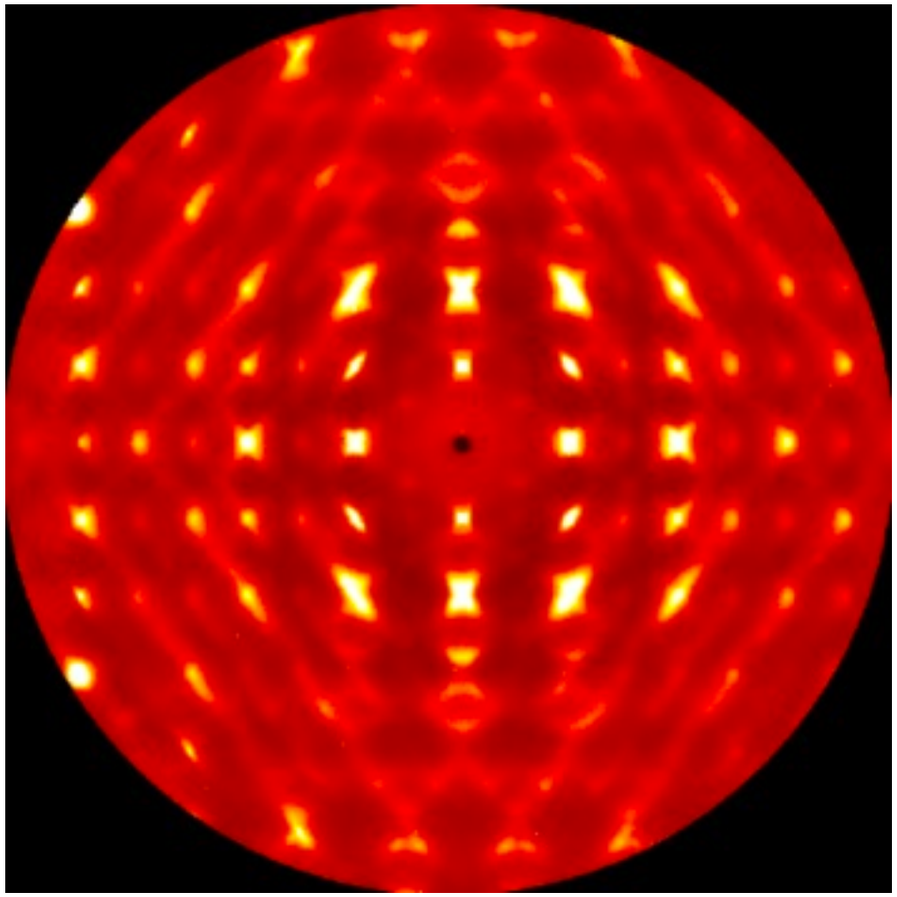
Single Crystal Diffuse Scattering using High-Energy X-rays



Stephan Rosenkranz, Ray Osborn
Materials Science Division
Argonne National Laboratory

Single Crystal Diffuse Scattering

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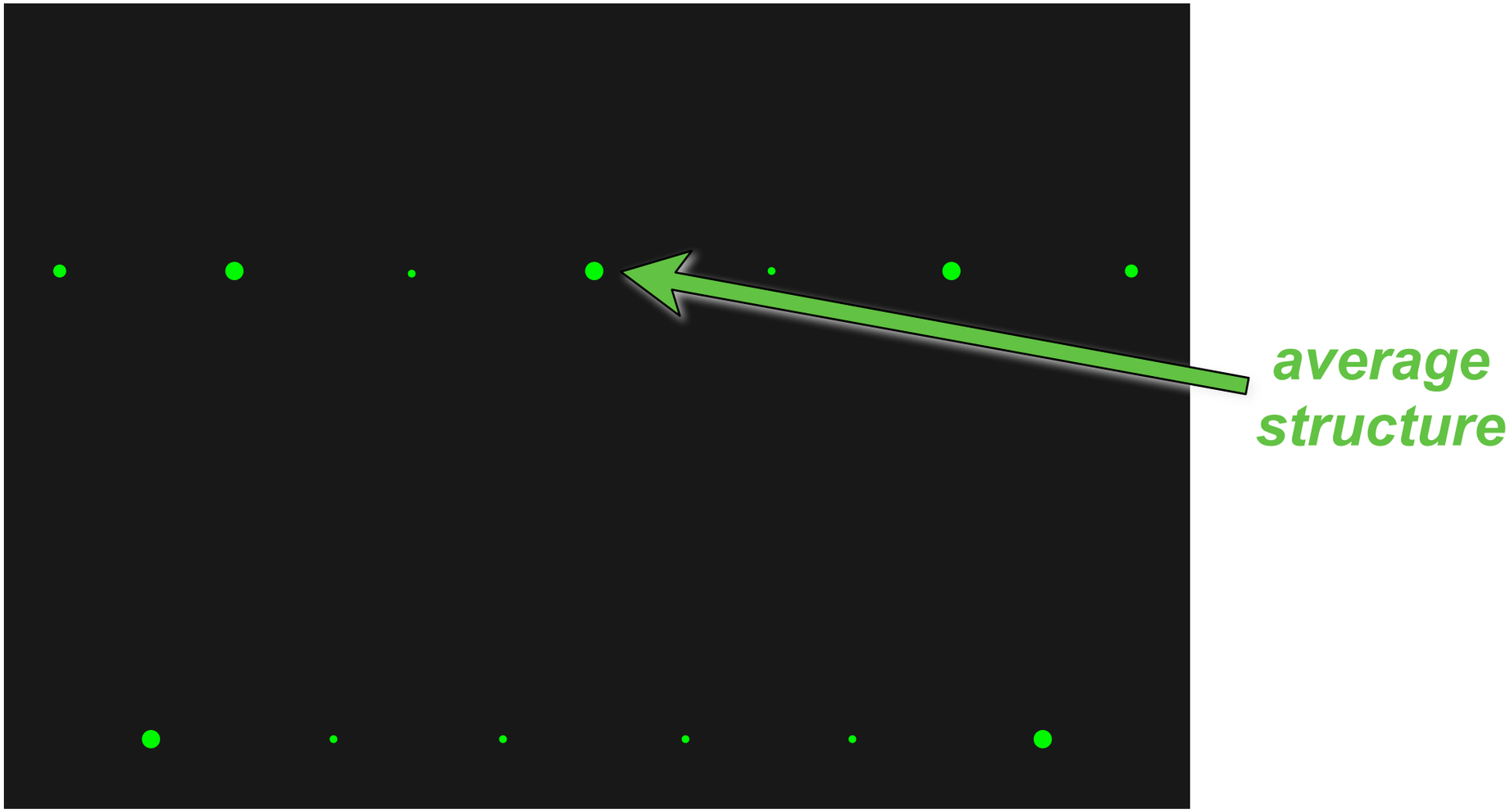
- Bragg Scattering
  - average structure, long range superstructures



Single Crystal Diffuse Scattering

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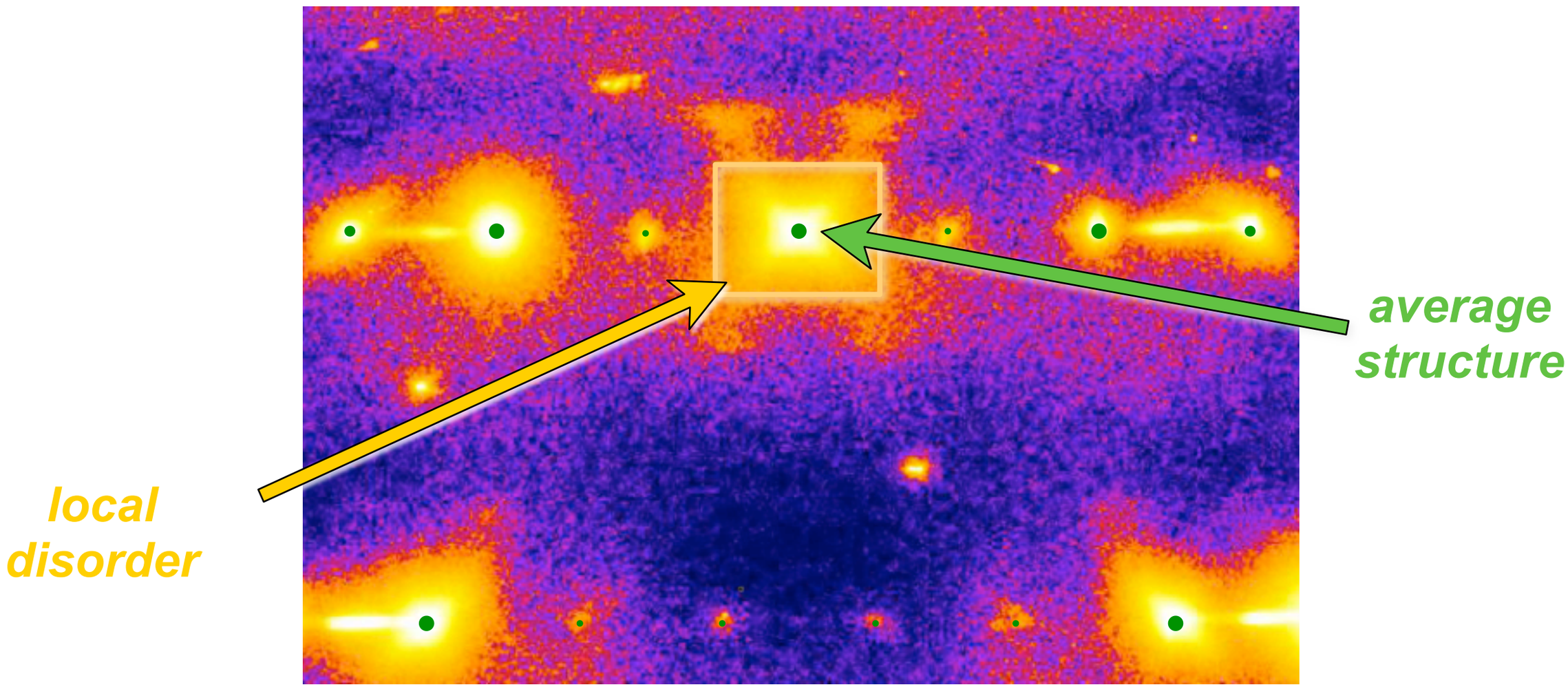
  - deviations from the average structure, topology of disorder



Single Crystal Diffuse Scattering

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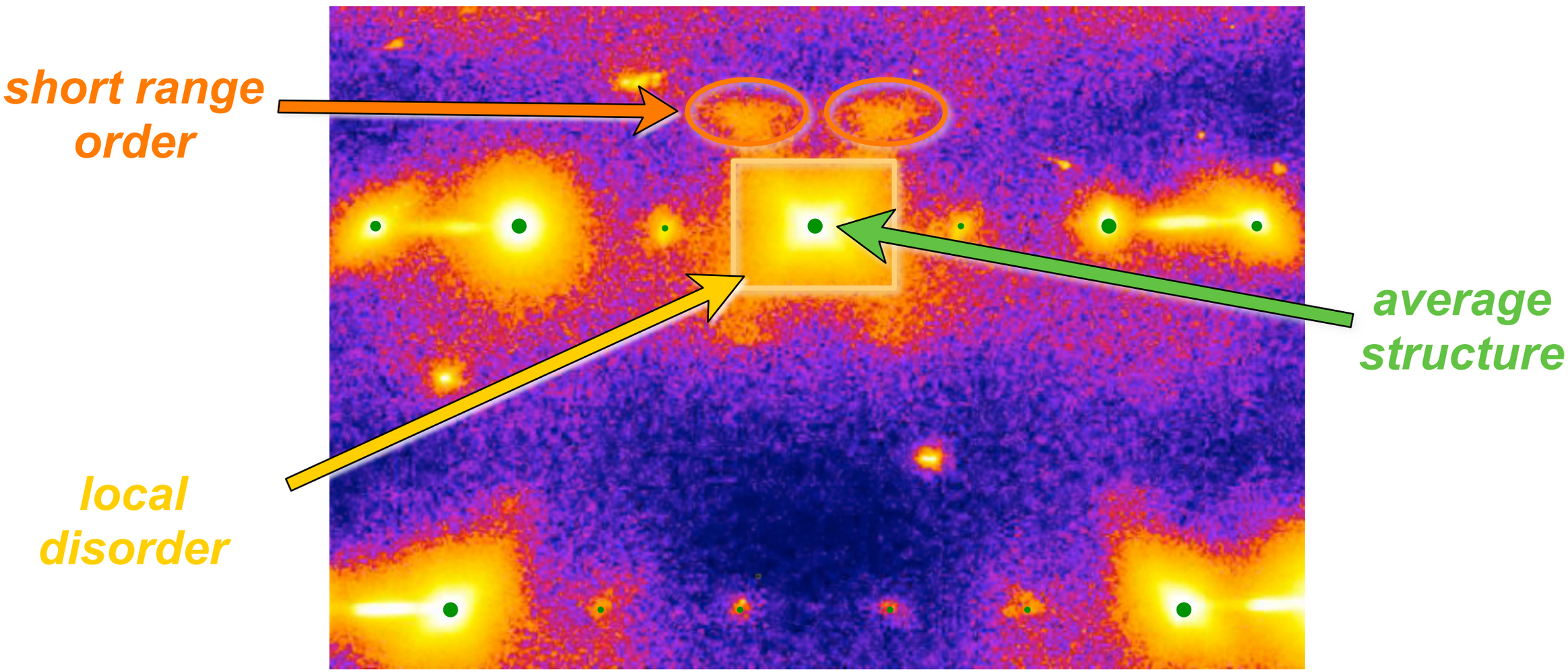
- Local Probes: single crystal diffuse scattering, PDF, EXAFS
  - deviations from the average structure, topology of disorder
  - short-range correlations



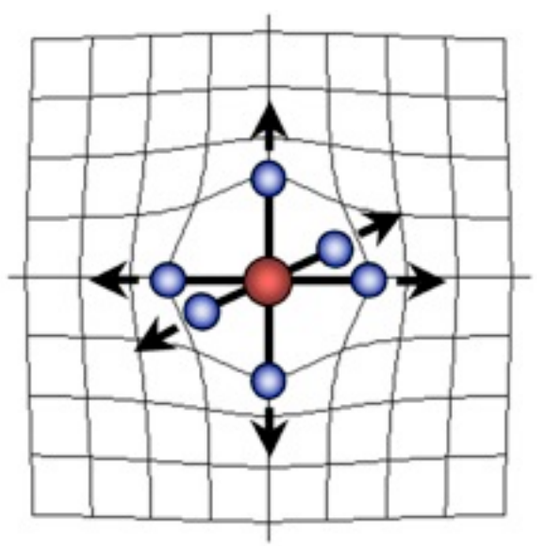
Emerging Phenomena in Systems with Complex Disorder

Emerging Phenomena in Systems with Complex Disorder

- Many emerging phenomena are governed by complex disorder and short range correlations on the 1-10 nm length scale
- disorder due to
  - vacancies, inhomogeneous distribution of dopants *extrinsic*
  - competing interactions, quantum fluctuations, geometric frustration *intrinsic*

    ➡ Colossal Magnetoresistance

Jahn-Teller polarons in CMR manganites



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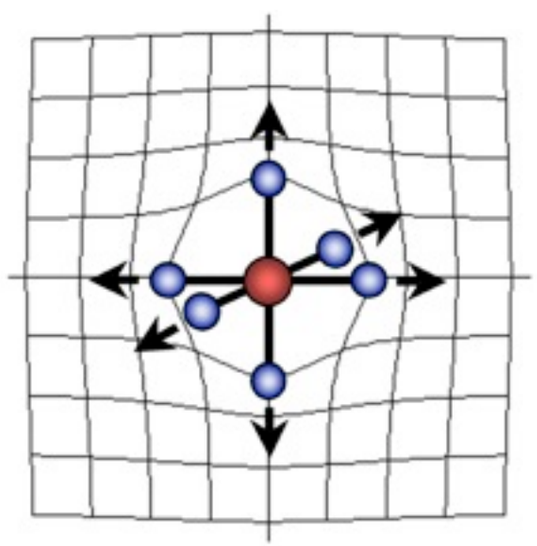
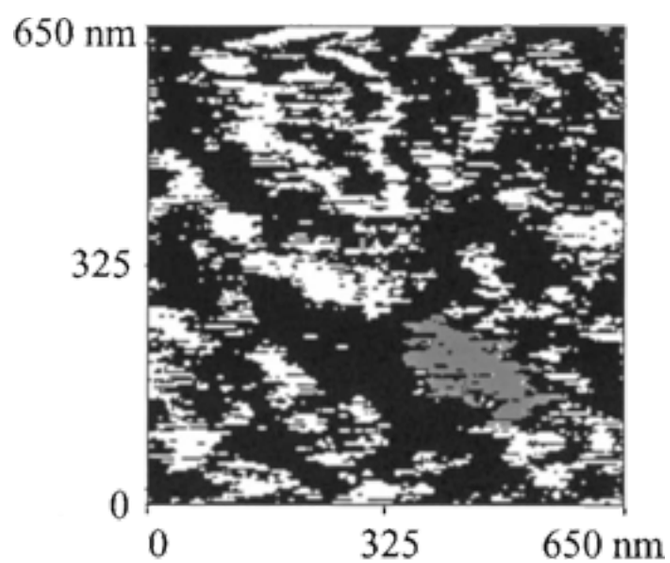


Polar nanodomains in relaxor ferroelectrics



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➡ Fast Ion Conduction
➡ Host-Guest Frameworks
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➡ Molecular Crystals
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➡ Doped Semiconductors

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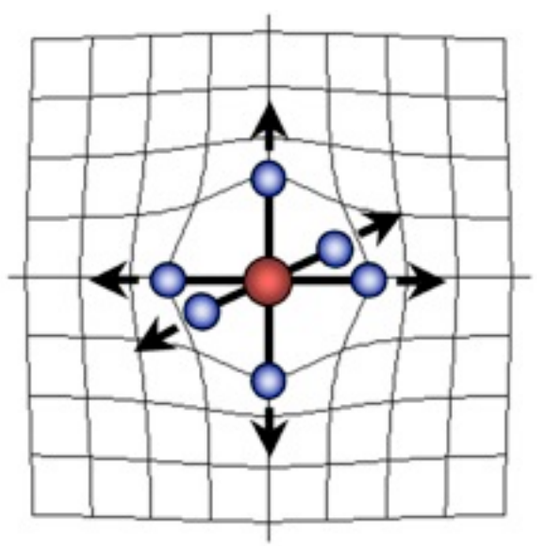

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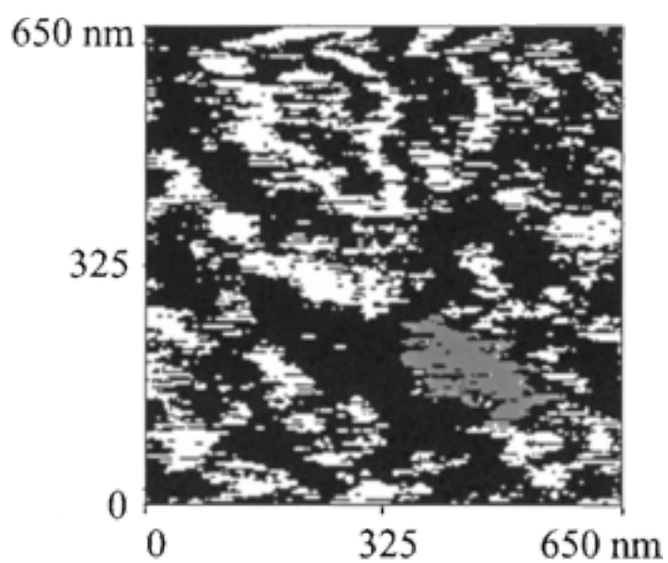
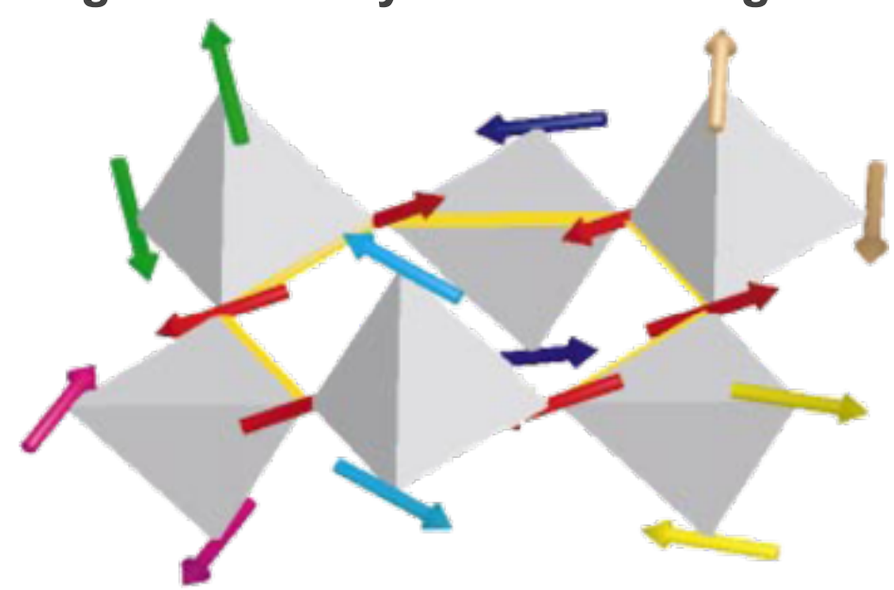


Hexagonal AF spin cluster in a geometrically frustrated magnet



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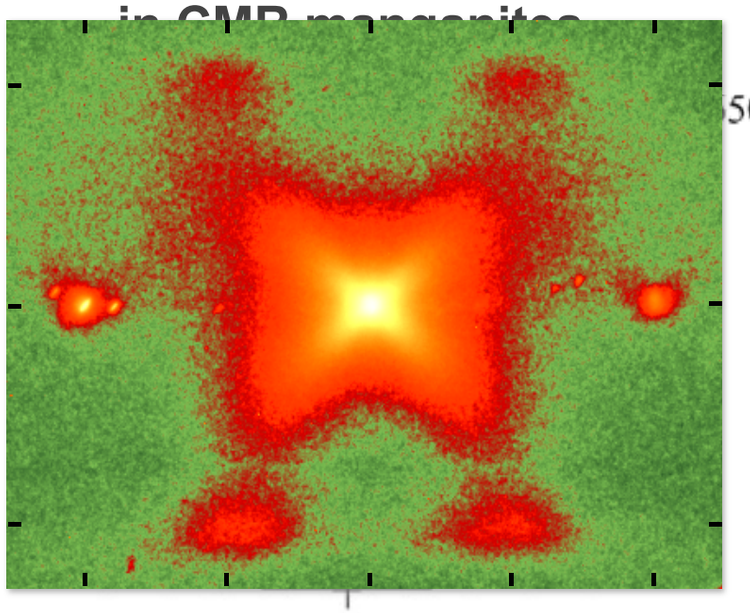

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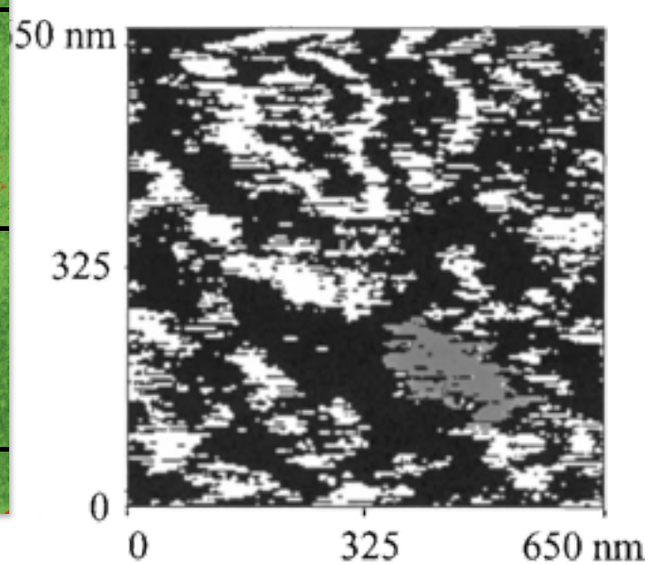

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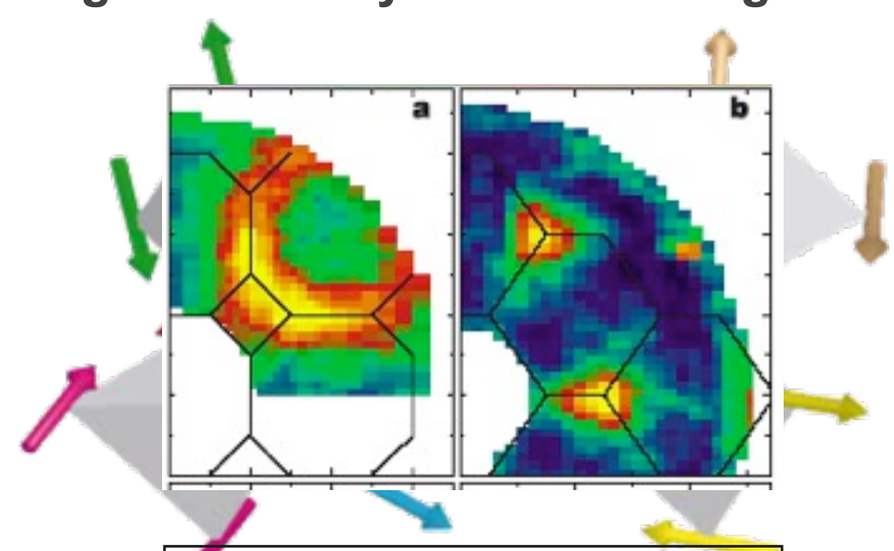
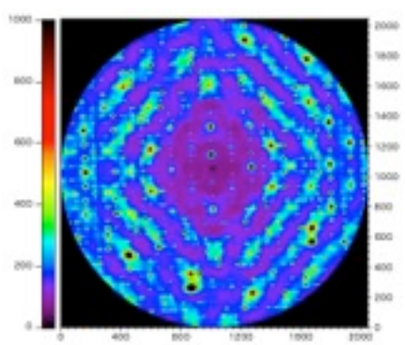
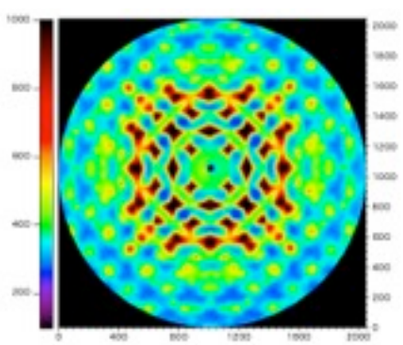


Lee *et al* Nature **418**, 856 (2002)

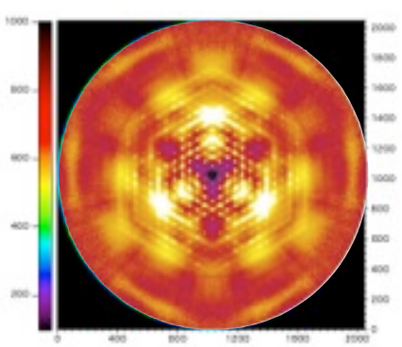
- superionics
- quasicrystals
- molecular disorder
- metallic alloys
- doped semiconductors
- microporous and mesoporous compounds
- host-guest systems
- colossal magnetoresistance
- relaxor ferroelectrics
- unconventional superconductors
- geometric frustration
- critical fluctuations
- hydrogen-bearing materials



Fast Ion Conduction

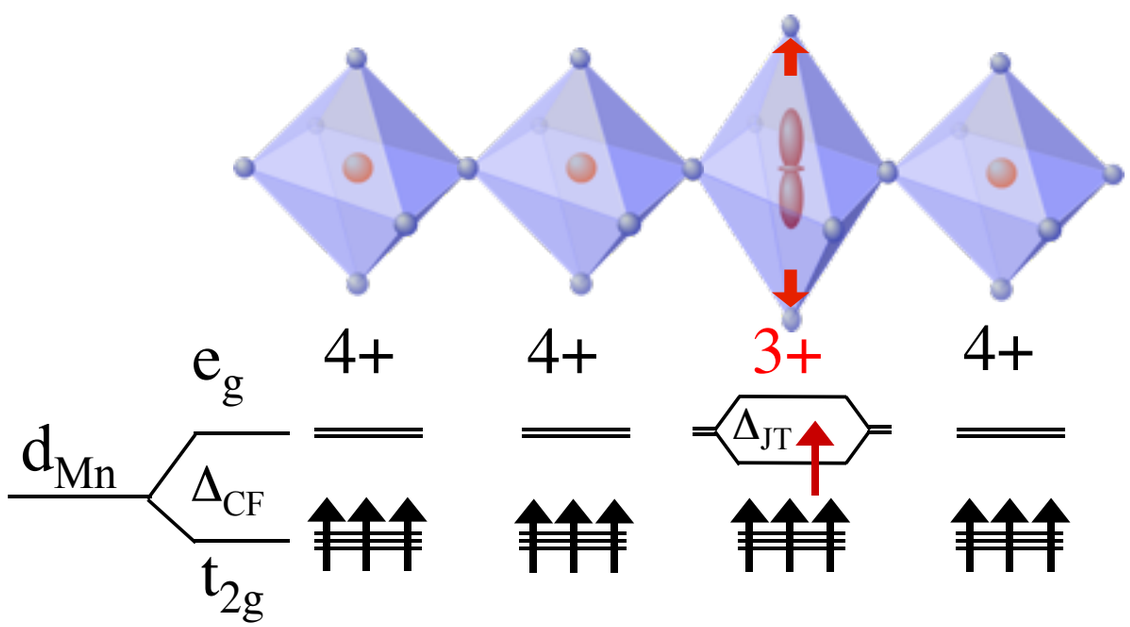


Relaxor Ferroelectricity



Molecular Solids

Diffuse Scattering from Jahn-Teller Polarons



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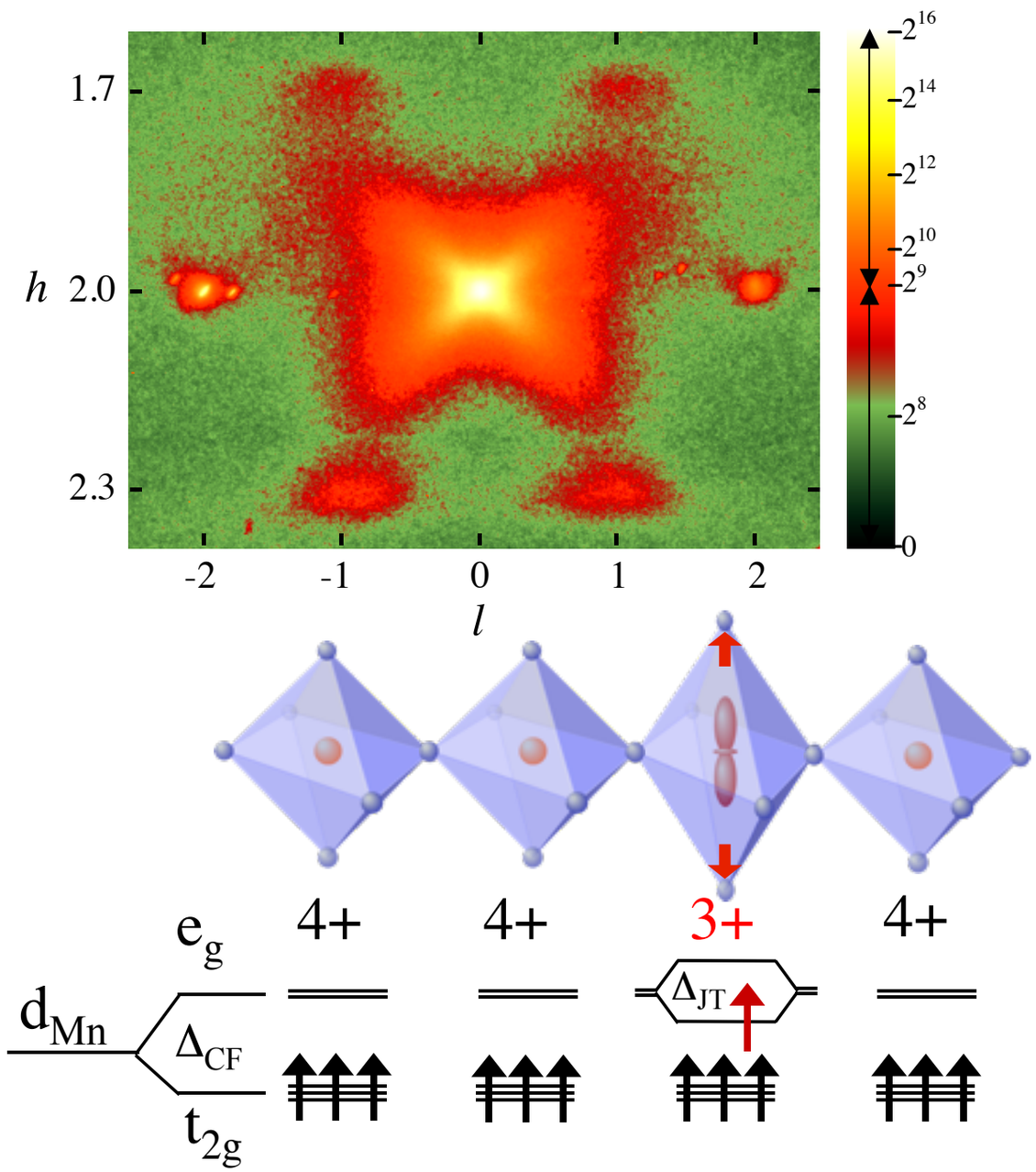

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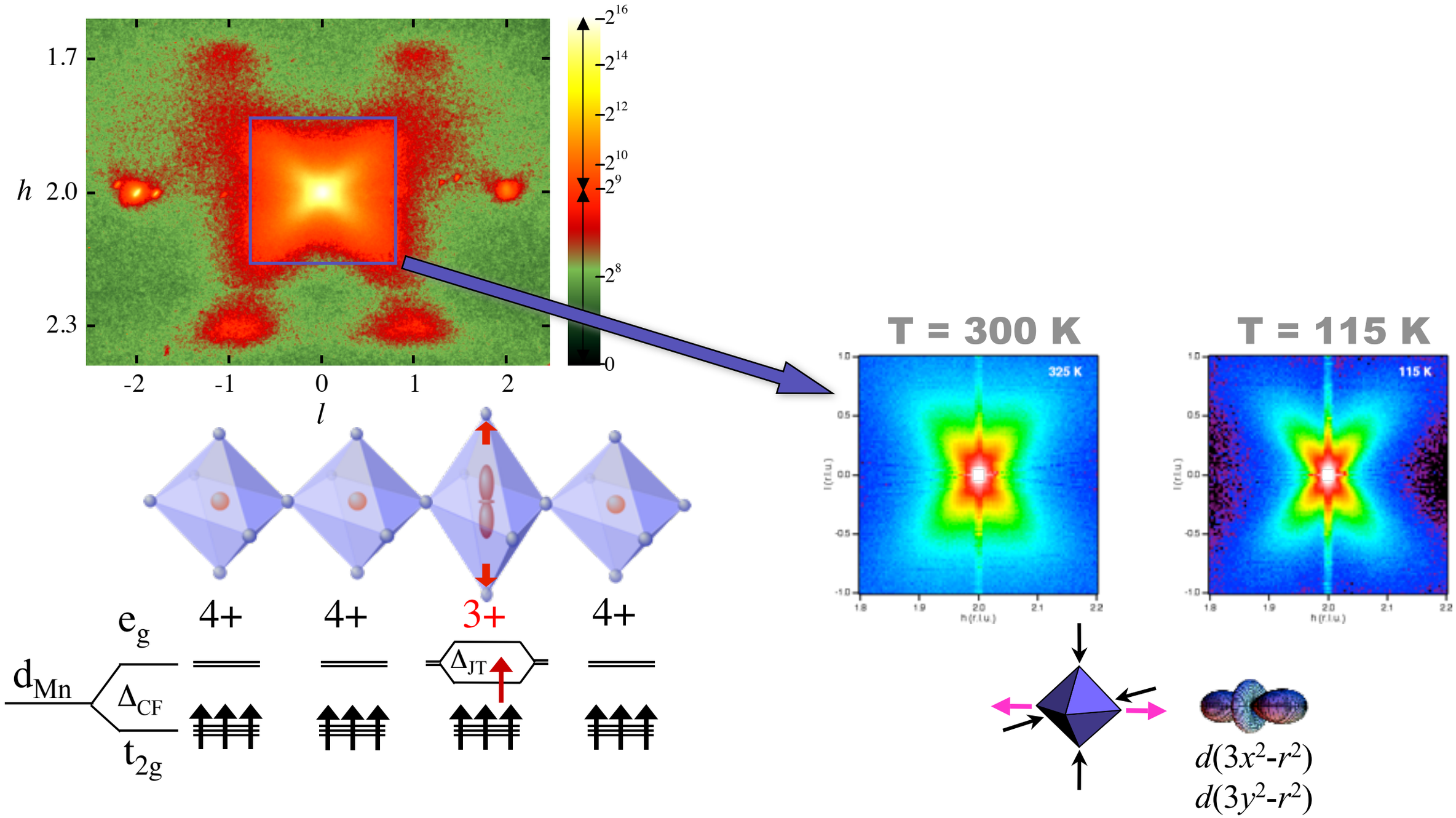

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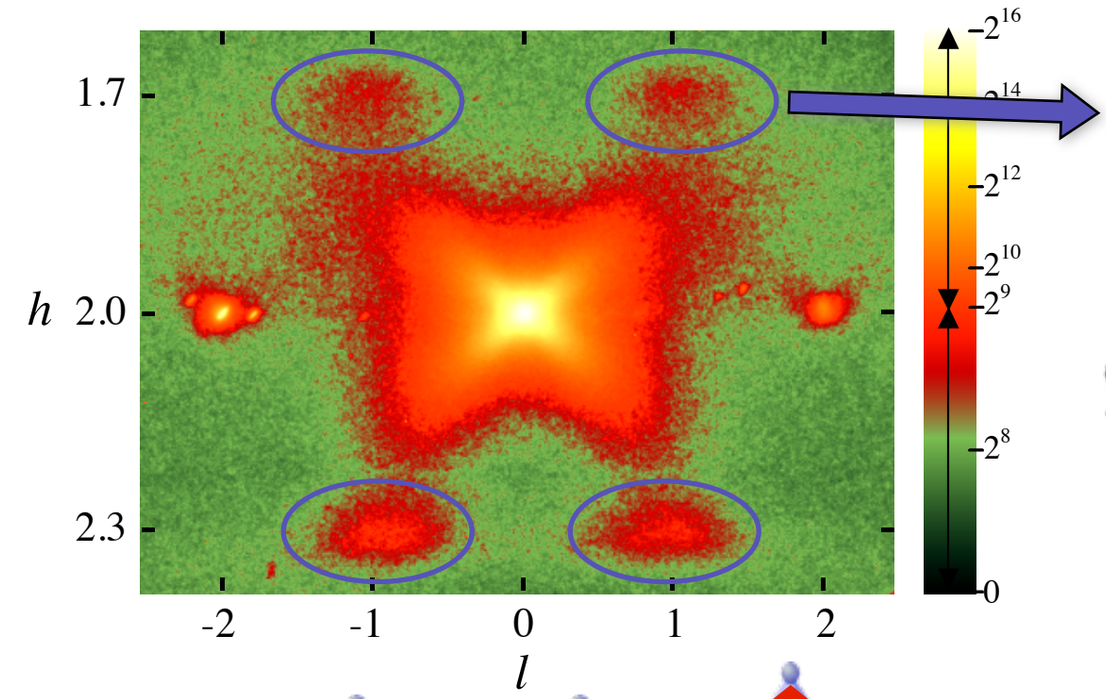
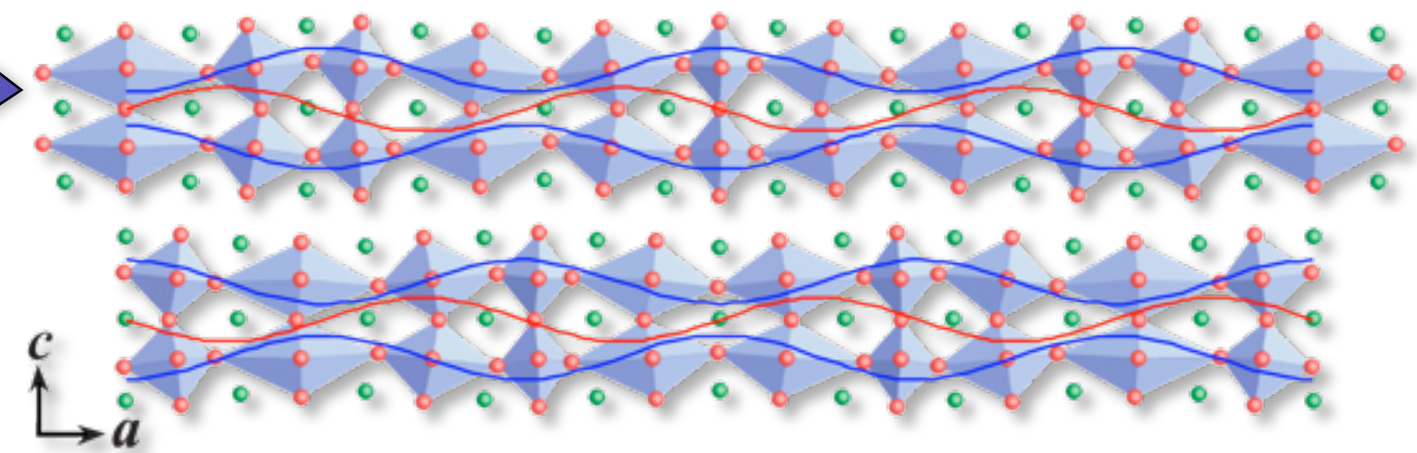
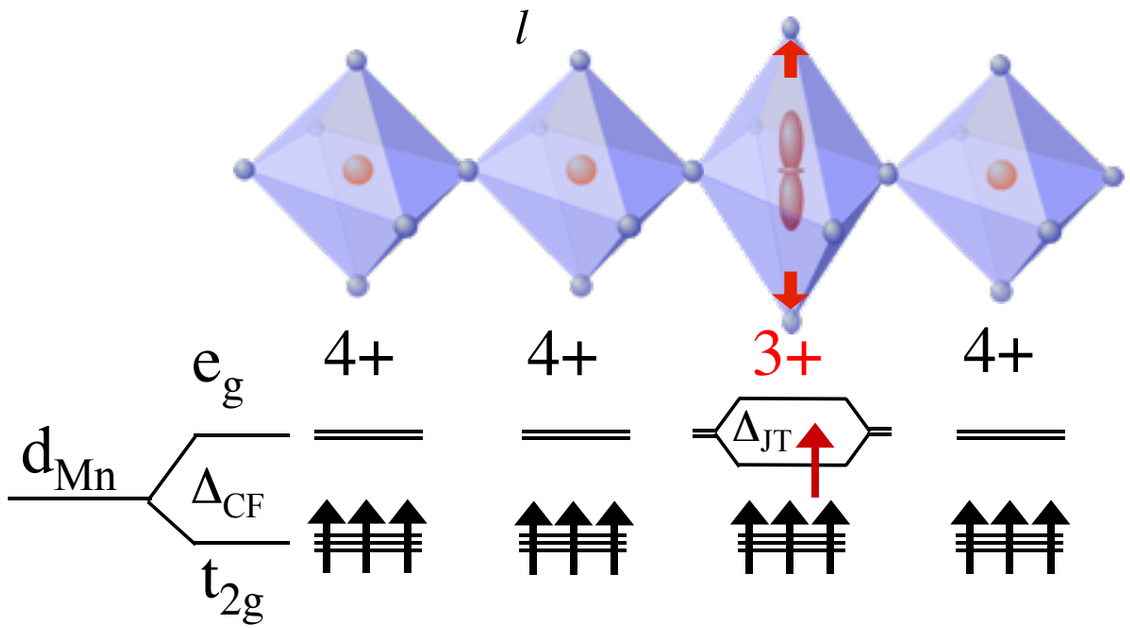
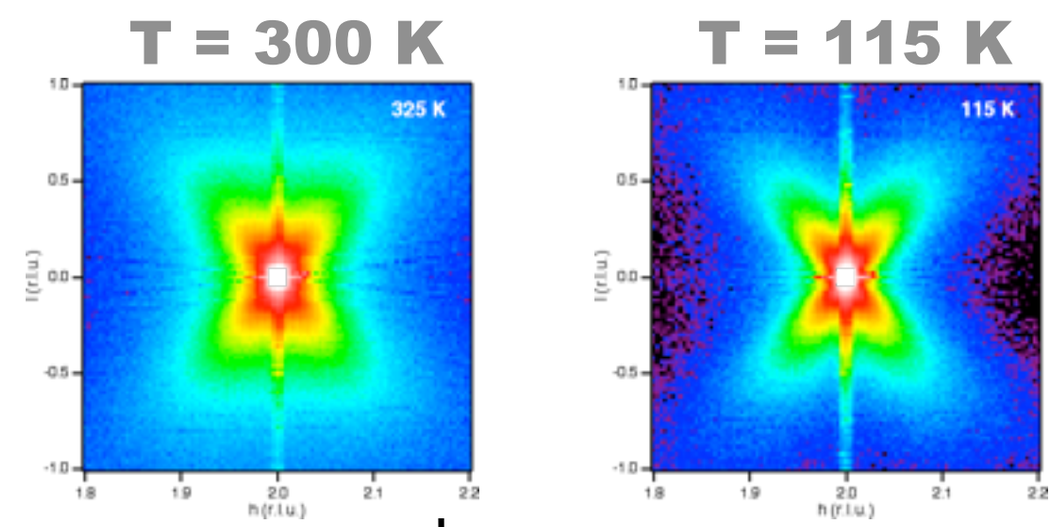
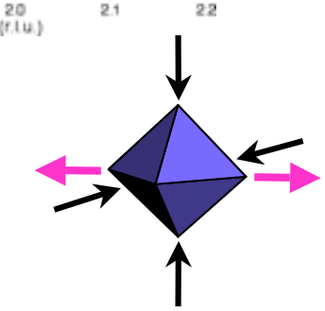










$d(3x^2\text{-}r^2)$
$d(3y^2\text{-}r^2)$

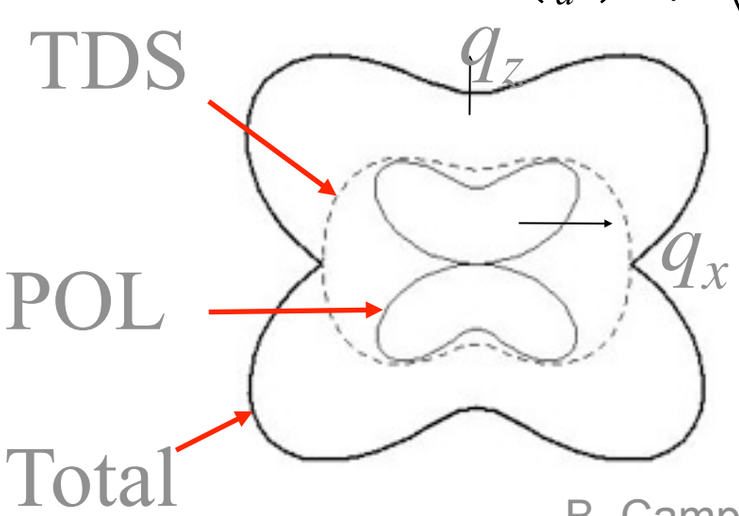
Modeling the Diffuse Scattering

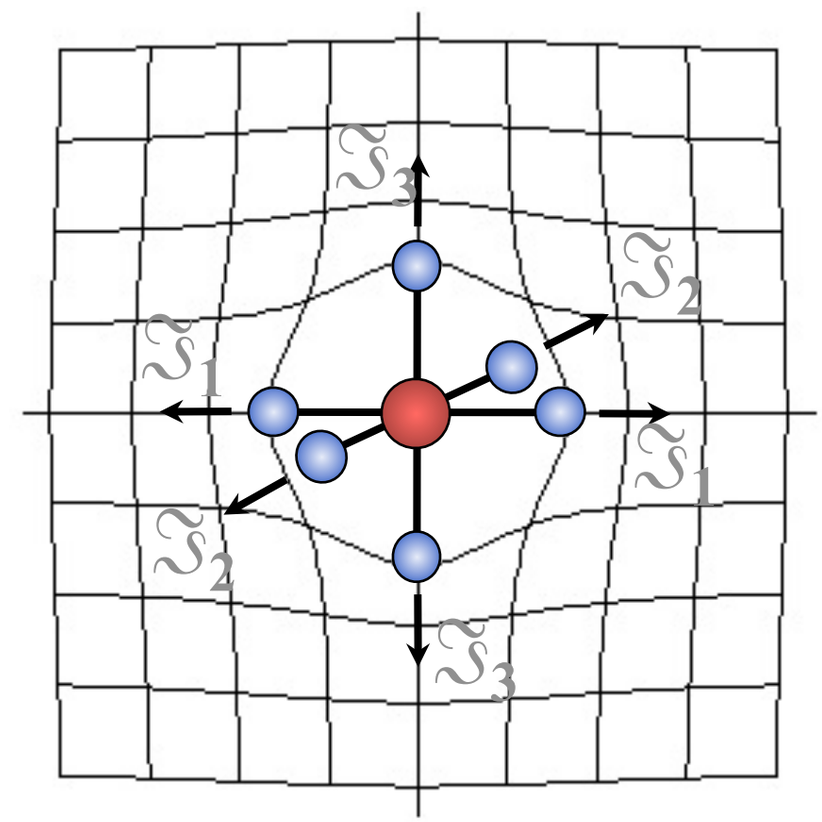
$$I(\mathbf{Q}) = \sum_{m,n} e^{i\mathbf{Q}\cdot(\mathbf{R}_m - \mathbf{R}_n)} f_m f_n e^{-W_m} e^{-W_n} \left\langle (\mathbf{Q}\cdot\mathbf{u}_m)(\mathbf{Q}\cdot\mathbf{u}_n) \right\rangle$$

$$I_{POL}(\mathbf{Q}) = N\left|F_{\mathbf{G}}\right|^2 \sum_{\alpha,\beta,\gamma,\delta} Q_\beta Q_\delta \left(\sum_{j,j'} \frac{\varepsilon_{\alpha,\mathbf{q},j}\, \varepsilon^*_{\beta,\mathbf{q},j}\, \varepsilon^*_{\gamma,\mathbf{q},j'}\, \varepsilon_{\delta,\mathbf{q},j'}}{\omega^2_{\mathbf{q},j}\, \omega^2_{\mathbf{q},j'}} \right) \sum_{m,n} \tilde{\mathfrak{I}}_{m,\alpha} \tilde{\mathfrak{I}}_{n,\gamma}\, e^{i\mathbf{q}\cdot(\mathbf{R}_m - \mathbf{R}_n)}$$

$$I_{TDS}(\mathbf{Q}) = N\left|F_{\mathbf{G}}\right|^2 \left(\frac{kT}{2M} \right) \sum_{\beta,\delta} Q_\beta Q_\delta \left(\sum_{j} \frac{\varepsilon^*_{\beta,\mathbf{q},j}\, \varepsilon_{\delta,\mathbf{q},j}}{\omega^2_{\mathbf{q},j}} \right)$$

$$u_{m,\delta} = \int \frac{d^3q}{\left(\frac{2\pi}{a}\right)^3} \sum_{\beta} \left(\sum_{j} \frac{\varepsilon^*_{\beta,\mathbf{q},j}\, \varepsilon_{\delta,\mathbf{q},j}}{\omega^2_{\mathbf{q},j}} \right) \sum_{n} \tilde{\mathfrak{I}}_{n,\beta}\, e^{i\mathbf{q}\cdot(\mathbf{R}_m - \mathbf{R}_n)}$$



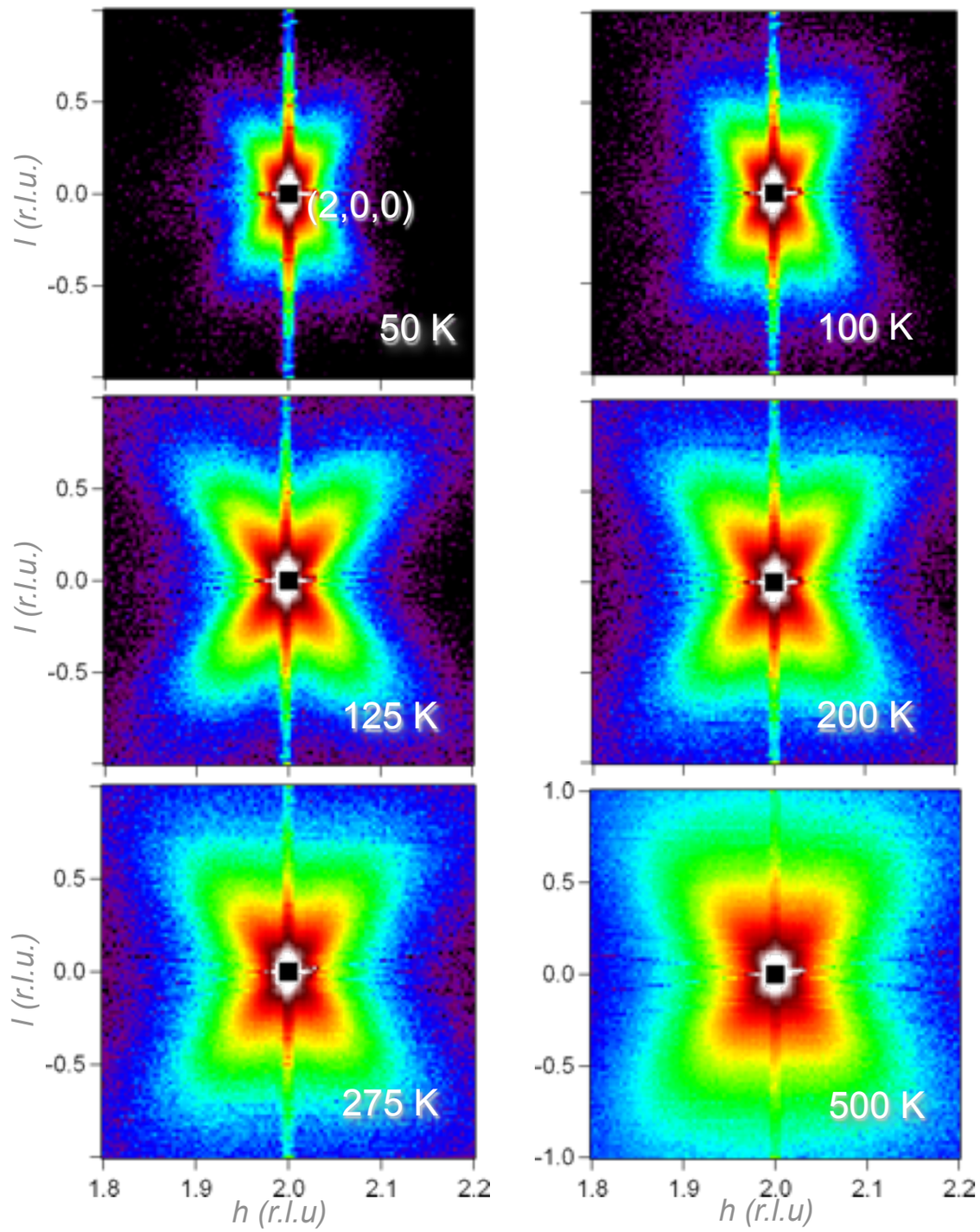


B. Campbell *et al* Phys. Rev. B. **67**, 020409 (2003)

Correlated Data

single crystal synchrotron x-ray scattering
11-ID-D, APS@Argonne

Correlated Data



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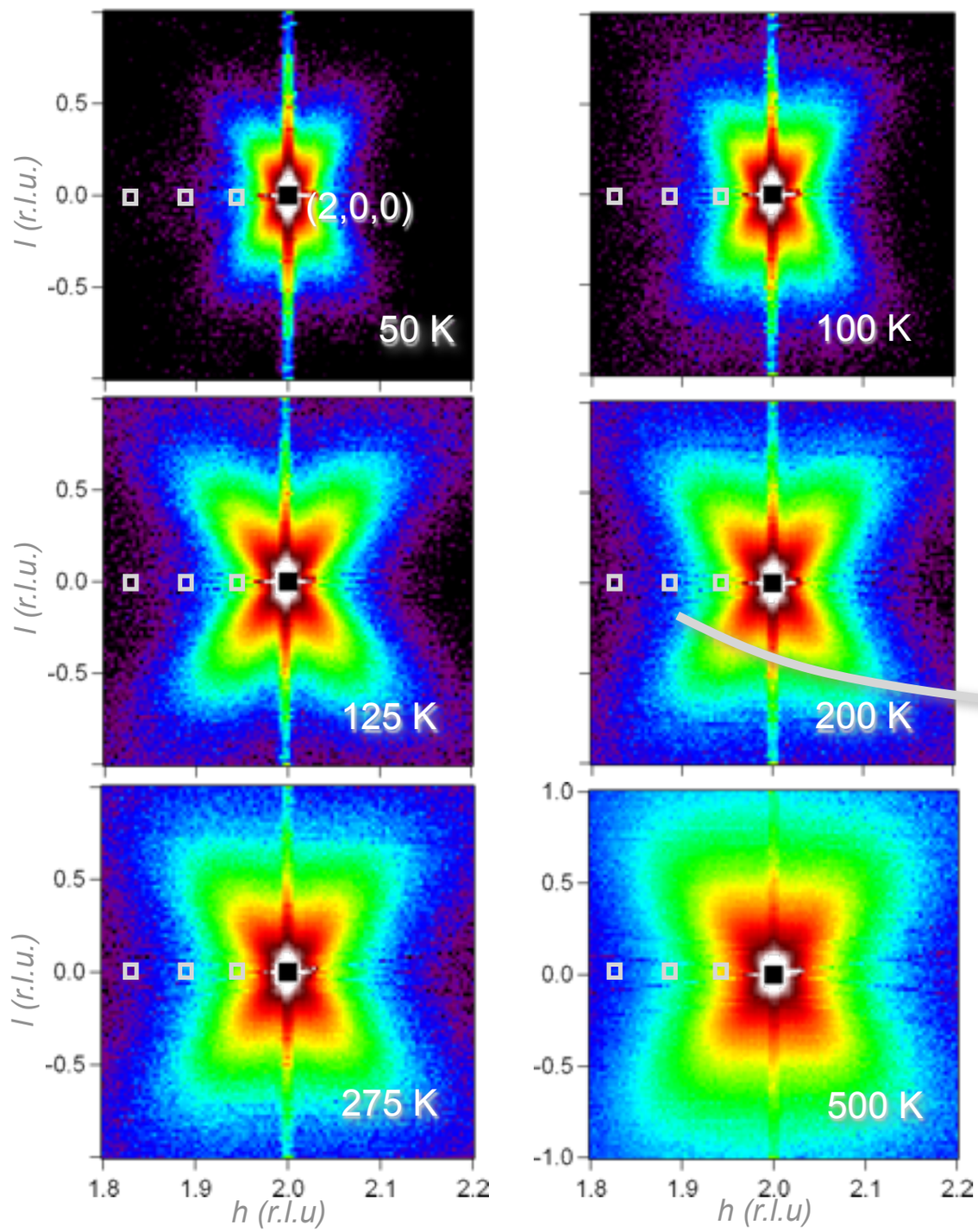

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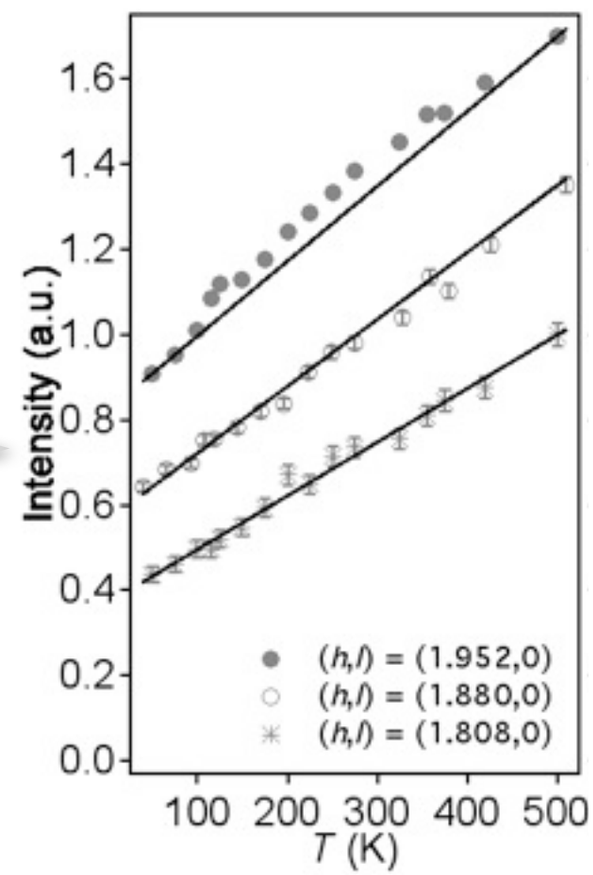

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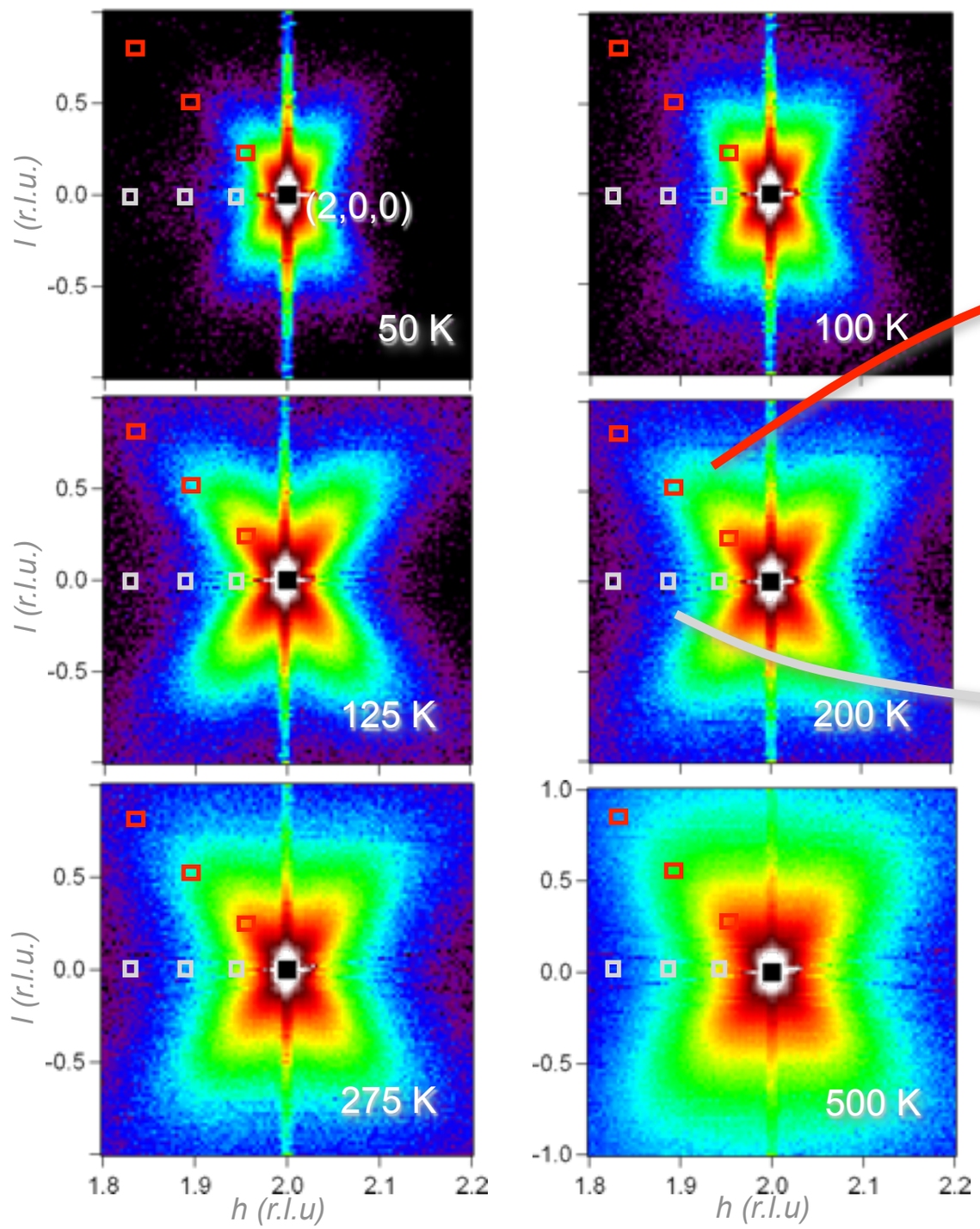

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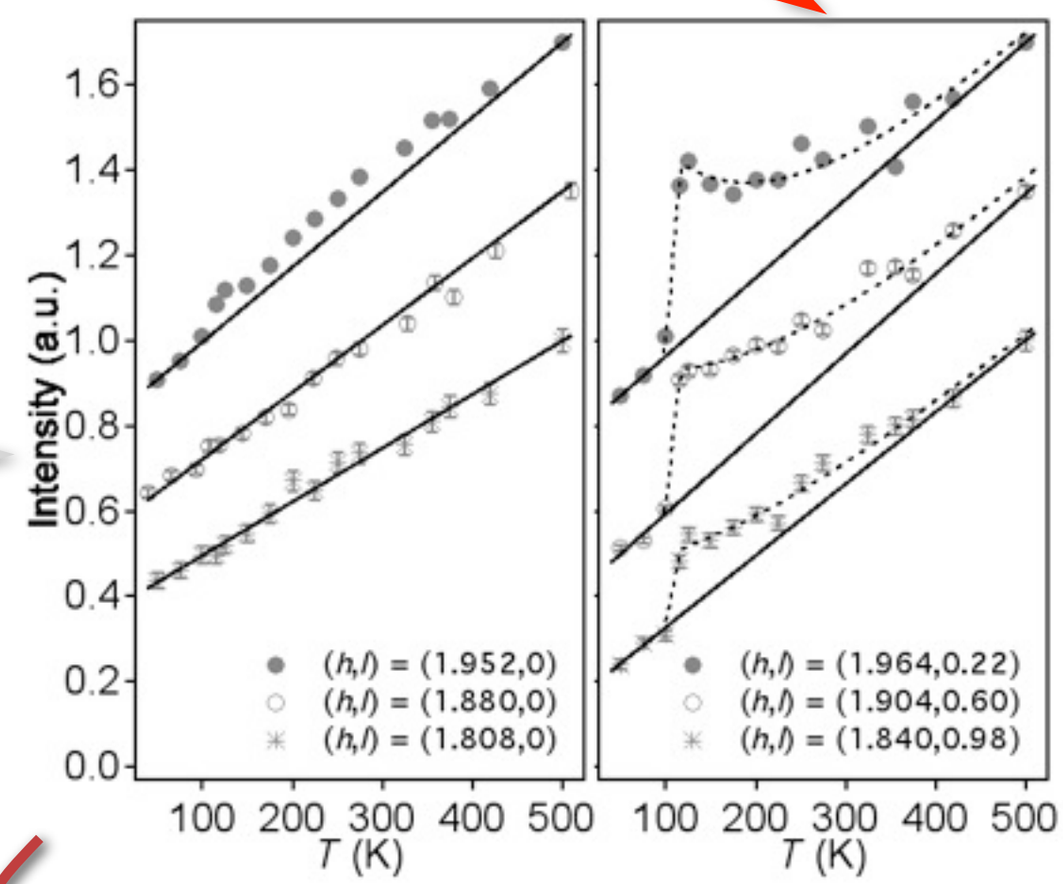
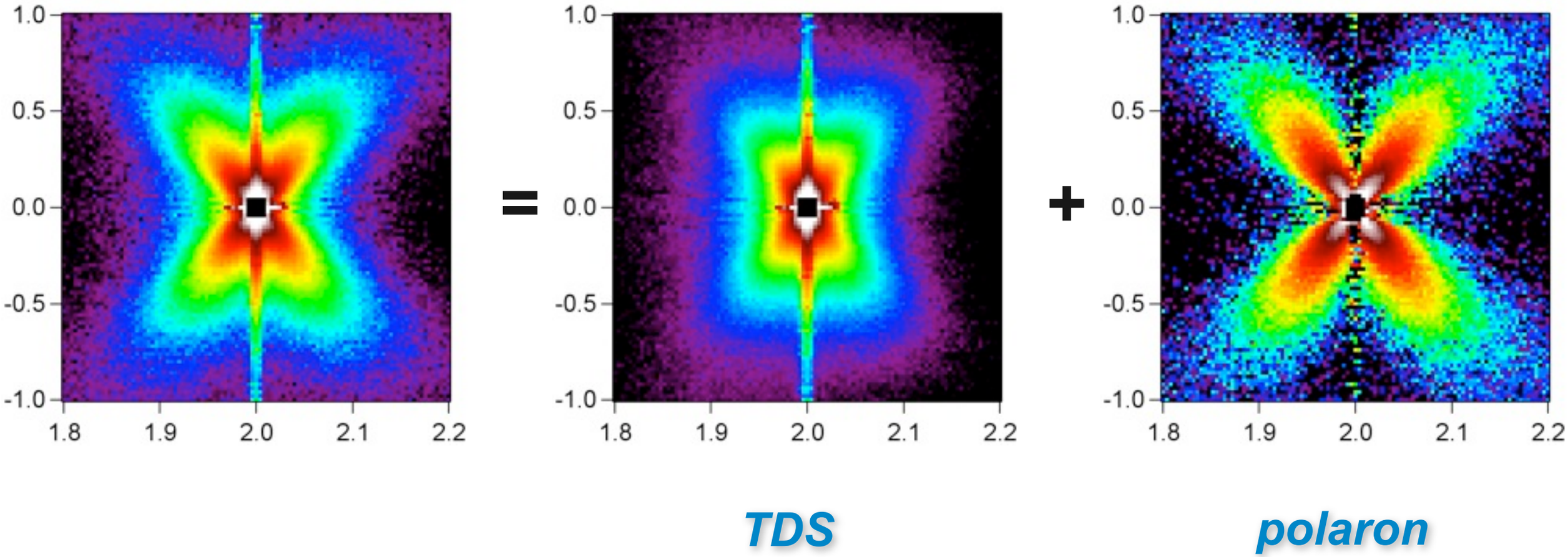


this allows us to subtract background from thermal diffuse scattering!

Results of Correlated Data Analysis



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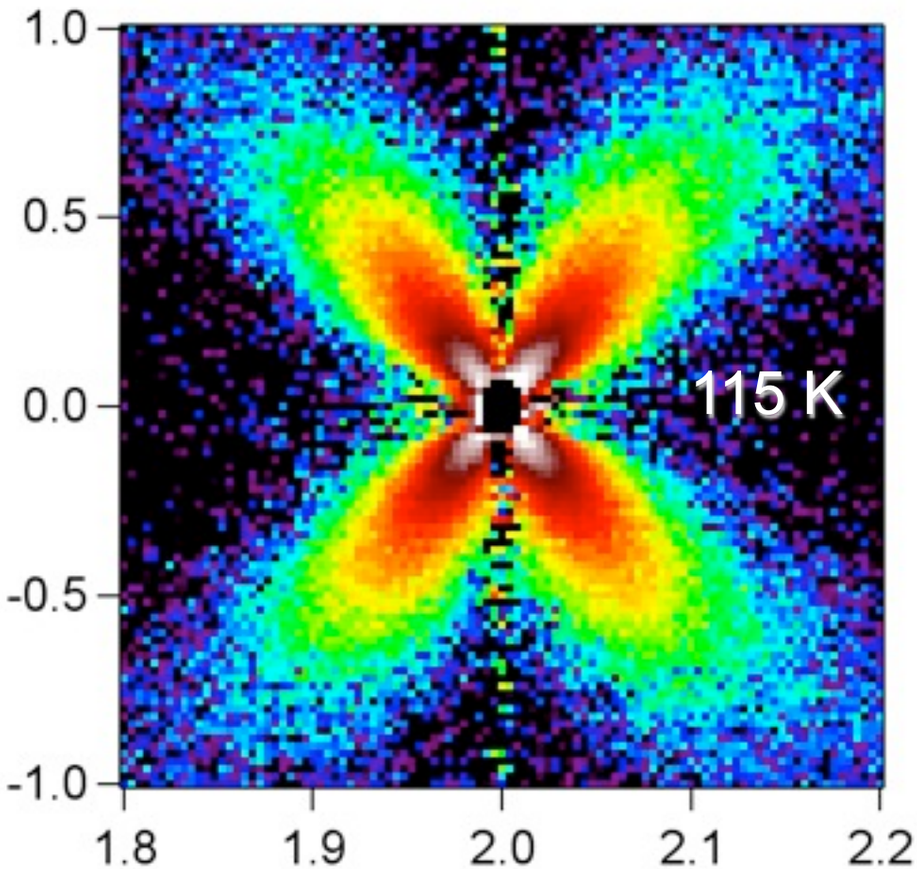

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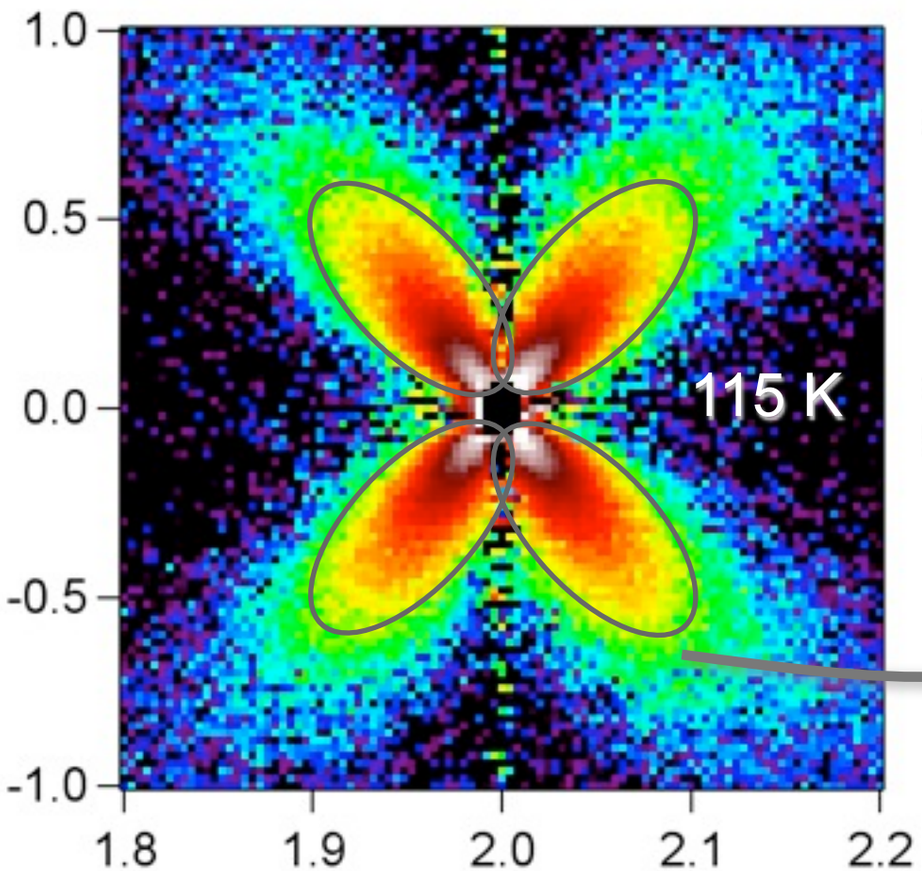

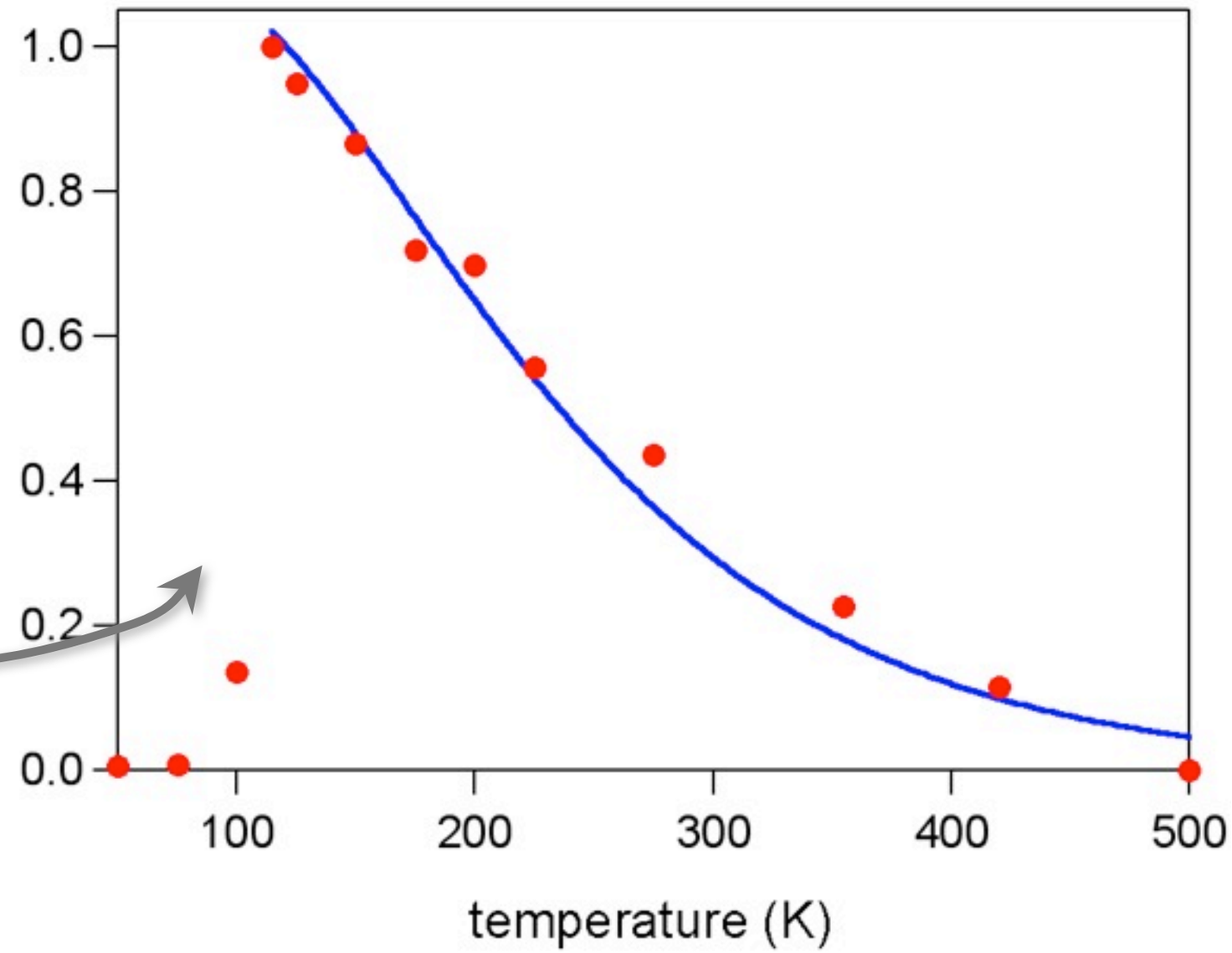

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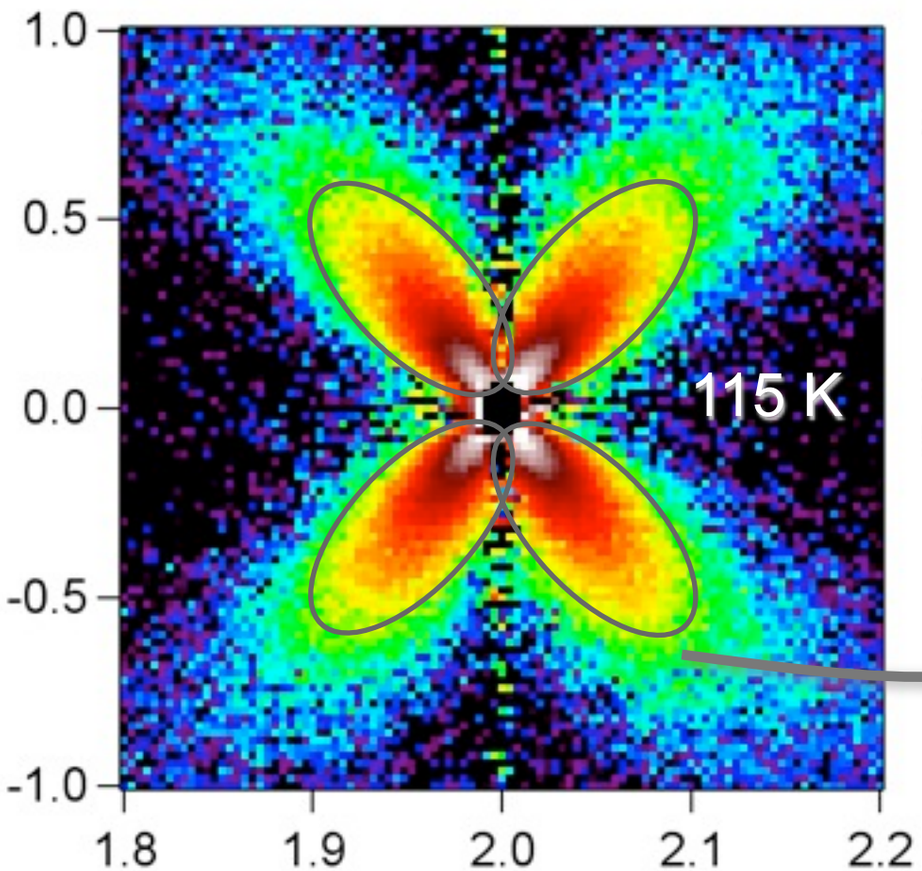

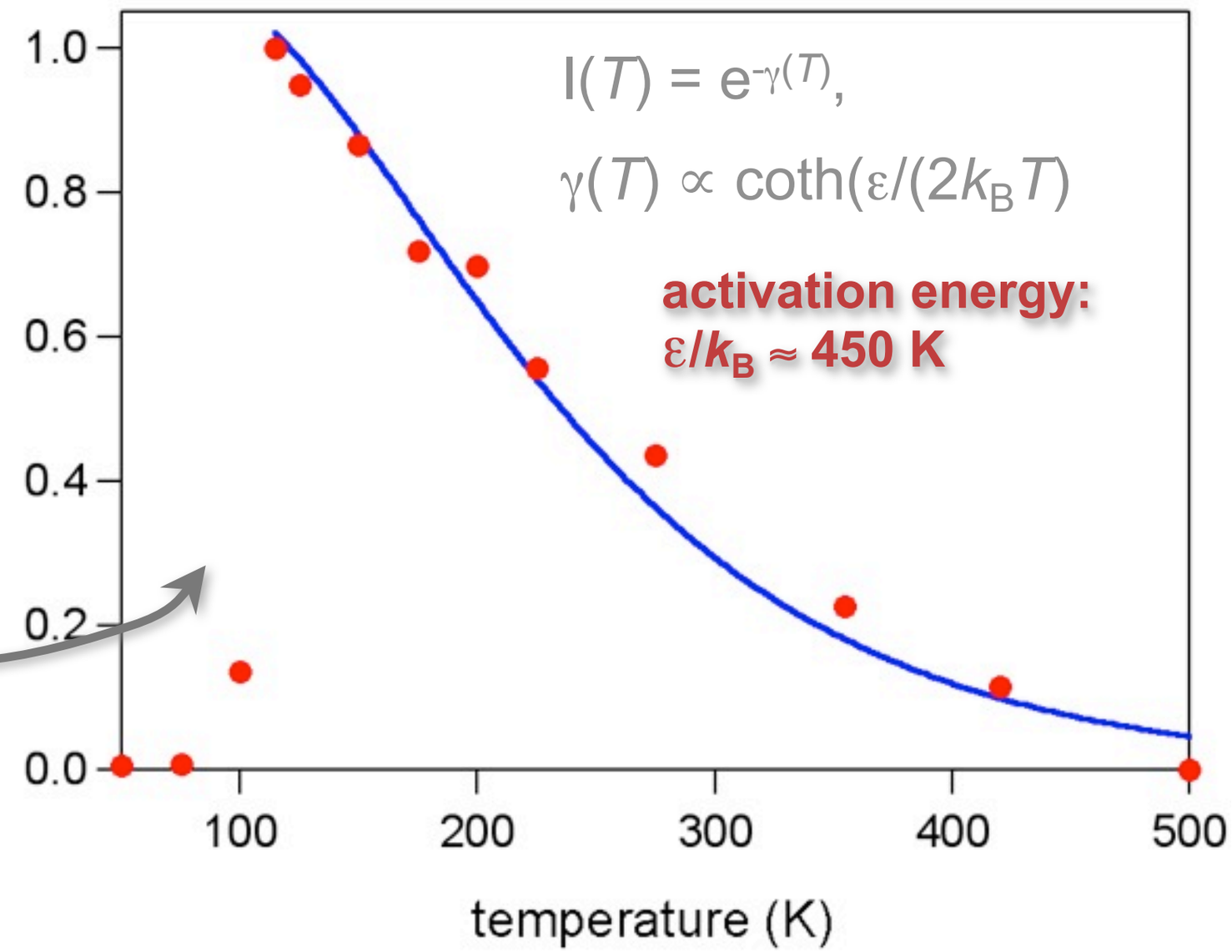

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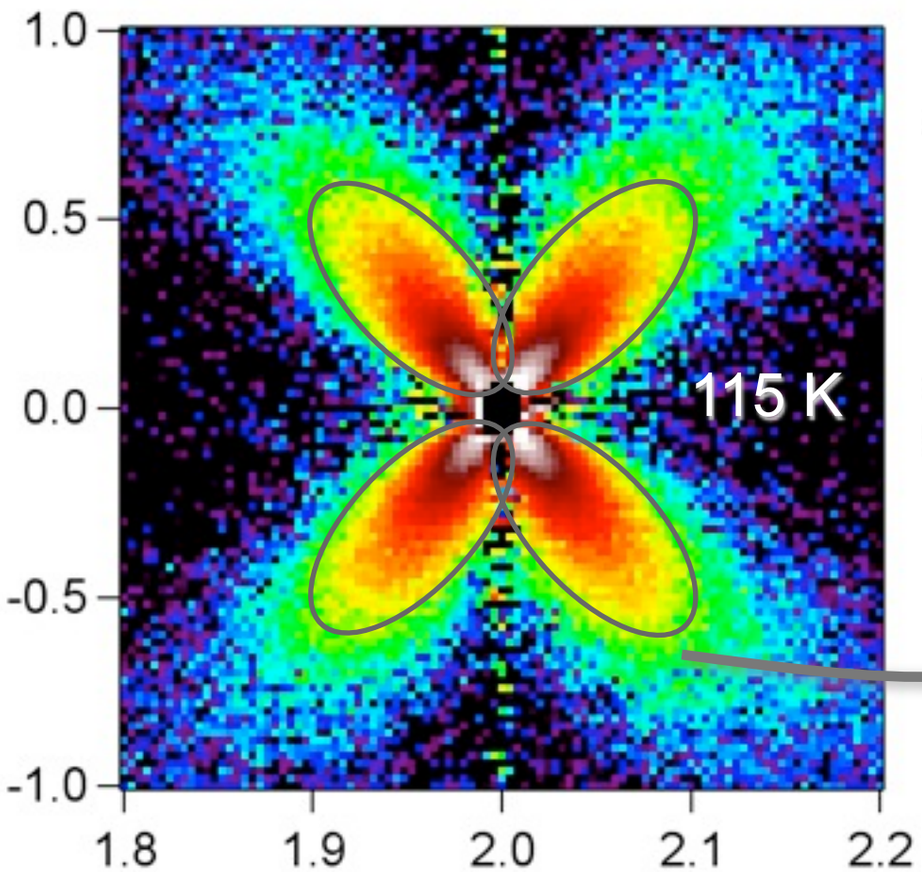

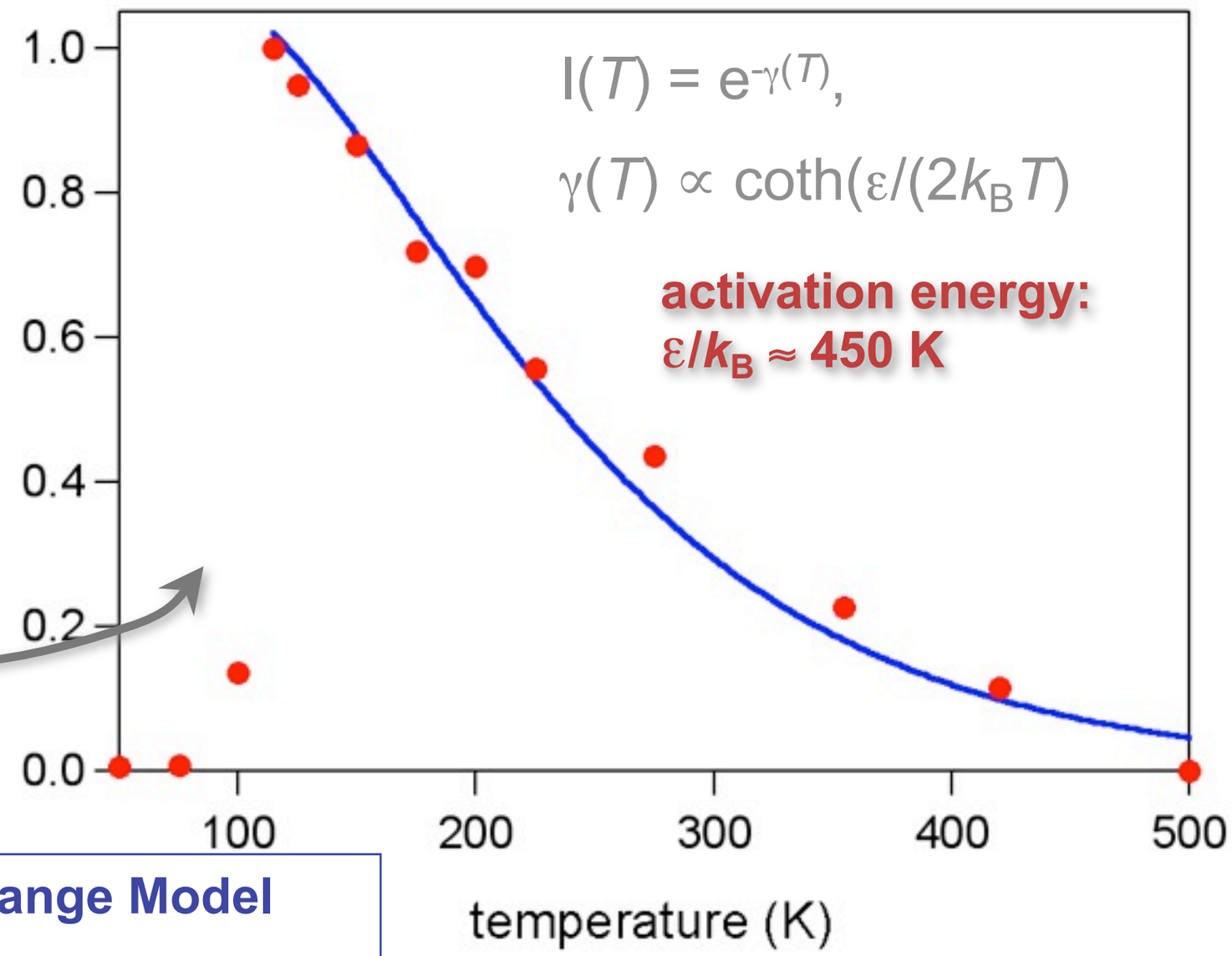

Holstein-Double Exchange Model

$$H = \sum_{ij\sigma} t_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} - J \sum_i \boldsymbol{S}_i \cdot \boldsymbol{\sigma}_i - h \sum_i \left(S^z_i + \sigma^z_i\right)$$
$$- g \sum_i n_i \left(b^{\dagger}_i + b_i\right) + \omega \sum_i b^{\dagger}_i b_i.$$

Edwards Adv. Phys. **51**, 1259 (2002)

Total Data: $\mathbf{S}(\mathbf{Q}, \mathrm{T}, x)$

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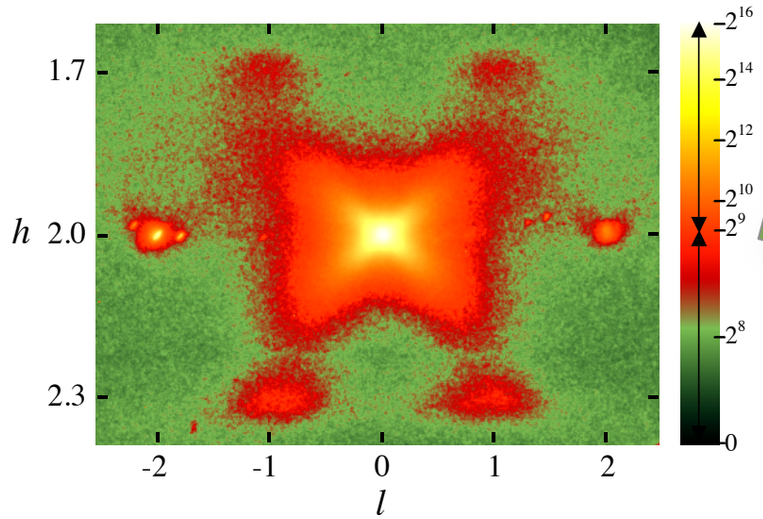

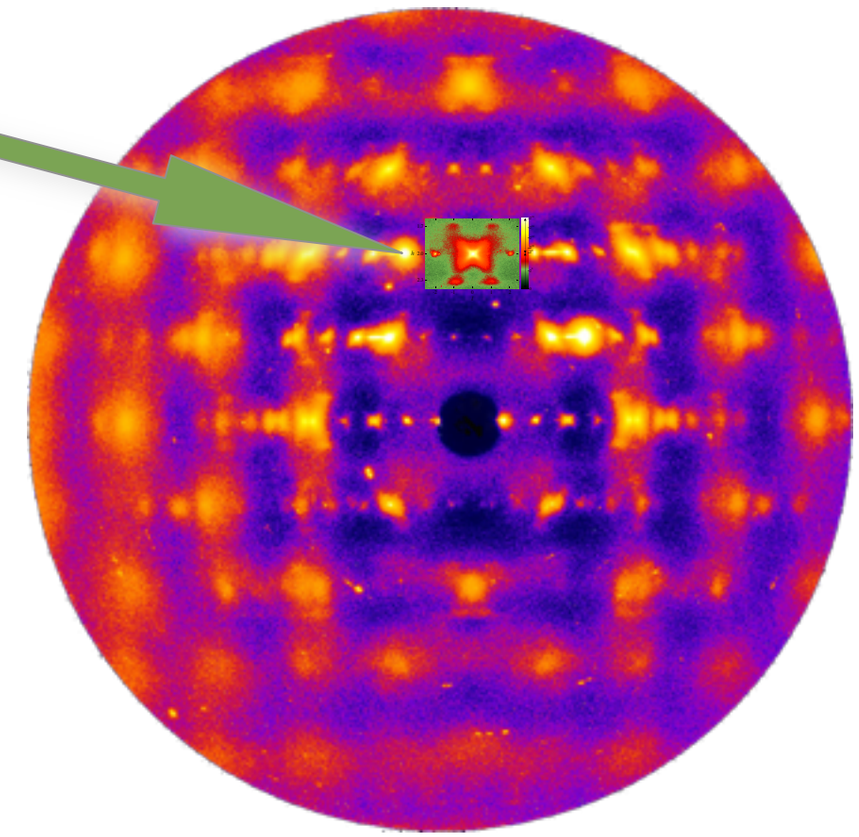

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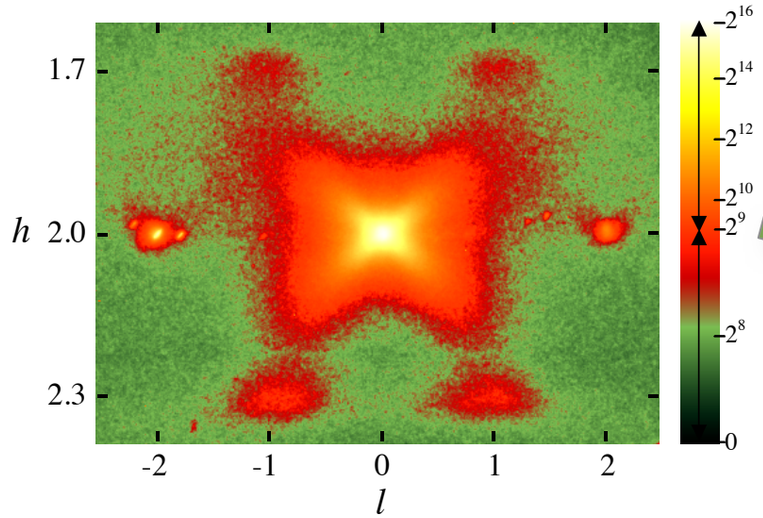
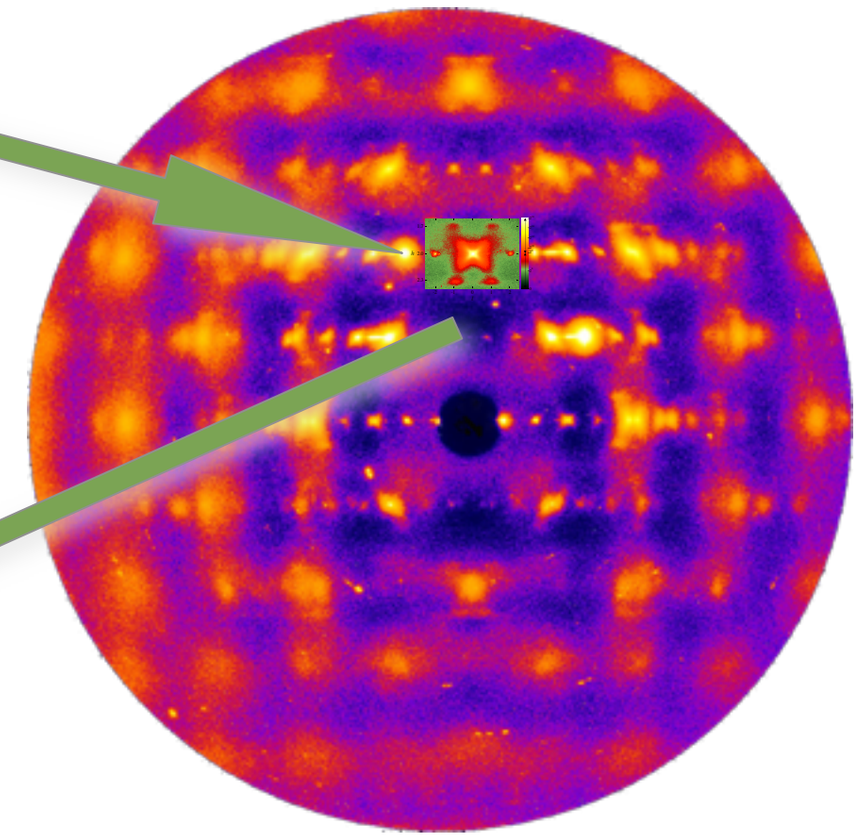
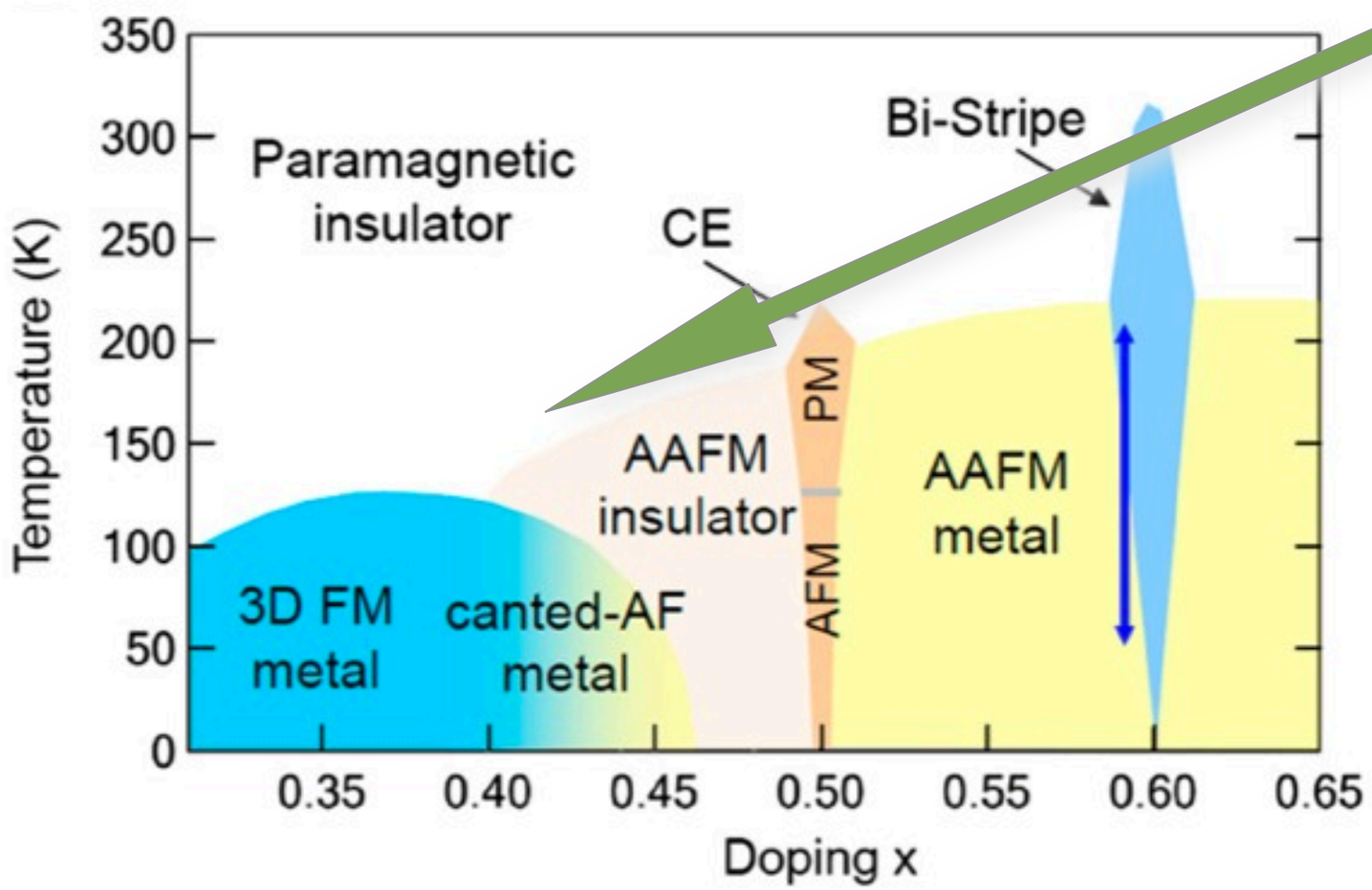




Phase Diagram of Bilayer Manganites



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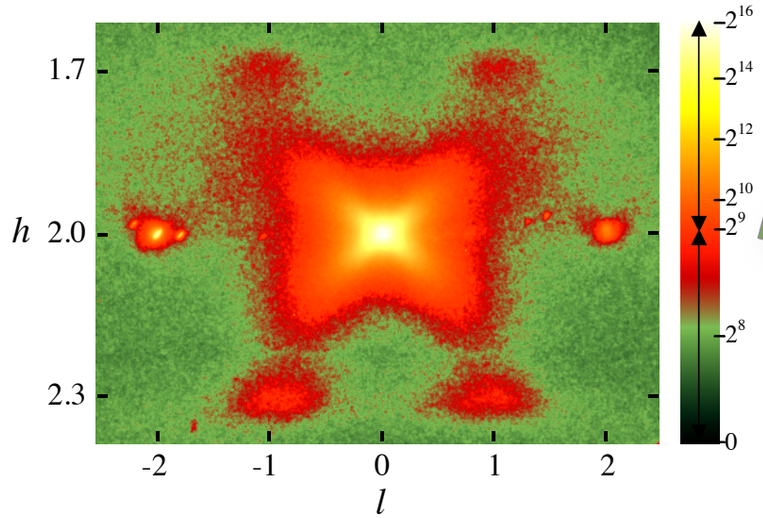

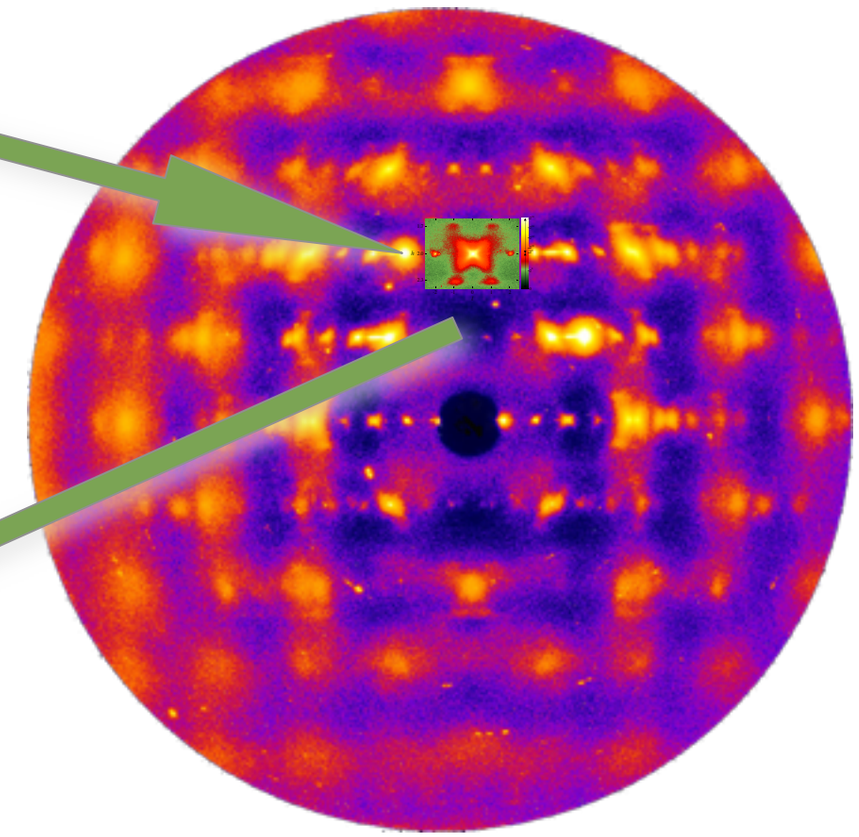

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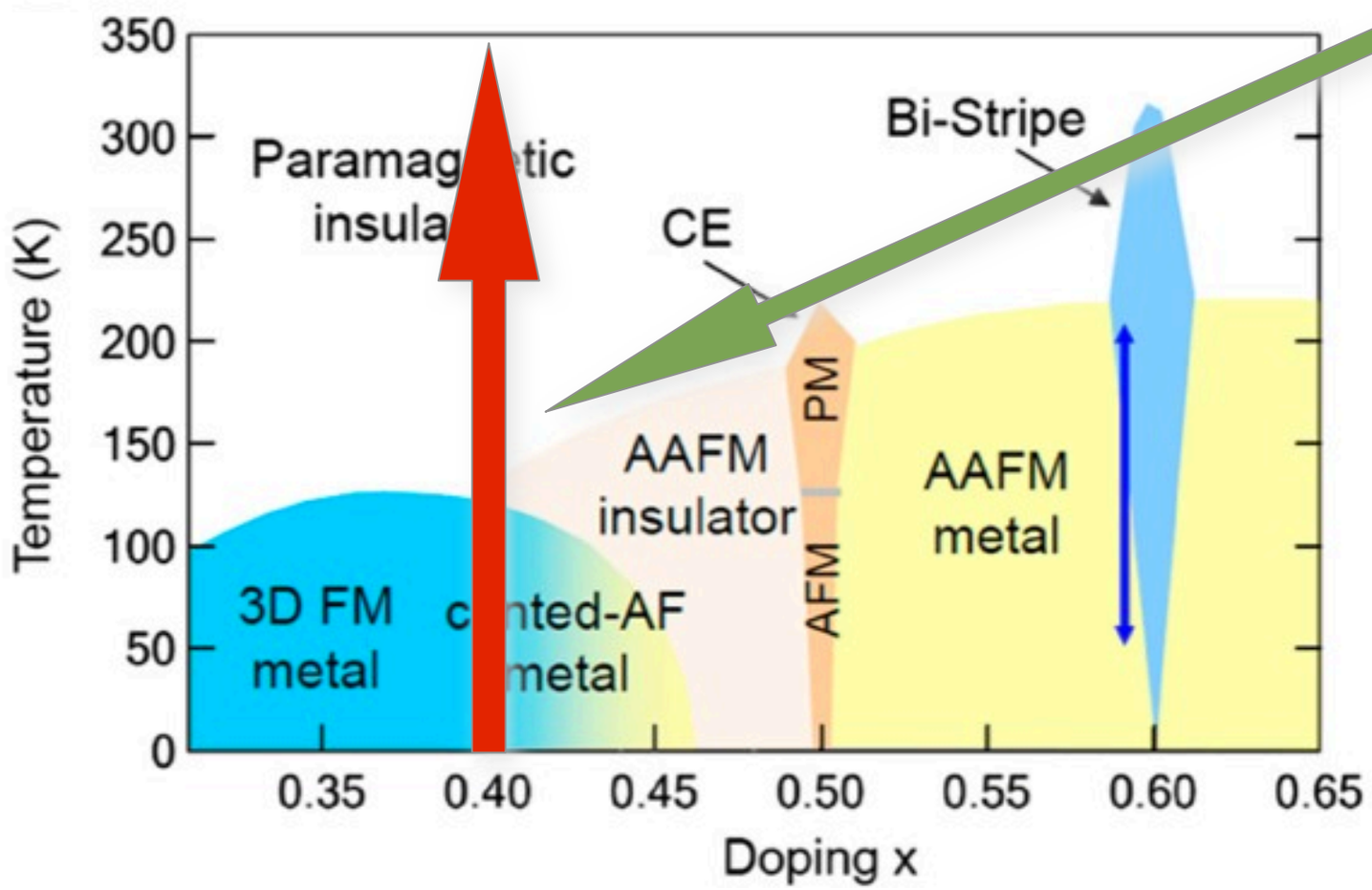
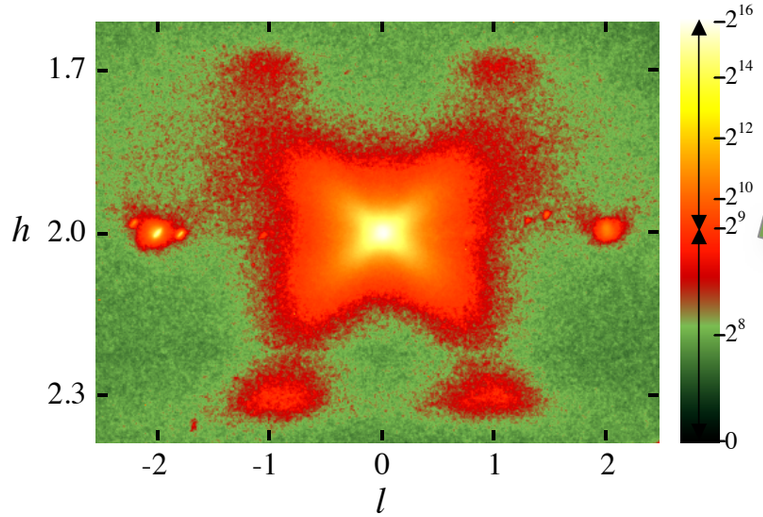
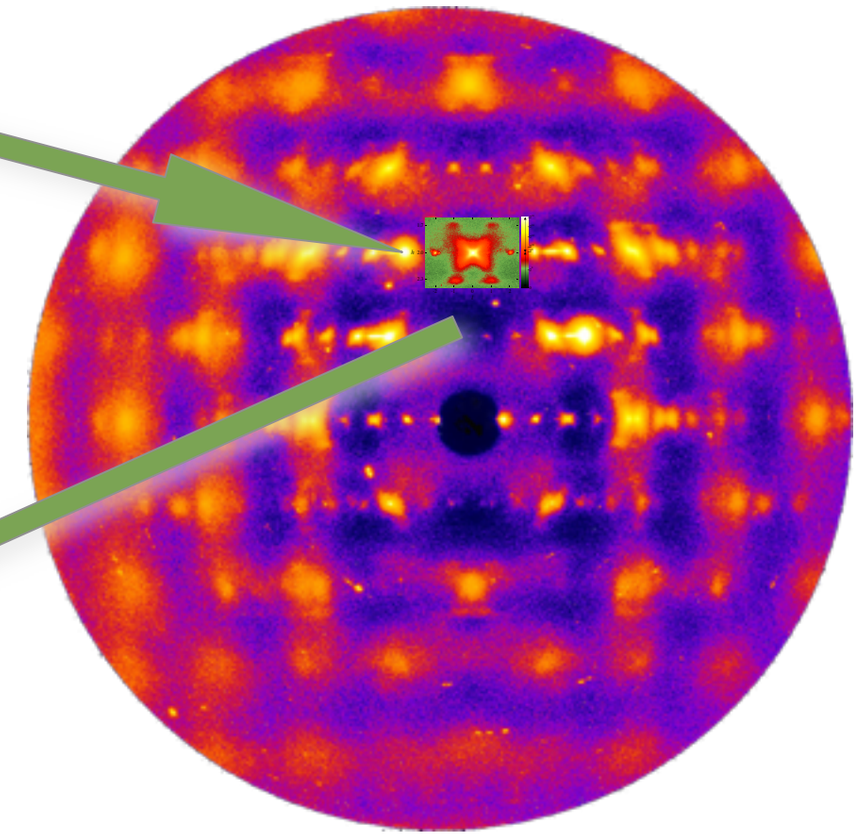
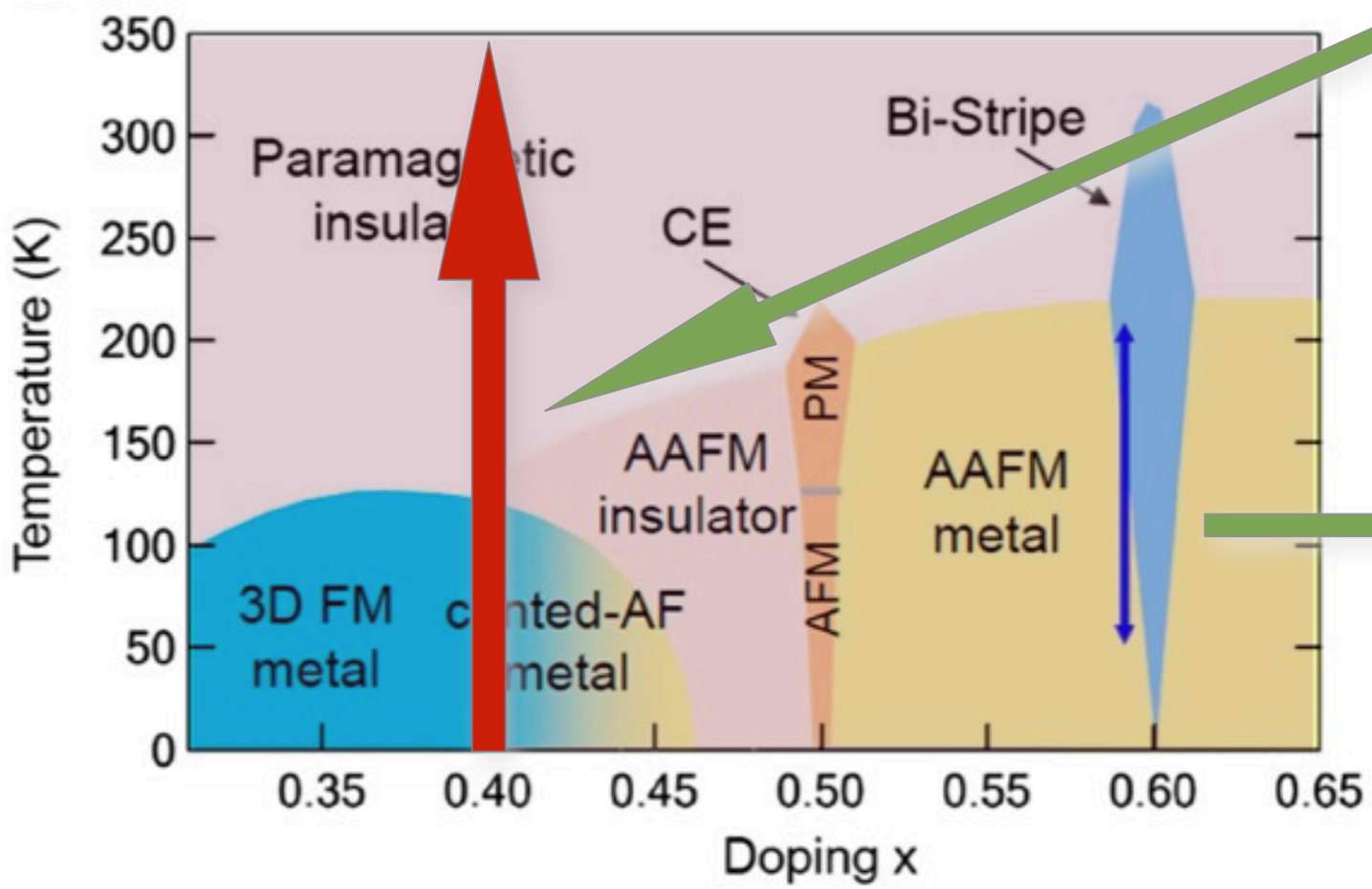


Total Data: S(Q, T, x)





Phase Diagram of Bilayer Manganites



Correlated Data Analysis/ Machine Learning

Argonne Grand Challenge LDRD on Data Driven Science

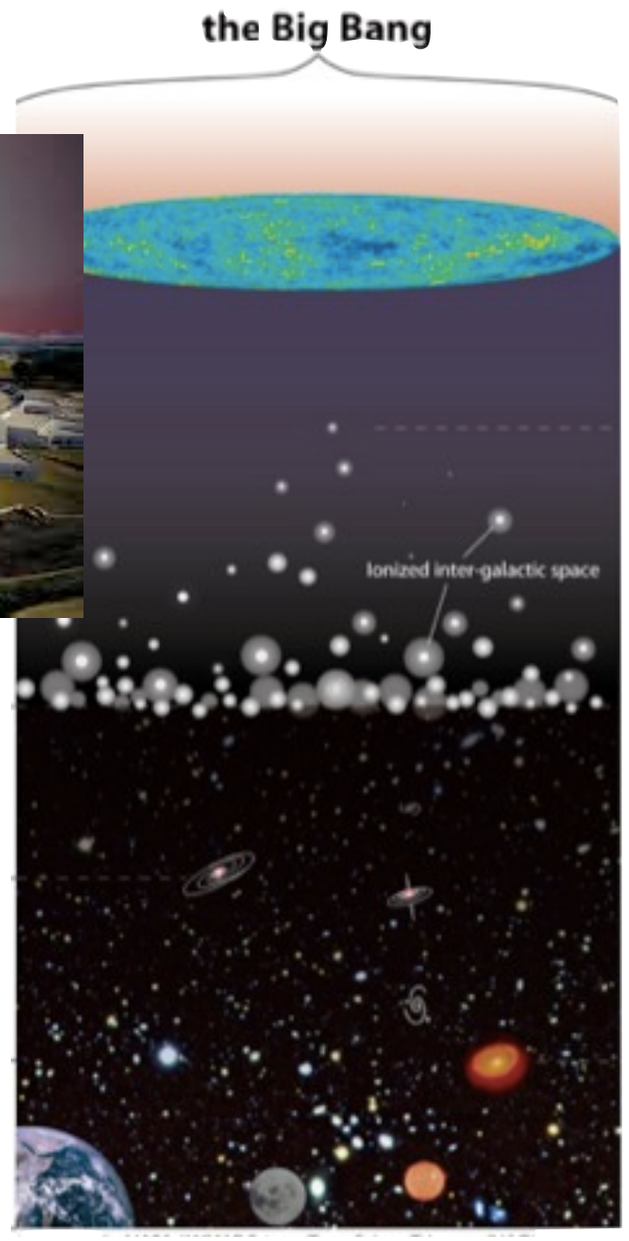


Image: Fusseis et al., Nature, 2009

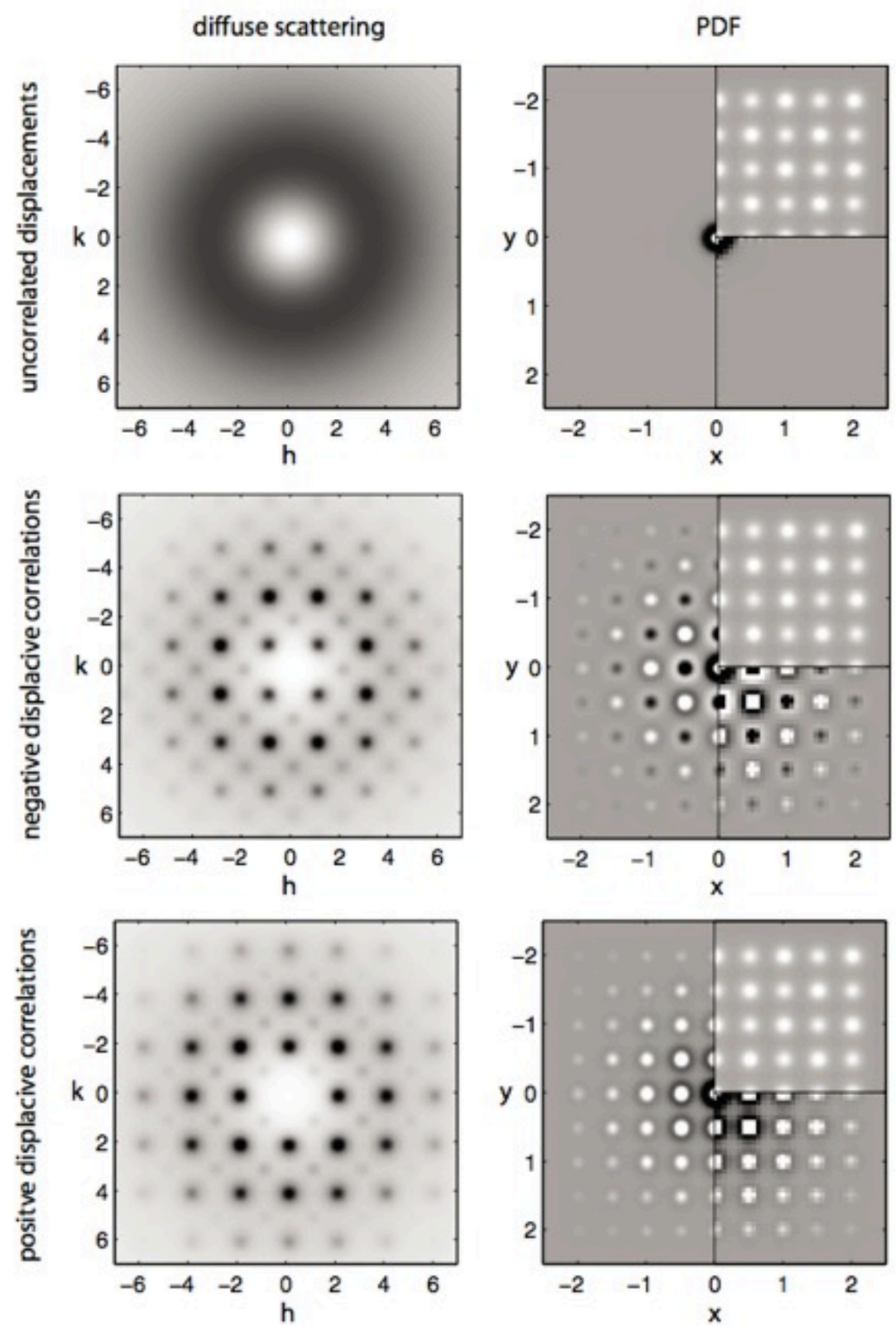
- **Integrating Simulation and Observation:**
  Discovery Engines for Big Data
  - PIs: Ian Foster, Salman Habib, Ray Osborn
    Co-PIs: Jon Almer, Karena Chapman, Lin Chen, Peter Chupas, David Tiede
  - Enable discovery by coupling experiment and modeling, in **cosmology and materials science**
  - Develop discovery engine platform for big data applications

This Grand Challenge LDRD is partnering with another LDRD to utilize the same computational infrastructure:

- **The Tao of Fusion:**
  Pathways for Big-Data Analysis of Energy Materials at Work
  - PI: Chris Jacobsen, Francesco De Carlo, Stefan Vogt
  - Pursue **scientific and infrastructure innovations at APS**, in partnership with “Discovery engines”

Three-Dimensional Pair Distribution Functions

- The ability to measure three-dimensional S(**Q**) over a wide range of reciprocal space provides the 3D analog of PDF measurements.
  - Total PDFs if Bragg peaks and diffuse scattering can be measured simultaneously
  - Δ-PDFs if the Bragg peaks are eliminated
    - using the punch and fill method
- This would allow a model-independent view of the measurements in real space.



238 Z. Kristallogr. 2012, 227, 238–247 / DOI 10.1524/zkri.2012.1504
© by Oldenbourg Wissenschaftsverlag, München

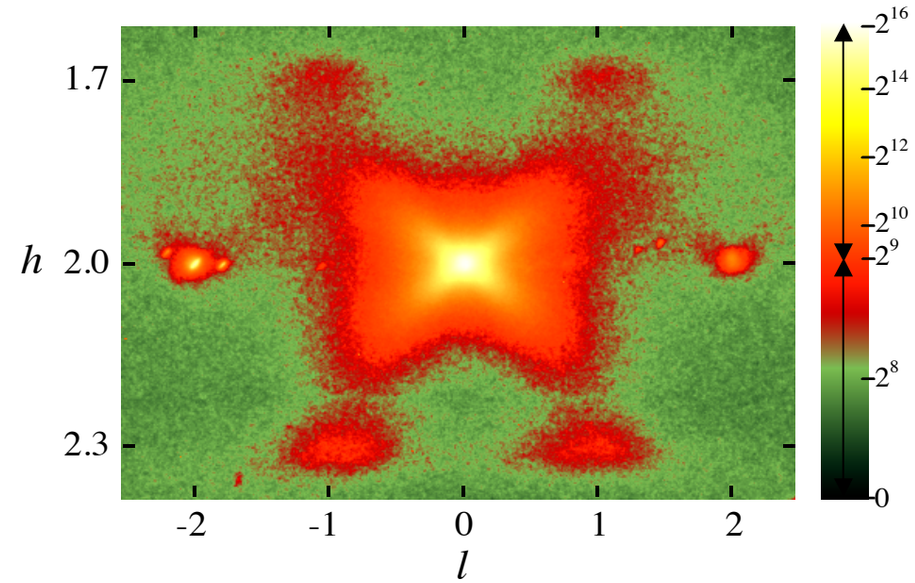
The three-dimensional pair distribution function analysis of disordered single crystals: basic concepts

Thomas Weber* and Arkadiy Simonov

Laboratory of Crystallography, ETH Zurich Wolfgang-Pauli-Str. 10, 8093 Zurich, Switzerland

Opportunities in diffuse scattering with APS upgrade

- Larger flux enables studies over larger range / finer step size of temperature / doping
- Higher resolution (?) enables measurements of diffuse scattering closer to Bragg peak.
  - higher intensity: ~ q^{-2}
  - more model sensitivity



- full flux at small beam size
  - enables measurements in extreme sample environments
    - high magnetic fields
    - high pressure.
  - magnetic scattering
  - “diffuse scattering imaging”
    - spatially resolved diffuse scattering:
      is complex disorder homogeneous through sample?
  - preserved resolution at shorter detector distance (Andreas Kreyssig, AMES)
    - large momentum coverage for relatively small angles, diffuse scattering setup within a vacuum chamber

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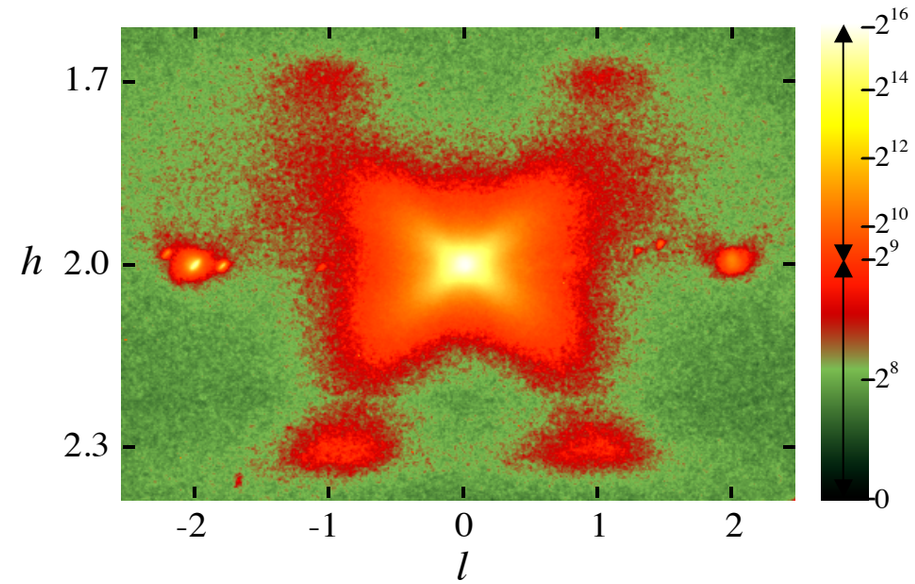

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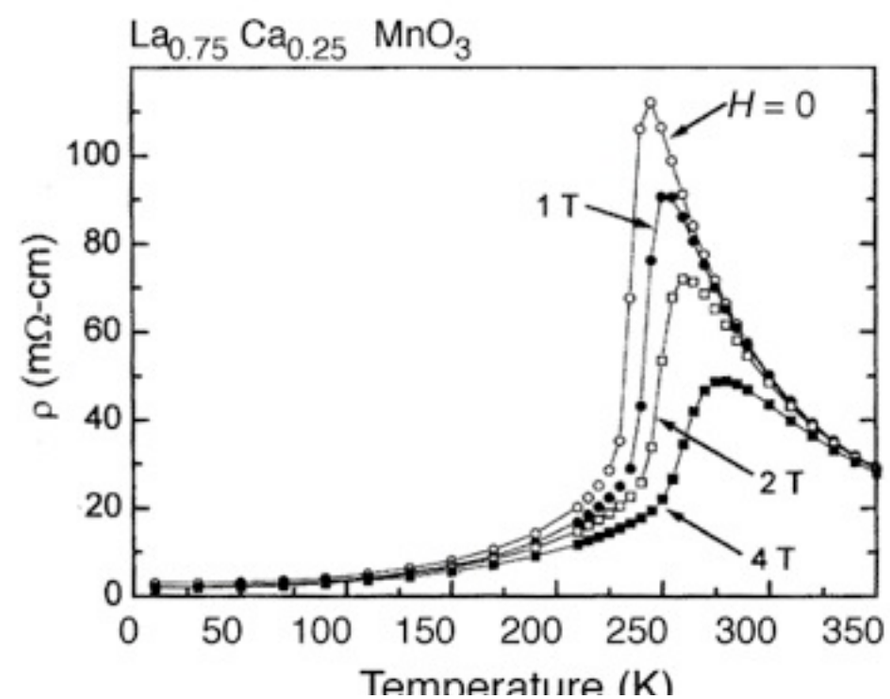

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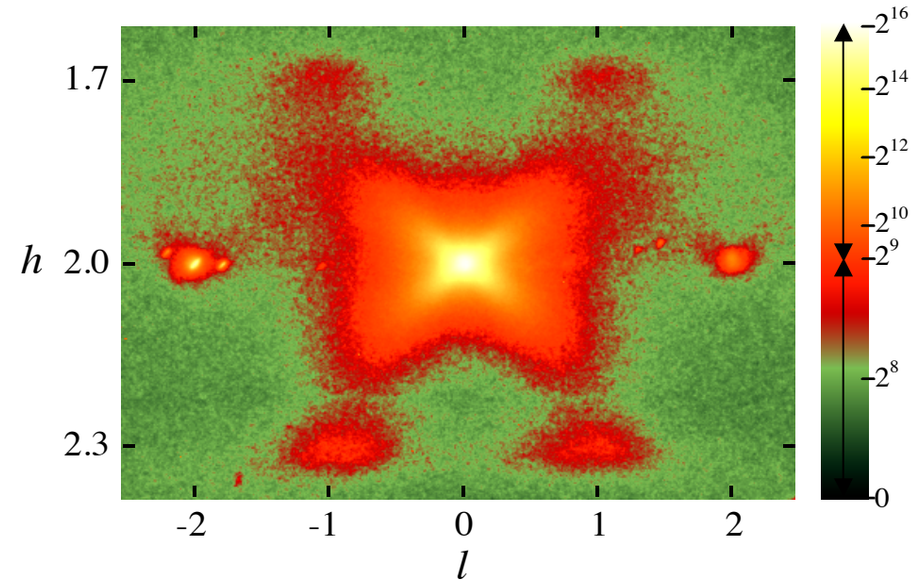

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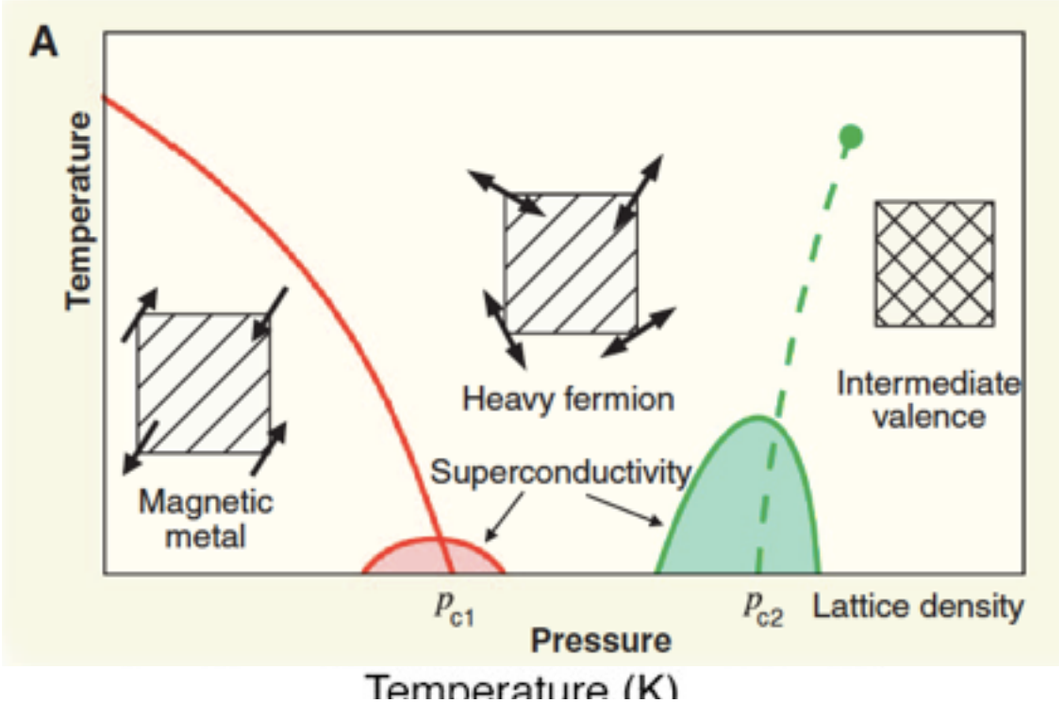

Example: nematicity in iron based superconductors

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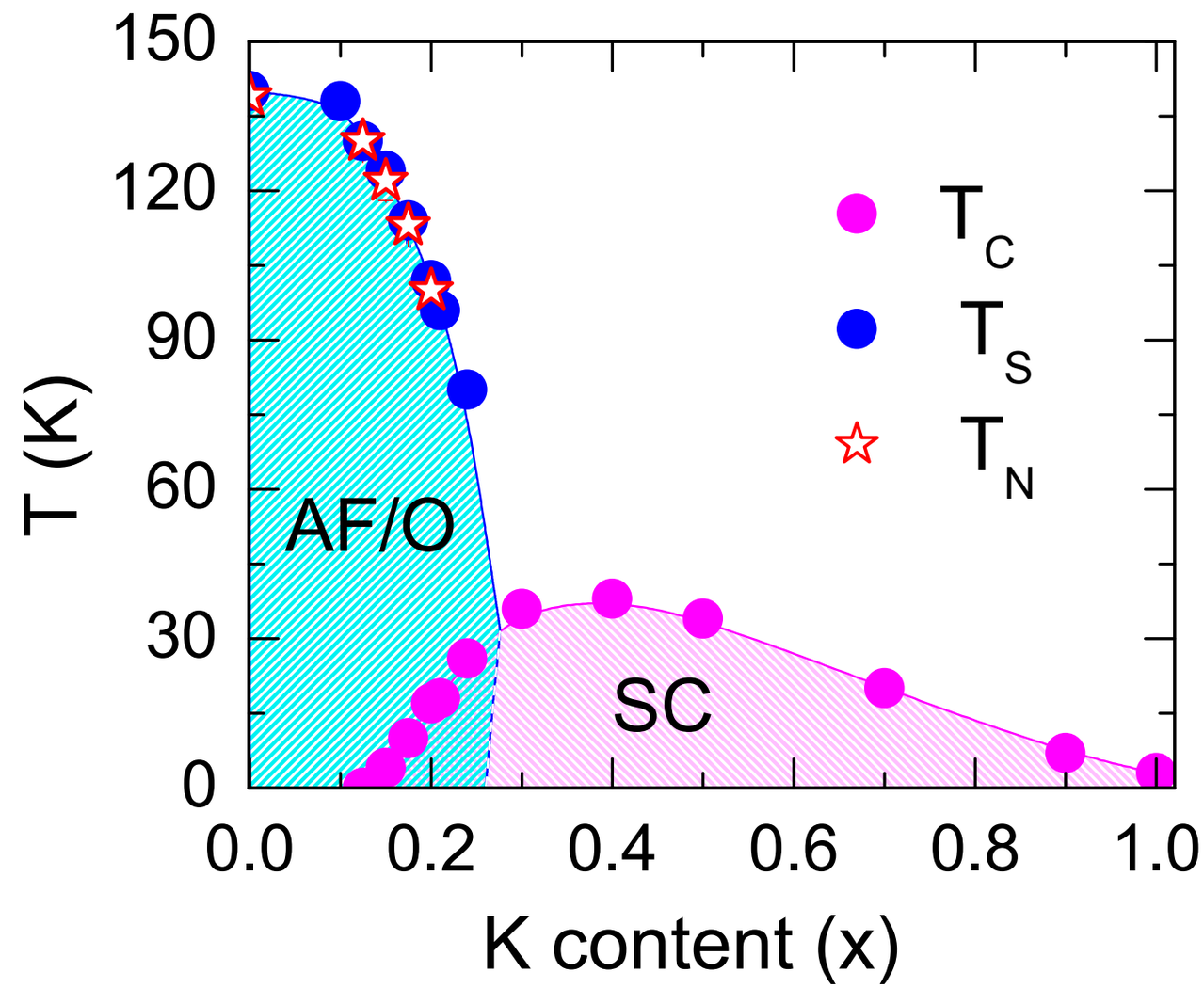

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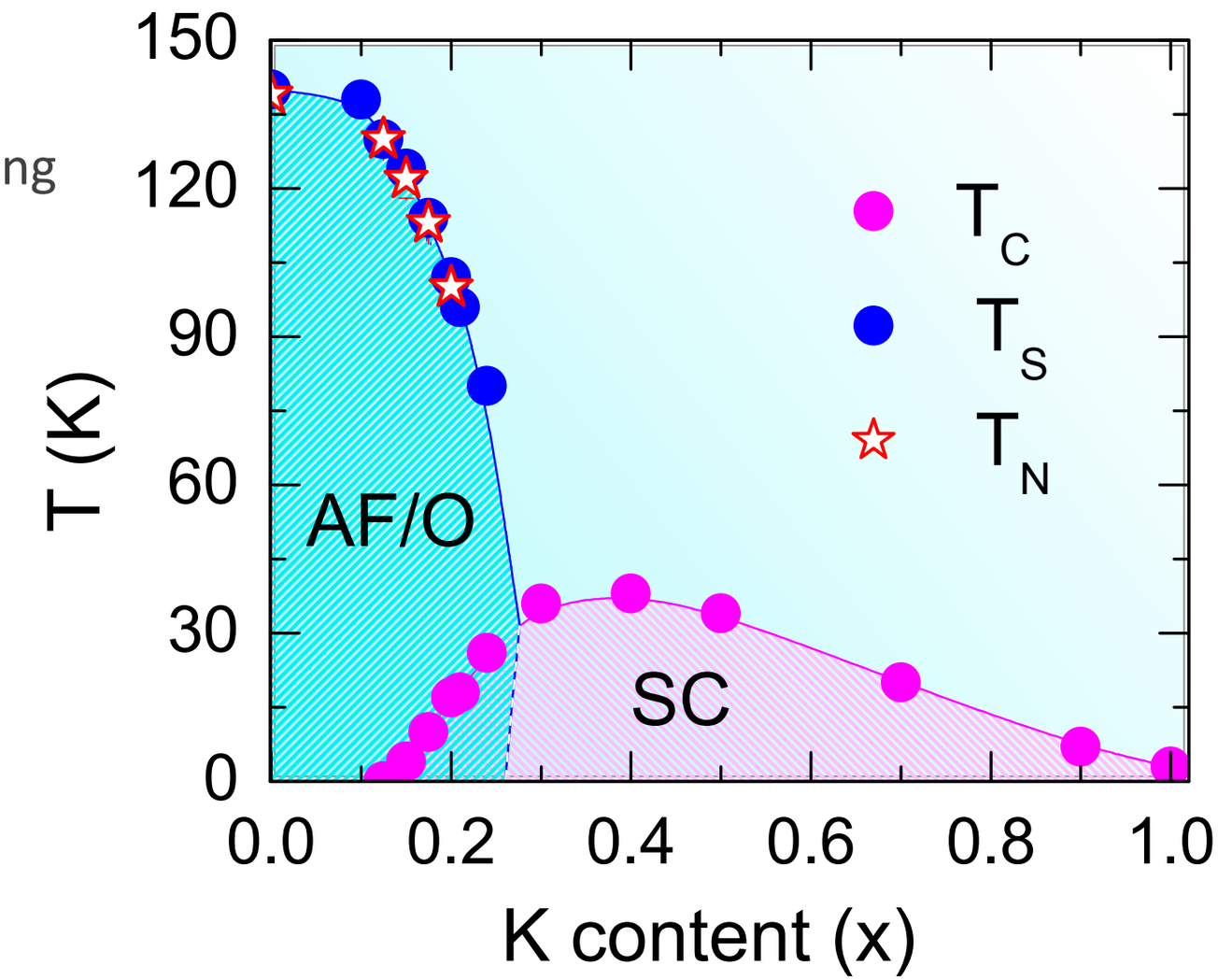

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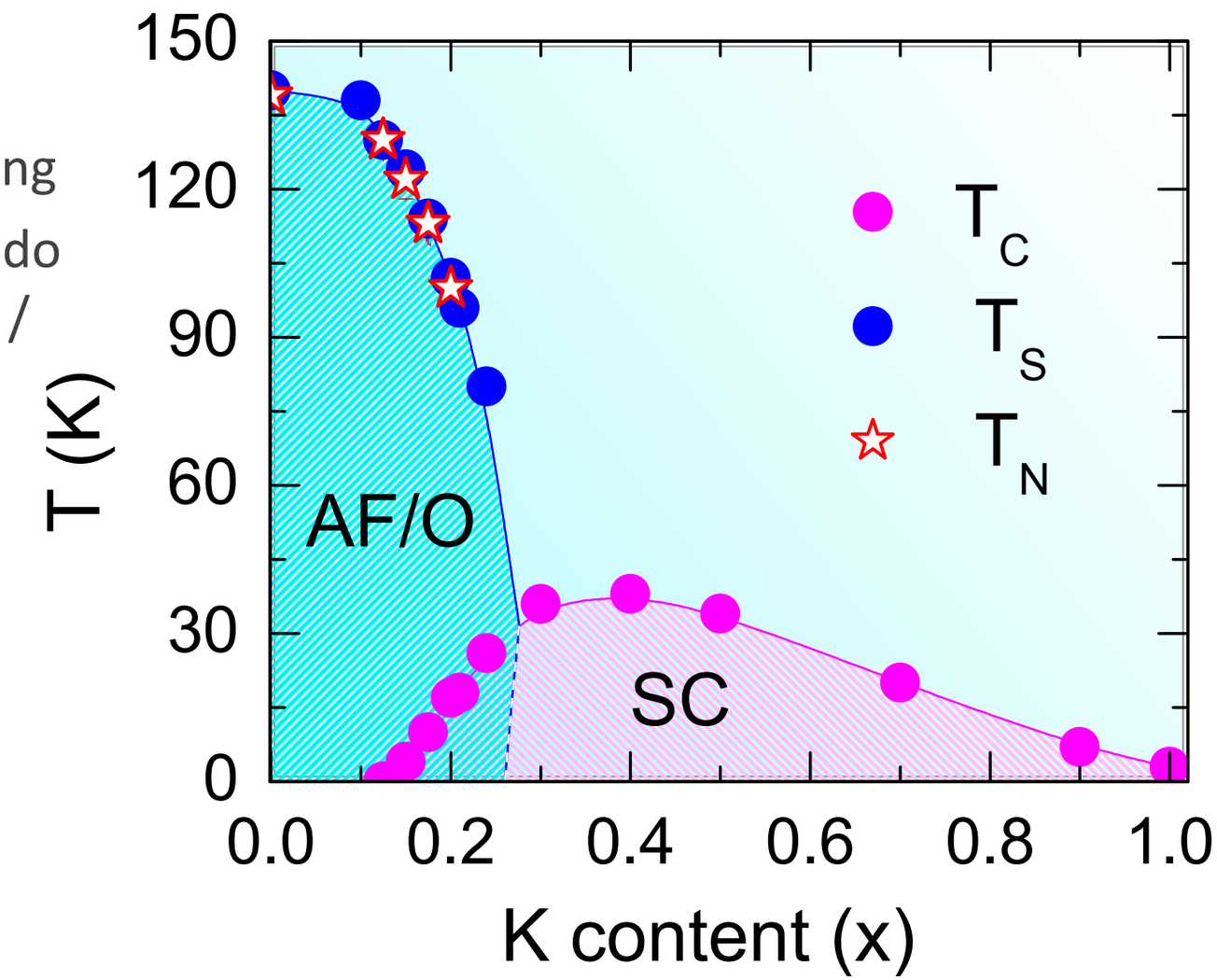
M.A. Tanatar *et al., Phys. Rev. B* **79**, 180508 (2009) (AMES Group)



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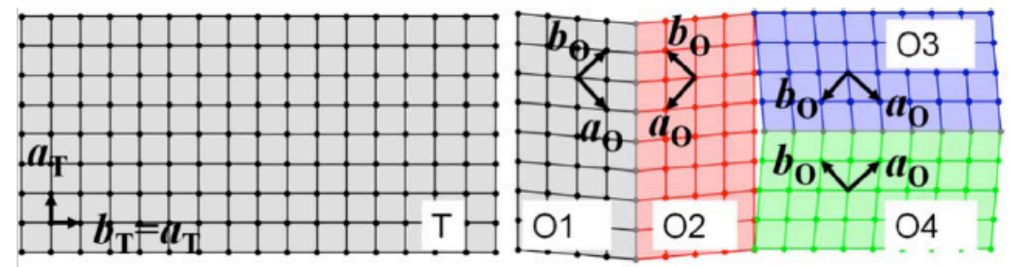
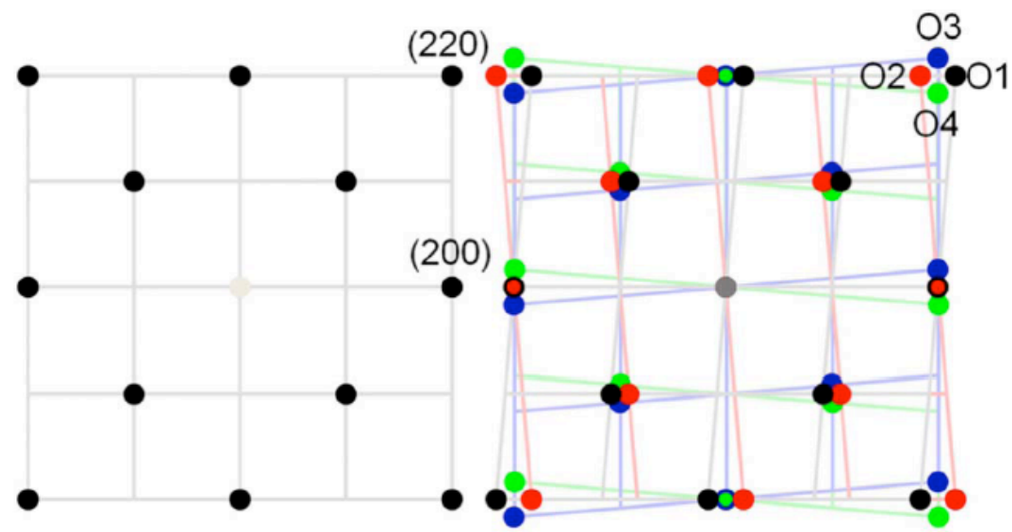
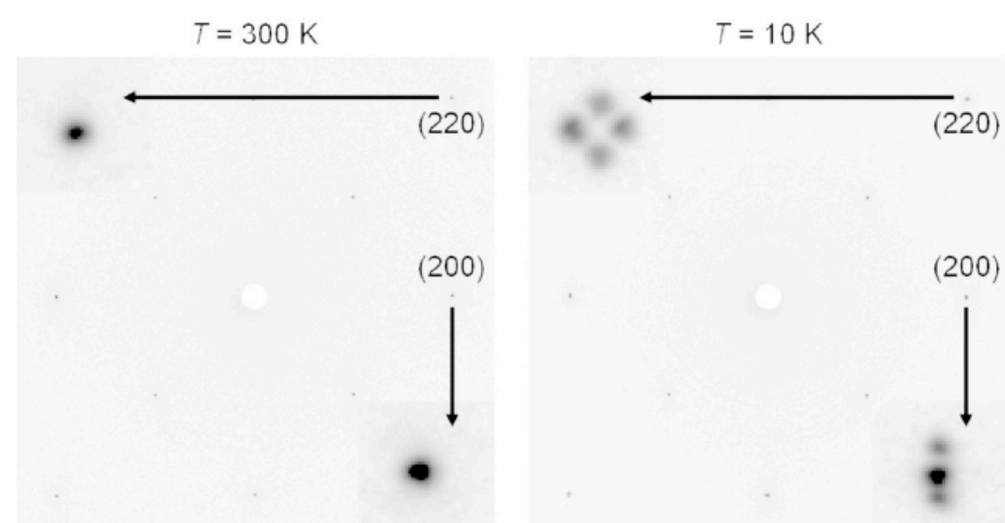
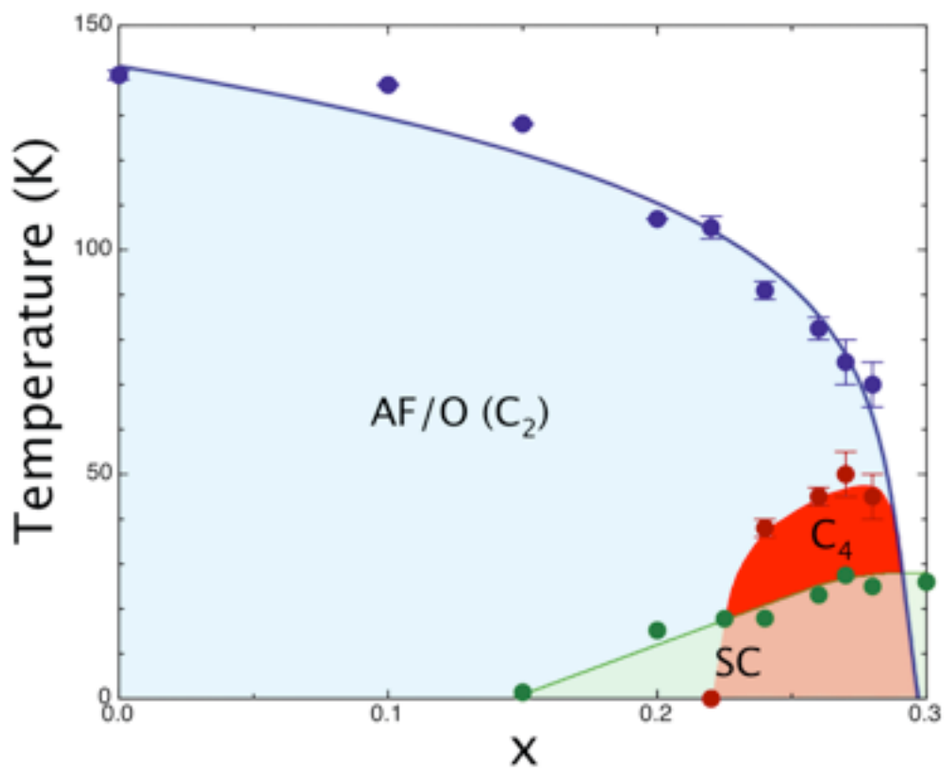








Conclusion

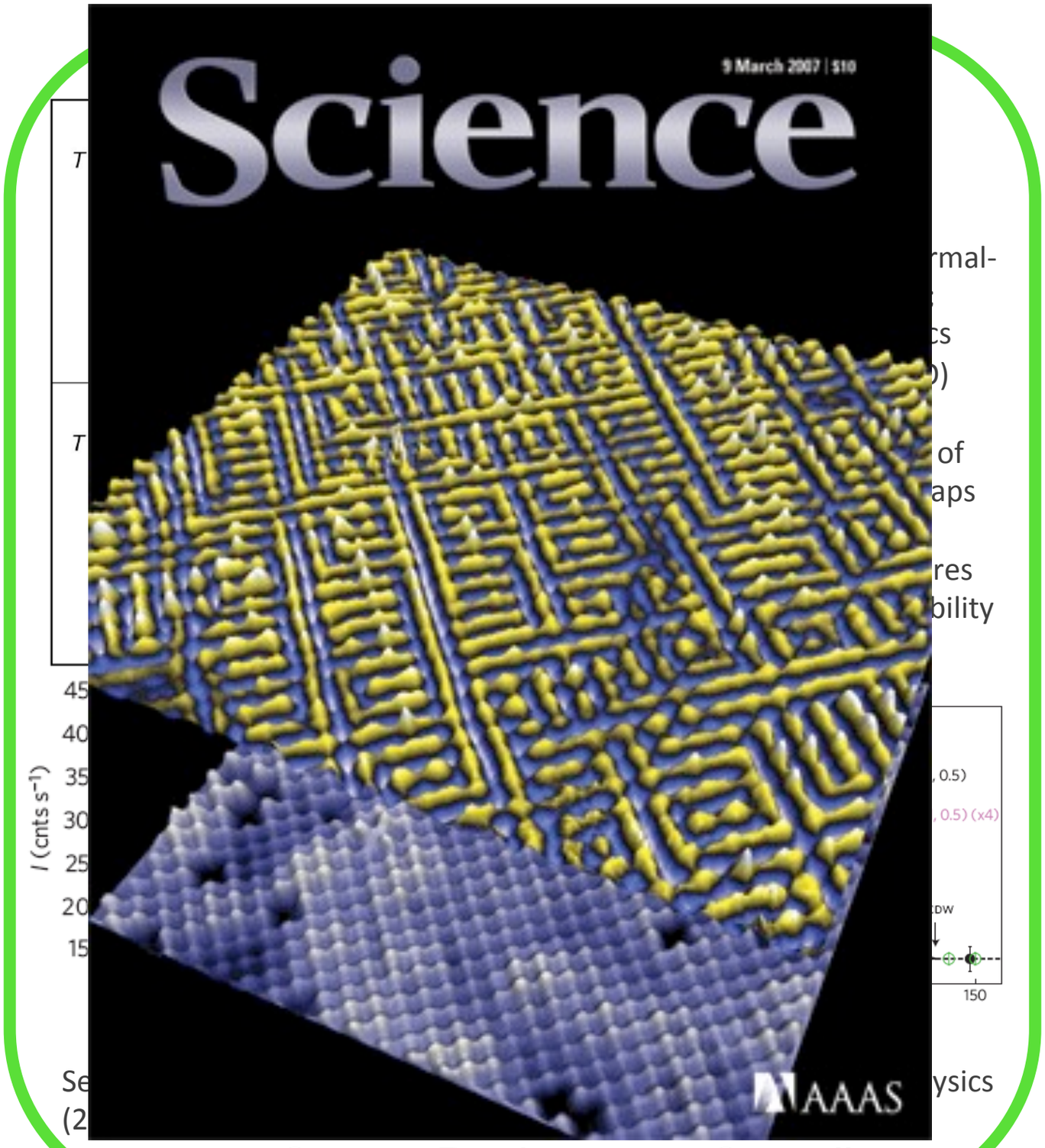
- Diffuse scattering with high-energy x-rays is a powerful probe of defects in crystalline solids
- It can play an essential role in understanding the role of defects in the functional properties of materials
- Advances in source brightness, detector technology, and computational power has the potential of transforming the technique into a more widely utilized materials science tool
- diffraction limited synchrotron light will enable new science in diffraction studies
  - detailed studies of weak diffraction signatures over wide ranges of temperature, doping, magnetic field, and external pressure
  - distinguish inhomogeneous effects from intrinsic short-range correlations induced by competing interactions in strongly correlated electron systems.

Conundrum of electronic phases in high-T_cs : Z. Islam

Opportunity
Detect very weak signature and exquisite details of phases that compete with the SC state in high-T_c cuprates using high energy x-ray scattering

Challenge
Phase-pure, high-quality, single-crystal samples, which are tiny, needed to be studied with comprehensive bulk sensitivity w/ (to show competition w/ SC state) &w/out an external magnetic field

DLSR strength
High flux, small, high-energy beam easily available



Samus Davis group, Cornell

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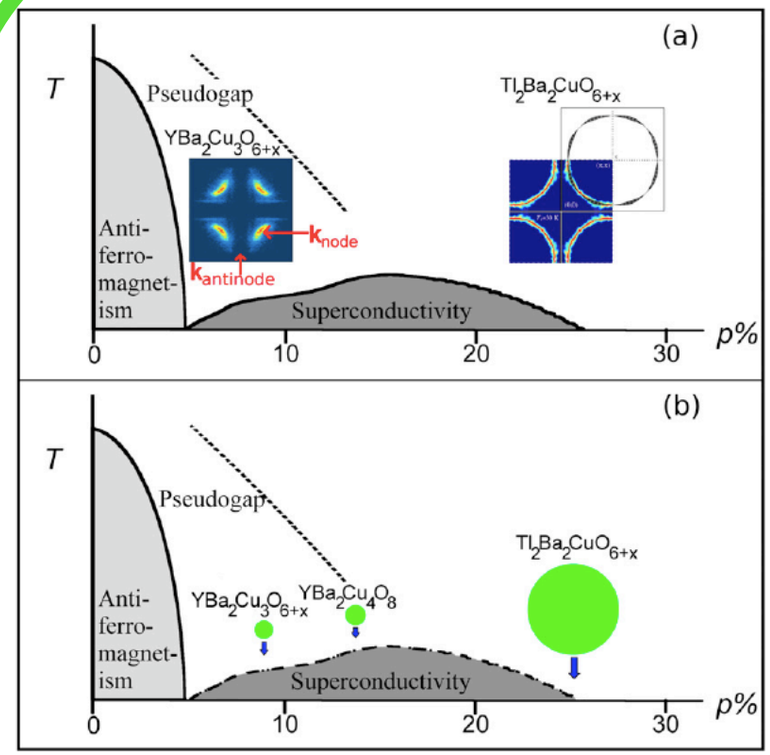
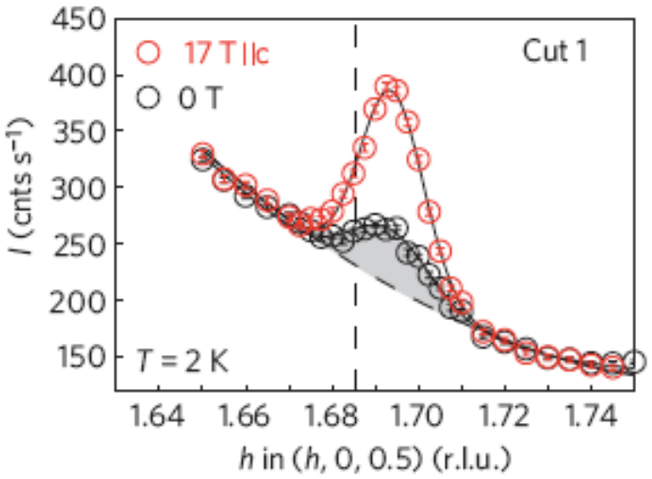
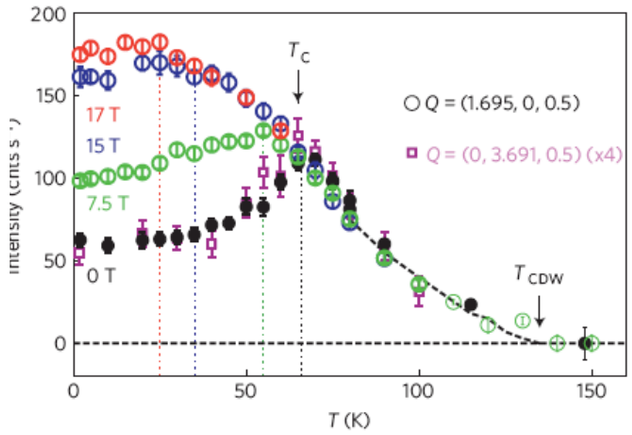


Overdoped: a large normal-state FS (ARPES & QO); Underdoped: Fermi arcs (ARPES) & small FS (QO)

HEXS shows formation of CDWs that introduce gaps and compete w/ SC; however, CDW signatures are at the fringe of visibility





Sebastian et al., Rep. Prog. Phys. **75**, 2012; Chang et al., Nature Physics (2012); Blackburn et al., PRL **110**, 137004 (2013)

Other opportunities in condensed matter: Z. Islam

Fluctuations of short-range order in high-T_c cuprates

Opportunity

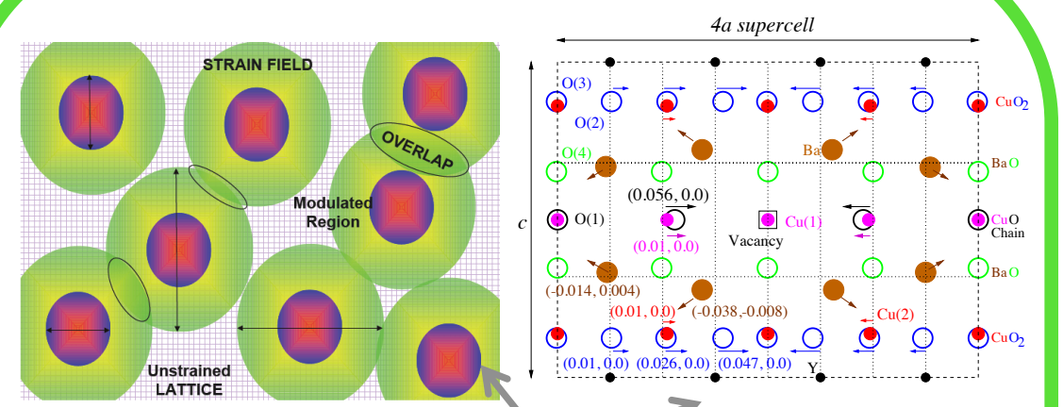
Understanding hierarchy of length scales reflecting competing and/or coexisting inhomogeneities that occur in high-T_c cuprates is essential to control them

Challenge

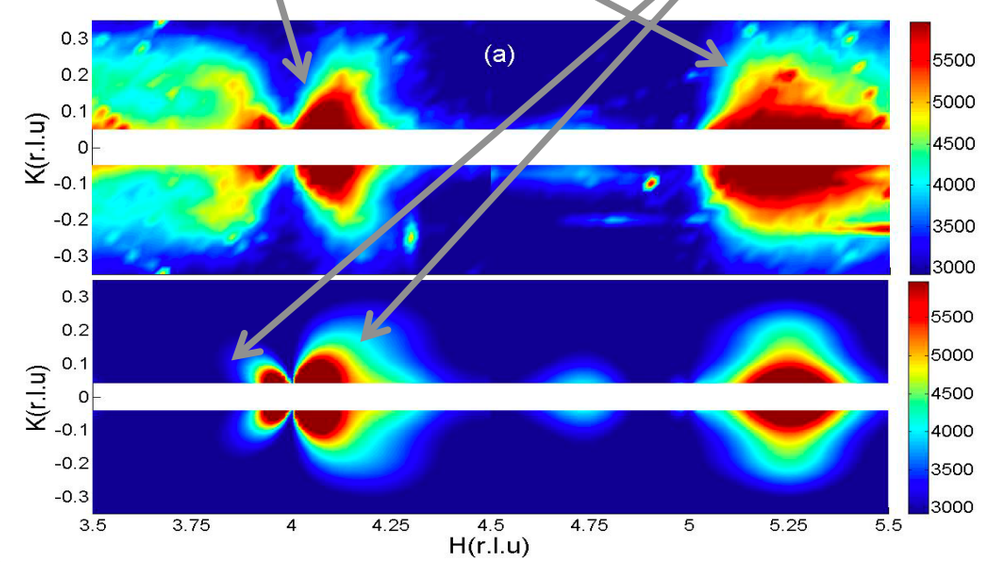
Nanoscale domains of ordered dopants (e.g. O in YBCO), strain field, electronic inhomogeneities seen by STM, & electron mean-free paths are of the same order. Construct 3D images of bulk correlations of these domains & determine their fluctuations

DLSR strength

Spatially resolved coherent diffraction will be enabled on weaker short-range order scattering



Super-lattice peaks from modulated regions, Huang scattering from long-range strain field, and a strong intensity asymmetry from their interference



X. Liu et al., PRB **78**, 134526 (2008)