Exploring Local Structural Evidence for Strong Electronic Correlations in the Spinel $LiRh_2O_4$

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BROOKHAVEN
NATIONAL LABORATORY

Outline

- Physics of Spinel Systems
  - Pyrochlore lattice promotes geometrical frustration
  - Charge, spin, orbital ordering
  - Metal to insulator transition

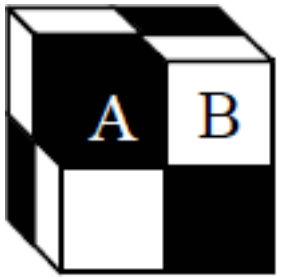
- Pair Distribution Function Analysis
  - Multi-scale probe
  - High throughput and fast measurement time
  - Customized endstation at NSLS

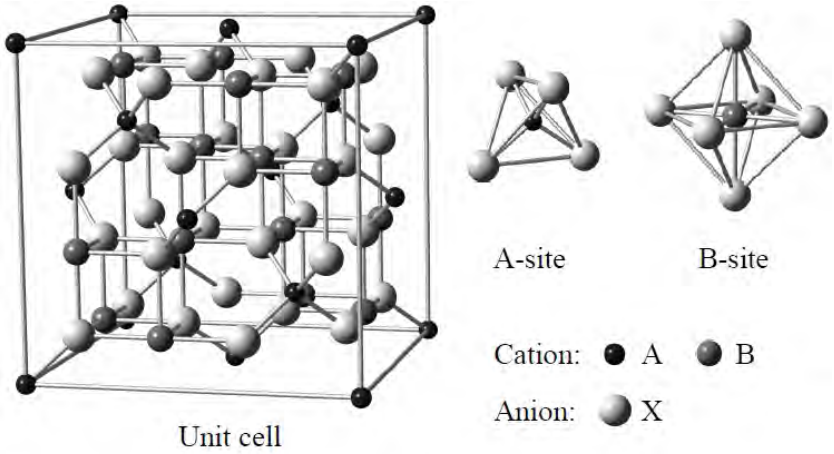
- Systems studied
  - $CuIr_2S_4$
  - $LiRh_2O_4$
  - $Cu(Ir_{1-x}Cr_x)_2S_4$

Overview of Spinel Systems

Spinel Structure

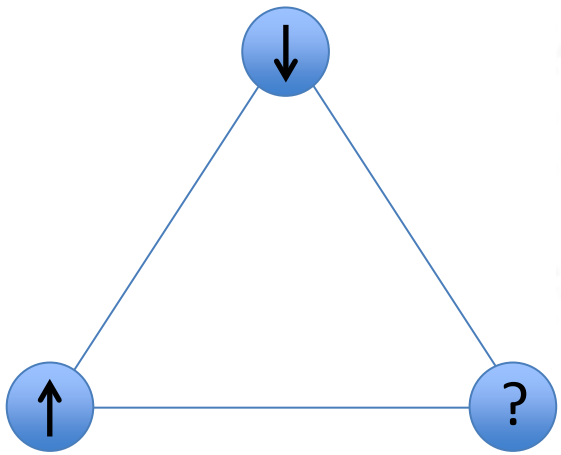
- Class of minerals named after $MgAl_2O_4$
- Cubic close-packed structure
- General formulation AB_2X_4
- Two metal environments: tetrahedral and octohedral

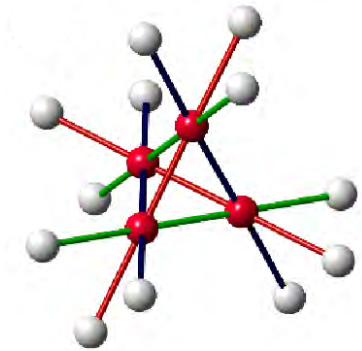


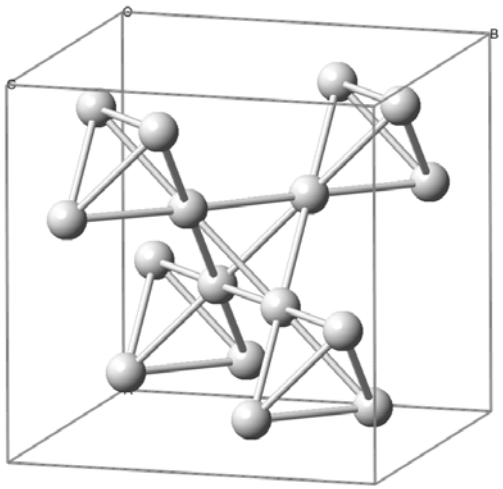


Spinel crystal structure: AB_2X_4

Interesting Physics in Spinels

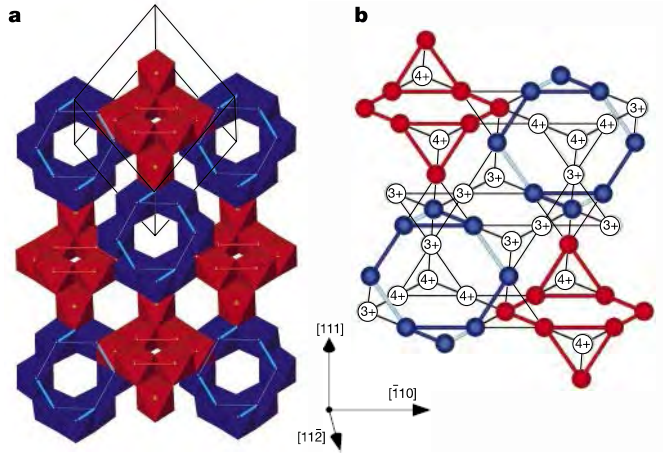




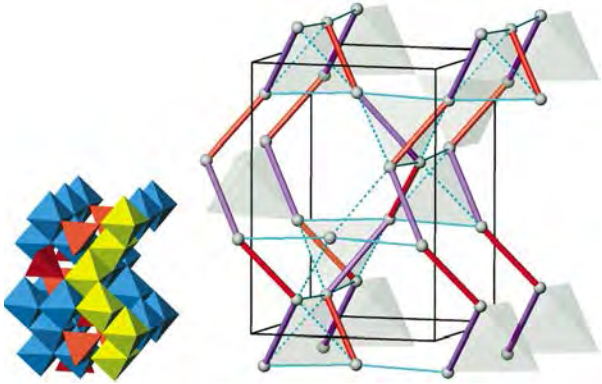


- Pyrochlore sublattice of corner shared B_4 tetrahedra
- Nearest neighbor Hamiltonian leads to Geometrical Frustration
  - Occurs for half integer spin or charge on B site
  - Degenerate lowest energy manifold
  - Ordering temperatures suppressed
- Possible ground states (lifting of degeneracy):
  - "Exotic" quantum ground state such as spin liquid
  - Frozen disordered state (spin glass)
  - System lifts degeneracy by distorting structure and forms long range order

Beautiful Complex Structures



Octamers in $CuIr_2S_4$



Helices in $MgTi_2O_4$

- Ground State Degeneracy lifted by structural distortion
- B ions dimerize into long and short bonds
- Complex Long Range ordering dramatically decreases symmetry

Experimental Technique: Pair Distribution Function

What does the PDF Approach Provide?

- “Total Scattering” approach -> information from all length scales.
- Disordered systems, local structural studies, multi-scale problems.
- High throughput (acquisition in mins) -> subtle changes in structure.
- Development of PDF program at NSLS/NSLS II is essential.

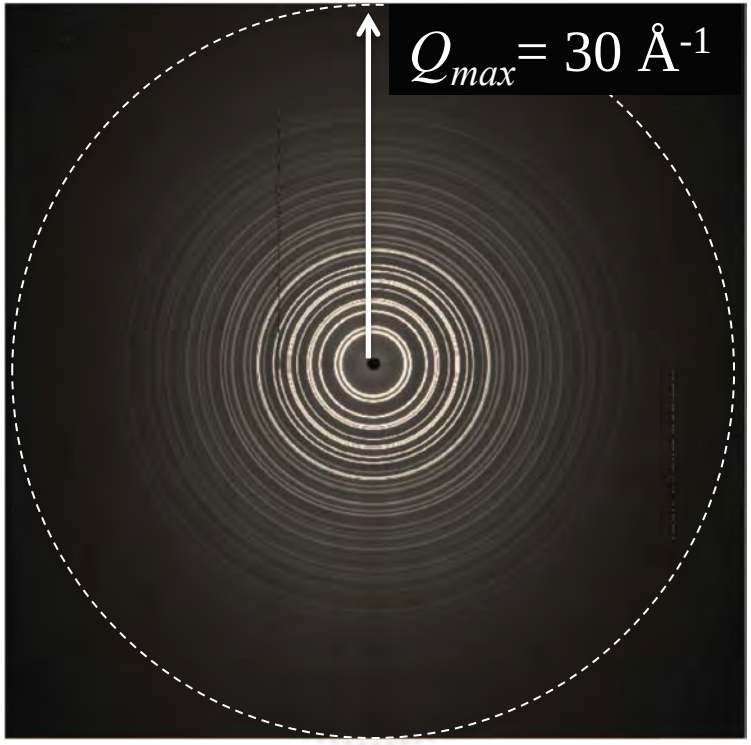
How is a PDF obtained?

Fourier transform of the total powder diffraction data (Bragg + diffuse)

$$G(r) = (2/\pi)\int_{Q_{min}}^{Q_{max}} Q[S(Q)-1]\sin(Qr)\,dQ = [\frac{1}{r}\sum_{ij}\frac{f_i f_j}{<f>^2}\delta(r-r_{ij})] - 4\pi r\rho_0$$

FT of Data

Model



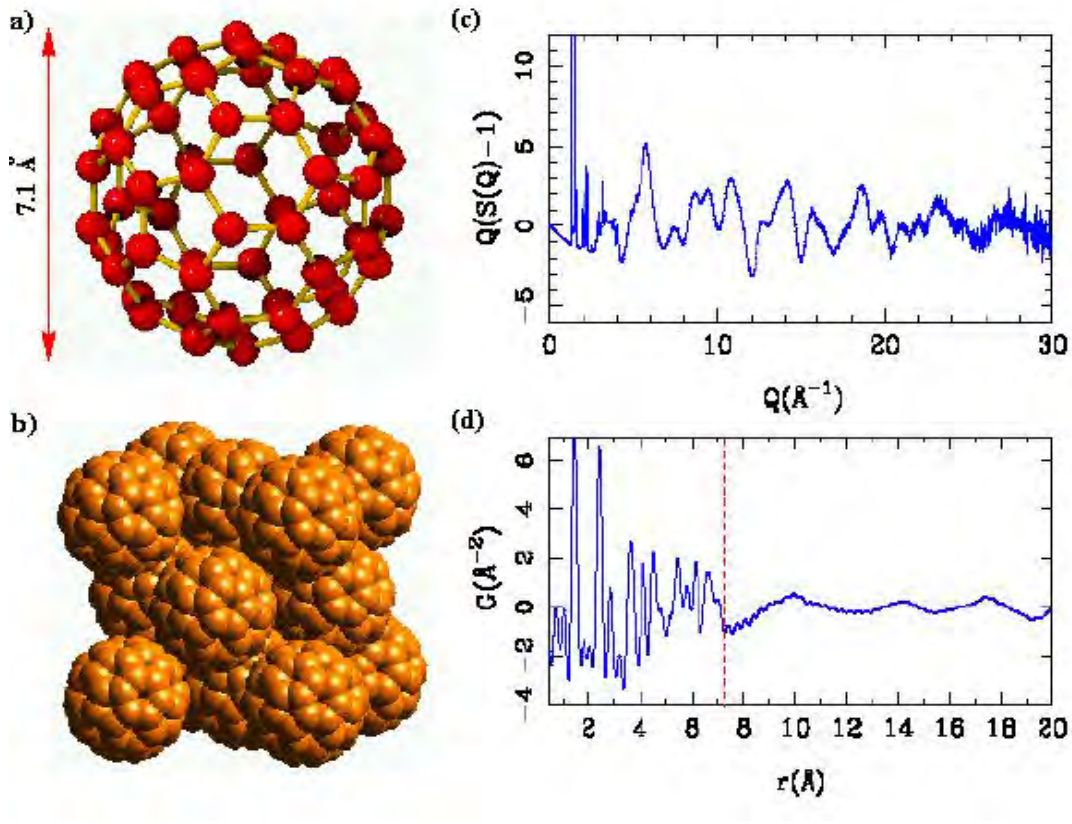
$S(Q)$ – normalized intensity

ρ_0 - number density

$Q = 4\pi\, Sin(\theta)/\lambda$

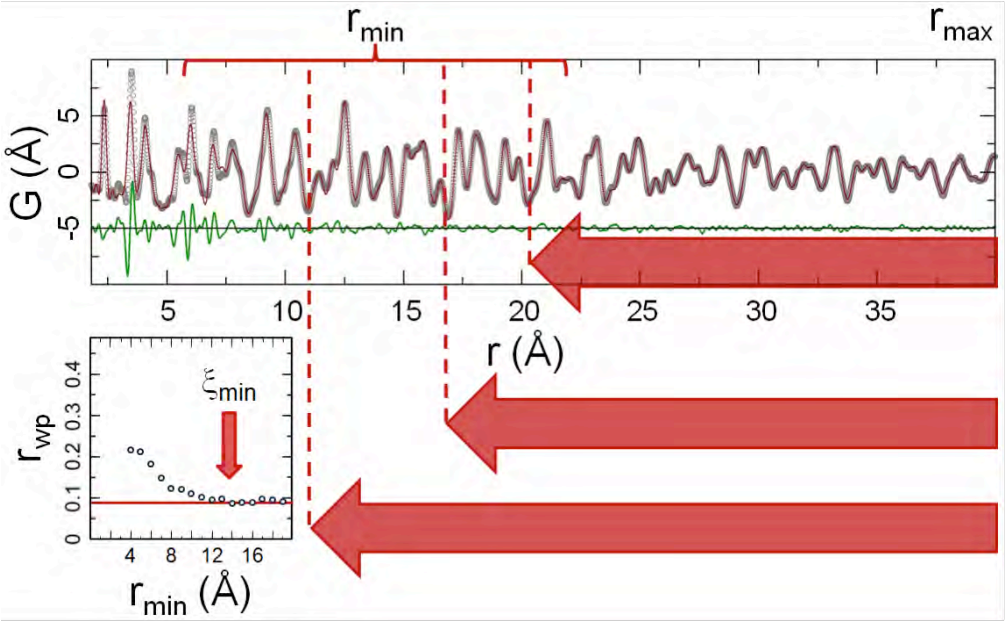
P.J. Chupas, X. Qiu, J.C. Hanson, P.L. Lee, C.P. Grey and S.J.L. Billinge, ***Rapid-acquisition pair distribution function (RA-PDF) analysis****, J. Appl. Cryst.****36****, 1342-1347 (2003).*

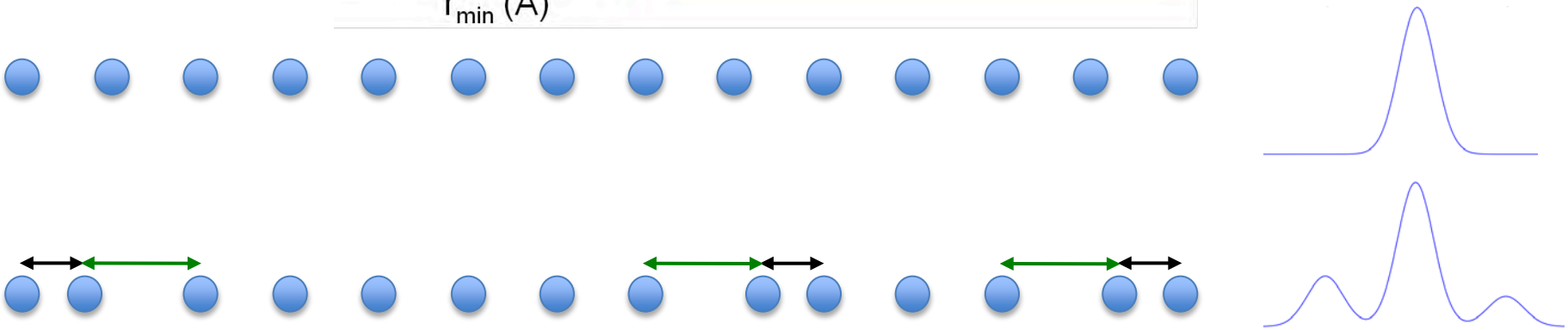
Pair Distribution Function



- Sit on an atom and look at your neighborhood
- G(r) gives the probability of finding a neighbor at distance r.
- PDF is experimentally accessible
- PDF gives the local structure

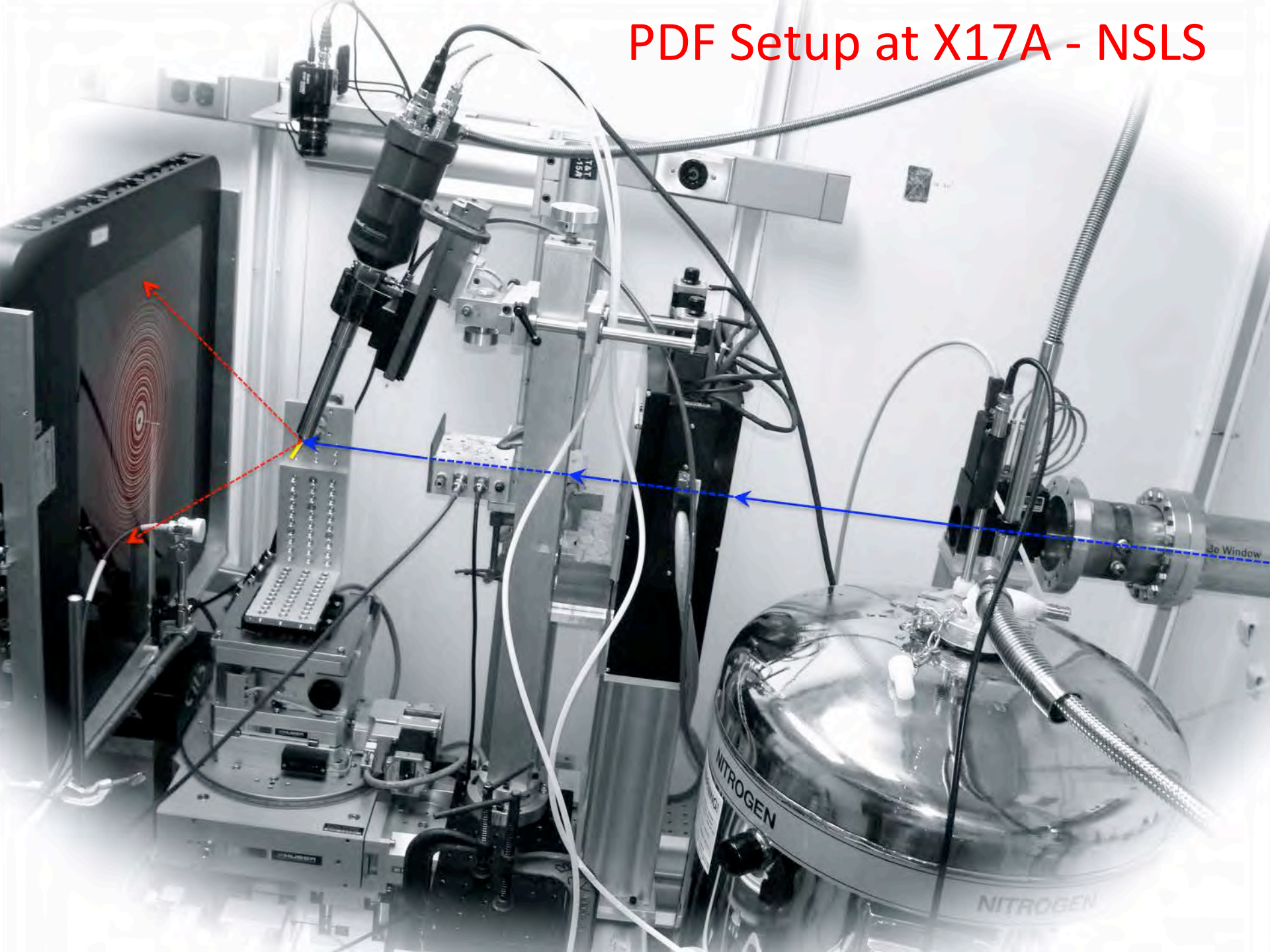
When is the PDF approach useful?





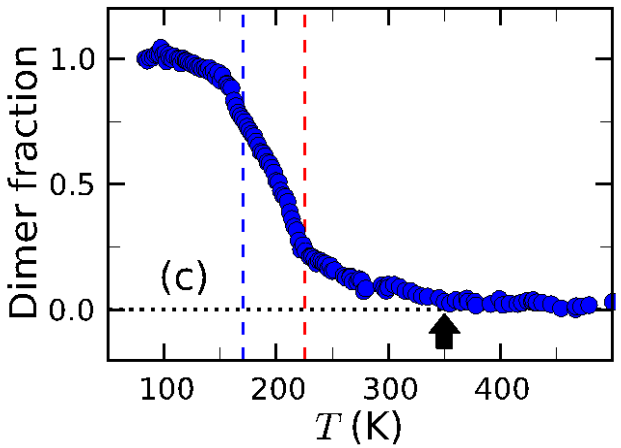
- Systems that display local distortion without long range order
- Identifying differences between local structure and average structure

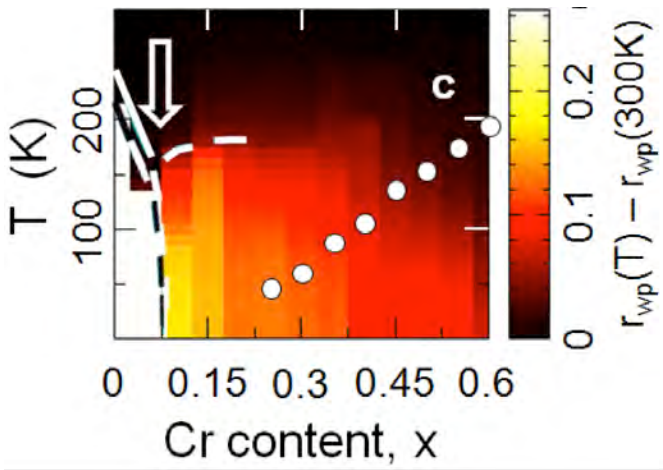
PDF Setup at X17A - NSLS



PDF Setup at X17A - NSLS

- Photon Energy 67 KeV (0.1839 Å)
- Qmax 28 – 30 Å
- Sample-to-detector distance 204.2 mm
- Beam size 0.5 x 0.5 mm
- Capillary transmission with detector centered configuration
- Temperature range 10 – 500 K

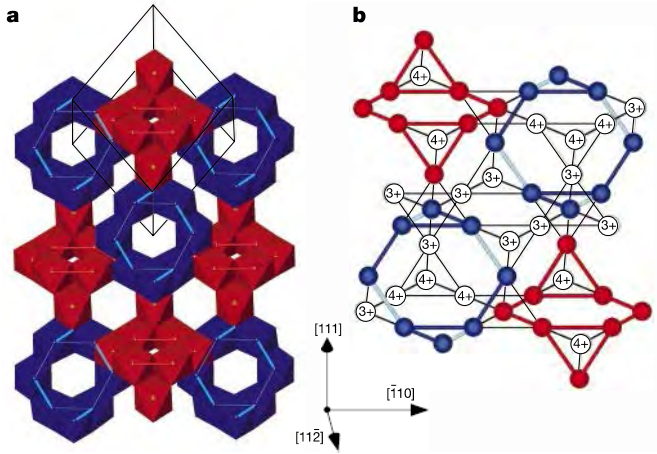




Rapid acquisition of scattering data (minutes per data set)

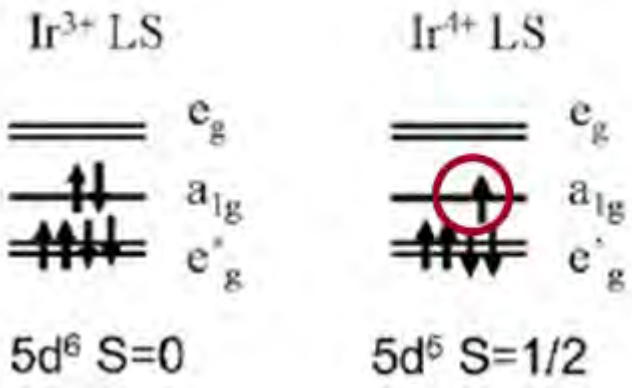
Can study subtle changes in structure

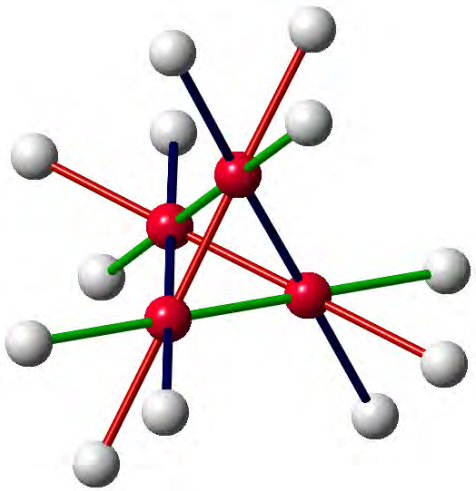
PDF Studies of Spinel Systems



1. $CuIr_2S_4$

Thiospinel $CuIr_2S_4$ Properties





- Ir in almost regular S_6 octahedra, CF splits *d* levels into t_{2g} triplet and e_g doublet
- Only t_{2g} levels are occupied (Ir^{3+} by 6 and Ir^{4+} by 5 electrons, nominal valence 3.5+)

PES, NMR, LDA: Cu^{1+} making $Ir^{3.5+}$ (half-integer!)

J. Matsuno *et al*., Phys. Rev. B **55**, R15979 (1997); K. Yagasaki *et al*., J. Phys. Soc. Jpn. **75**, 074706 (2006).

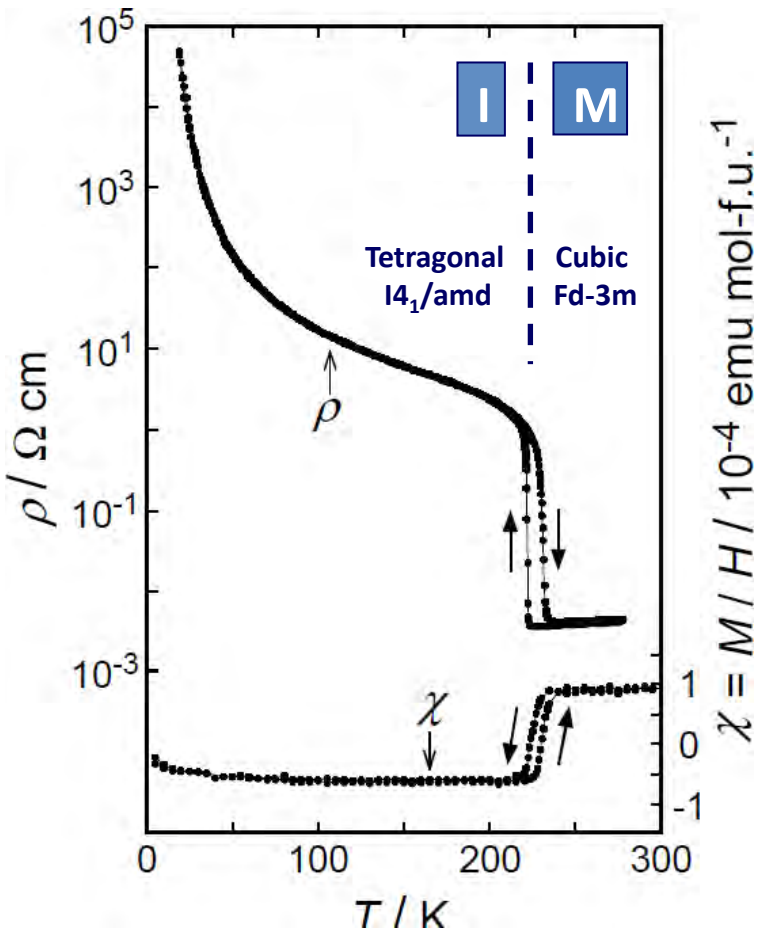
Thiospinel $CuIr_2S_4$ Properties

High-T phase (HMP)

- Metallic
- Pauli paramagnetic
  (NMR, Mössbauer, Magnetic susceptibility)
- Cubic (Fd-3m)

Low-T phase (LIP)

- Insulating
- Diamagnetic (nonmagnetic)
- Tetragonal ($I4_1$/amd) – *original assessment*

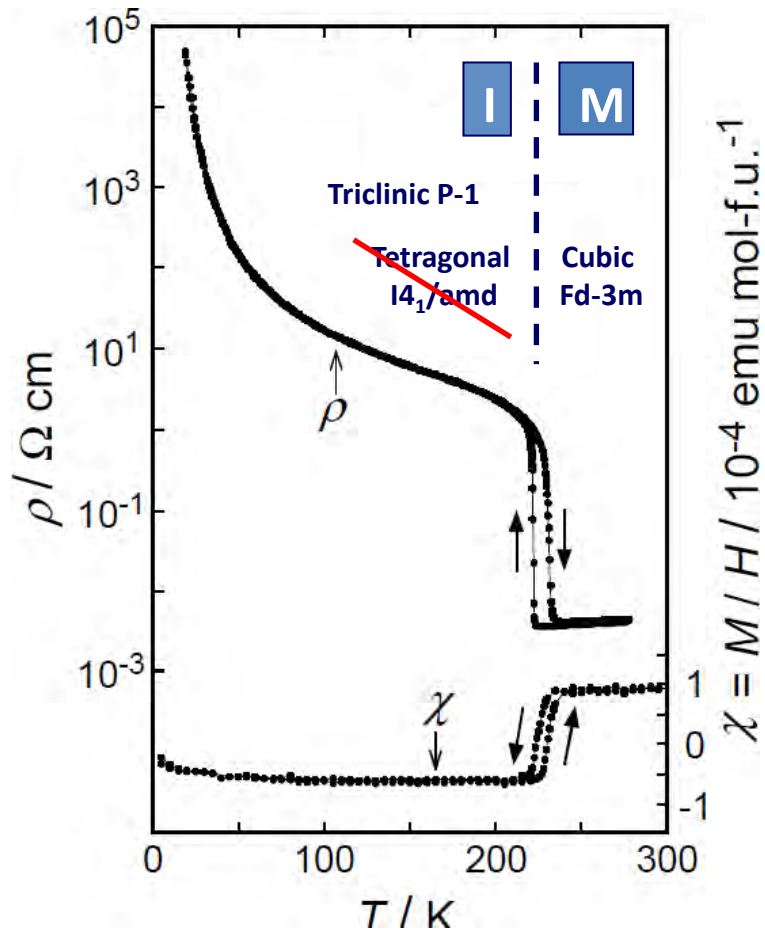


S. Nagata *et al.*, Physica B **194-196**, 1077 (1994); T. Furubayashi *et al.*, J. Phys. Soc. Jpn. **63**, 3333 (1994).

Thiospinel $CuIr_2S_4$ Properties

High-T phase (HMP)

- Metallic
- Pauli paramagnetic
  (NMR, Mössbauer, Magnetic susceptibility)
- Cubic (Fd-3m)
- Ir charge nominally 3.5+
- Nearest neighbor Ir-Ir distance ~ 3.5 Å

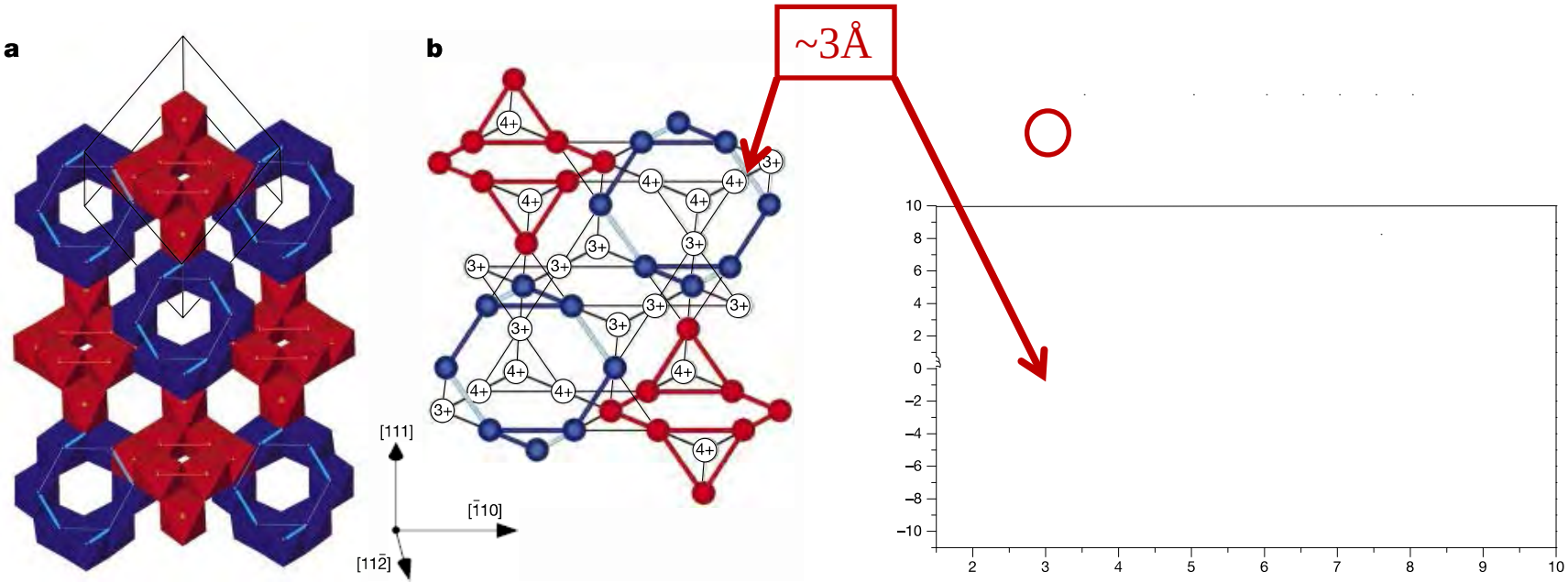


Low-T phase (LIP)

- Insulating
- Diamagnetic (nonmagnetic)
- Tetragonal ($I4_1$/amd) – *original assessment*
- Long range charge and orbital ordering
- Triclinic (P-1) – *updated assessment*
- Nearest neighbor Ir distance: 3.0 Å when dimerized, 3.5 Å otherwise

Very strong lattice response to dimer state: 0.5 Å difference in n.n. bondlength

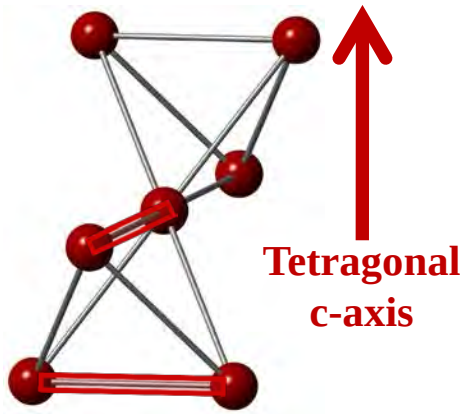
$CuIr_2S_4$ Structure

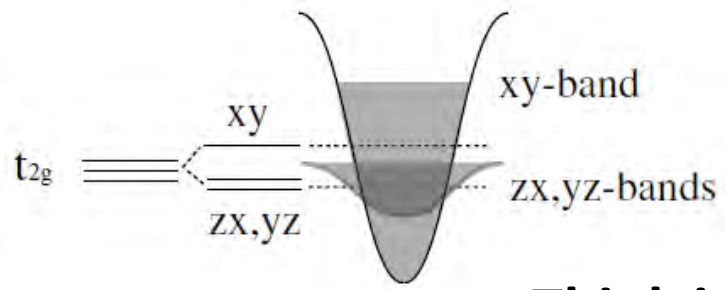


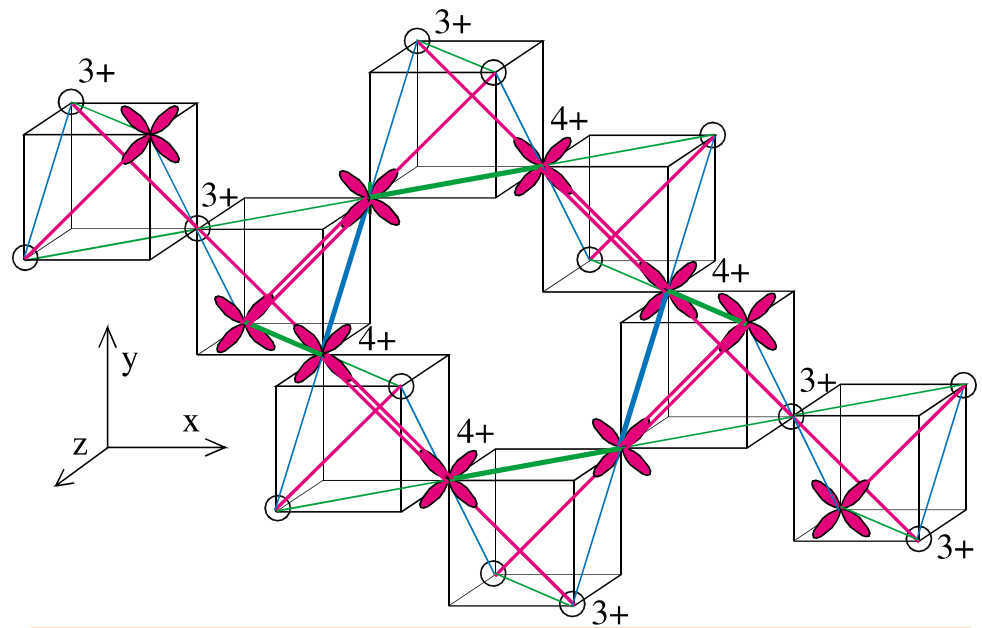
- Low-T structure is triclinic and low symmetry
- Ir ions are arranged in octahedral units:
  - Red octahedra contain non-dimerized Ir^{4+} ions
  - Blue octahedra contain dimerized Ir^{3+} dimerized
- Dimers are spin singlets with significantly shorter bond length
- Dimerization only occurs along two (symmetry related) Ir chains
- Unusual for a 3D system!

P.G. Radaelli *et al.*, Nature **416**, 155 (2002).

Understanding $CuIr_2S_4$ Low-T Structure





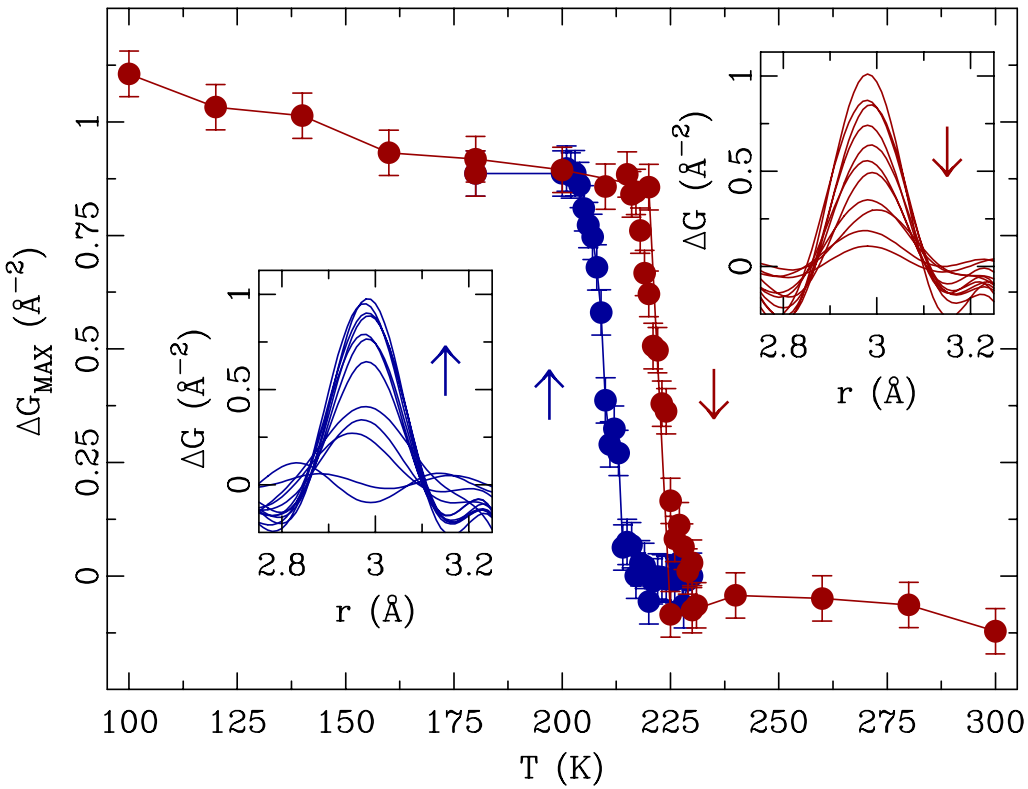


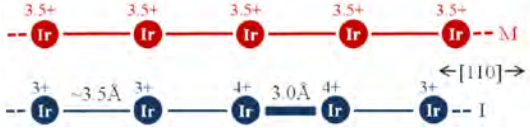
D.I. Khomskii and T. Mizokawa, PRL **94**, 156402 (2005).

Think in 1D, not 3D

- Strongest overlap of Ir orbitals is between same orbitals along 1D chain
- Tetragonal distortion modifies CF and splits triply degenerate t_{2g} band
  - zx, yz bands are lower in energy and completely filled
  - xy band is broader and higher in energy with ¾ filling (1.5 electrons)
- 1D partially filled band results in Peierls or CDW transition
- Ir chains along xy direction tetramerize (Ir^{3+}-Ir^{3+}-Ir^{4+}-Ir^{4+}) and Ir^{4+} form spin singlets
- Same mechanism at work in $MgTi_2O_4$

PDF Study of $CuIr_2S_4$





← Cr doped

- Short (dimerized) bond can be directly seen in PDF and tracked across MIT
- Clean hysteretic behavior observed
- Local dimers disappear along with LRO at MIT
- Substitution of small amounts of Cr (5%) destroys local dimers

$CuIr_2S_4$ Questions

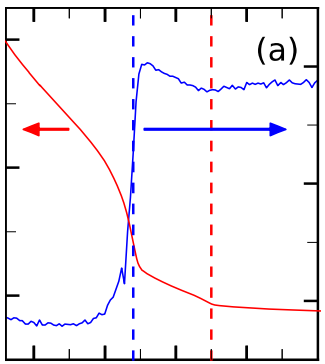
In $CuIr_2S_4$ everything happens at once

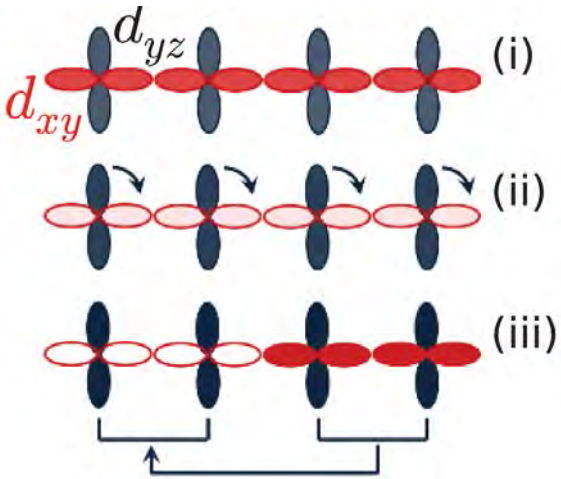
- Structural transition
- Metal to insulator transition
- Charge ordering
- Orbital ordering
- Spin singlet formation (magnetic ordering)

What is driving the Physics?

2. $LiRh_2O_4$

$LiRh_2O_4$

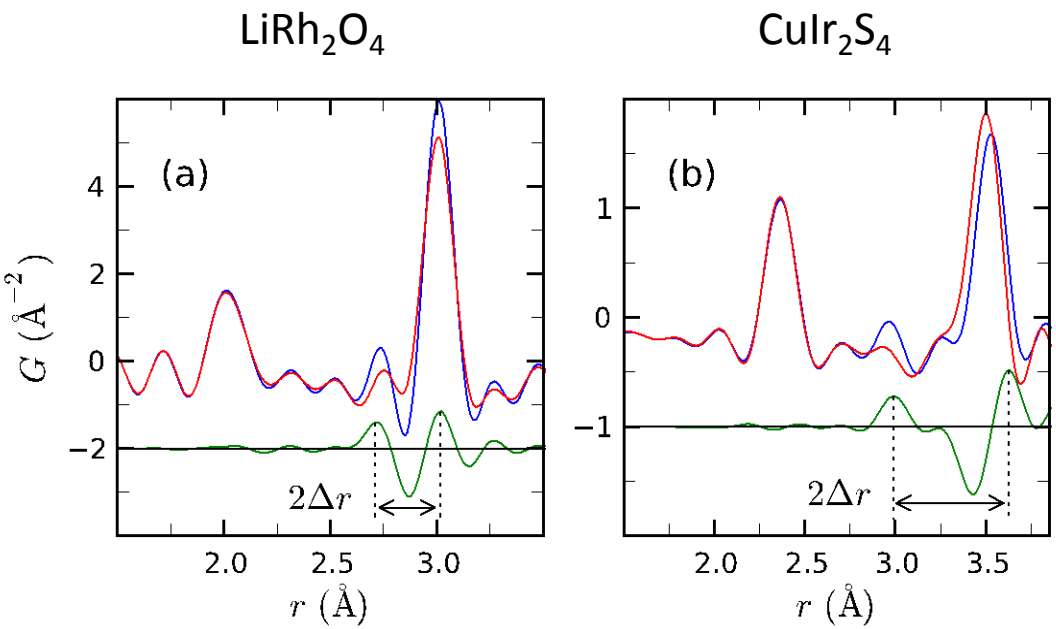


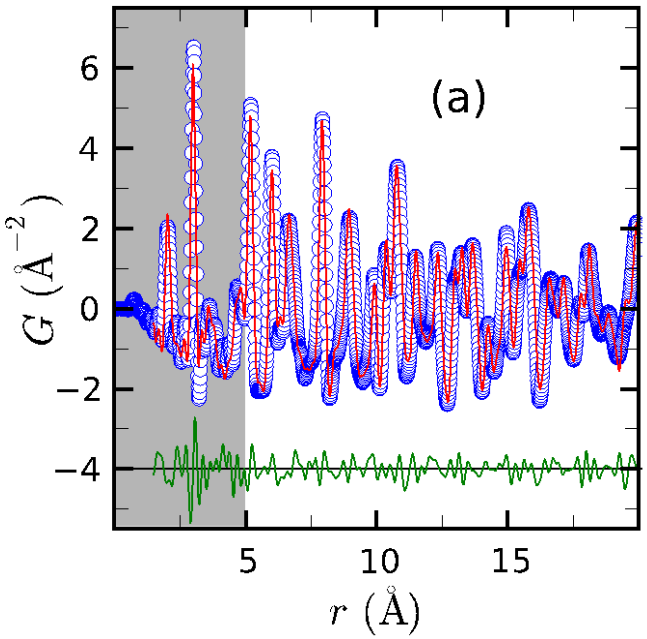


- Transition metal spinel similar to $CuIr_2S_4$
  - Spinel with cubic structure at 300K
  - Non-integer spin and charge on B-site (Rh nominally 3.5+)
  - MIT transition accompanied by structural distortion
  - LRO Rh^{4+} dimers assumed, but not directly observed (low-T structure unsolved)
- Important difference: MIT occurs in two stages
  - Band Jahn-Teller transition at 225 K breaks degeneracy of t_{2g} levels
  - Precursor to charge density wave formation (Peierls transition) at 170 K
  - Model system for understanding MIT in TM-spinels?

Y. Okamoto *et al.*, Phys. Rev. Lett. **101**, 086404 (2008).

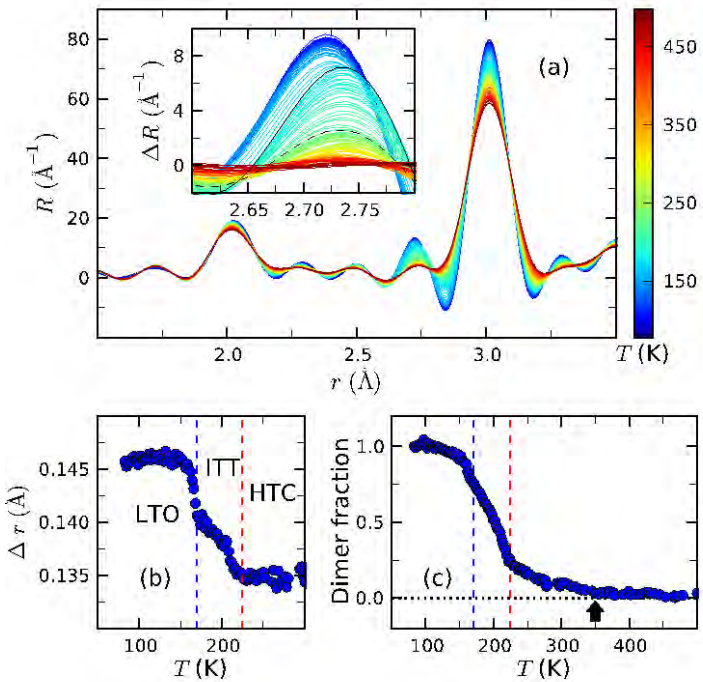
PDF Study of $LiRh_2O_4$

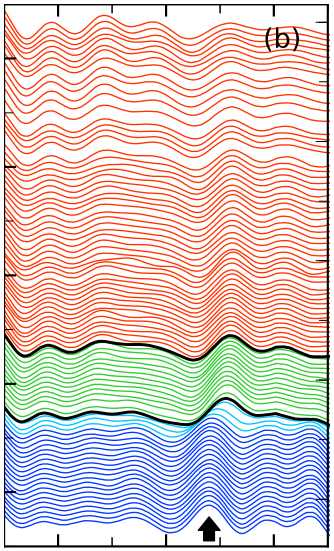




- PDF provides direct evidence for dimer formation at low-T (similar to $CuIr_2S_4$)
- What happens as we warm the system?
  - In the ITT phase the $I4_1/amd$ model does not fit the data well
  - Evidence for SRO dimers above the phase transition?

PDF Study of $LiRh_2O_4$

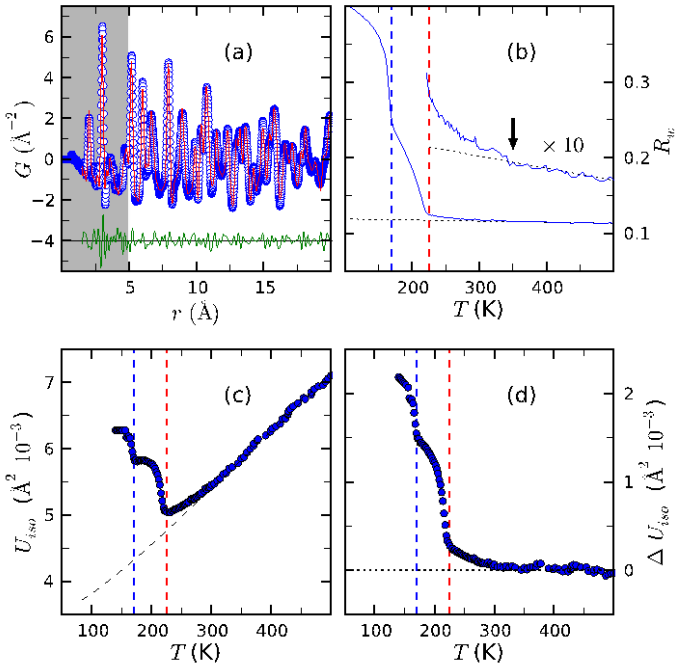


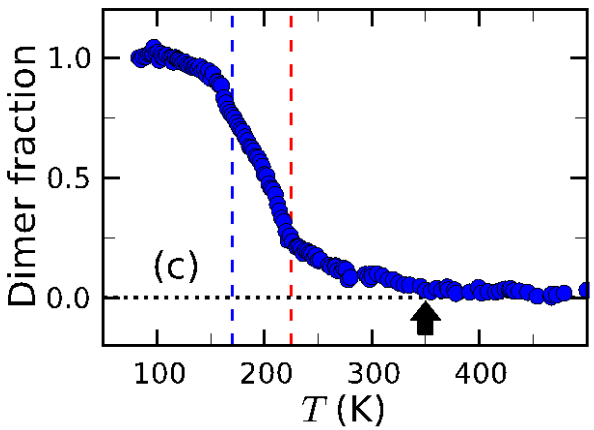


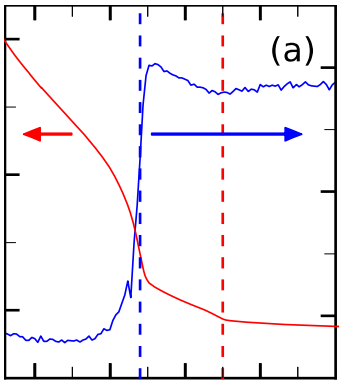
Evidence for SRO dimers above the phase transition?

- Yes! It appears that dimers persist all through the ITT phase and into HTO phase
- Size of distortion changes abruptly at LTO/ITT transition, but dimers survive
- Not like $CuIr_2S_4$!

PDF Study of $LiRh_2O_4$

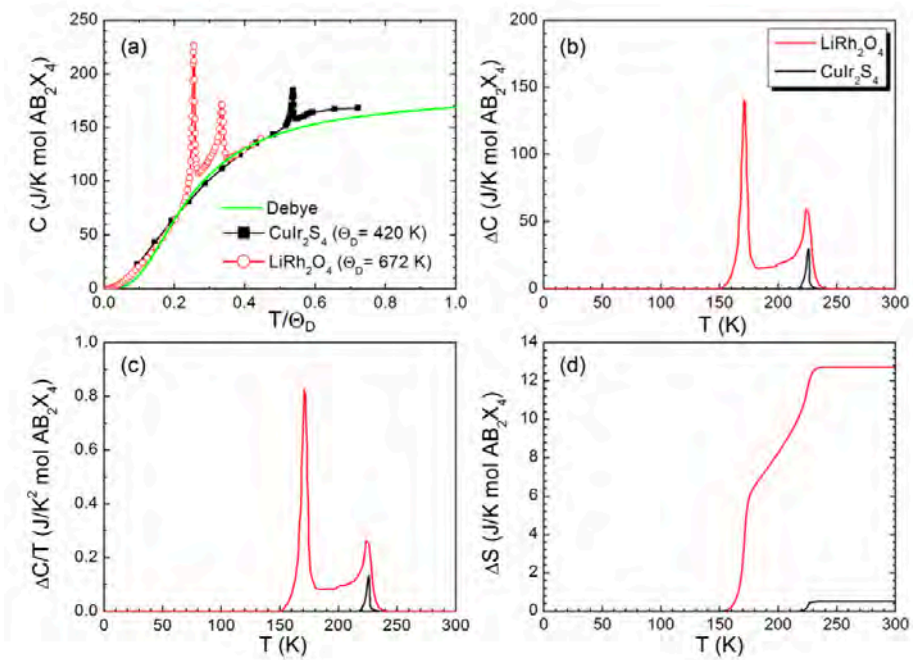


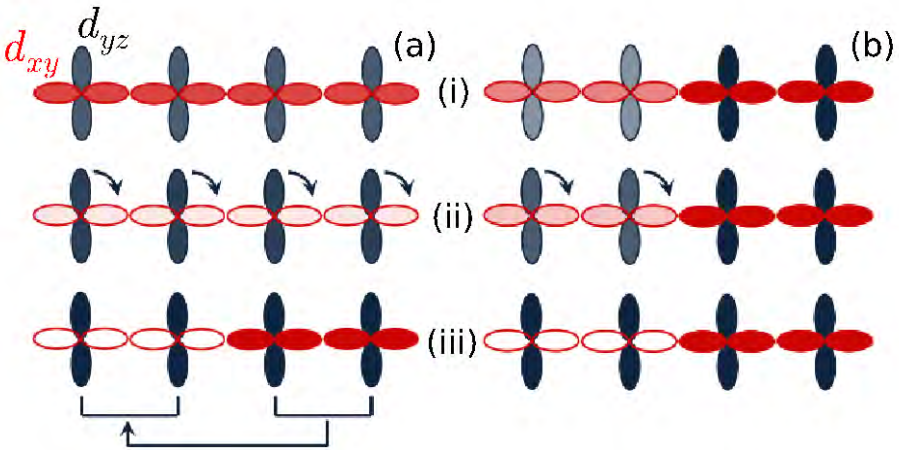




- Evidence for SRO dimers into the HTC phase
- Dimer fraction correlates well with electrical measurements
- Local structure is driving the Physics

Strong Electron Correlation in $LiRh_2O_4$

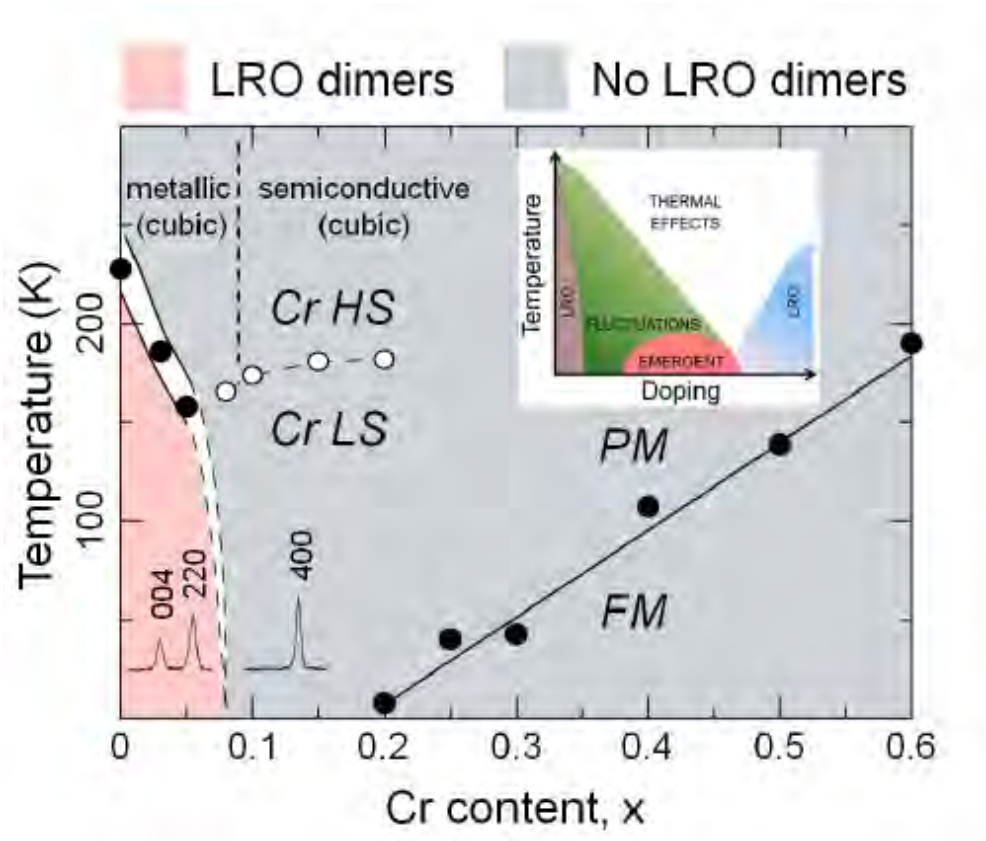




- Physics in $LiRh_2O_4$ and $CuIr_2S_4$ qualitatively different
- Khomskii model (orbital Peierls transition) cannot explain CDW at high-T
- All experimental evidence points to strong electronic correlation
- Low-T structure remains unsolved.

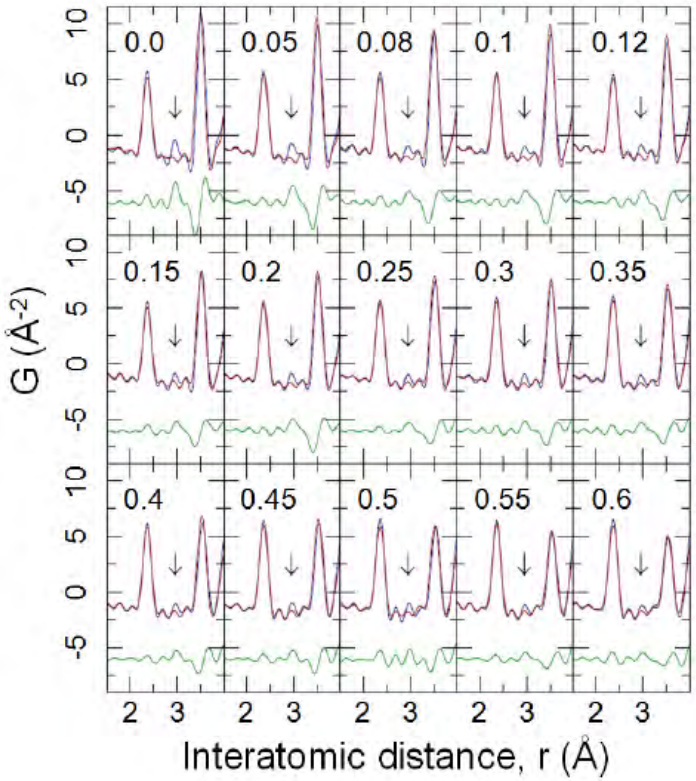
3. $Cu(Ir_{1-x}Cr_x)_2S_4$

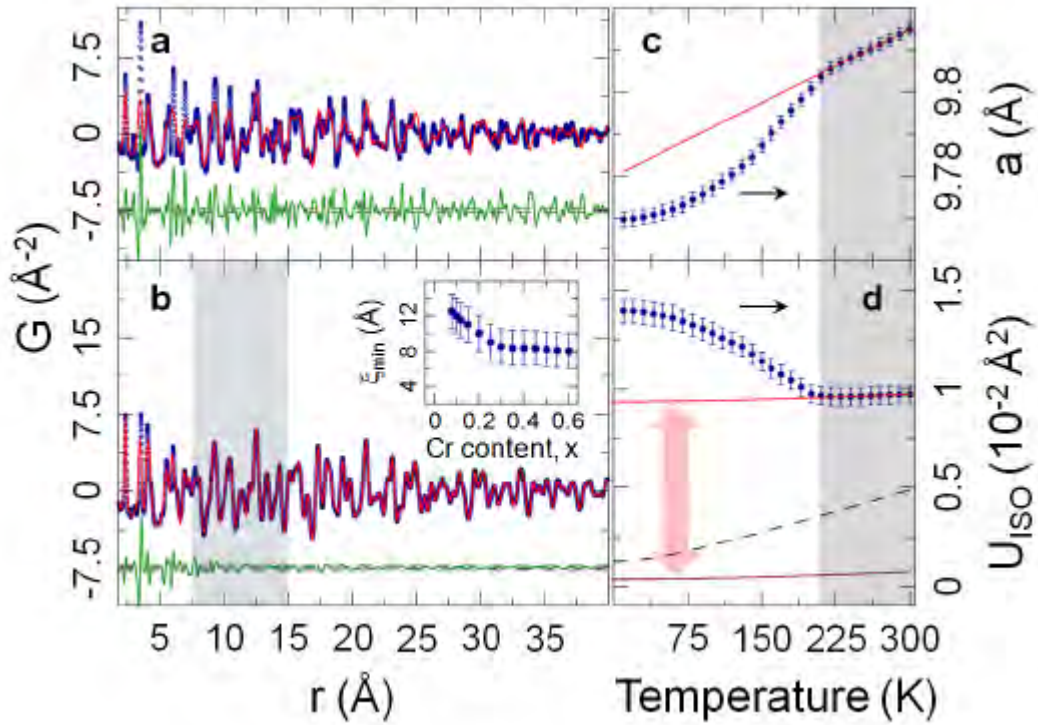
Average Structure Phase Diagram of $Cu(Ir_{1-x}Cr_x)_2S_4$



- MIT only occurs close to the Ir endmember
- Doping quickly suppresses LRO dimers
- FM metallic state emerges at higher doping
- Anomolies in resistivity and susceptibility associated with Cr HS to LS transition

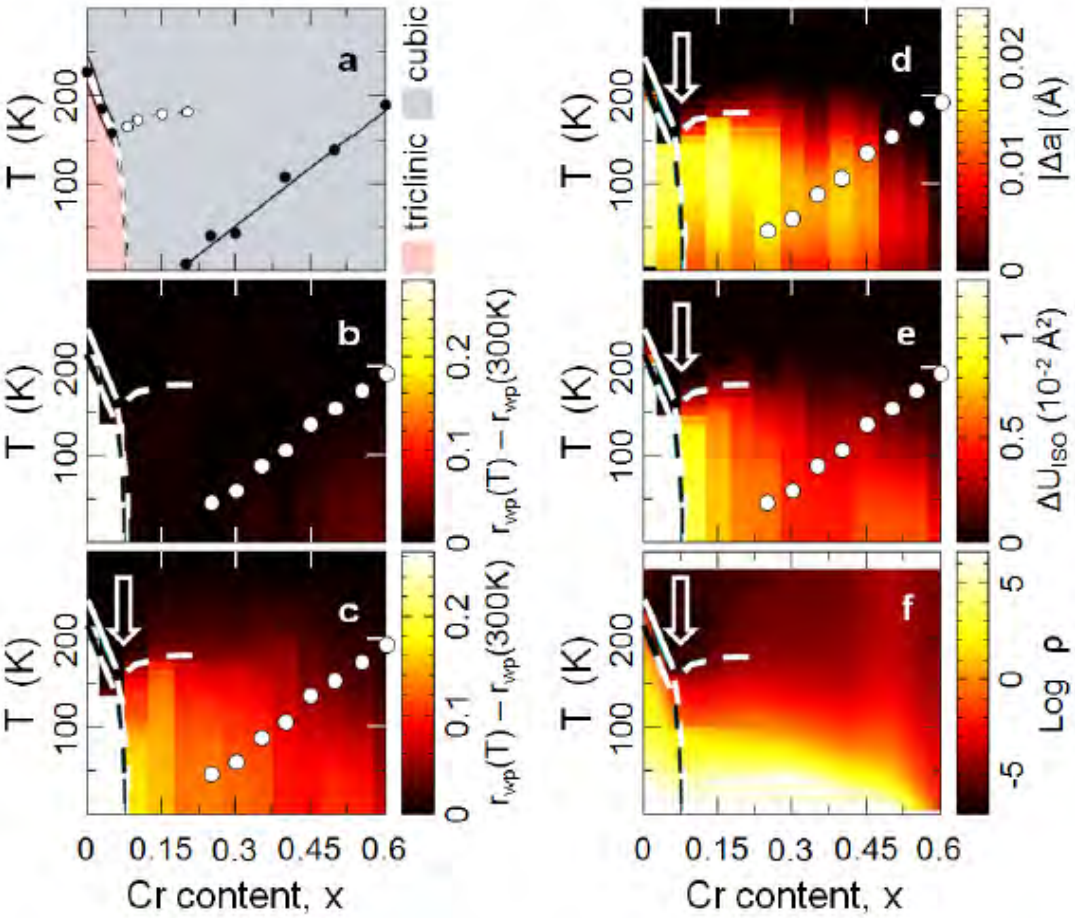
Local Structure of $Cu(Ir_{1-x}Cr_x)_2S_4$





- PDF study shows that dimers persist locally up to x = 0.6
- Competition between a PM metallic state and DM insulating charge ordered state
- First observation of nanoscale phase coexistence in irridates.

Local Structure Phase Diagram of $Cu(Ir_{1-x}Cr_x)_2S_4$



- Average structure and local structure produce very different phase diagrams
- Local structure correlates well with macroscopic measurements (resistivity)

Conclusions

- Evidence for Strong Electronic Correlations in $LiRh_2O_4$
- $Cu(Ir_{1-x}Cr_x)_2S_4$ model system for studying nano-scale phase separation/competition
- Local structure is intimately tied to macroscopic properties in complex materials
- Understanding local structure is essential to solve materials science problems
- PDF is an excellent tool for multi-scale problems
- Development of PDF at NSLS/NSLS II is essential

Thank you

BNL

Simon Billinge
Emil Bozin
Pavol Juhas
Milinda Abeykoon

Alexei Tsvelik
Weiguo Yin

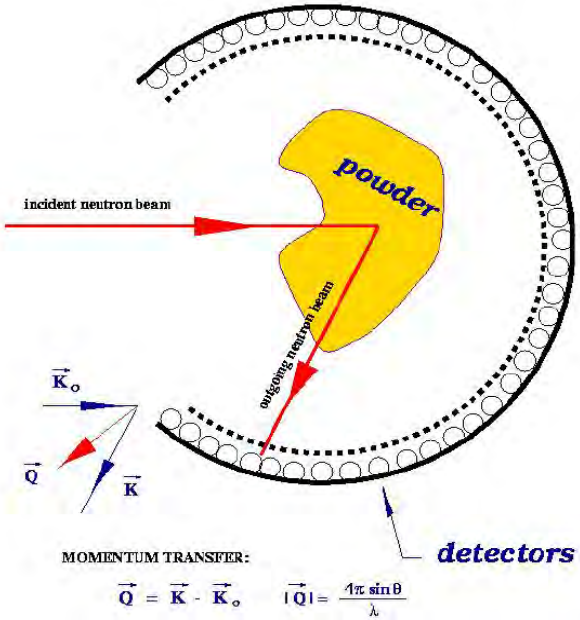
ANL

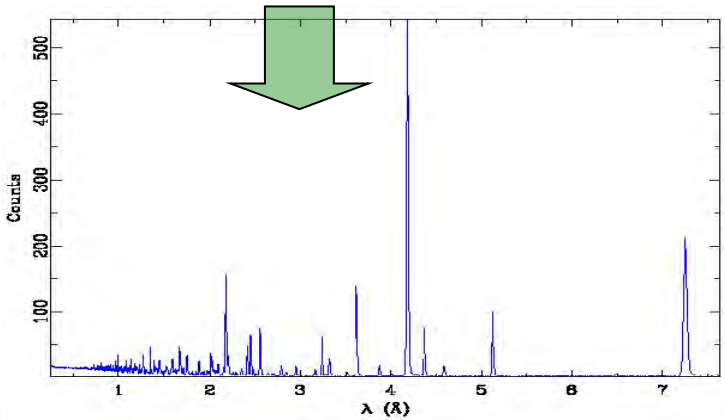
John Mitchell

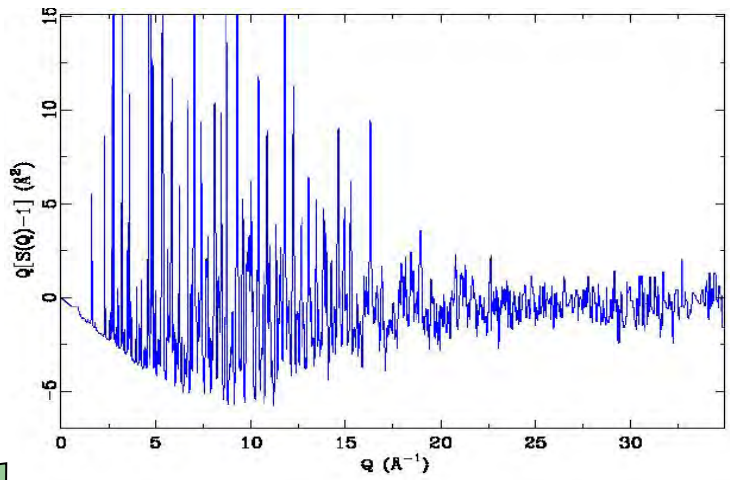
Radaelli

Regardless of the specific implementation, geometrical frustration is intimately intertwined with all these phenomena, since, at the classical mean field level, spin or charge configurations minimizing nearest-neighbour Coulomb or exchange energy form a degenerate lowest energy manifold. In most cases, this induces a suppression of the ordering temperatures much below what is expected based on the strength of the interactions. How the degeneracy is eventually lifted on cooling is a matter of intense theoretical and experimental interest, but, essentially, there are three possibilities. The system can retain its cubic symmetry, remains fluctuating down to low temperatures and may eventually settle in an 'exotic' quantum ground state such as a 'spin liquid', with unusual excitation spectra. A second possibility, which is realized in ice, is that the system 'freezes' in a disordered configuration, such as a spin glass, with residual low-temperature entropy. Alternatively, the system can lift the degeneracy, resulting in long-range charge or spin ordering. This is usually accompanied by a distortion of its crystal structure. When the latter happens, the resulting crystal structures are usually extremely complex, and only a handful of cases have been solved to date.

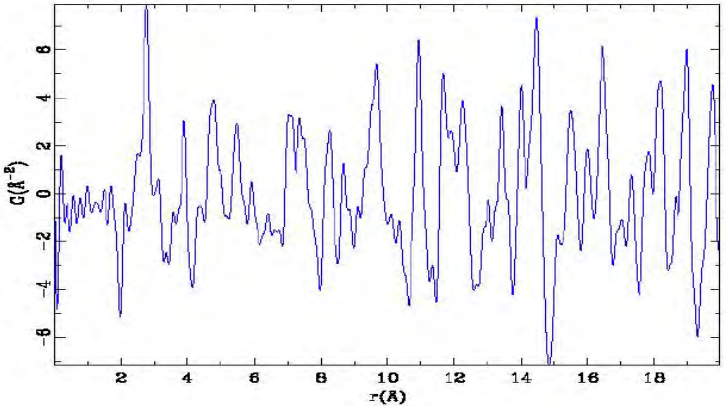
How is a PDF obtained?



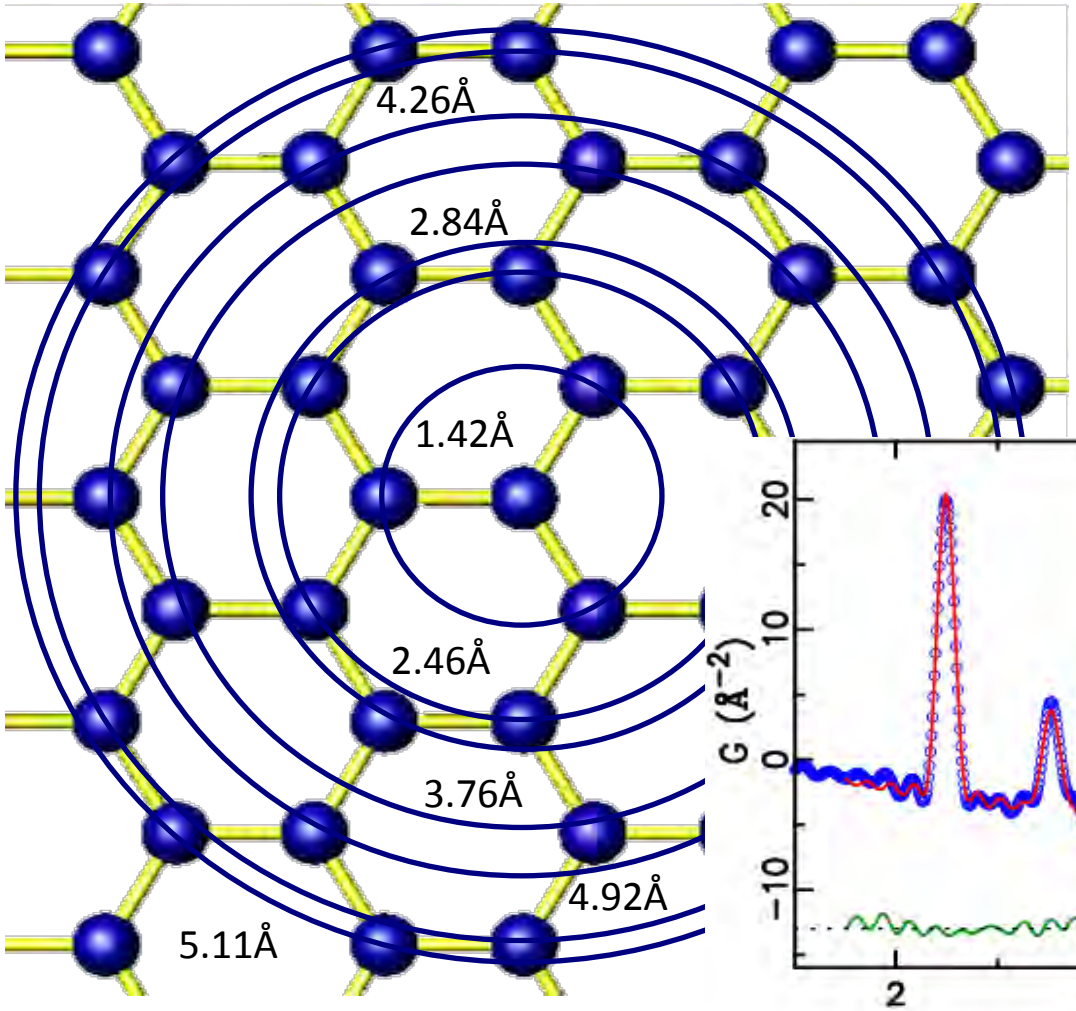
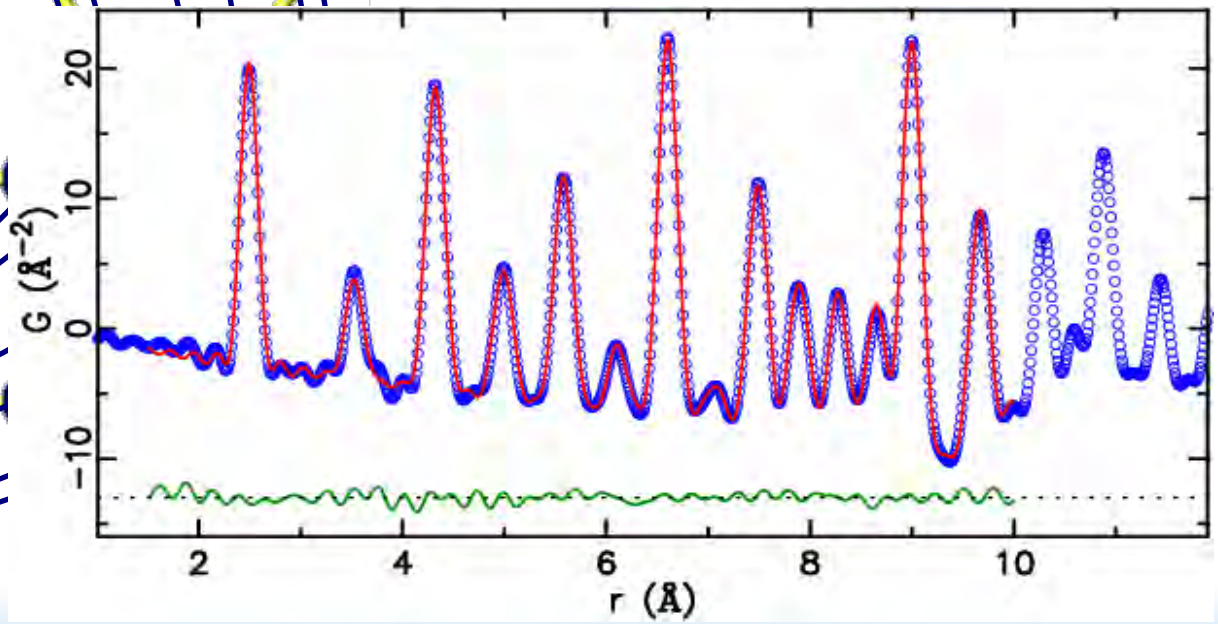




$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin Qr dQ$$



Pair Distribution Function



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