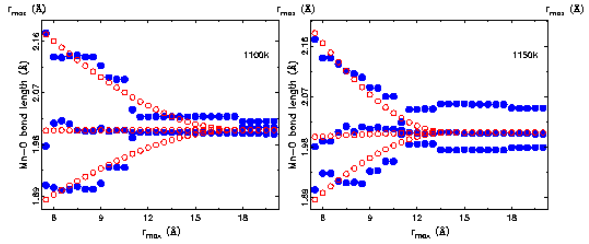
O'

R

R-dependent fits vs T

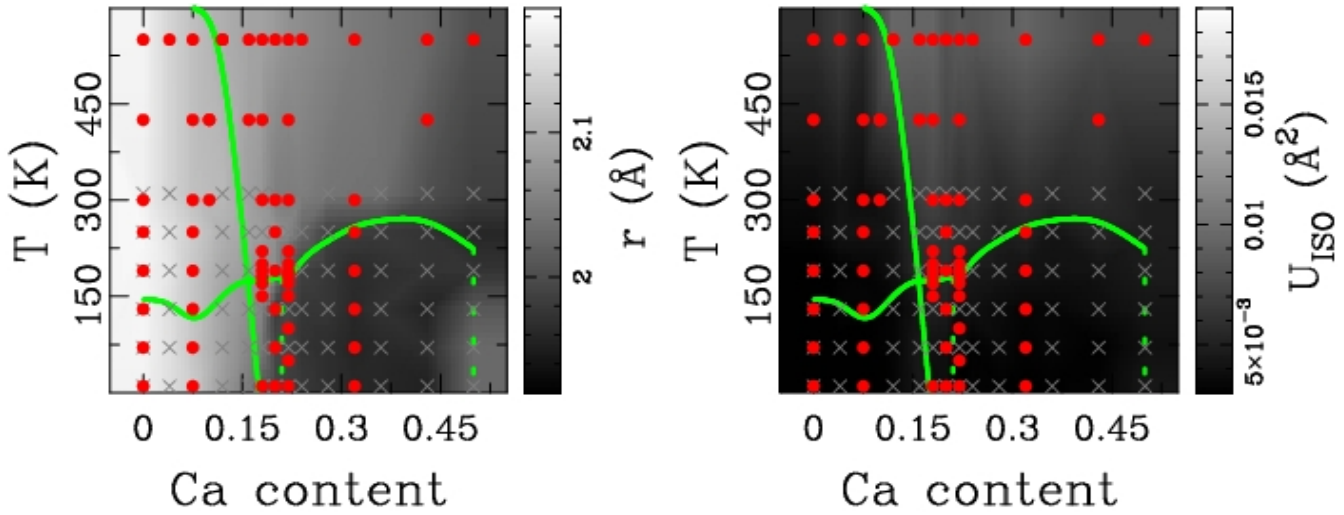






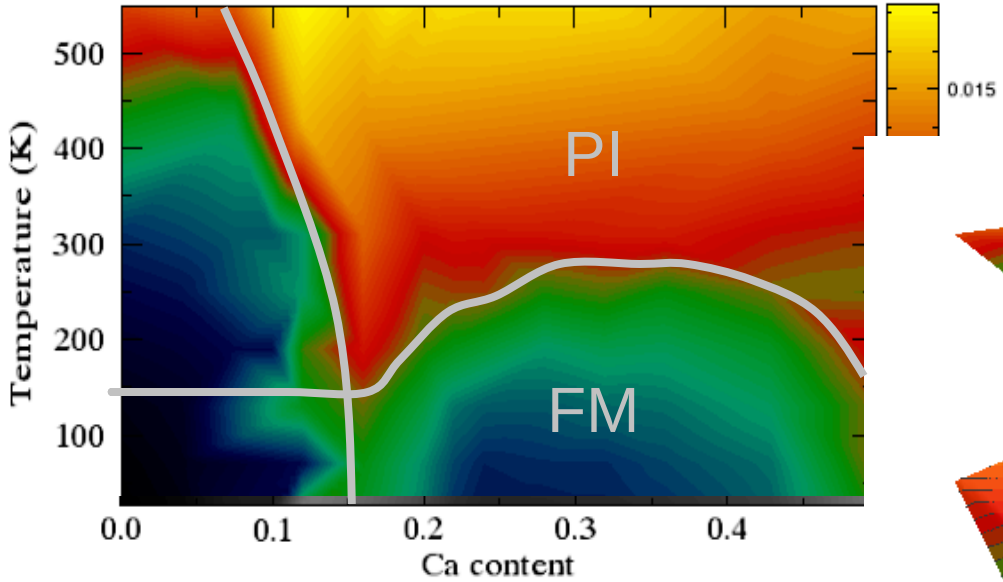
$$f\left(r,d\right)=\left[1-\frac{3r}{2d}+\frac{1}{2}\left(\frac{r}{d}\right)^{3}\right]\Theta(d-r)$$

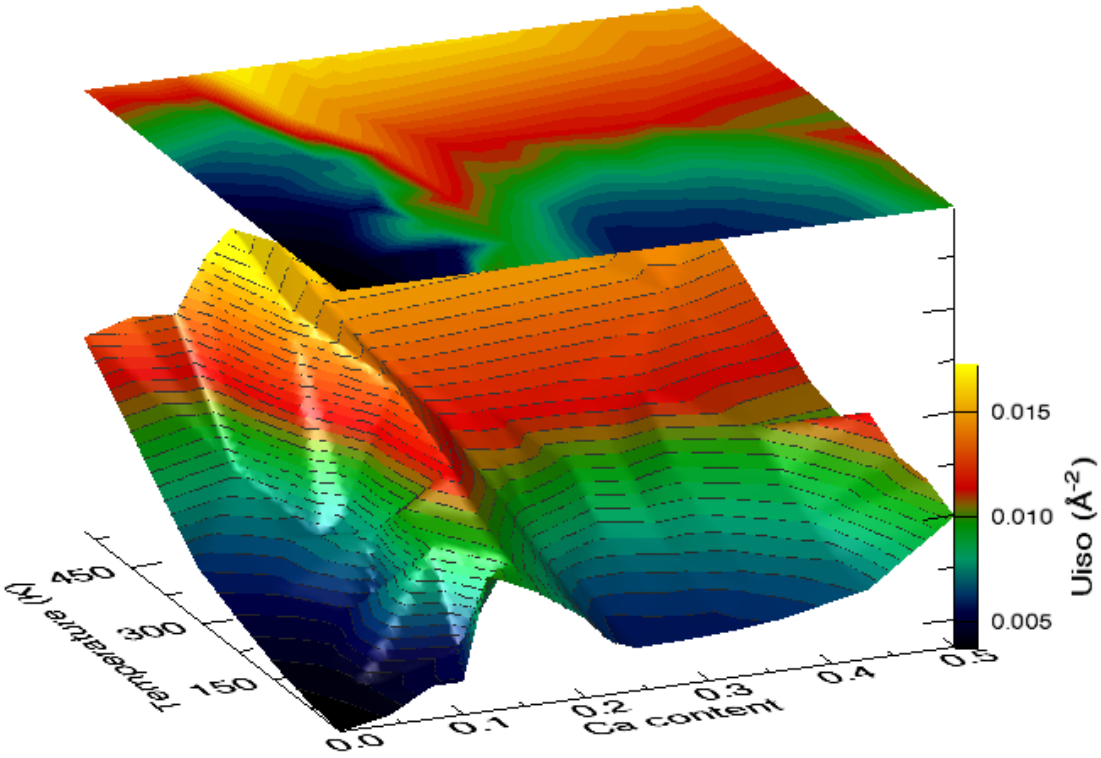
$La_{1-x}Ca_xMnO_3$ and colossal magnetoresistance



- Key point is that understand colossal magnetoresistance, we need many data points throughout the phase diagram.
- High throughput local structural studies!

Remarkable dataset: Phase diagram emerges from single refined parameters





- Phase diagram draws itself from the parameters
- Unexpected detail emerges and demands interpretation

Summary

- Using PDF we can see structural response to charge-symmetry breaking
- Can see it when it *short*- or *long*-range ordered
- Can detect the structure/symmetry of the local distortions
- Can measure the size
- Effect never shrinks to a single-site, presumably due to strain
- Can map the effects out vs. T and doping

Case study #2: Dimers in $CuIr_2S_4$

Why is it interesting?

1. Frustration

2. Metal-insulator transitions

3. Carrier localization and broken symmetry states at low-temperature

4. Signal from broken symmetry state is large (colossal)!

$CuIr_2S_4$, Why is it interesting?

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Spinel structure

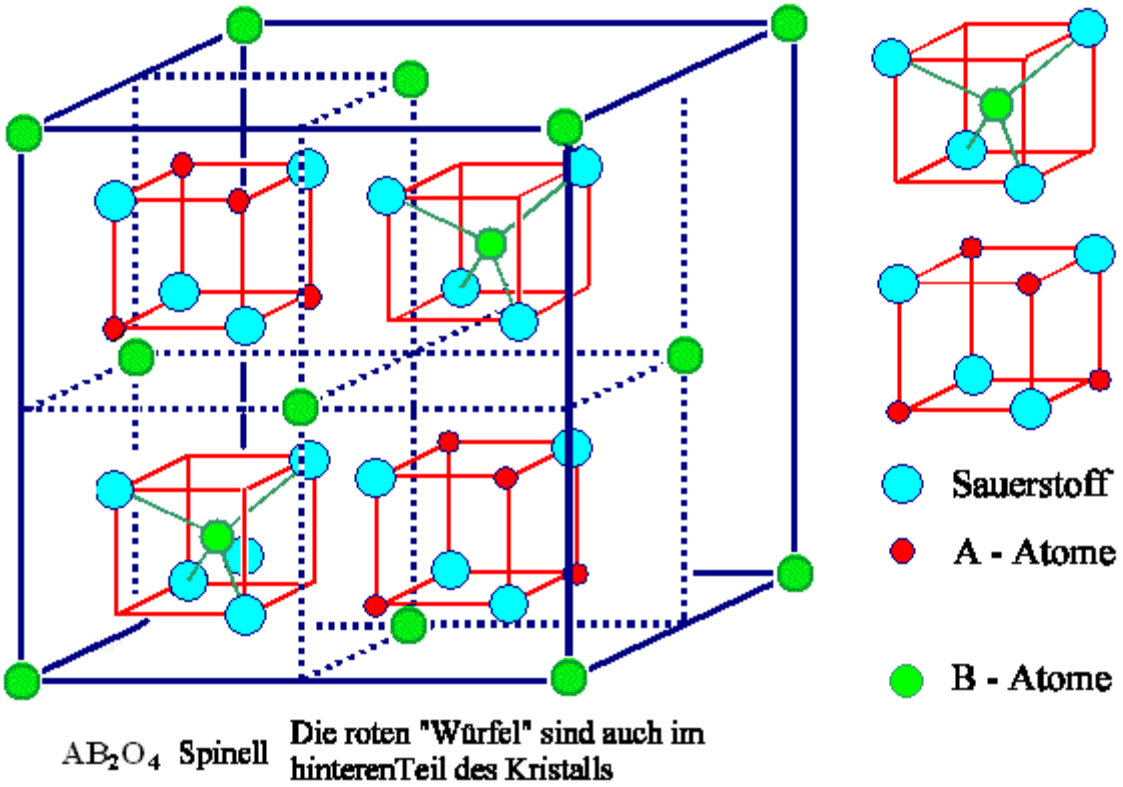
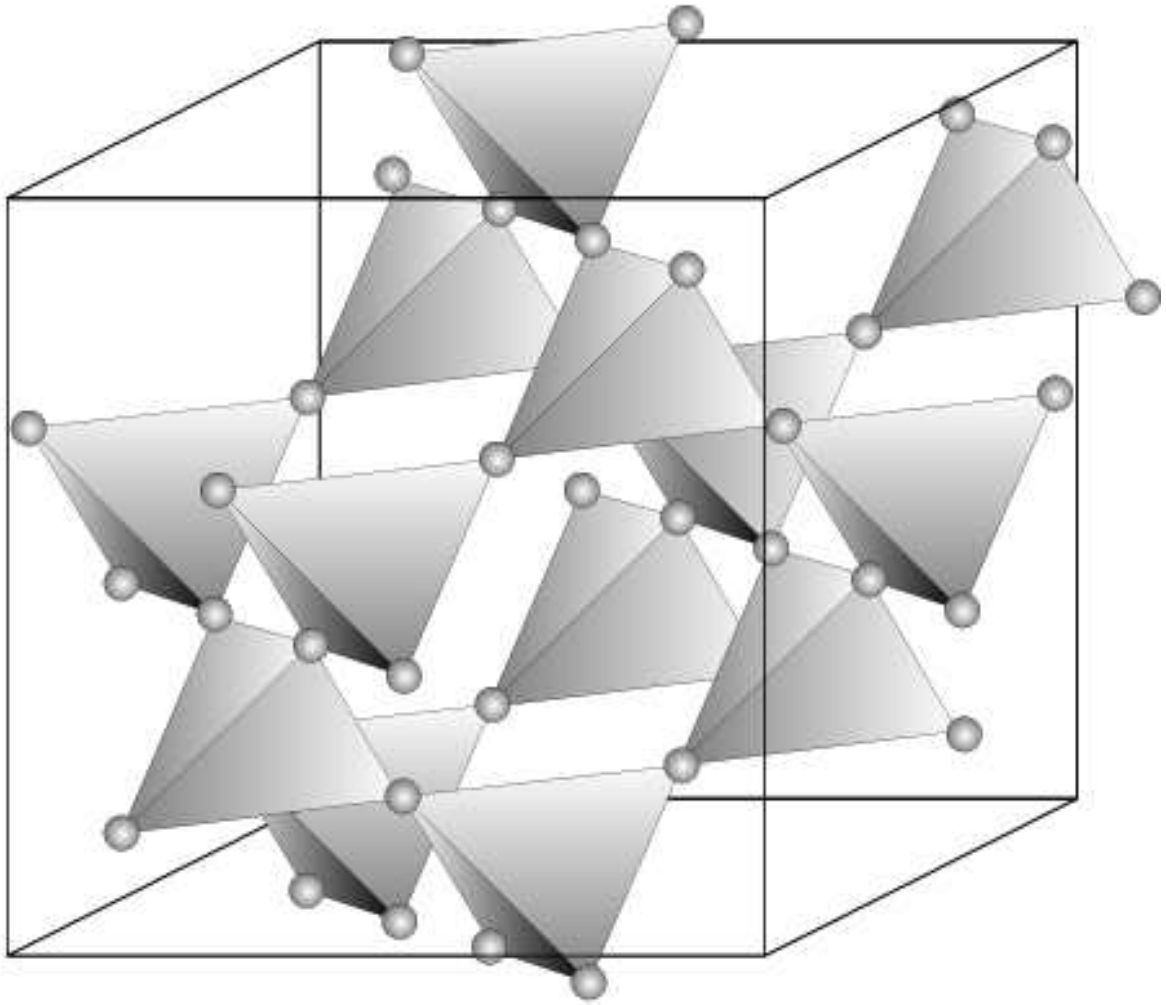
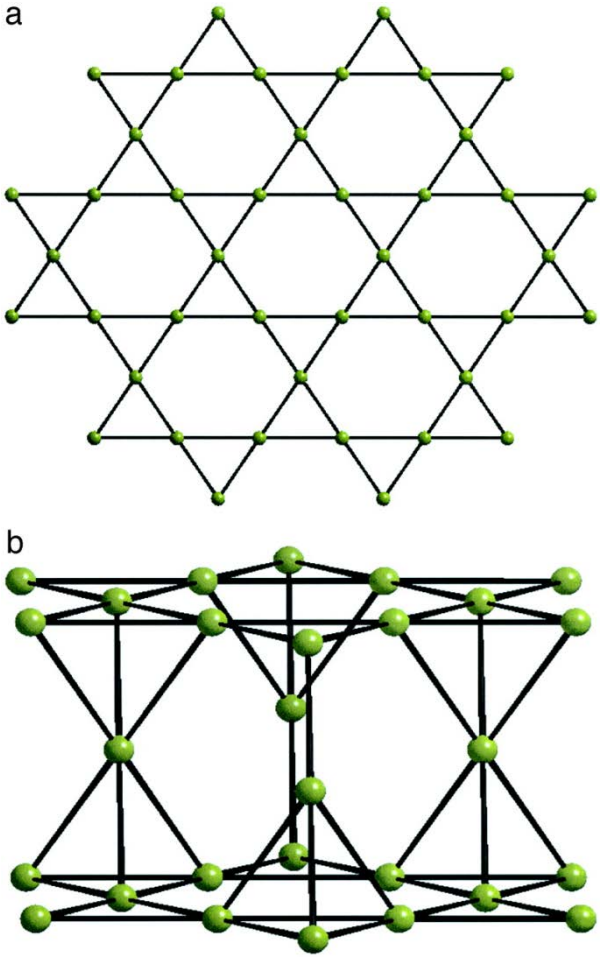


Image credit: http://www.tf.uni-kiel.de/matwis/amat/def_en/kap_2/basics/b2_1_6.html

But the B atoms form a pyrochlore lattice of corner shared tetrahedra => frustration





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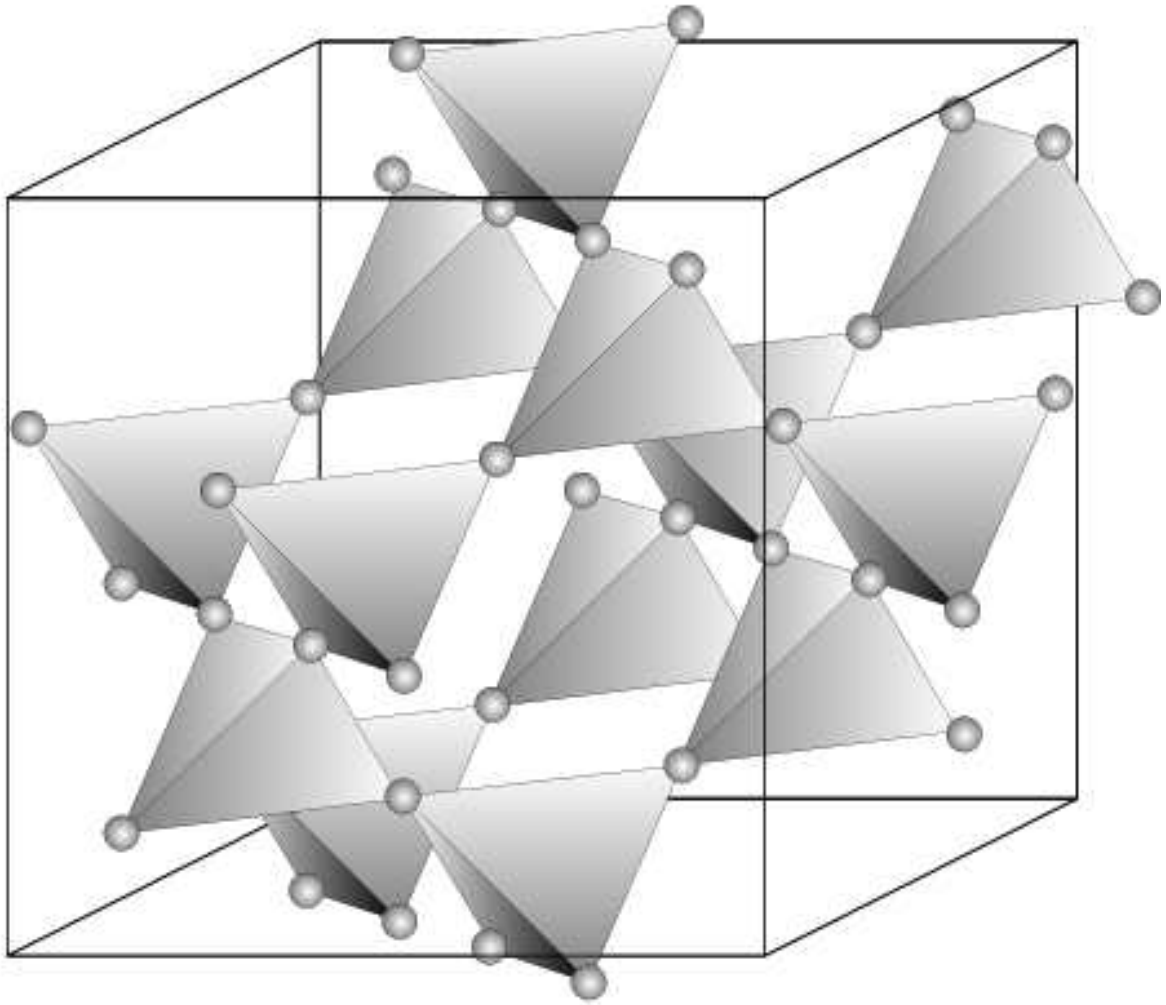
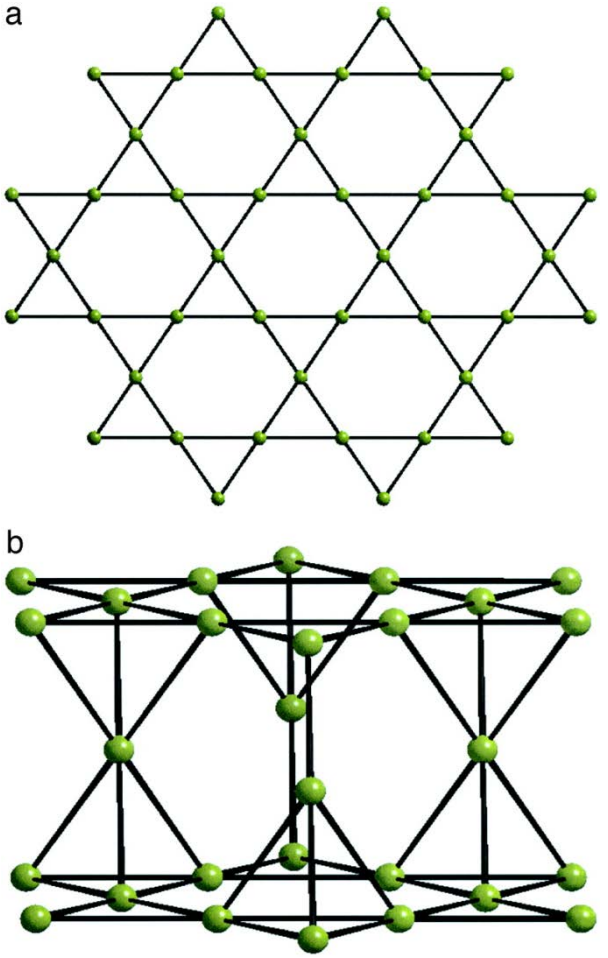
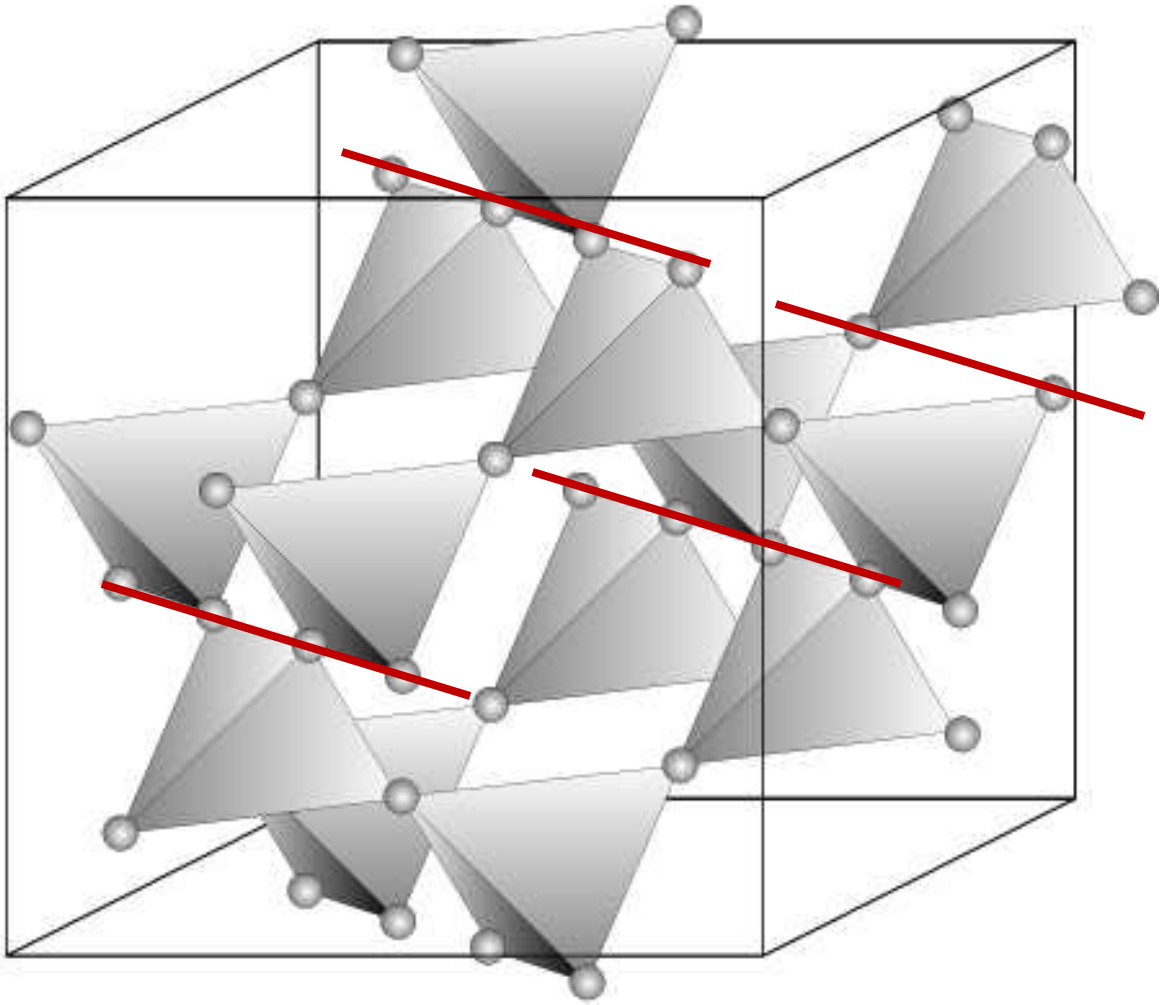




But the B atoms form a pyrochlore lattice of corner shared tetrahedra => low dimensional physics!



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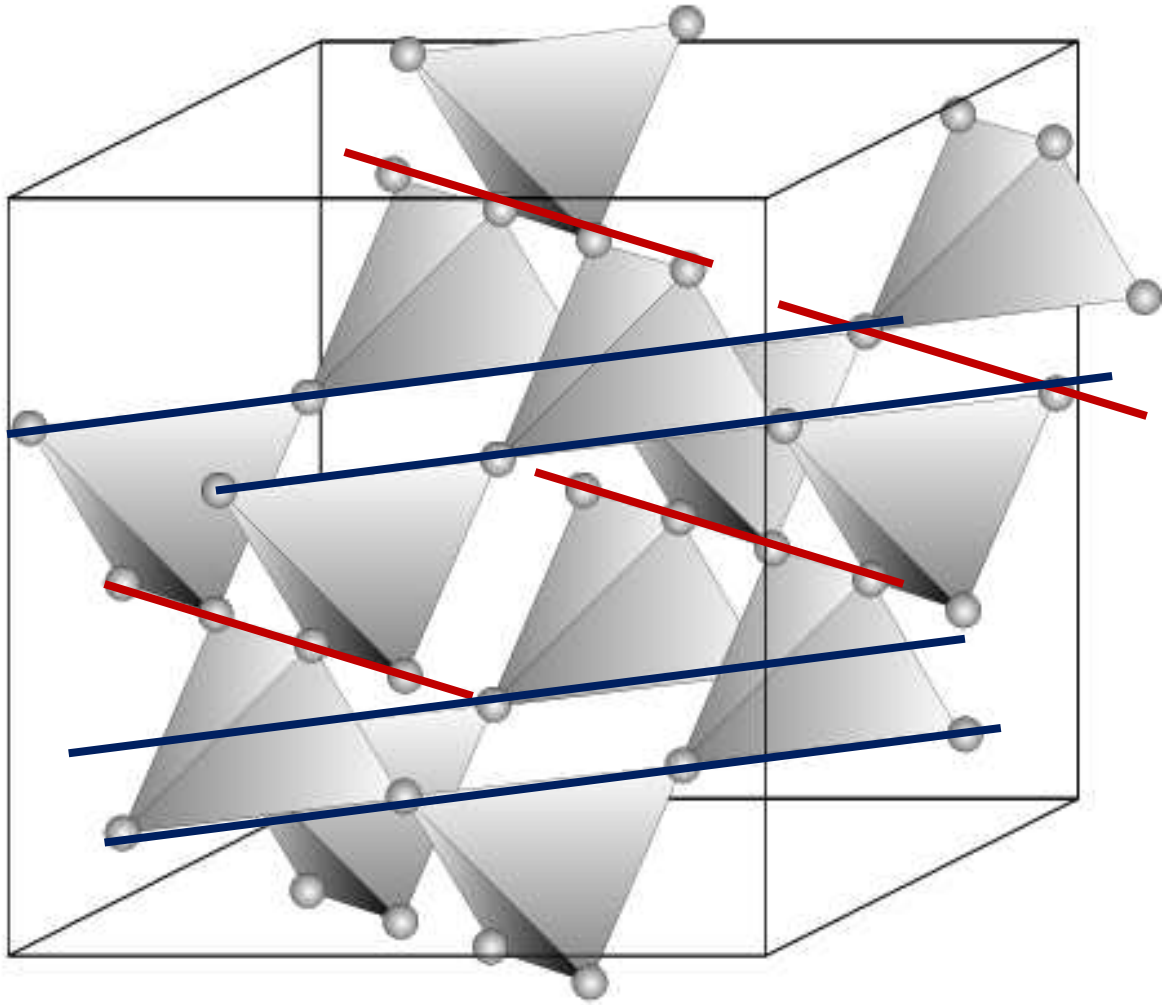

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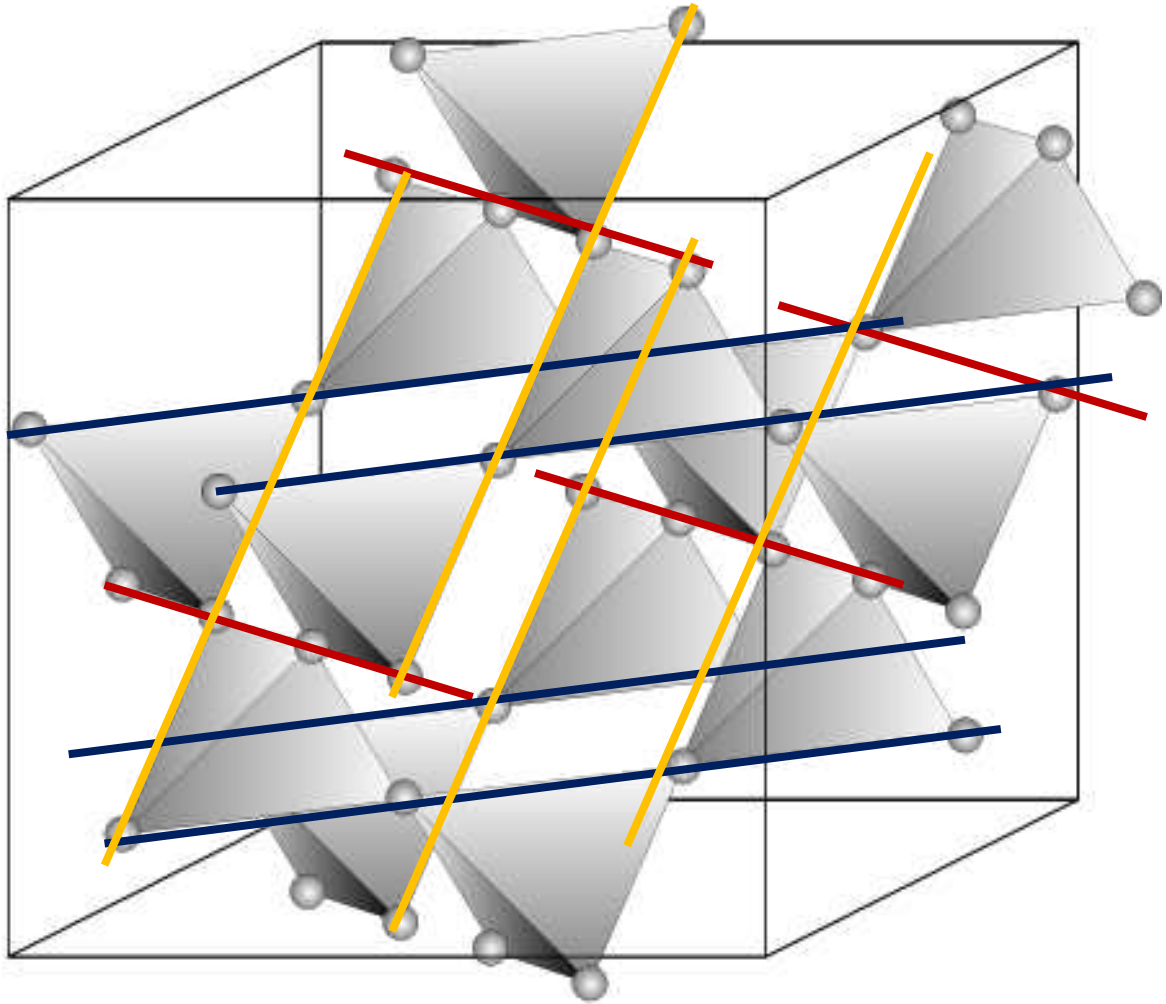
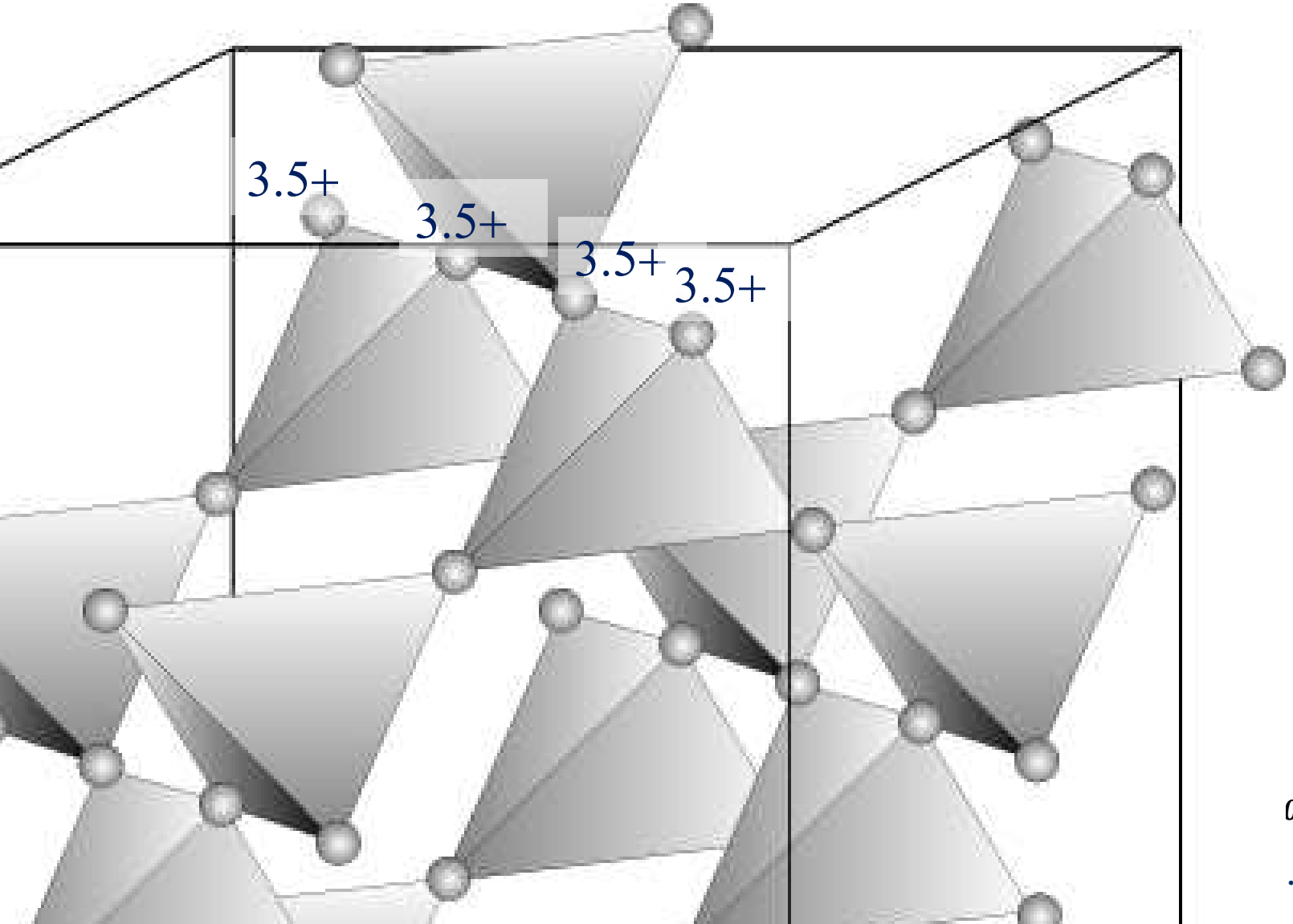
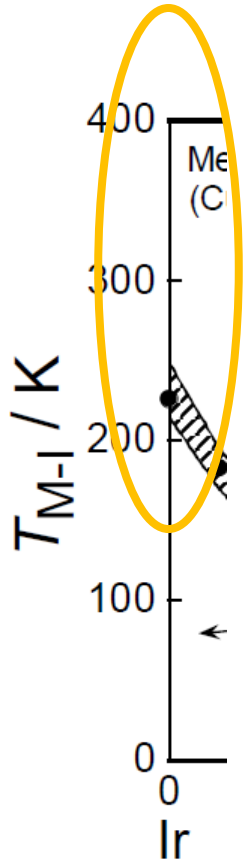


$CuIr_2S_4$





05).

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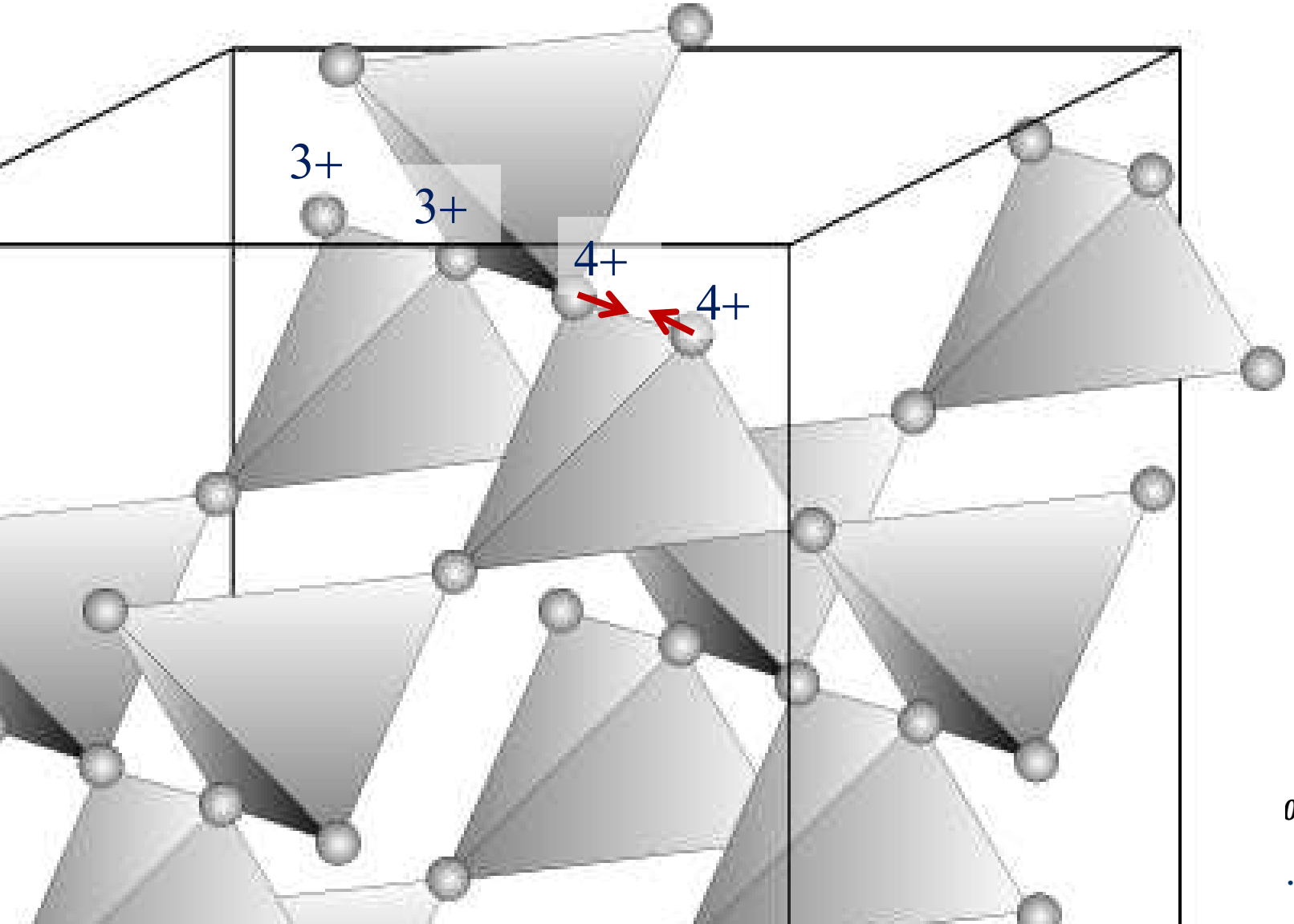
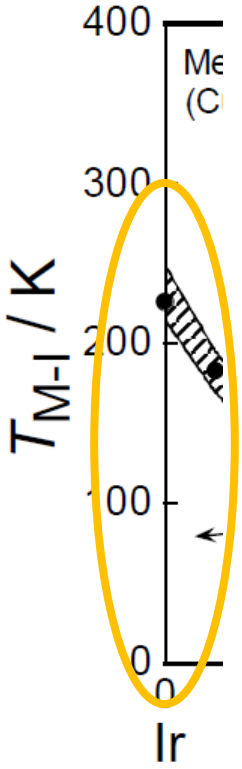
$CuIr_2S_4$





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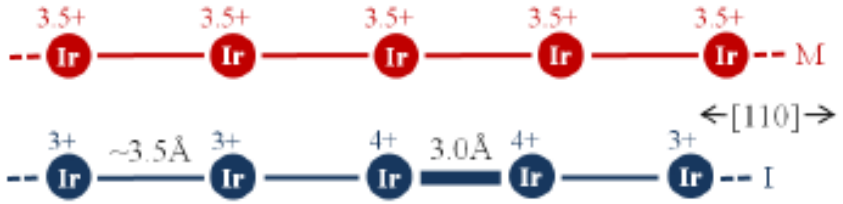
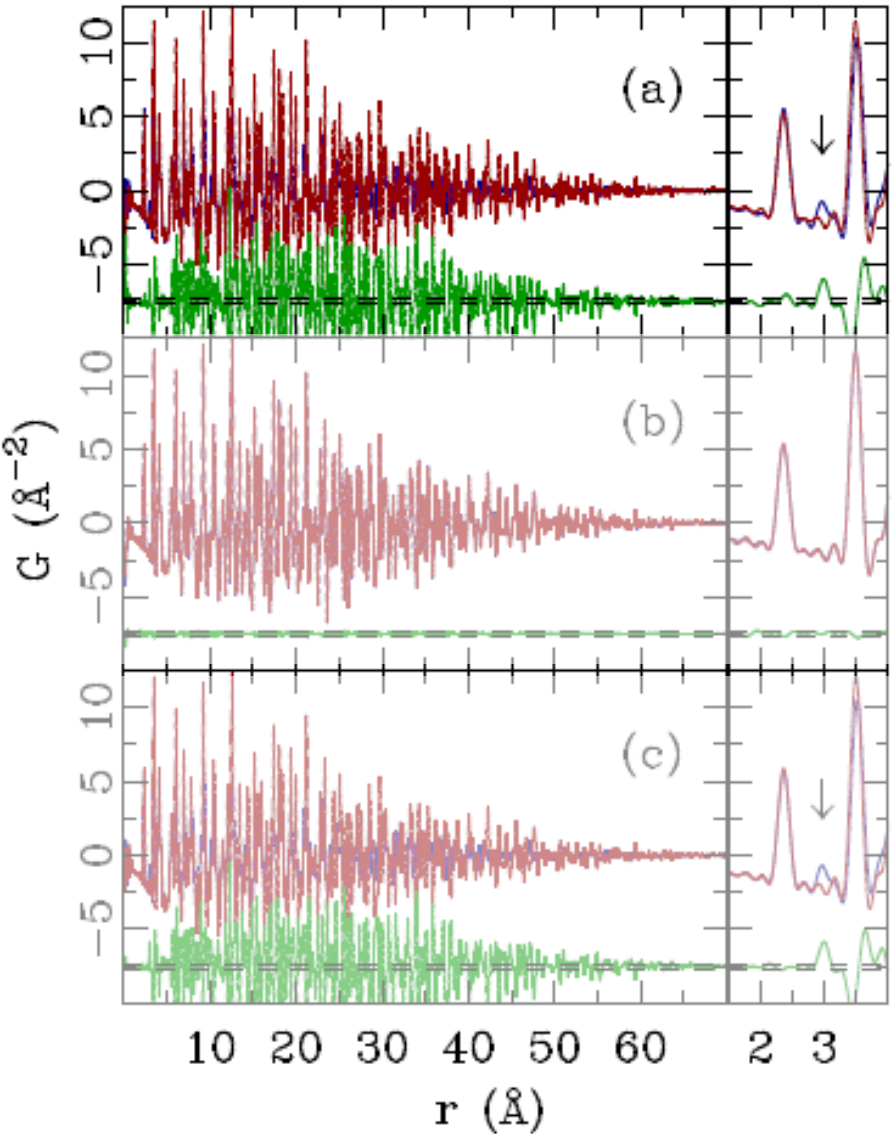
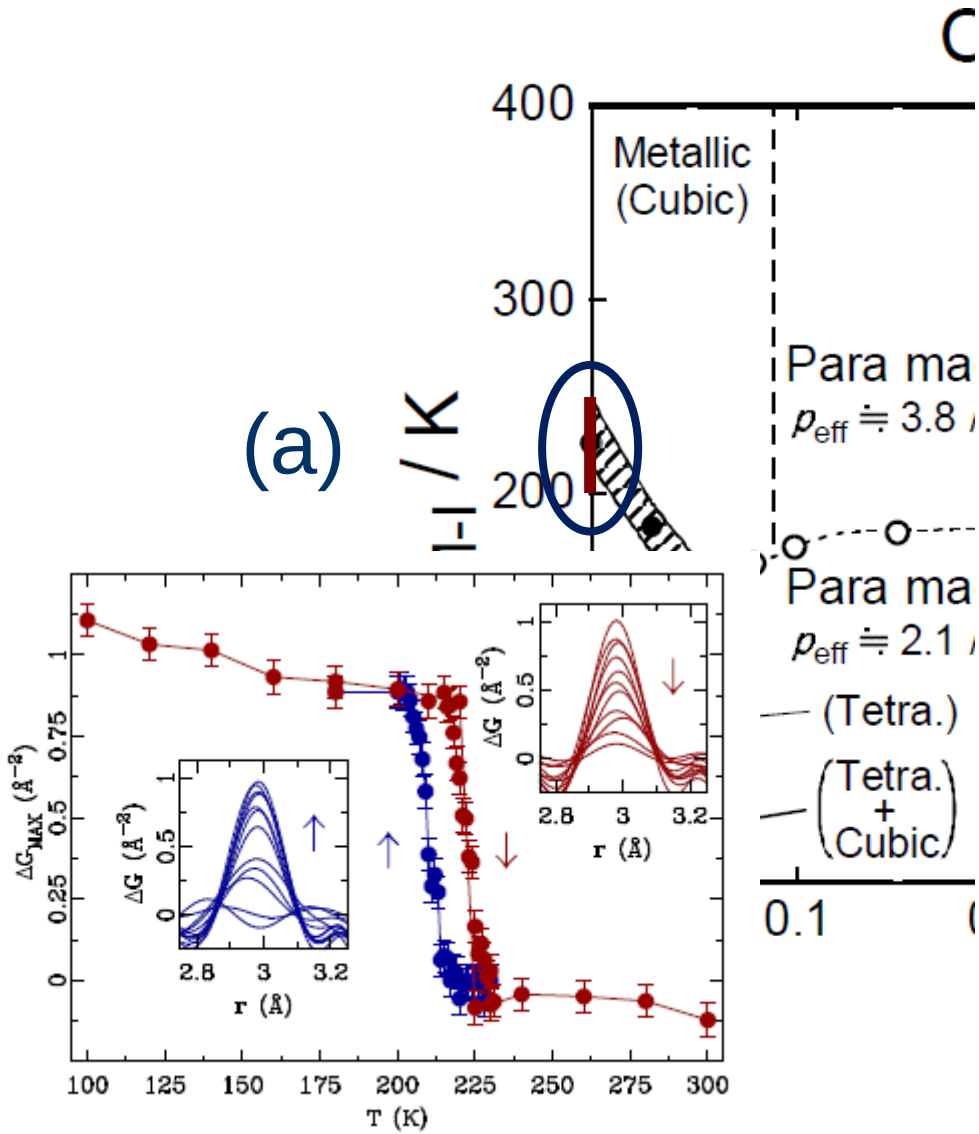
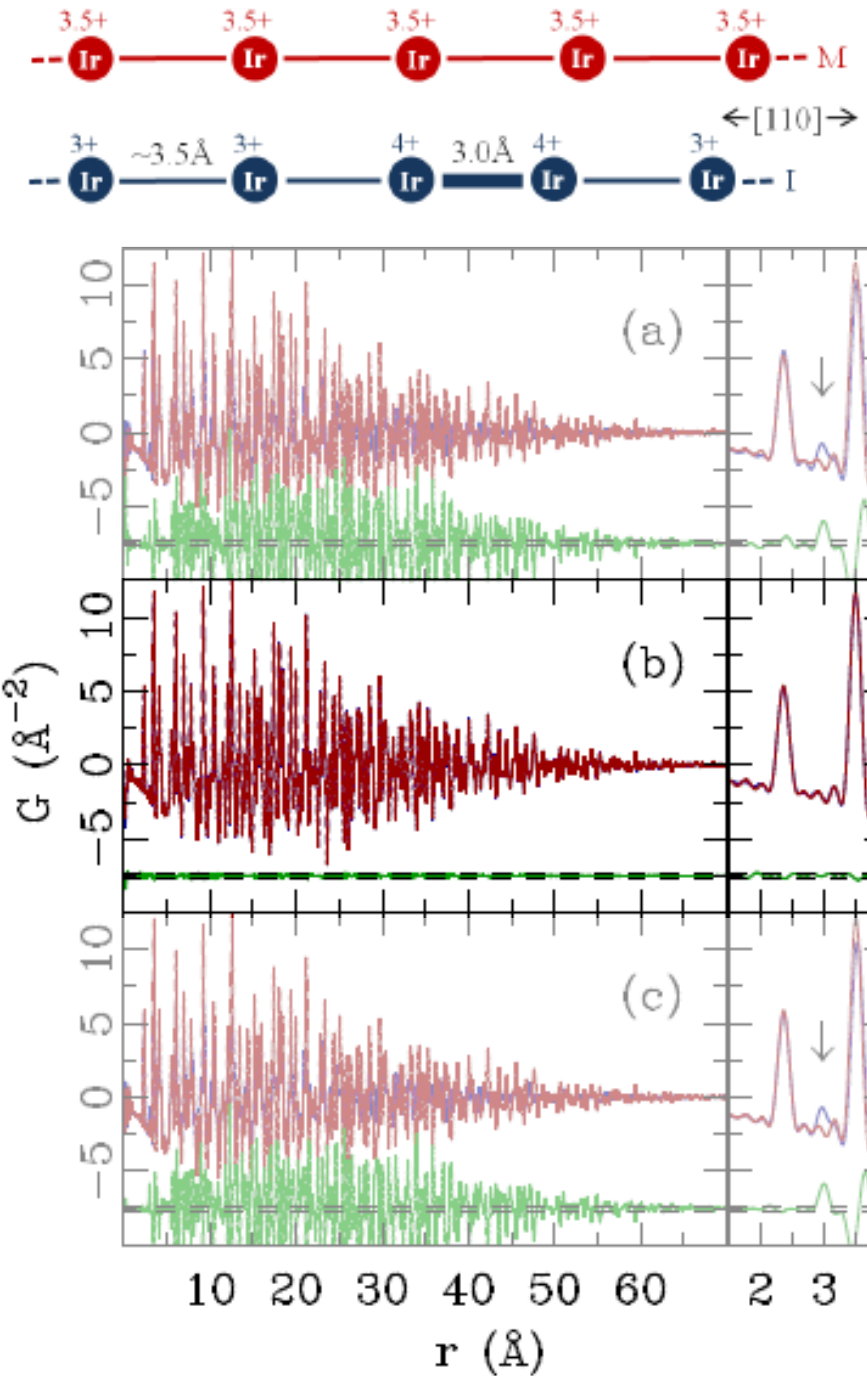

3.5+
Ir
M
←[110]→
3+
~3.5Å
4+
3.0Å
I


(a)
(b)
(c)
G (Å^{-2})
10 20 30 40 50 60
2 3
r (Å)

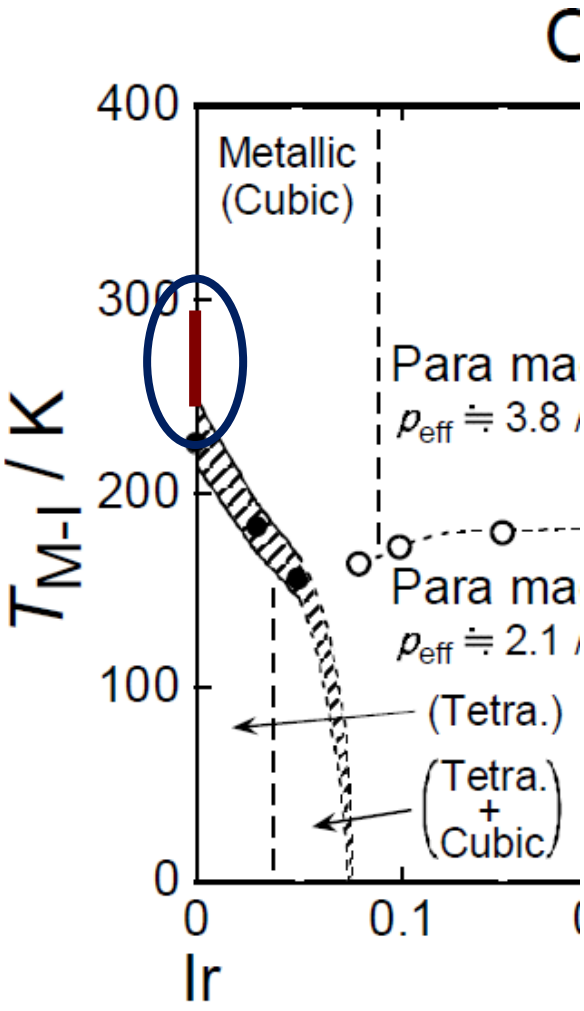
$CuIr_2S_4$


(a)
400
300
200
T-I / K
Metallic
(Cubic)
Para ma
p_{eff} ≒ 3.8
Para ma
p_{eff} ≒ 2.1
(Tetra.)
(Tetra.
+
Cubic)
0.1
ΔG_{MAX} (Å^{-2})
0 0.25 0.5 0.75 1
100 125 150 175 200 225 250 275 300
T (K)
ΔG (Å^{-2})
0 0.5 1
2.8 3 3.2
r (Å)



$CuIr_2S_4$

(b)



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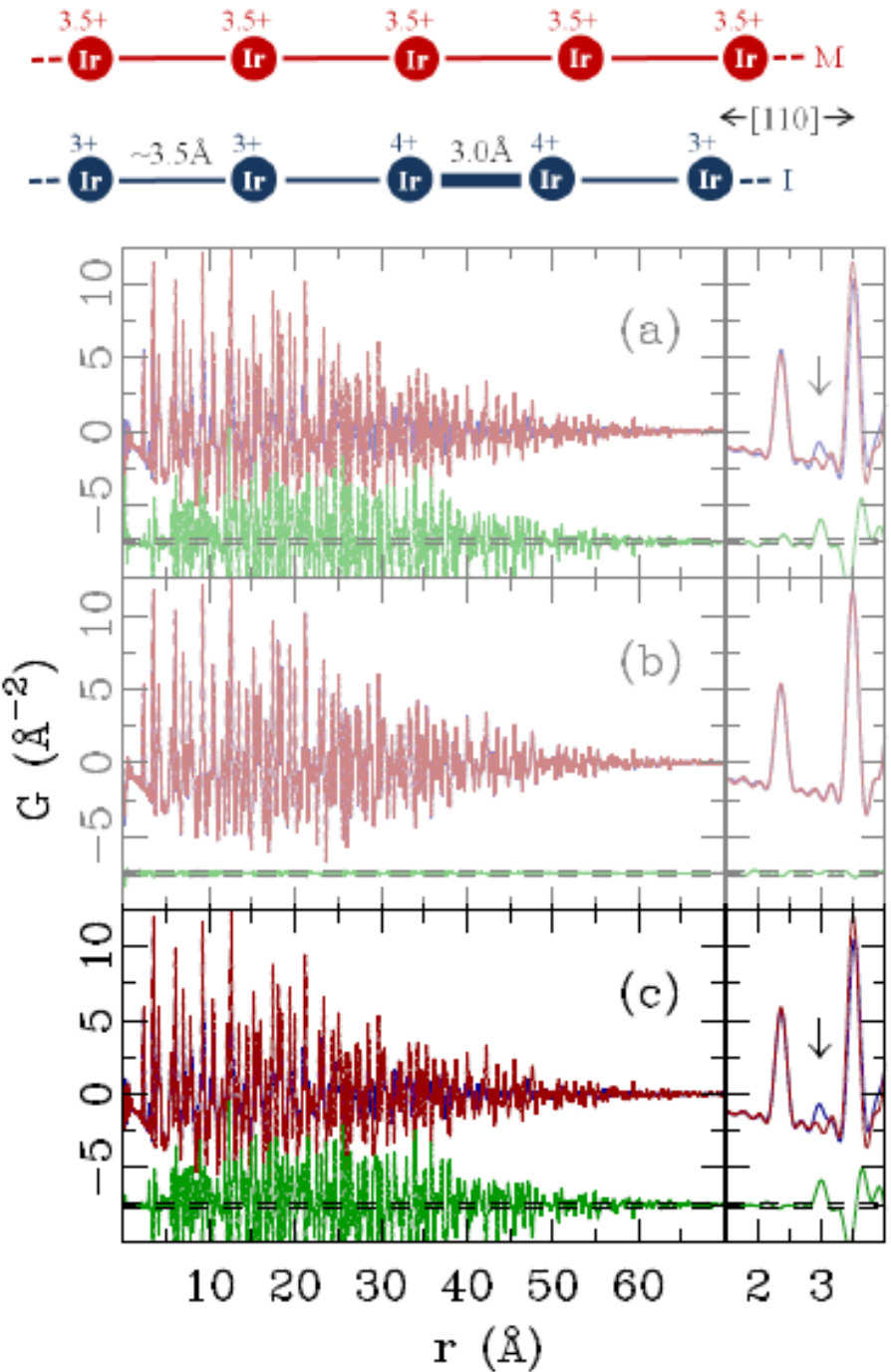
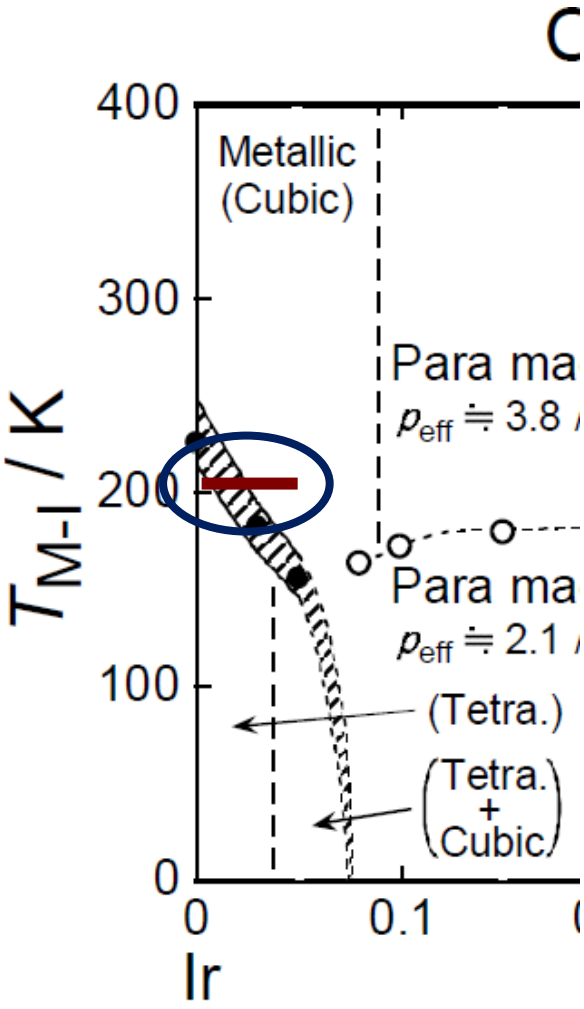

3.5+
Ir
M
←[110]→
3+
~3.5Å
4+
3.0Å
I
(a)
(b)
(c)
G (Å^{-2})
10 20 30 40 50 60
2 3
r (Å)

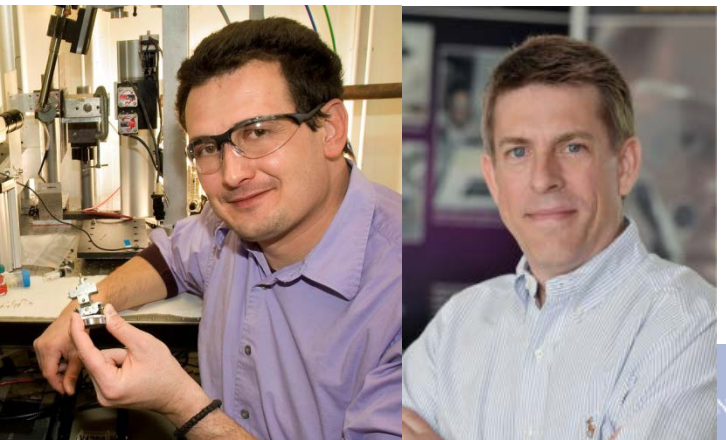
$CuIr_2S_4$

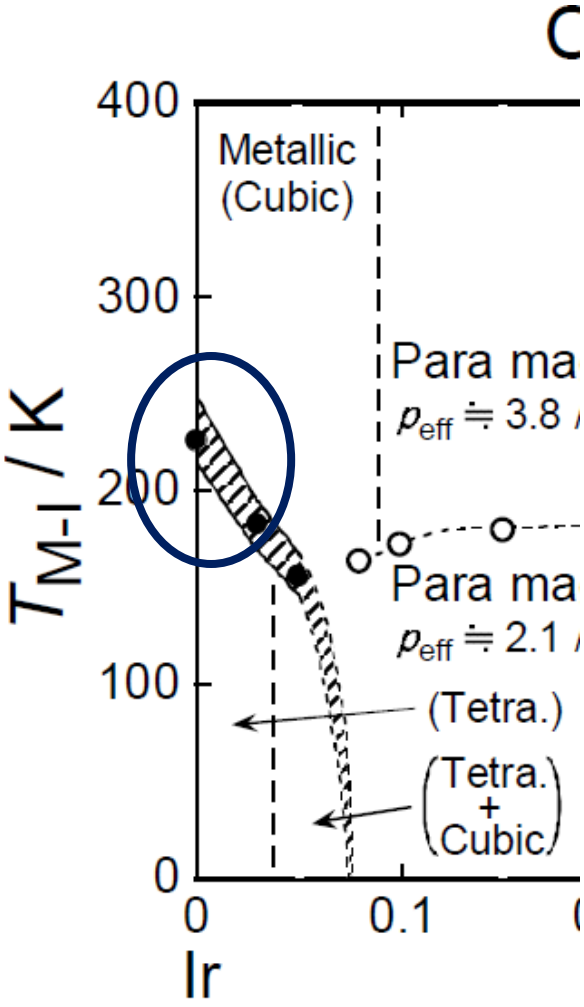
(c)


Metallic
(Cubic)
Para ma
$p_{eff} \fallingdotseq 3.8$
Para ma
$p_{eff} \fallingdotseq 2.1$
(Tetra.)
(Tetra.)
+
Cubic
T_{M-I} / K
400
300
200
100
0
0
0.1
Ir

Summary

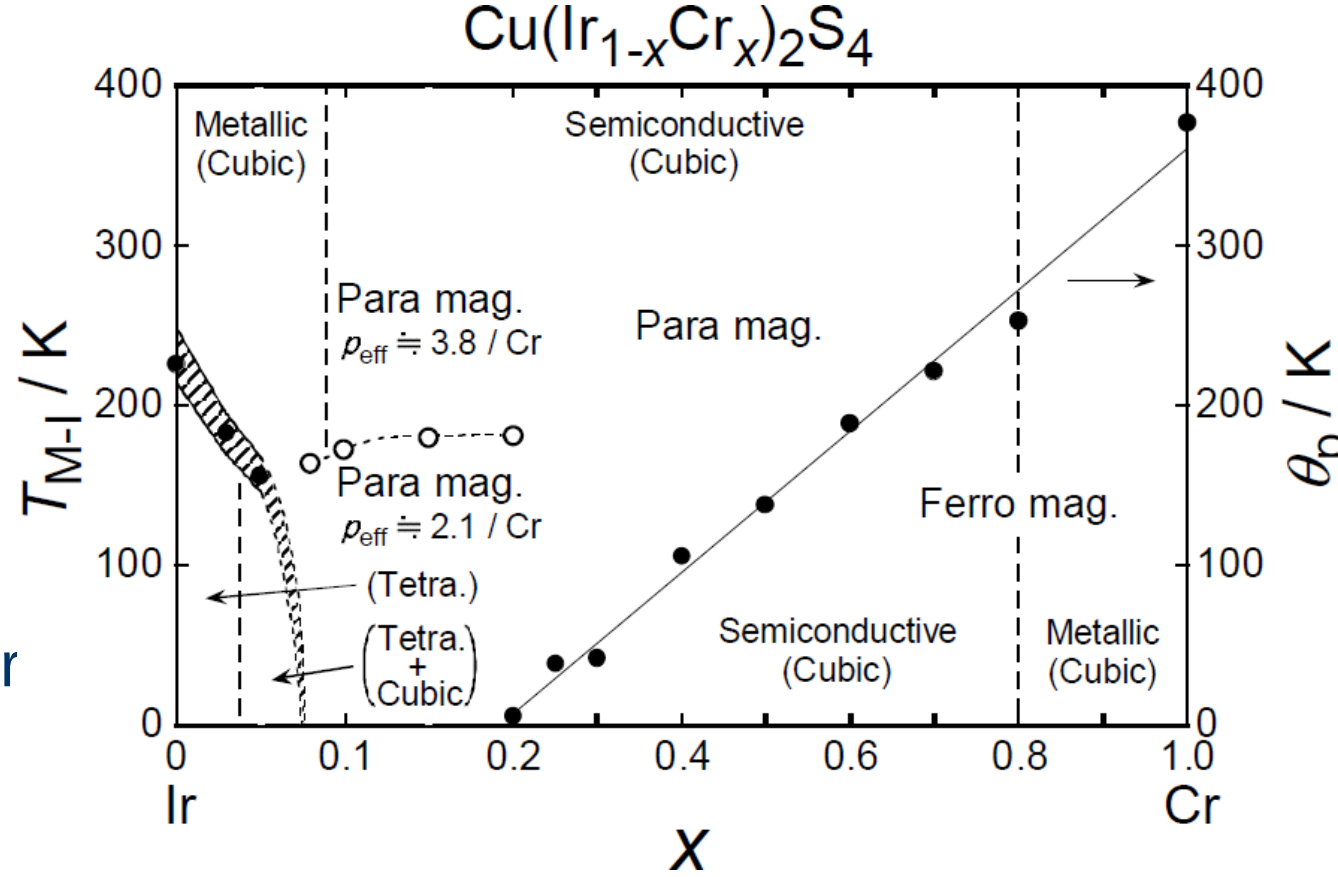
- Local dimers disappear at the MI transition
- E. S. Božin et al., *Phys. Rev. Lett.* **106**, 045501 (2011).





$CuIr_2S_4$ with Cr doped on the Ir site

- At high temperature it is a paramagnetic metal
- At low temperature it is a diamagnetic insulator
- At high doping it is a ferromagnetic metal
- Ir^{4+} dimers form at the MI transition and order => structural phase transition
- Collaboration with John Mitchell (ANL)



S. Nagata, Chin. J. Phys. 43, 772 (2005).

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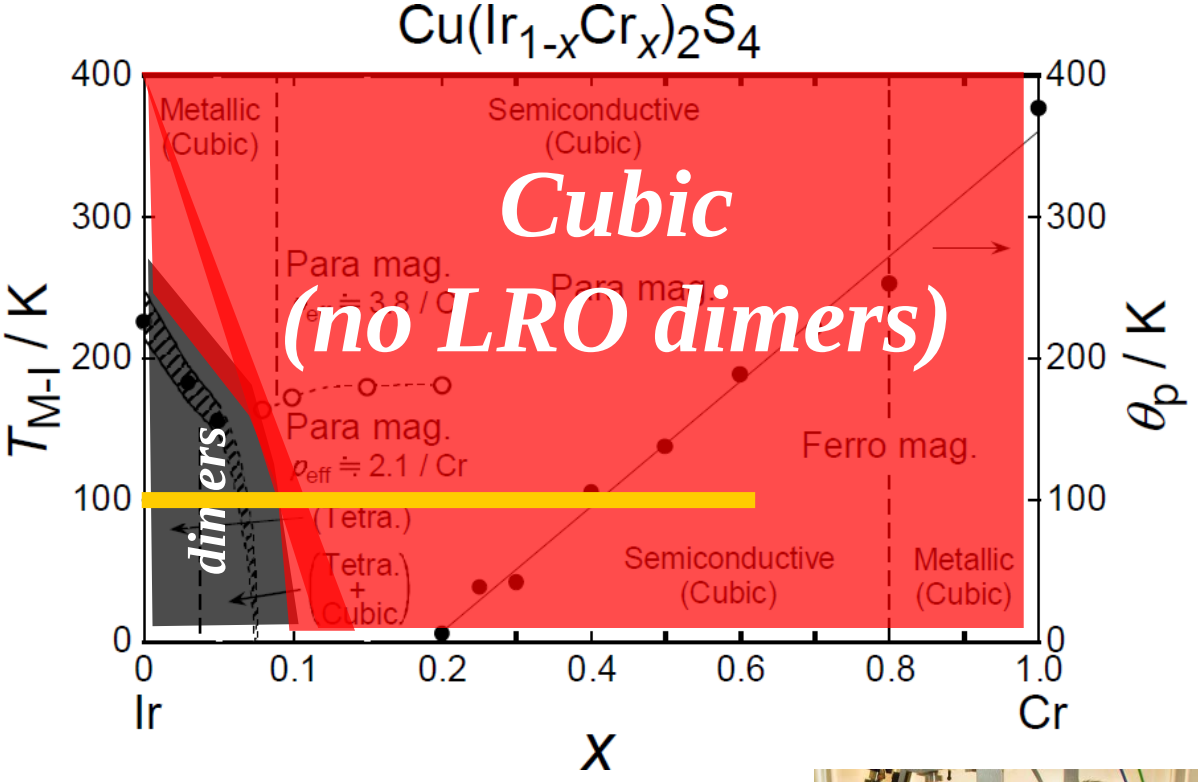
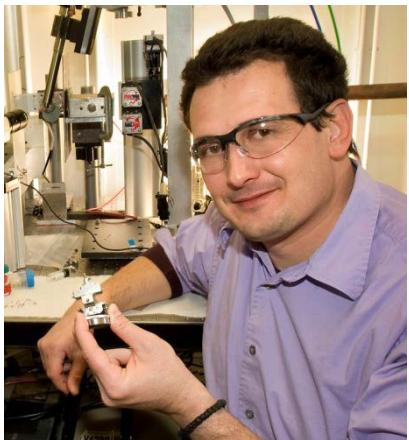
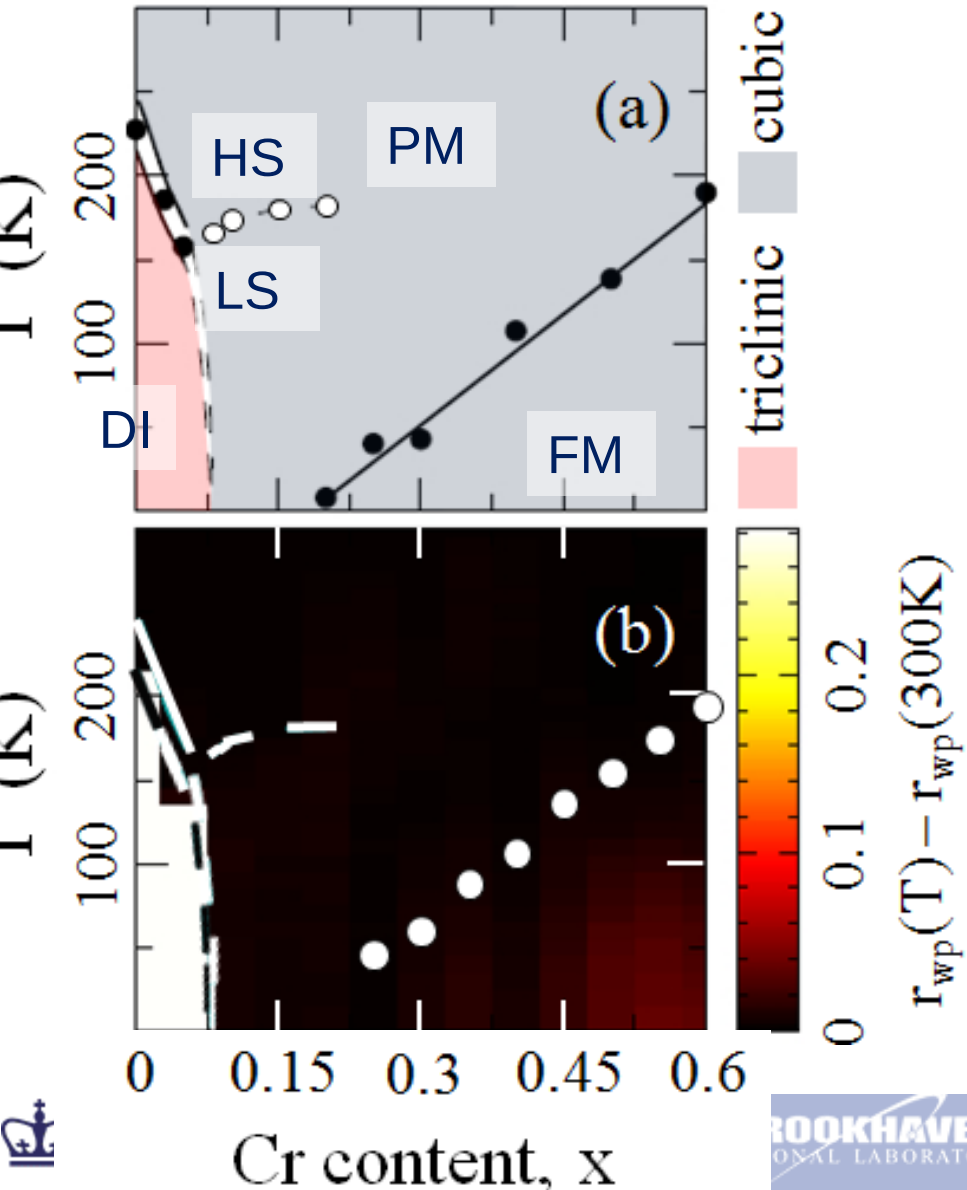
- Collaboration with John Mitchell (Argonne)





S. Nagata, Chin. J. Phys. 43, 772 (2005).

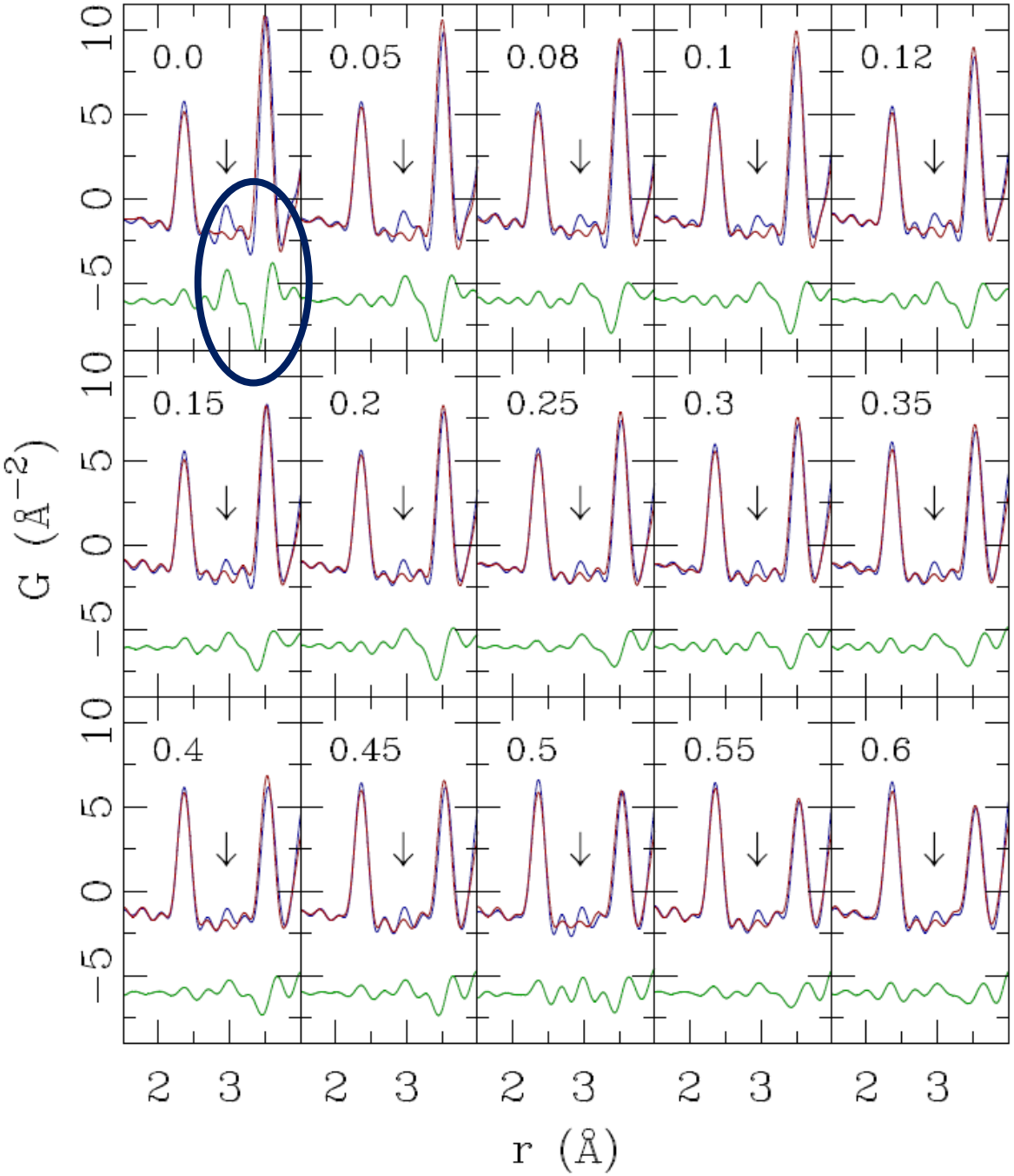
Average structure



Average structure:

- Top: Canonical phase diagram from Nagata

- Bottom: Agreement factor of *Cubic* model fit to PDF over wide-range of r
- => PDF data agrees on the average structure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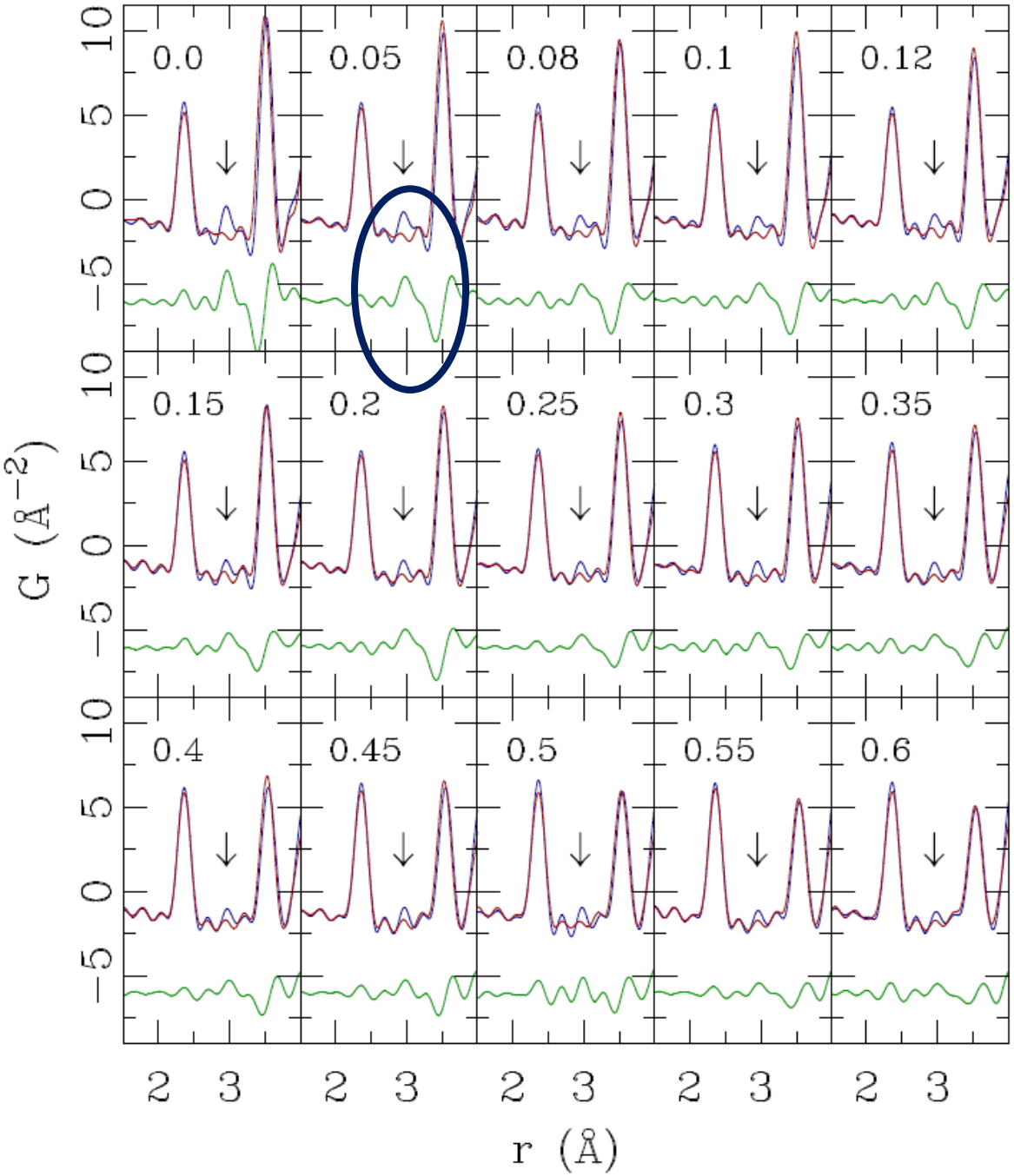
G (Å^{-2})
r (Å)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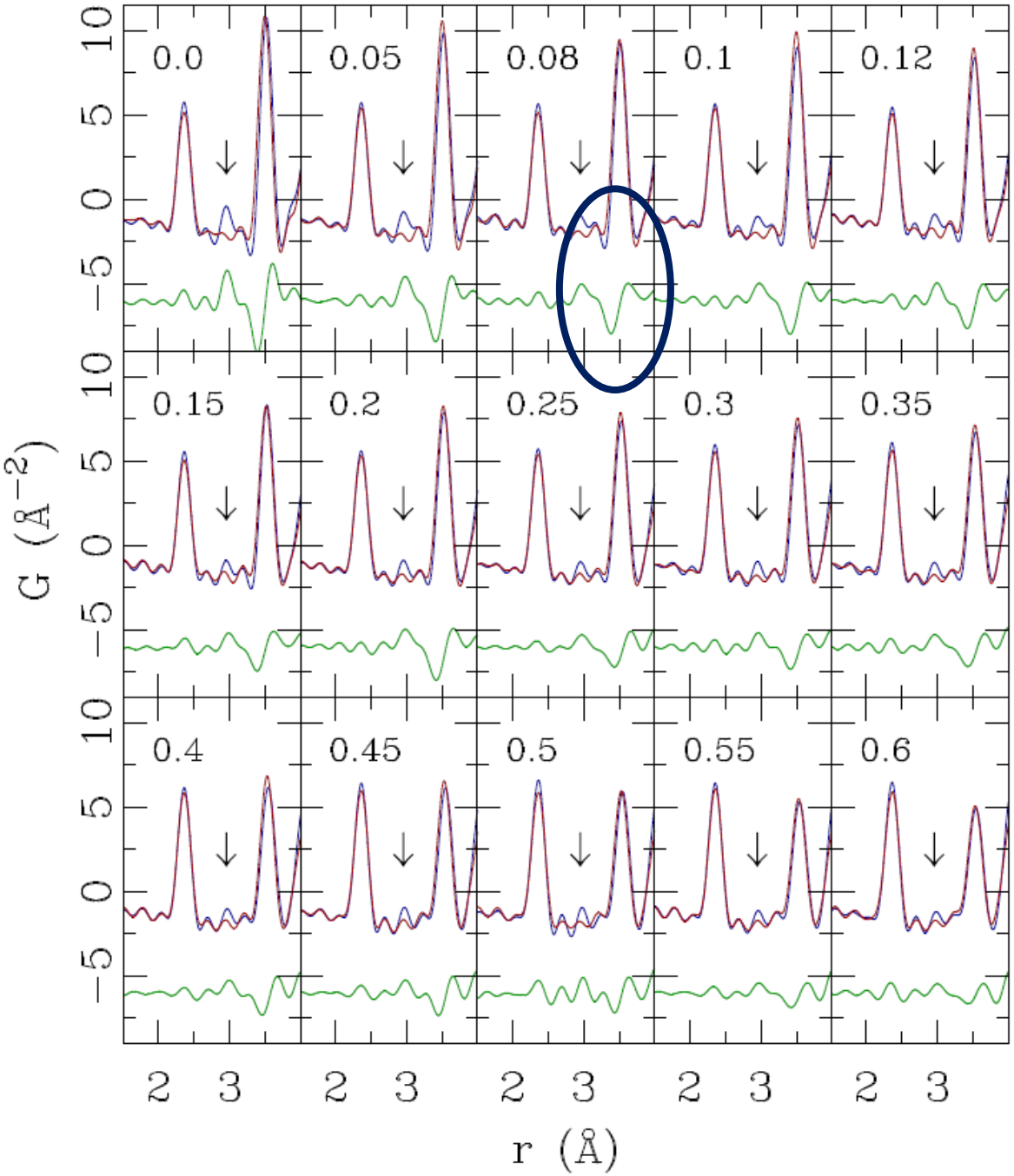
r (Å)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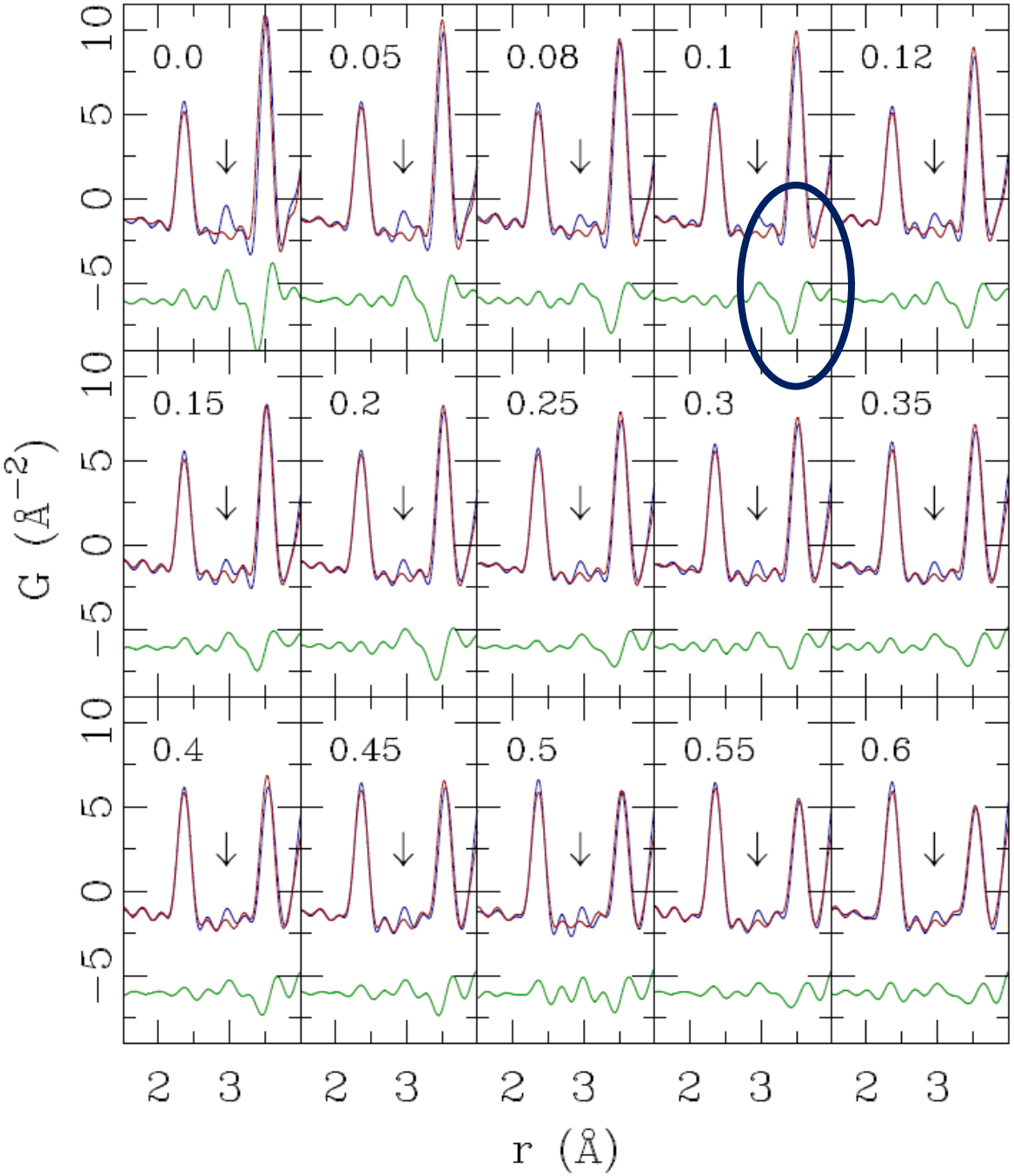
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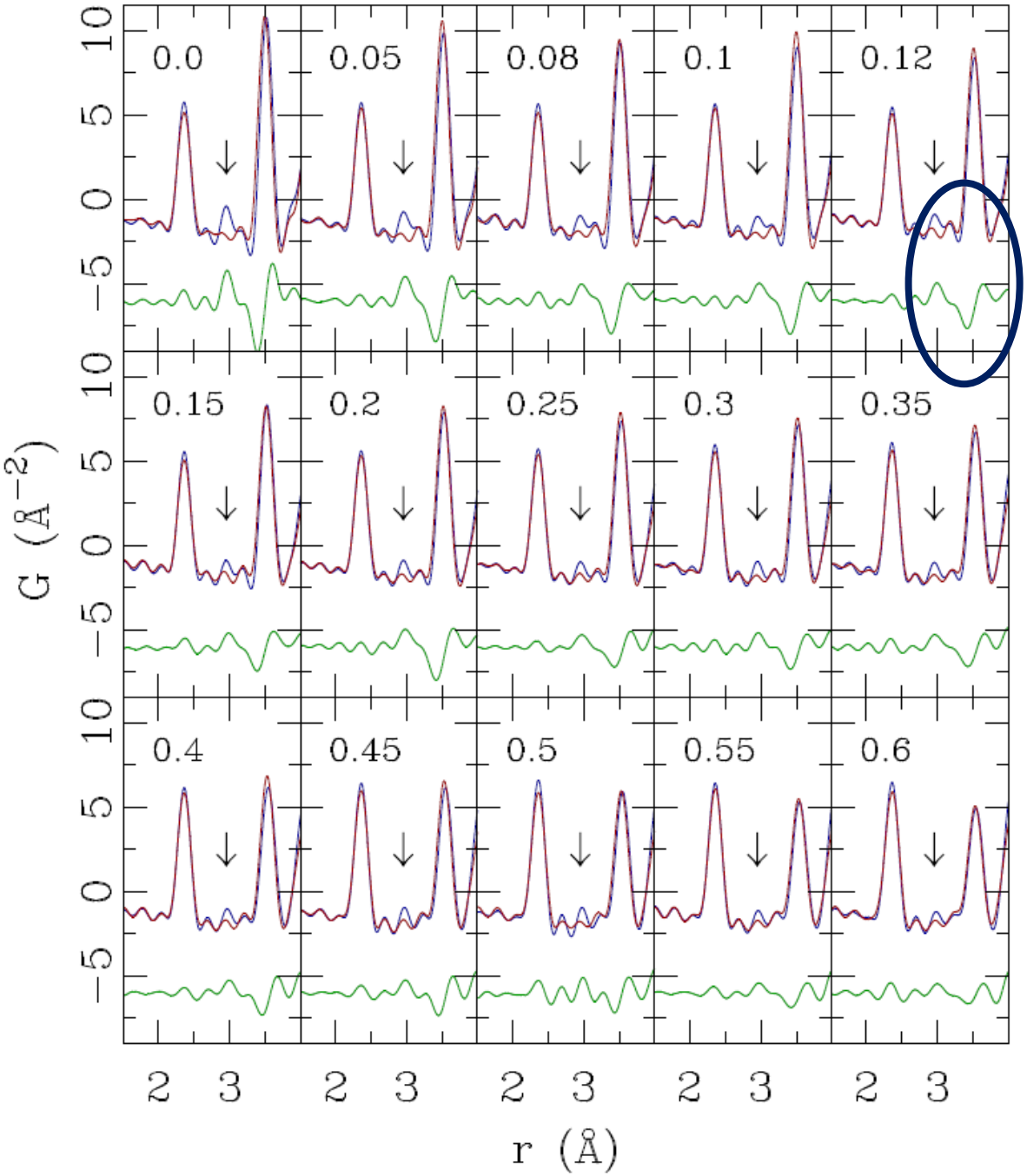
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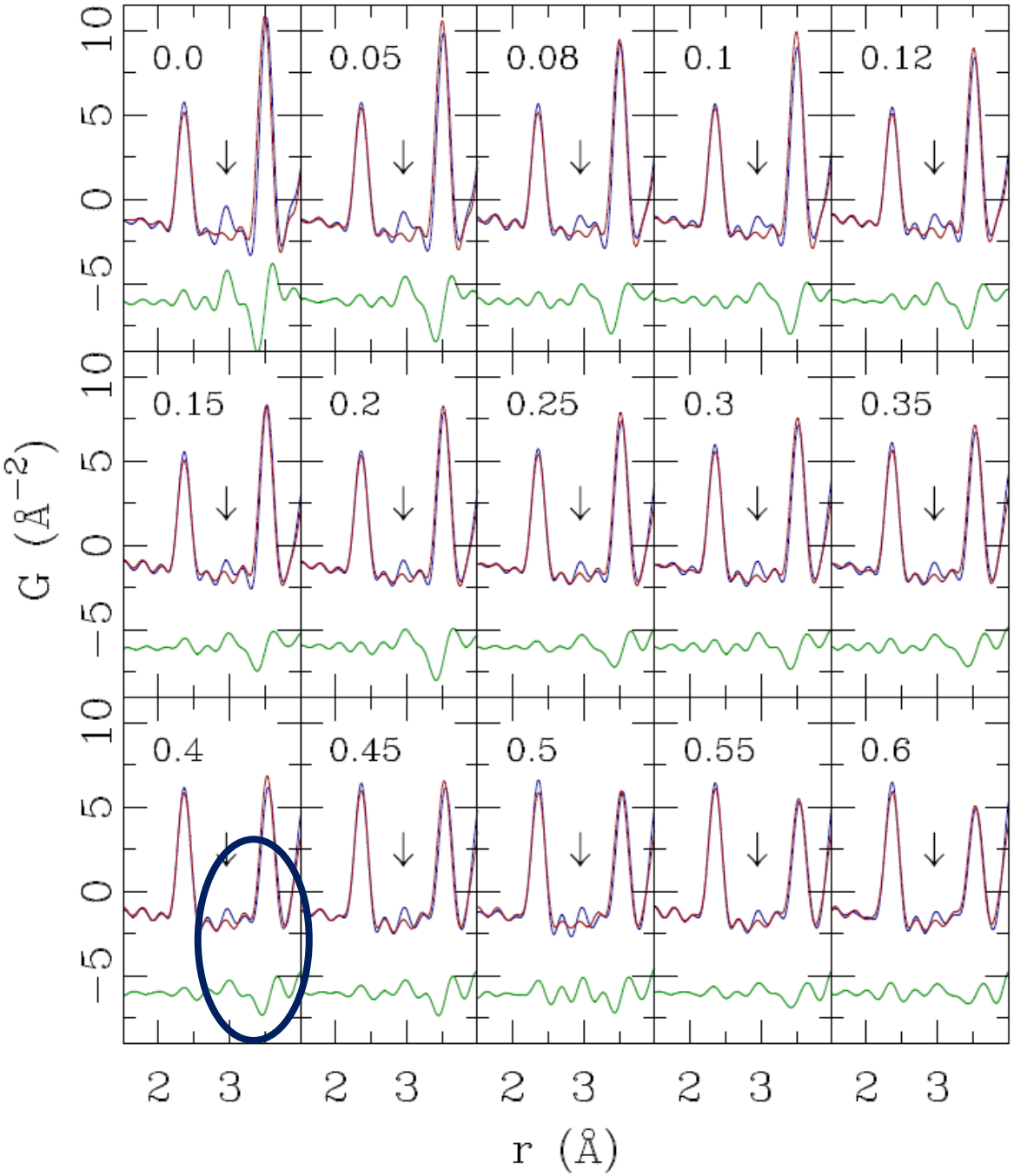
G (Å^{-2})
r (Å)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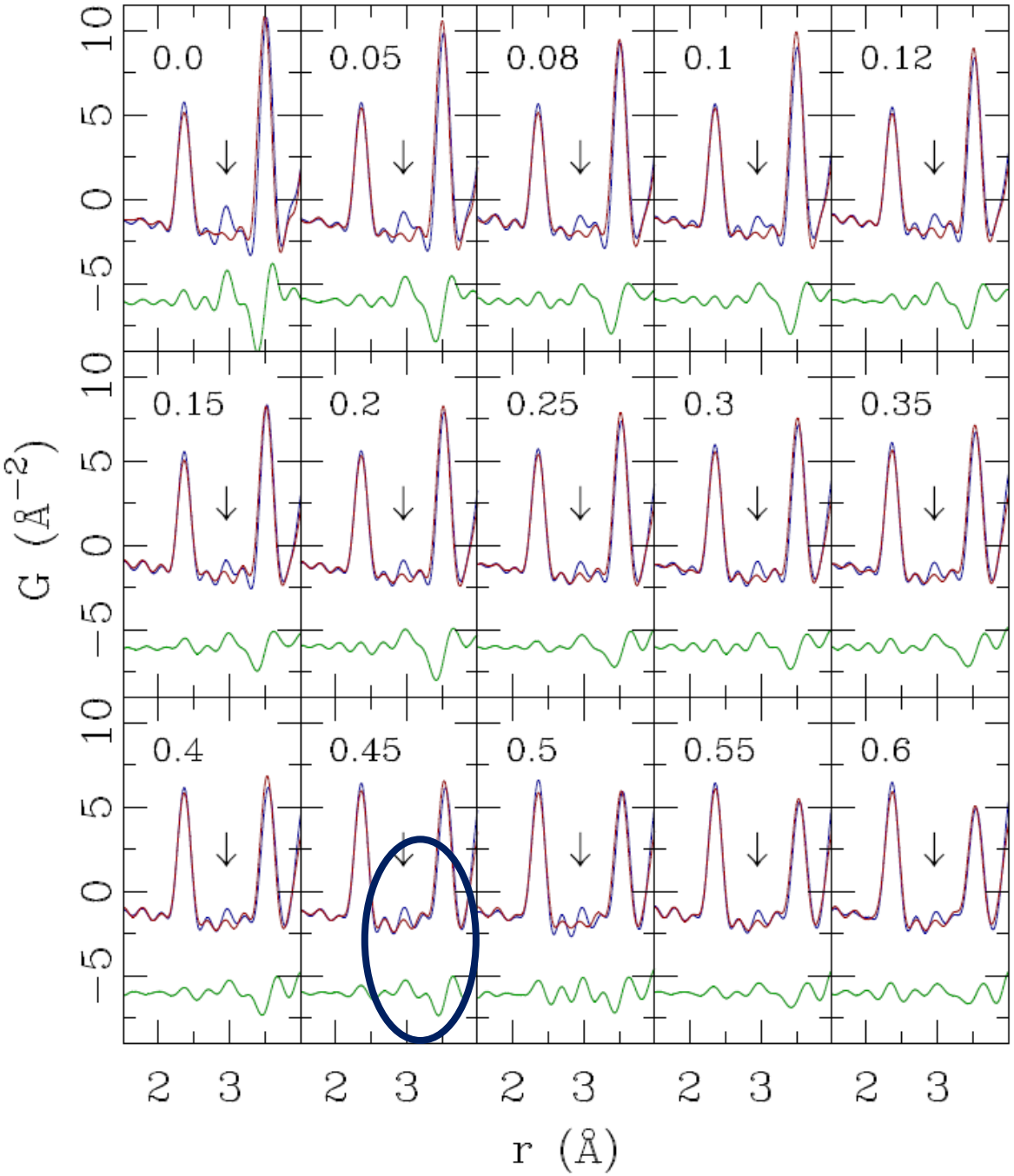
r (Å)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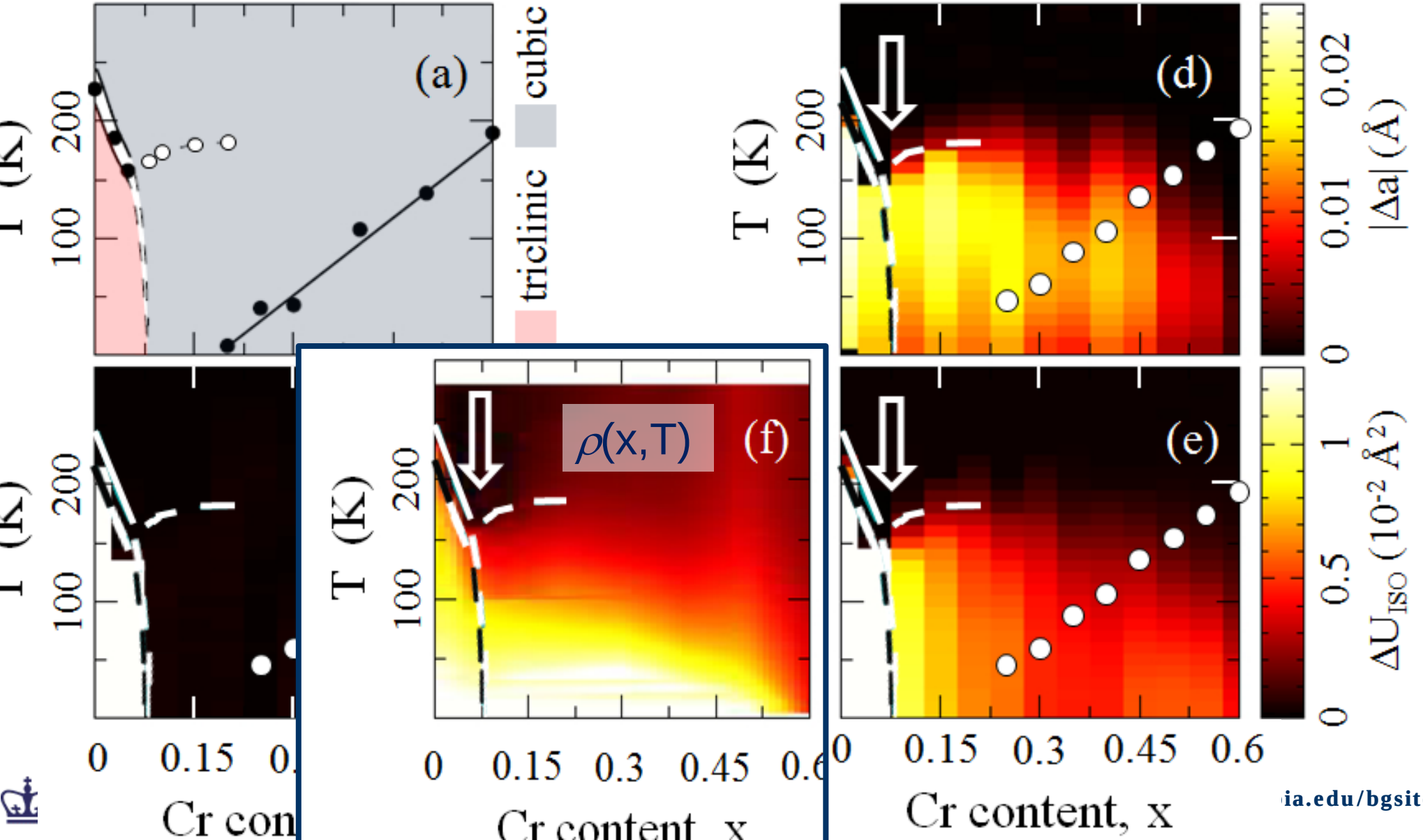
G (Å^{-2})
r (Å)

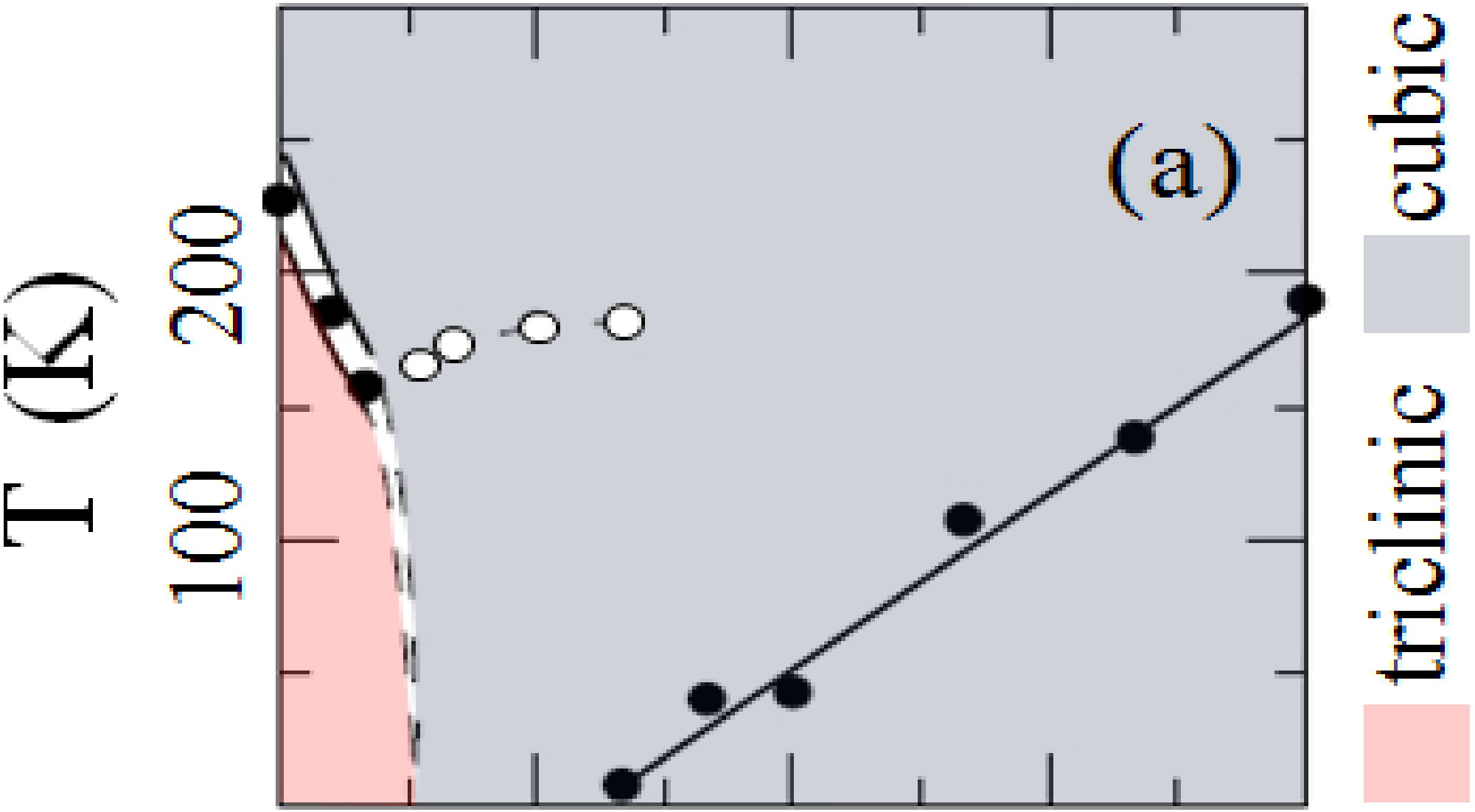
E. S. Božin, SJLB et al., *Sci. Rep*. **4**, 4081 (2014).

Avg str

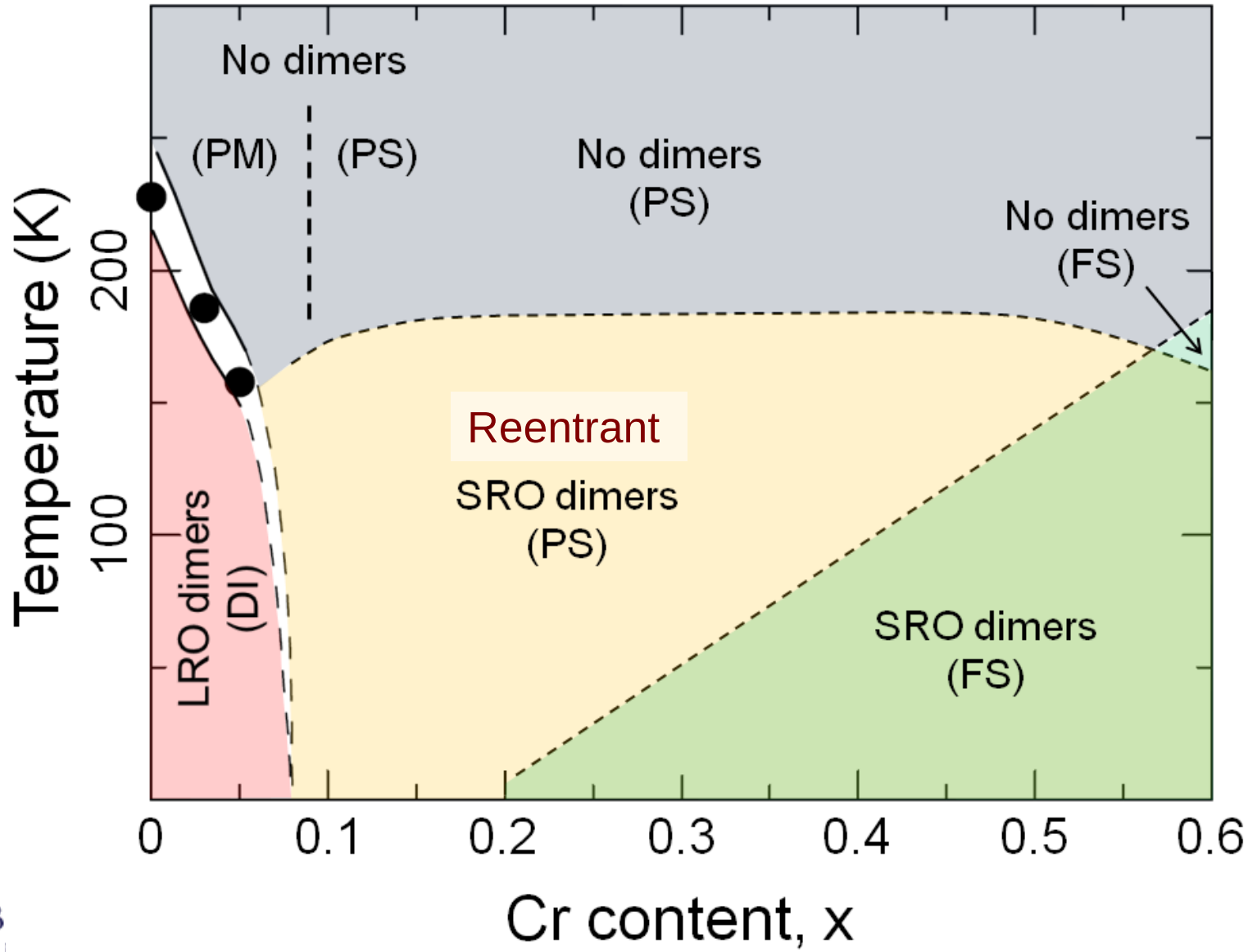
Local str



Average phase diagram

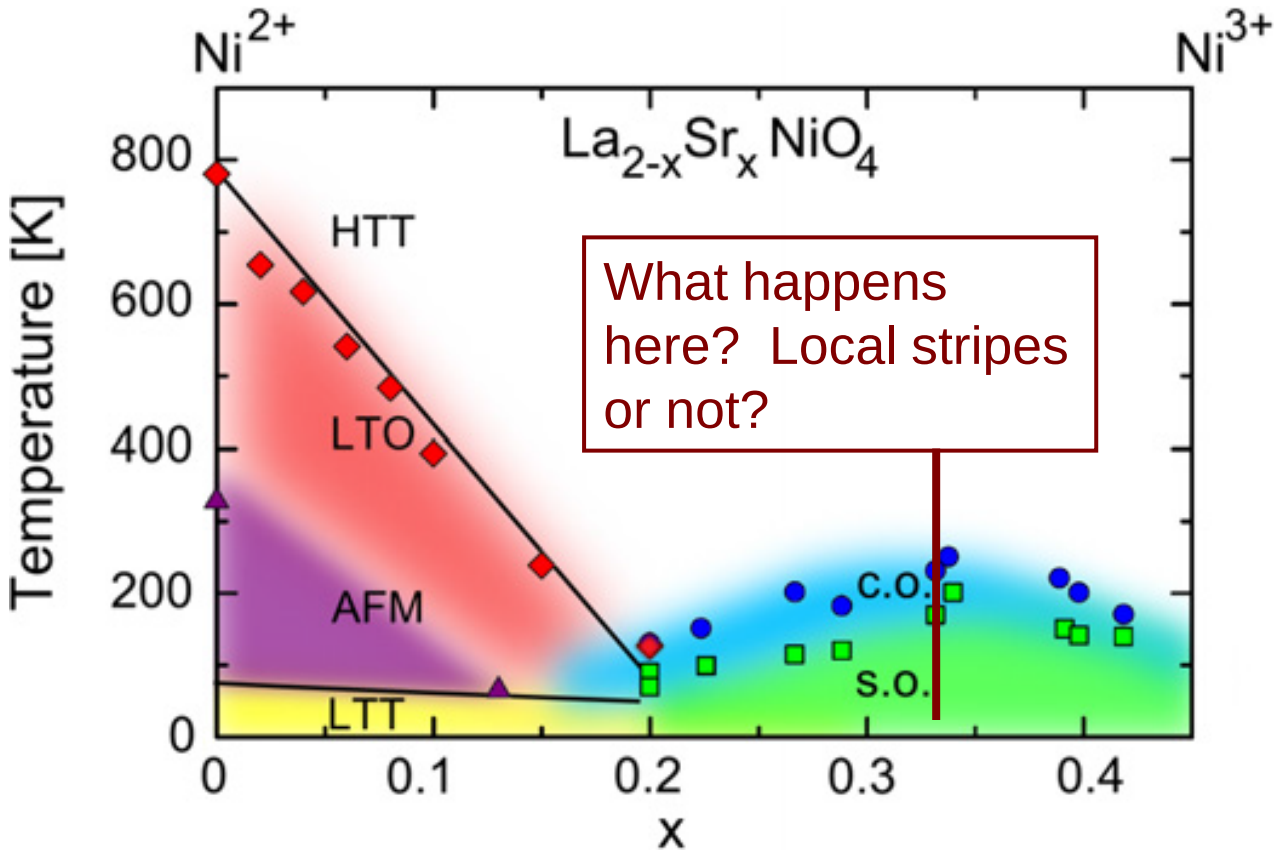


Local phase diagram

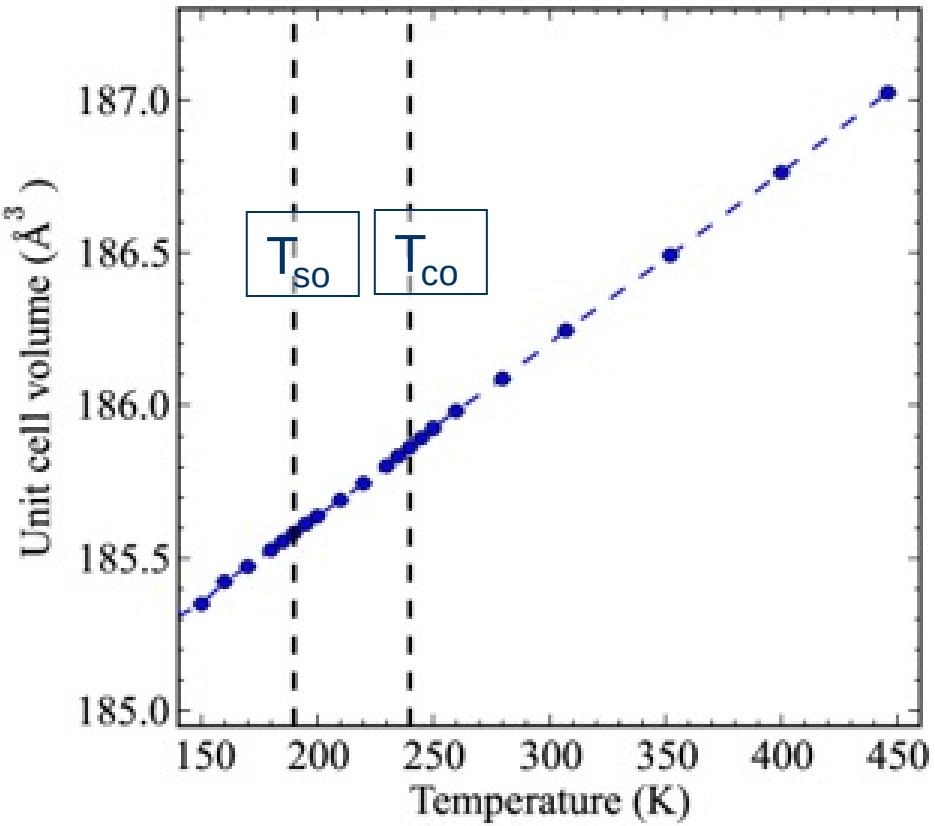


Case #3: Towards the cuprates…..Nickelate! - Fruit fly of correlated stripe materials

- Holger Ulbrich, Markus Braden Physica C 481 (2012) 31–45
- CO superlattice peak

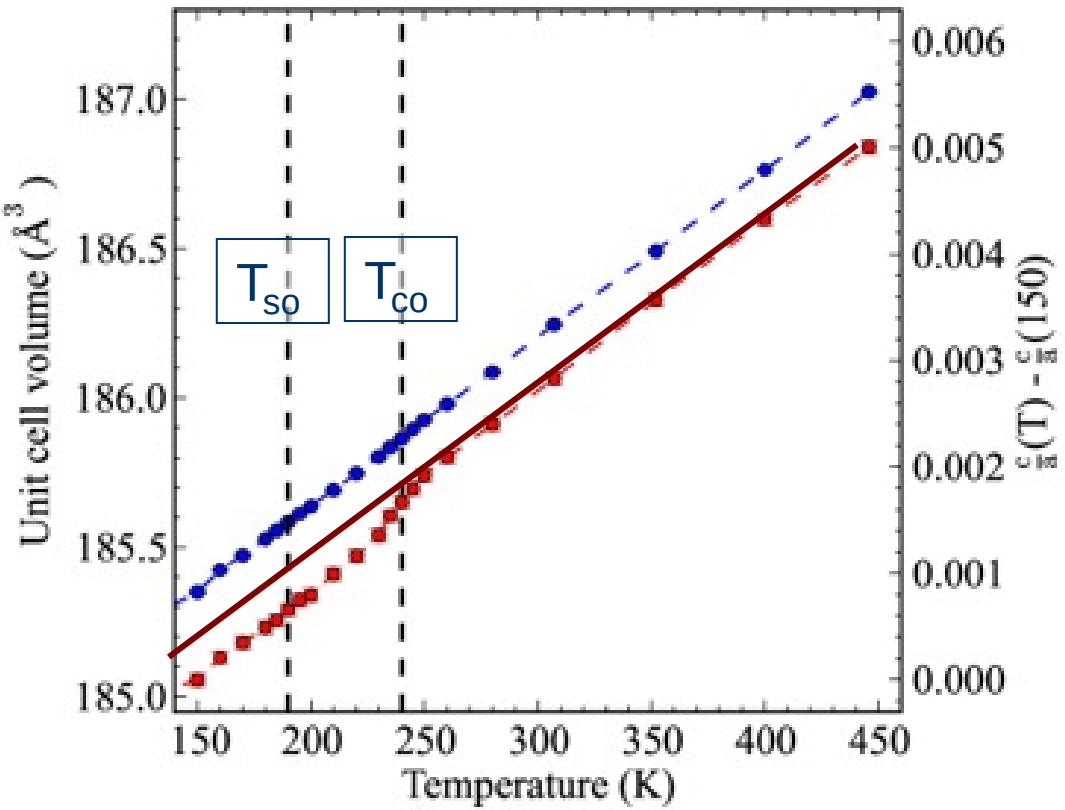


LSNO

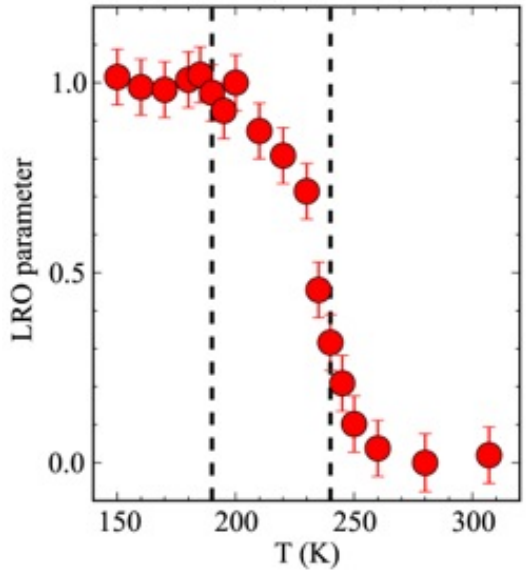


- Unit cell Volume vs T
- No response to spin or charge order
- From neutron powder diffraction data

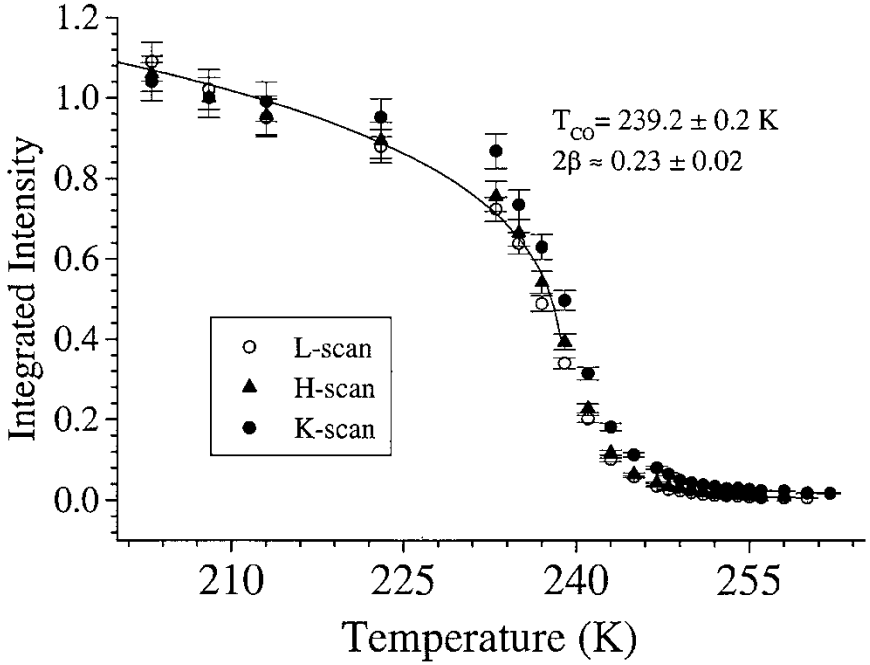
LSNO



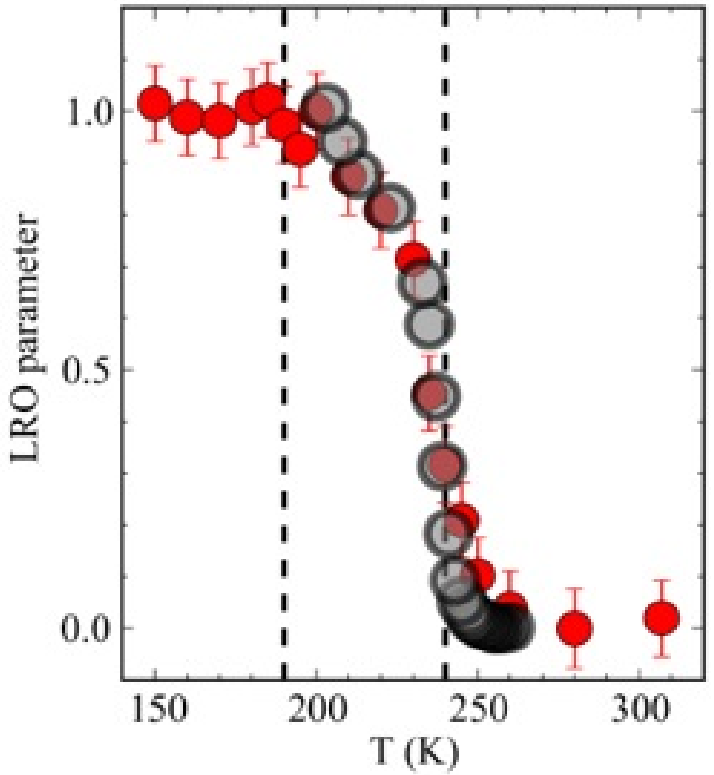
- No response in cell volume
- However, significant response in c/a ratio (red)



Charge order in LSNO



- Top: Charge order superlattice peak behavior from single crystal neutron (Braden et al)



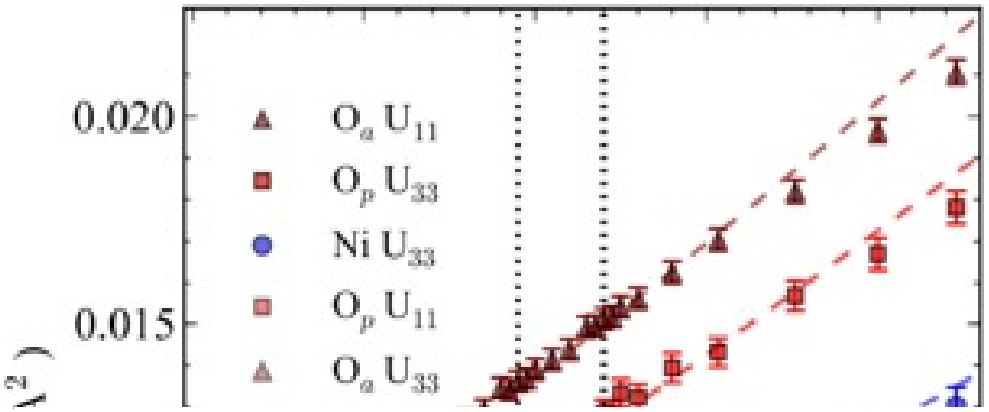
- Bottom: make an order parameter from the c/a behavior by taking the difference and normalizing
- Superimpose CO SL peak order parameter

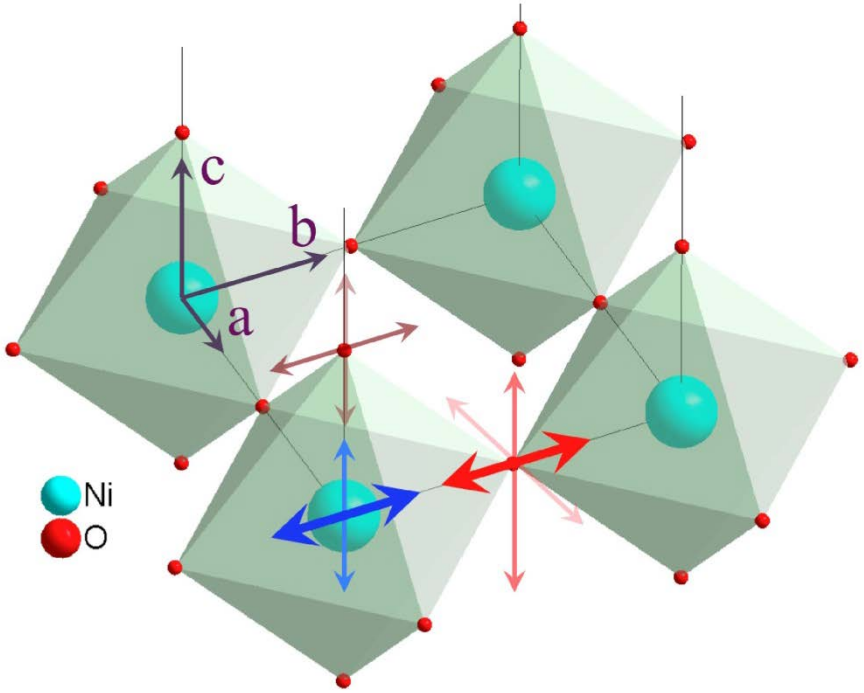
Summary

c/a ratio anomaly is sensitive to the Long Range Charge Order (LRCO)

Milinda Abeykoon, SJLB et al., *Phys. Rev. Lett*. **111**, 096404 (2013).

Local Structure





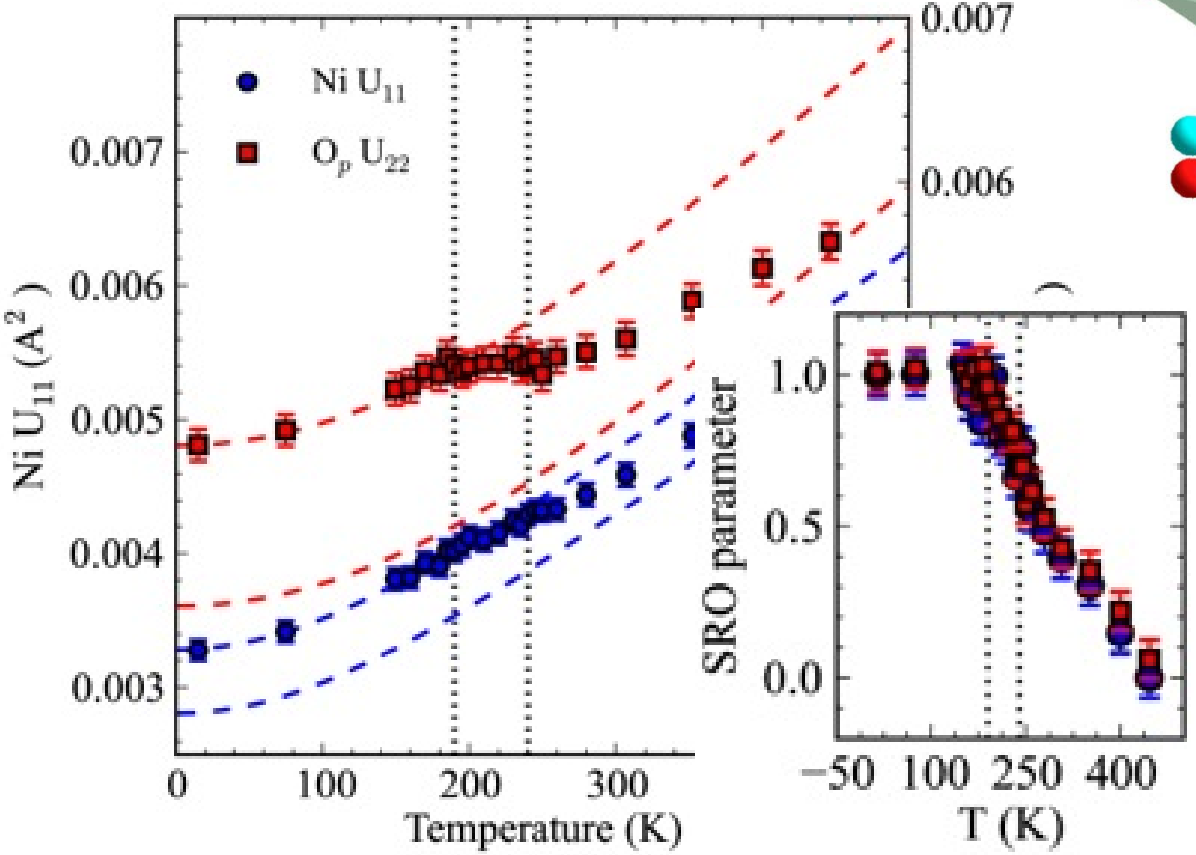
- Atomic disorder away from the high symmetry HTT model will appear in the atomic displacement parameters (ADPs)

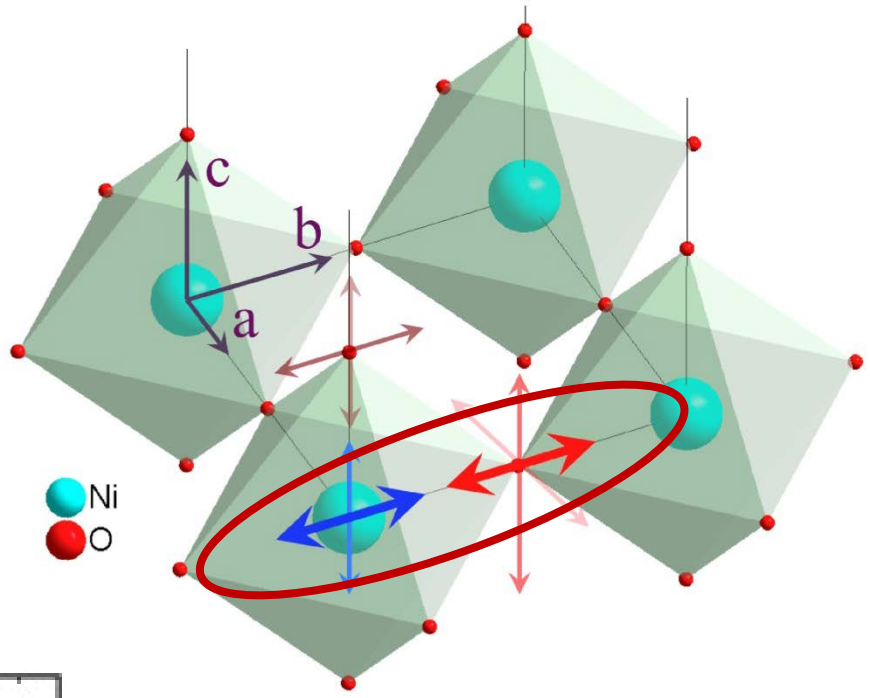
  Nothing much happening at T_{co} or T_{so}

  But which motions are these?

LSNO local structure

- ADPs of atomic displacements PARALLEL to the Ni-O bond





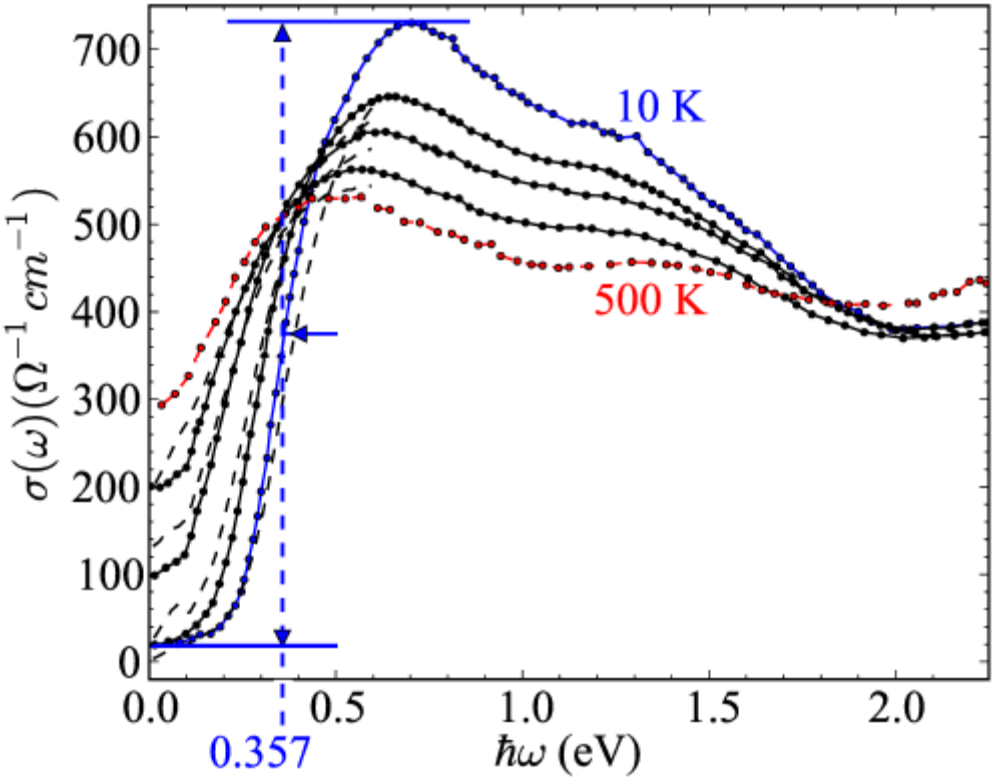
Large response at T_{co} / T_{so}

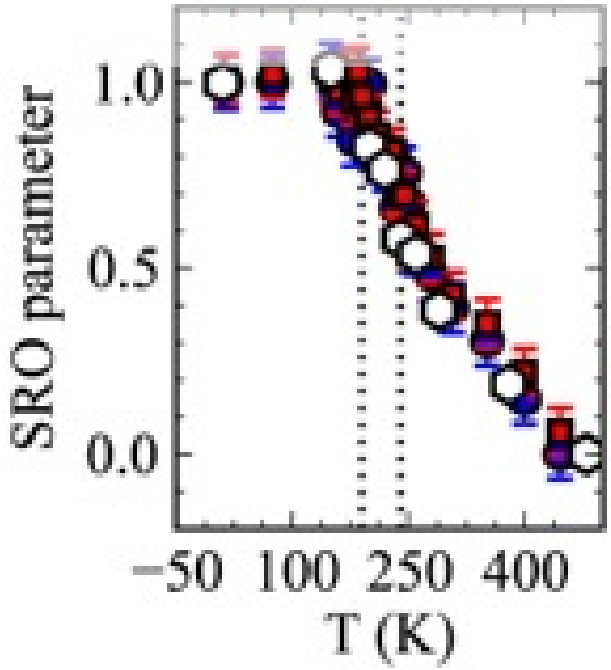
Extra disorder due to charge localization disappears only over a wide temperature range to ~$2T_{co}$

What about the properties?

Milinda Abeykoon, SJLB et al., *Phys. Rev. Lett*. **111**, 096404 (2013).

- Pseudogap from optical conductivity measurements
- Katsufuji et al. PRB 1996



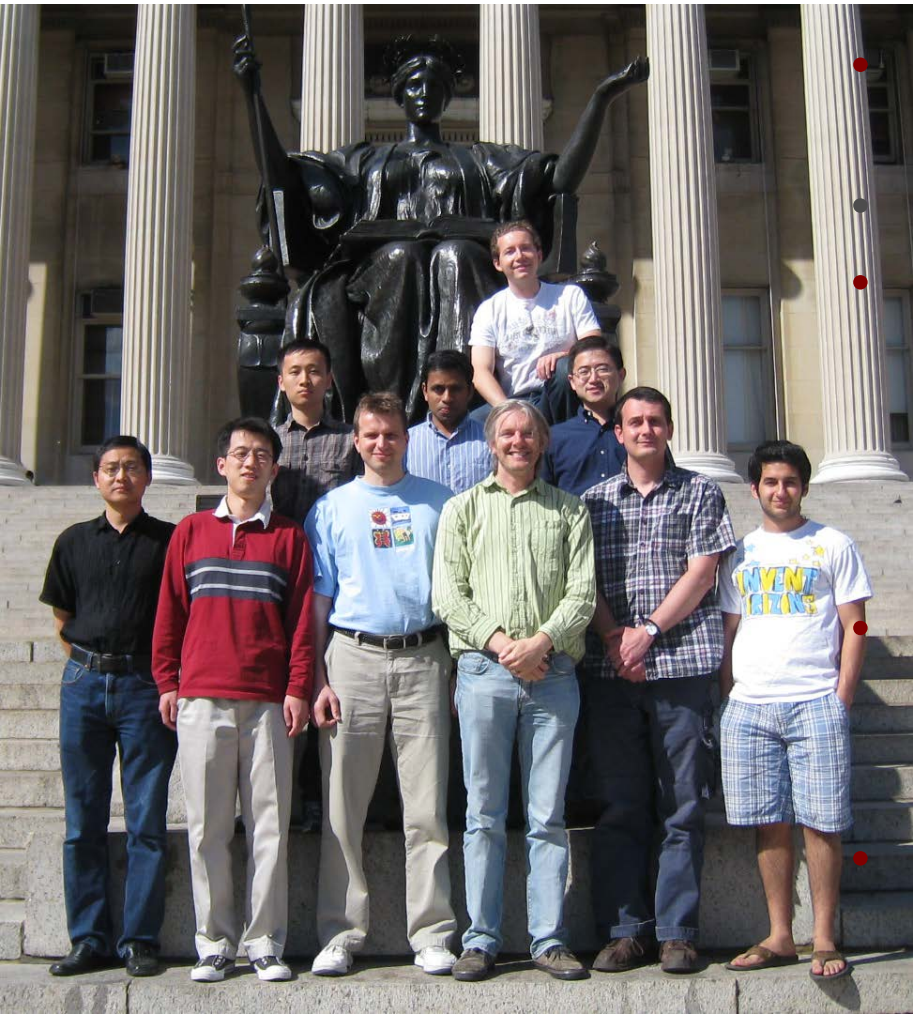


- Magnitude of the PG follows the LOCAL order parameter
- PG related to the presence/absence of local stripes rather than LRCO

Summary

- Symmetry broken electronic states can be seen in PDF measurements
- They are visible and may be characterized even when they are short-range ordered or disordered
- In the cuprates, the appearance of SRO CDWs seems to correlate with the pseudogap
- Strain most likely plays an important role in determining the morphology of the stripes – competition between electronic and lattice system

Acknowledgements



- A special thank you to all my current and former students and post-docs
- Emil Bozin, Milinda Abeykoon, Pavol Juhas
- Also my many wonderful collaborators, in particular from the work described here: John Mitchell, John Tranquada, Weiguo Yin, Genda Gu, Phil Duxbury
- Facilities:
  - NSLS (and people therein)
  - Lujan Center LANL (and people therein)
- Funding: DOE-BES