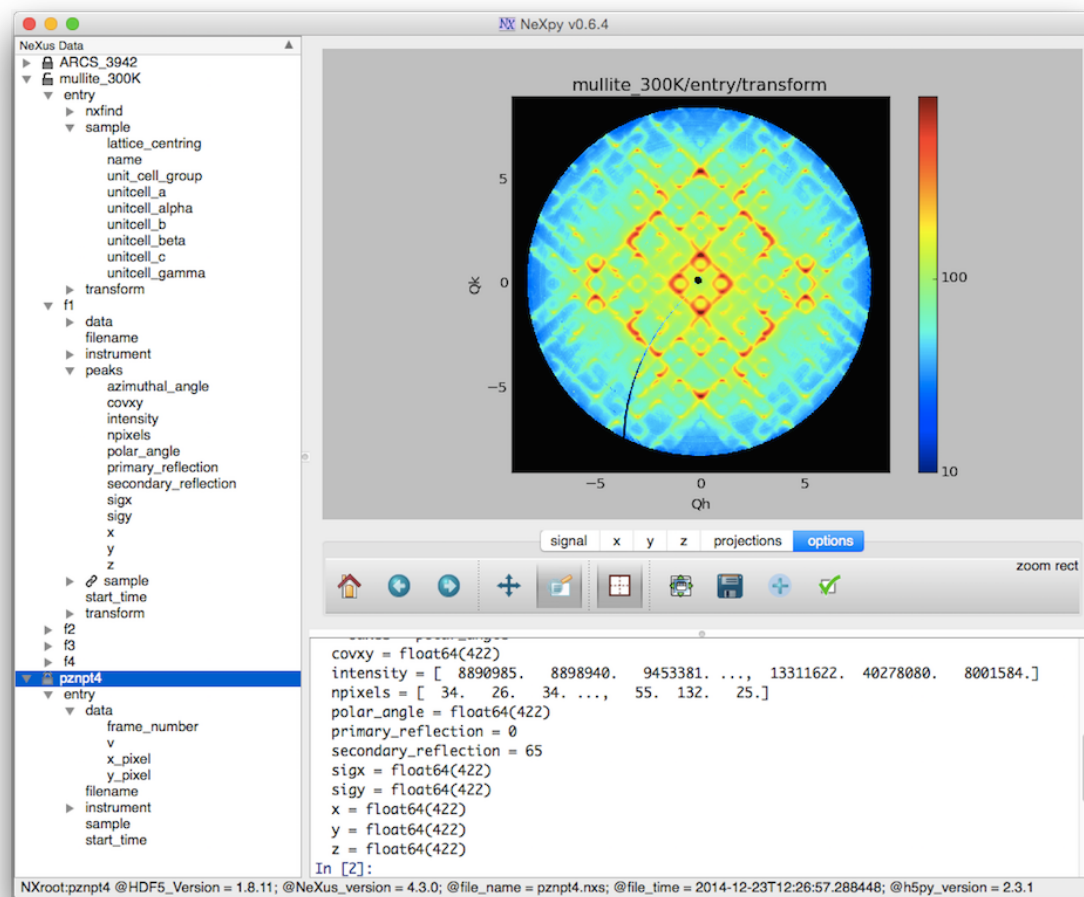


# Single Crystal Diffuse Scattering

Ray Osborn

Neutron and X-ray Scattering Group  
Materials Science Division  
Argonne National Laboratory

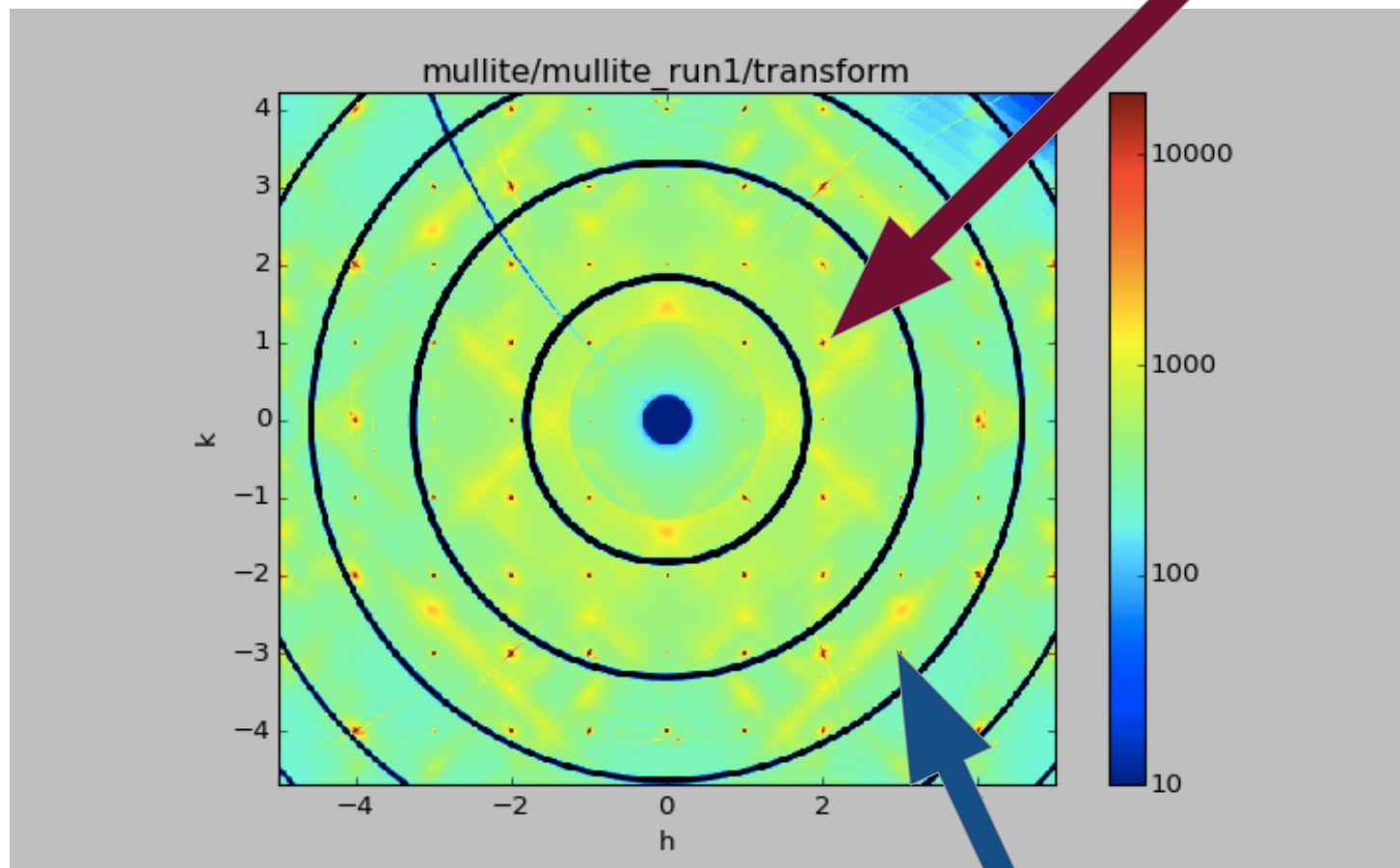


# Outline

- ▶ What is diffuse scattering?
  - What does it look like?
  - What causes it?
  - Who started it?
- ▶ What is it good for?
  - A random walk through disordered materials
- ▶ How do I model it?
  - A few equations
  - Rules of thumb
- ▶ Case Study 1: Diffuse scattering from vacancies in mullite
- ▶ Case Study 2: Huang scattering in bilayer manganites
- ▶ How do I look at static disorder?
  - Neutrons vs X-rays
  - Corelli - Diffuse scattering with elastic discrimination
- ▶ Diffuse scattering - the musical

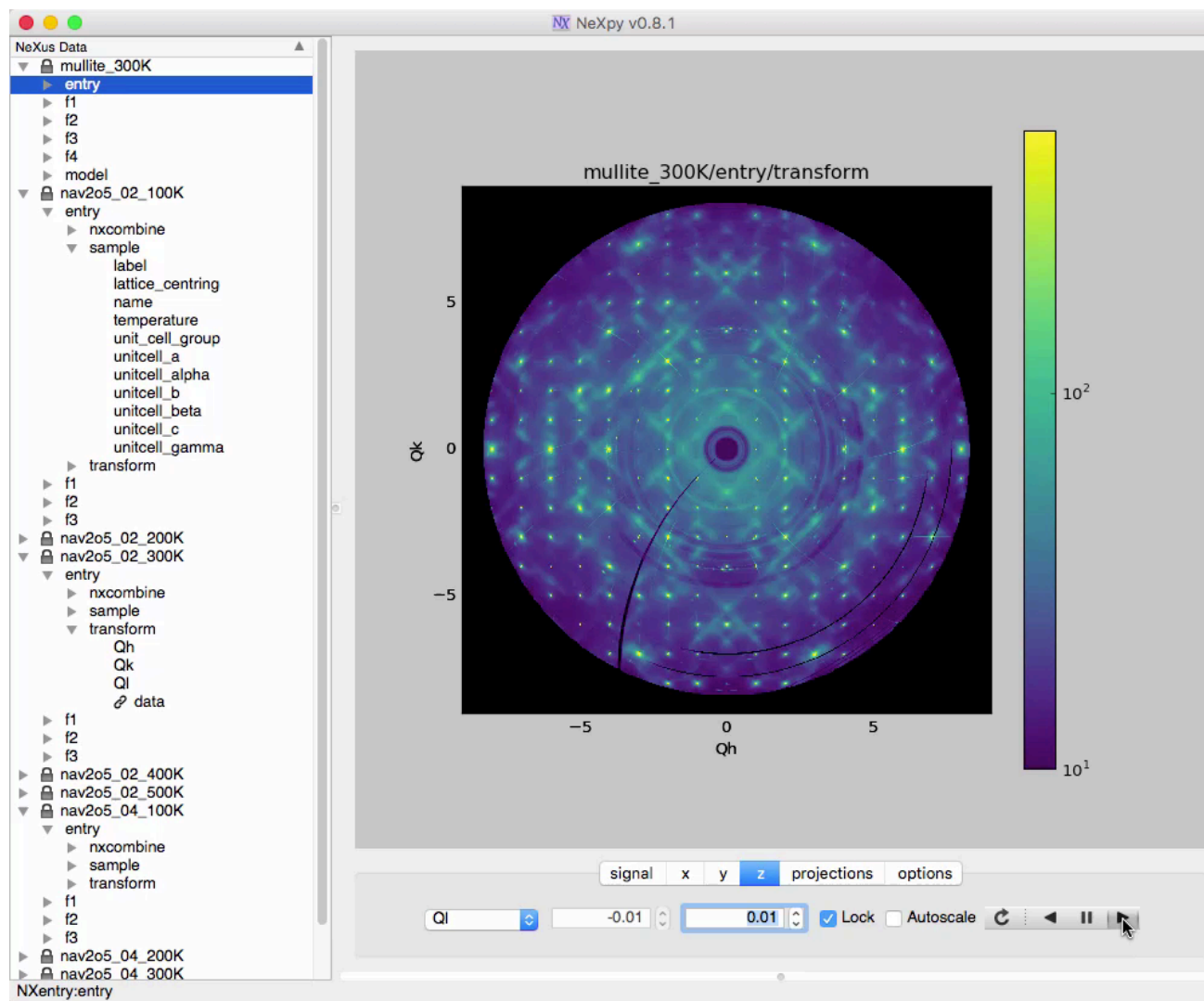
# Bragg Scattering vs Diffuse Scattering

Bragg Scattering  
Average Structure



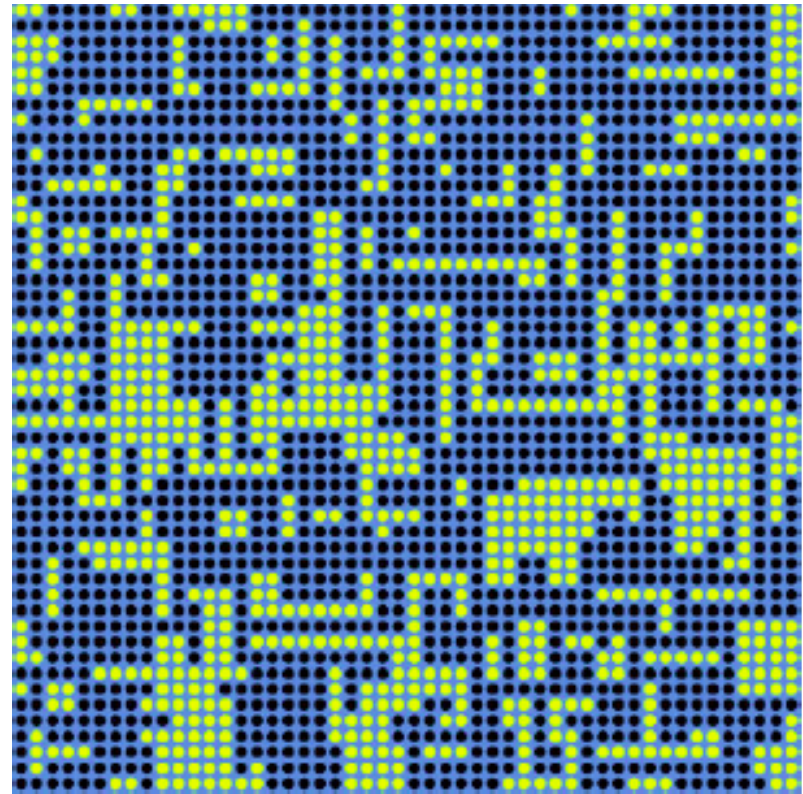
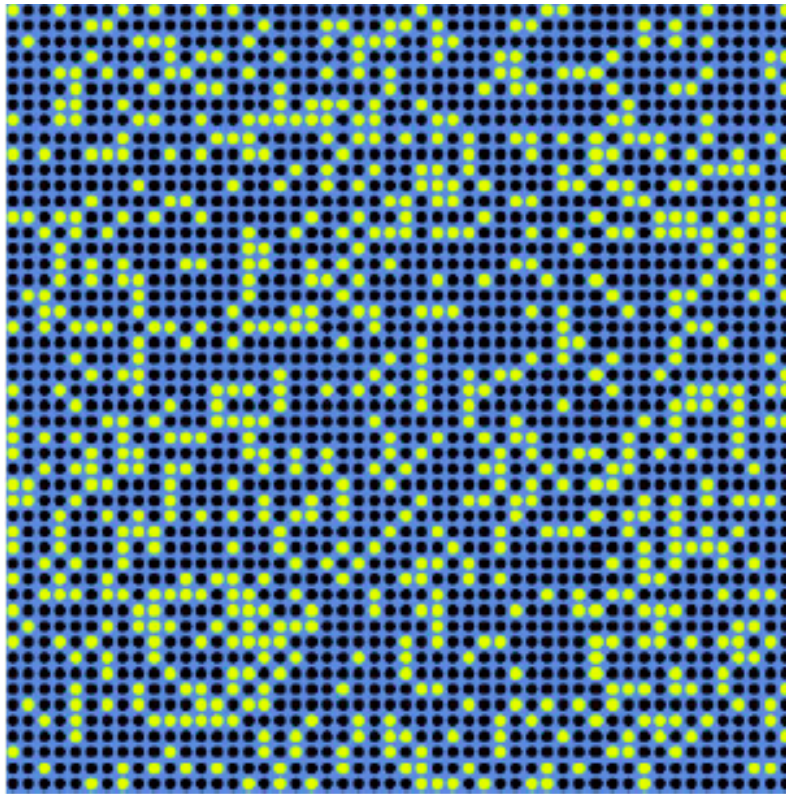
Diffuse Scattering  
Deviations from the Average Structure

# Single Crystal Diffuse Scattering in 3D



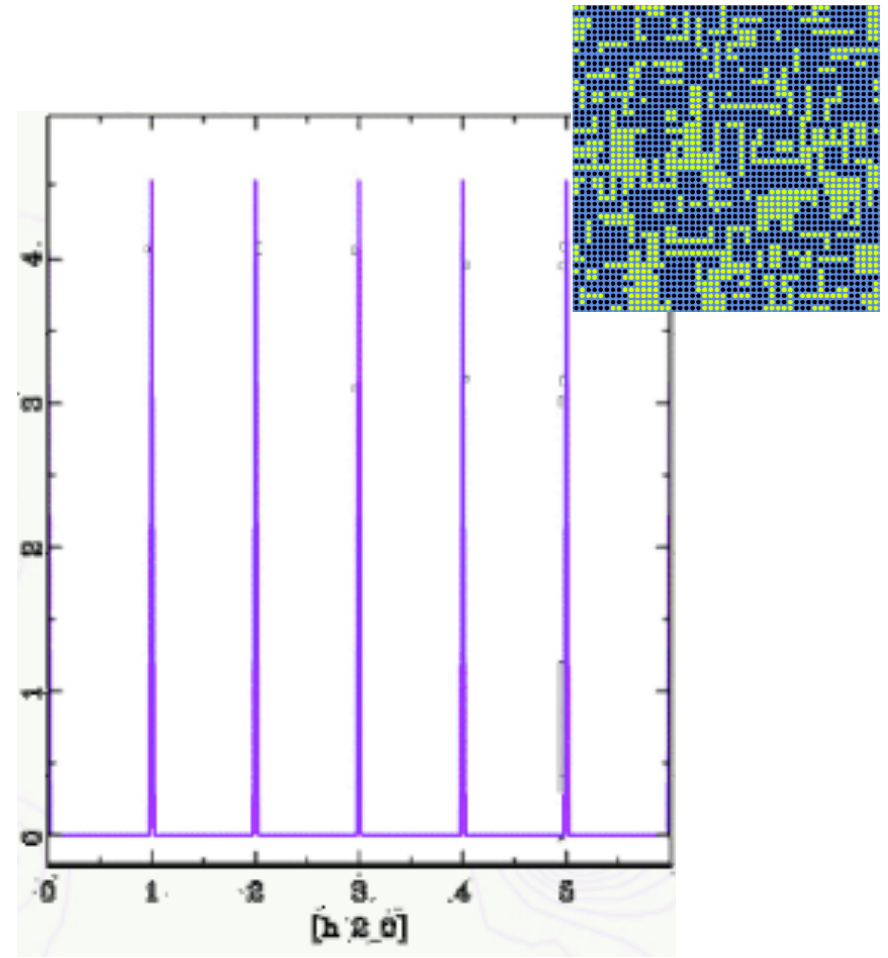
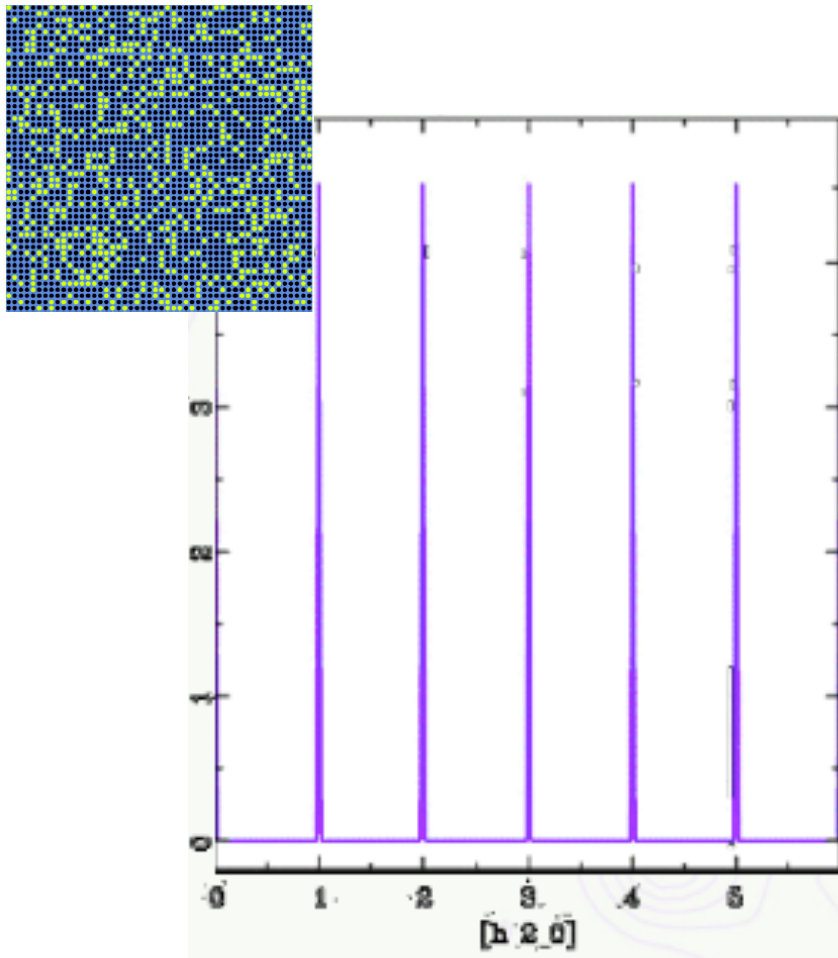
# Simple Example of Disorder

- ▶ In these examples, 30% of atoms (blue dots) have been replaced by vacancies (green dots)
  - Left-Hand-Side: random substitution
  - Right-Hand-Side: high probability of vacancy clusters
    - Thanks to Thomas Proffen



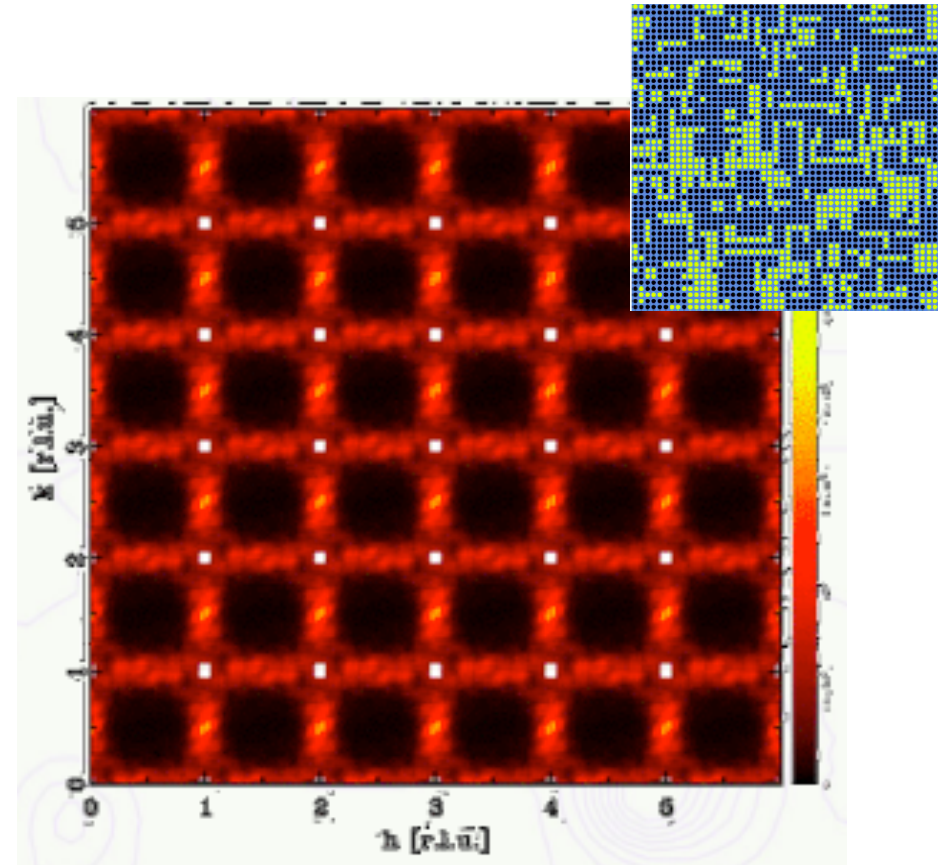
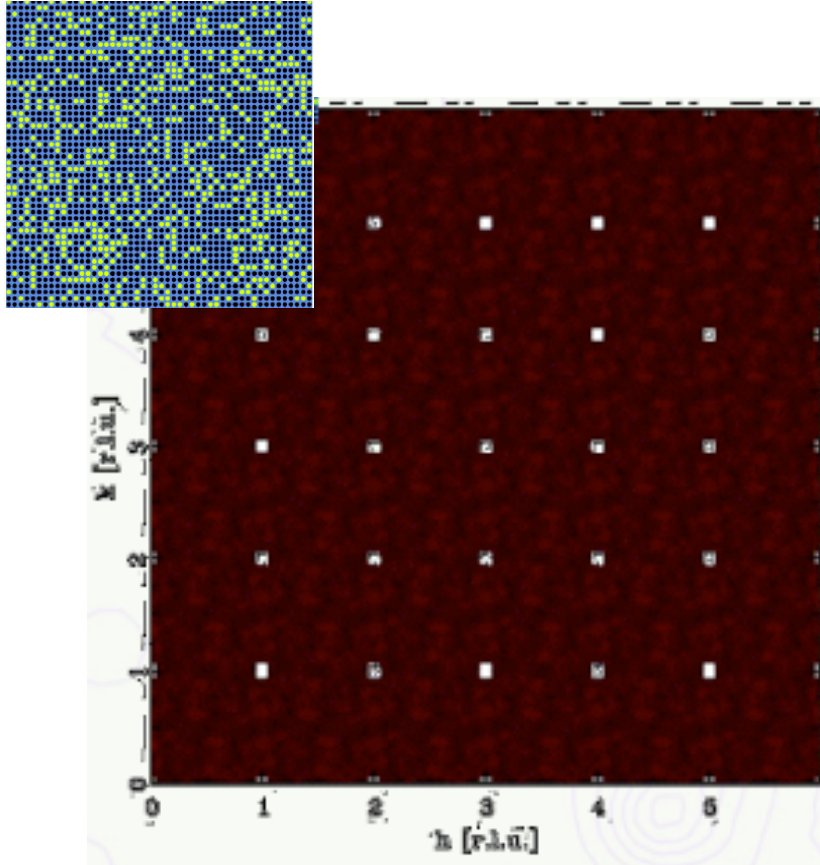
# Bragg Scattering

- ▶ Bragg scattering is determined by the average structure.
  - Since the average vacancy occupation is identical, both examples have identical Bragg peaks

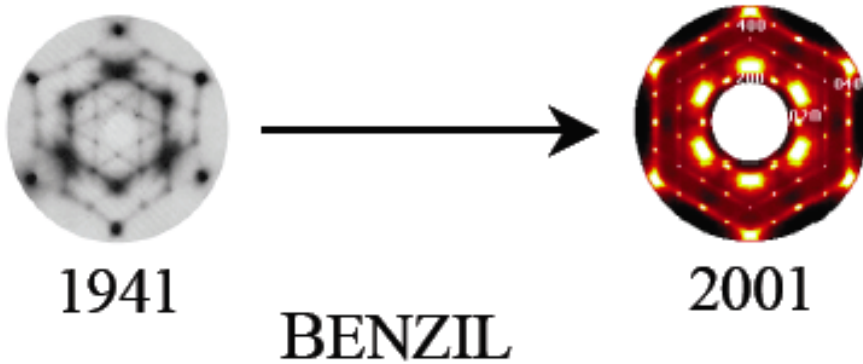


# Diffuse Scattering

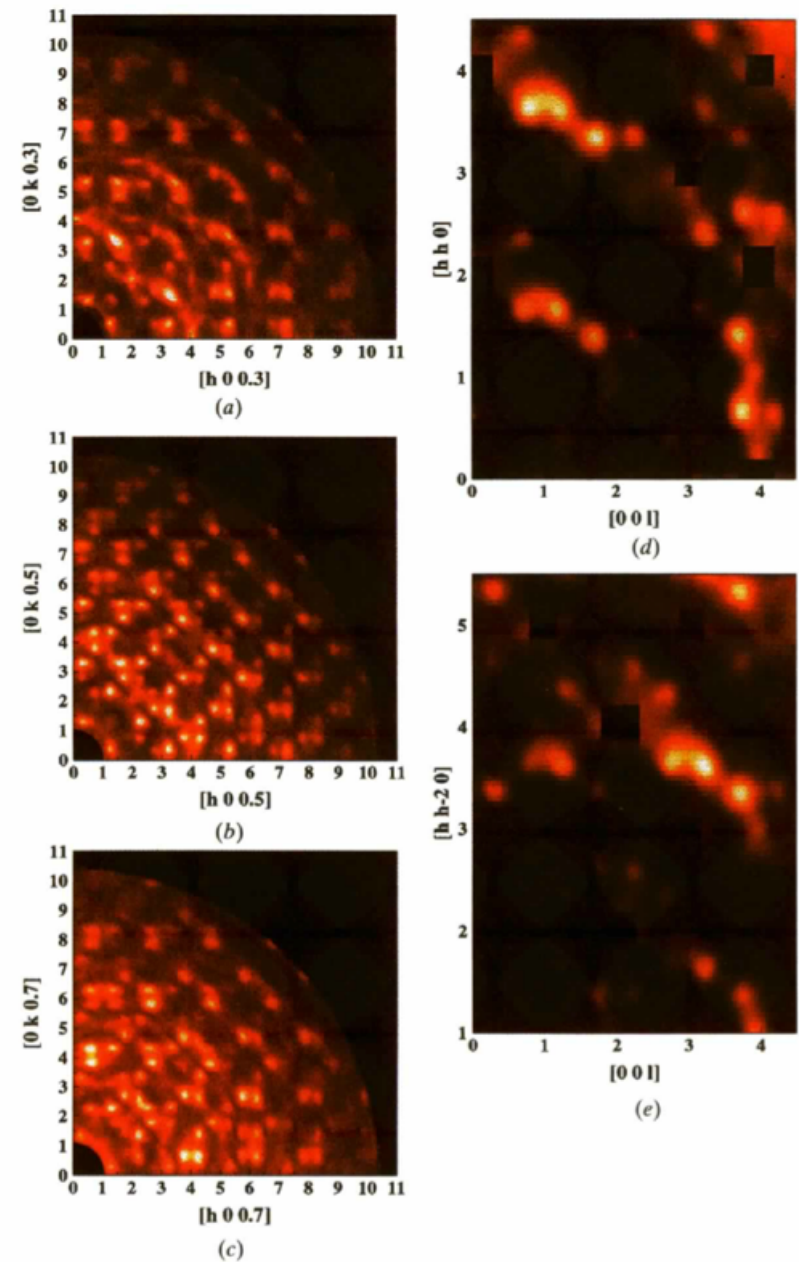
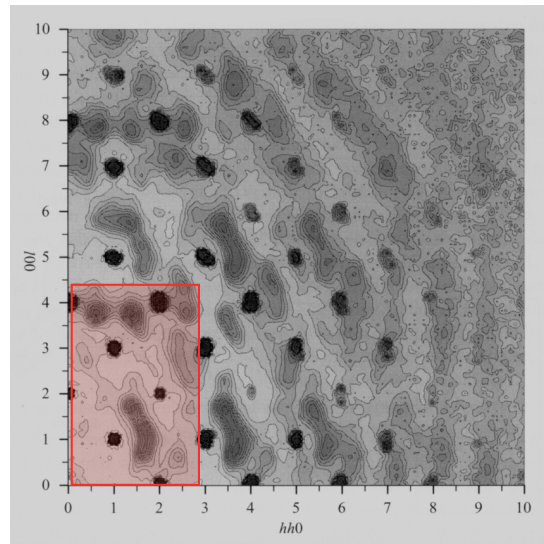
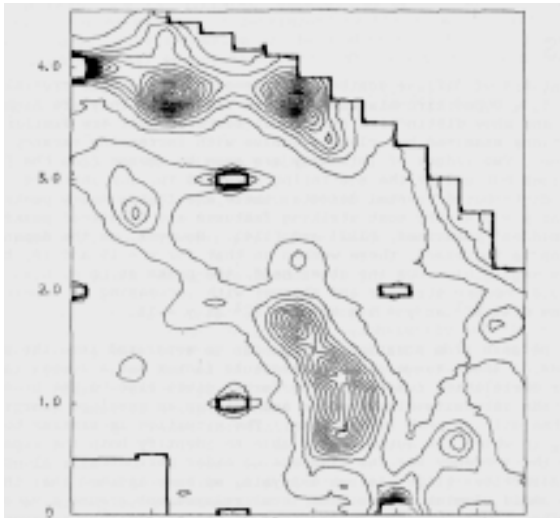
- ▶ The diffuse scattering is quite different in the two examples
  - Random vacancy distributions lead to a constant background (Laue monotonic scattering)
  - Vacancy clusters produce rods of diffuse scattering connecting the Bragg peaks



# An Ultra-Short History of Advances in Diffuse Scattering



Yttria-Stabilized Zirconia



T. Proffen and T. R. Welberry J. Appl. Cryst. **31**, 318 (1998)

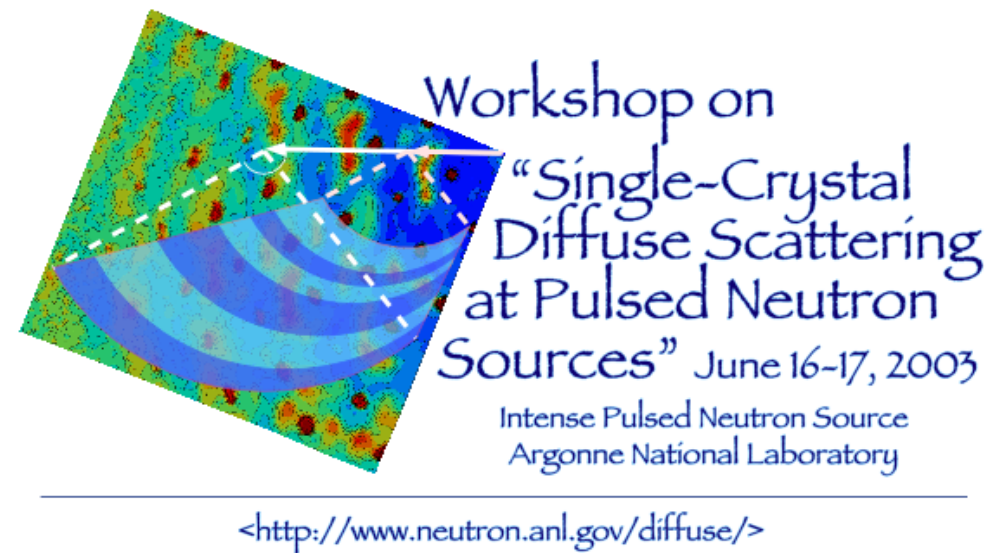
# What is it good for?



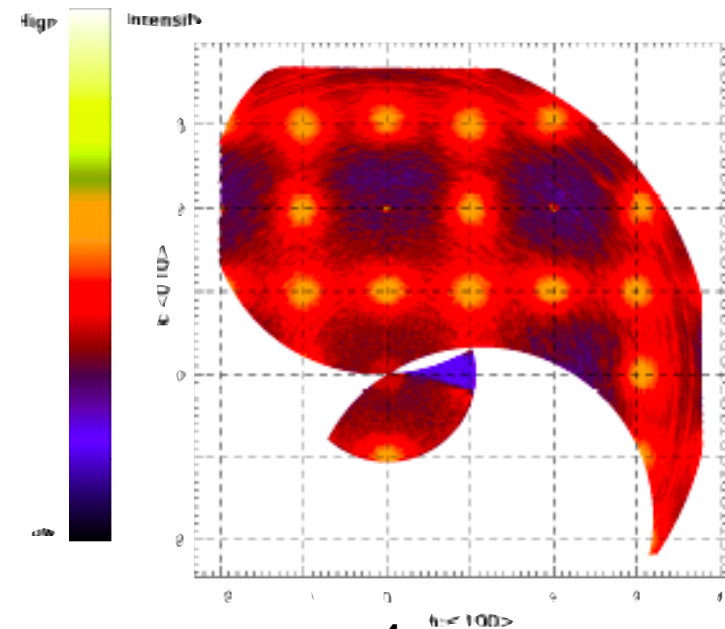
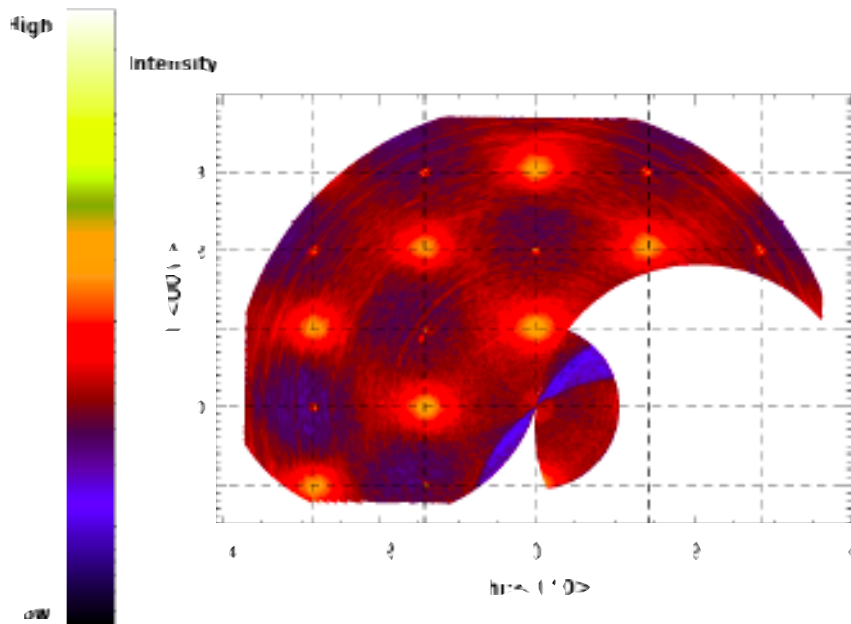
# Science Impacted by Diffuse Scattering

## ► Subjects identified at the *Workshop on Single Crystal Diffuse Scattering at Pulsed Neutron Sources*

- Stripes in cuprate superconductors
- Orbital correlations in transition metal oxides (including CMR)
- Nanodomains in relaxor ferroelectrics
- Defect correlations in fast-ion conductors
- Geometrically frustrated systems
- Critical fluctuations at quantum phase transitions
- Orientational disorder in molecular crystals
- Rigid unit modes in framework structures
- Quasicrystals
- Atomic and magnetic defects in metallic alloys
- Molecular magnets
- Defect correlations in doped semiconductors
- Microporous and mesoporous compounds
- Host-guest systems
- Hydrogen-bearing materials
- Soft matter - protein configurational disorder using polarization analysis of spin-incoherence
- Low-dimensional systems
- Intercalates
- Structural phase transitions in geological materials

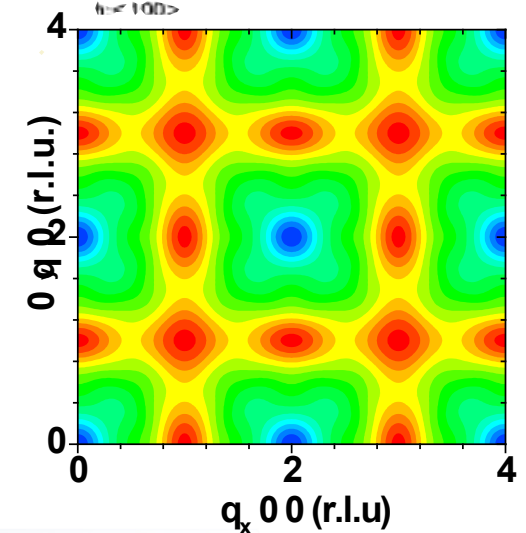


# Diffuse Scattering from Metallic Alloys

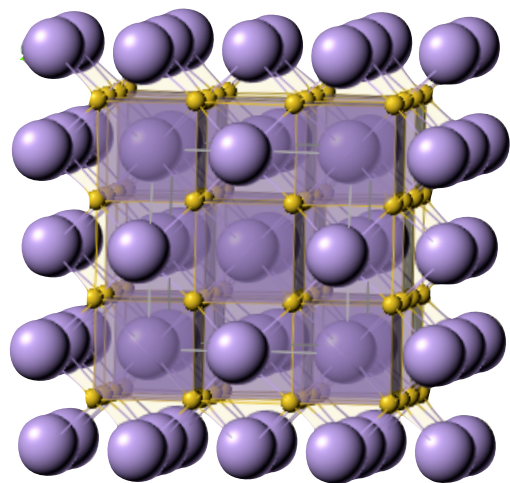


## Short-range Order in Null Matrix $^{62}\text{Ni}_{0.52}\text{Pt}_{0.52}$

J. A. Rodriguez, S. C. Moss, J. L. Robertson, J. R. D. Copley, D. A. Neumann, and J. Major  
 Phys. Rev. B **74**, 104115



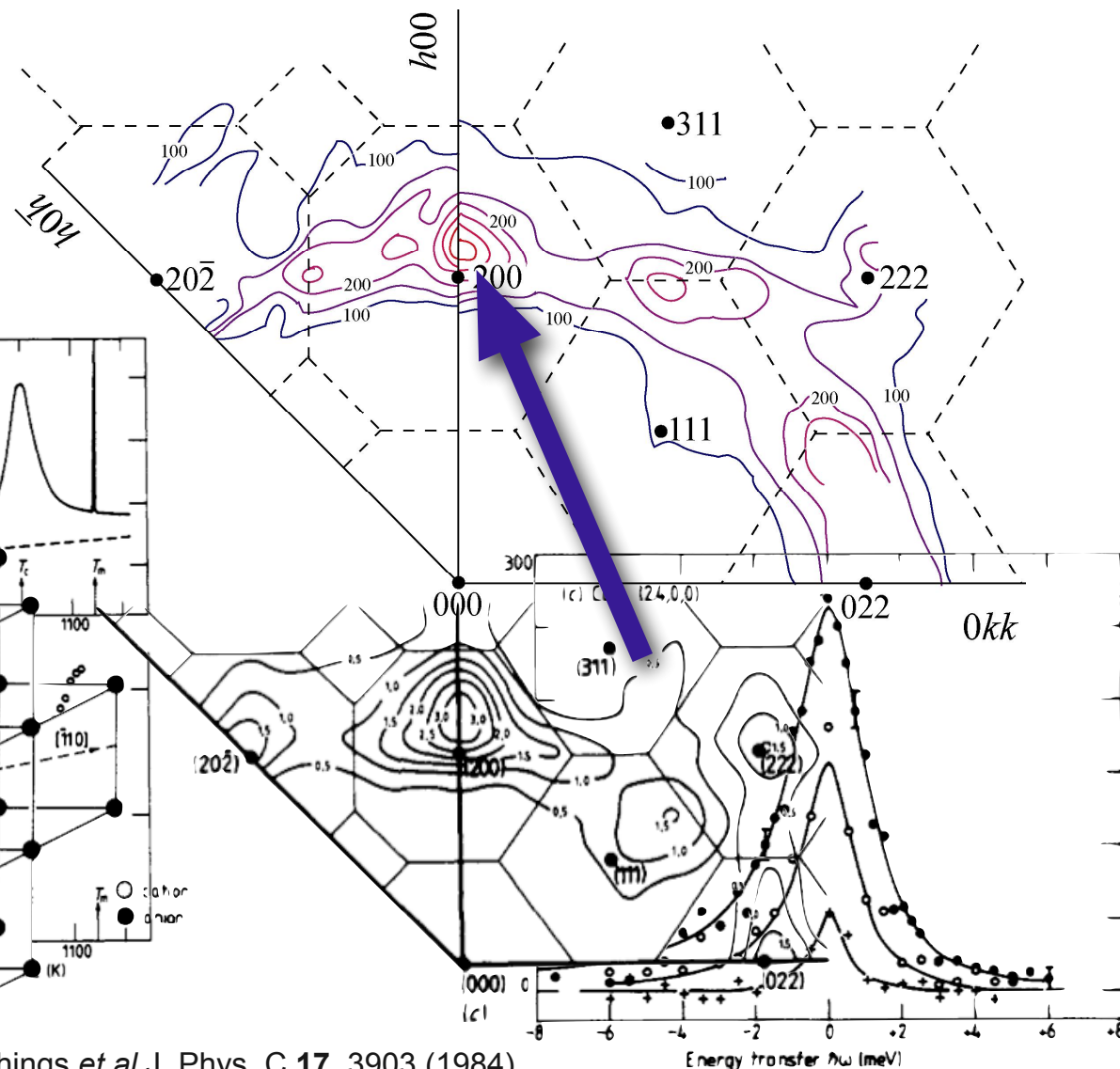
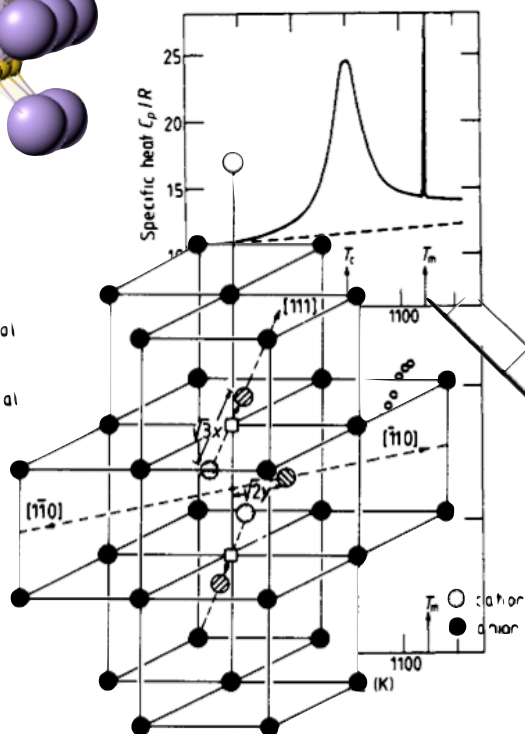
# Diffuse Scattering from a Fast-Ion Conductor



**CaF<sub>2</sub>**

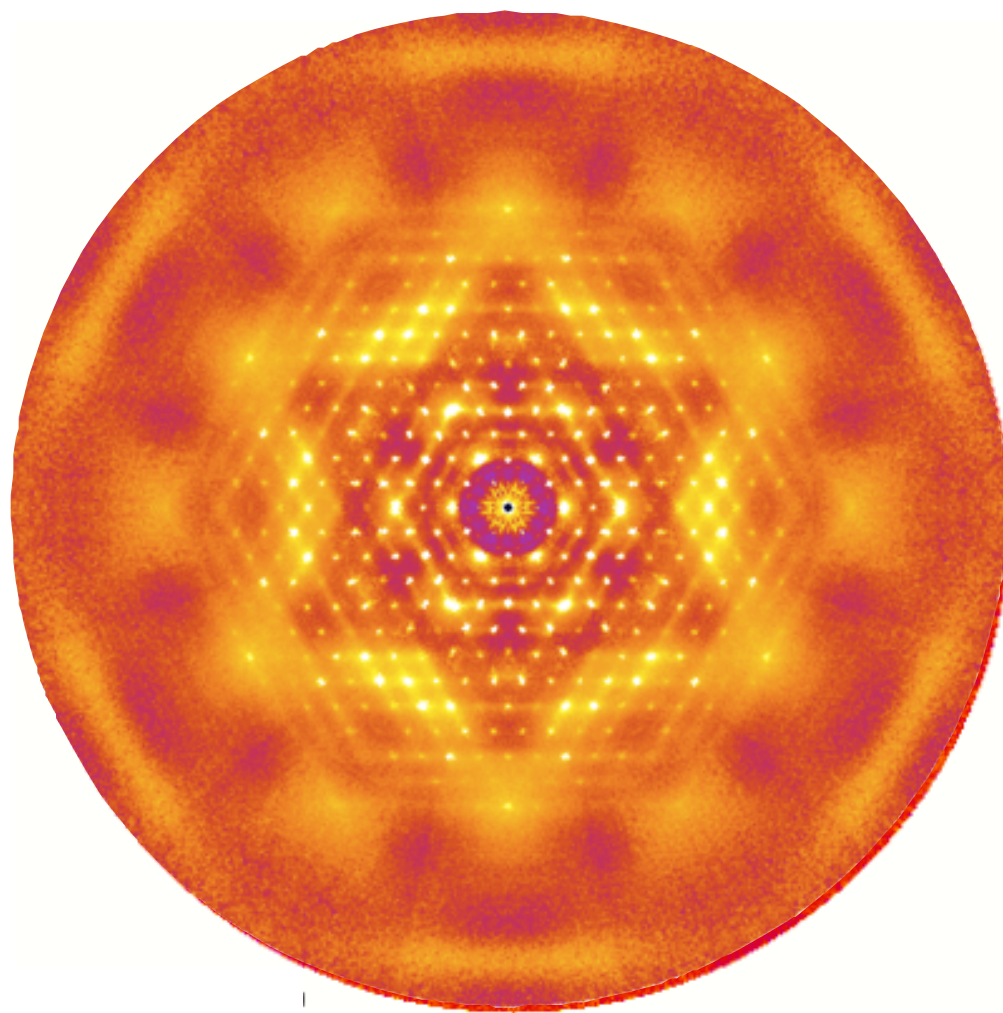
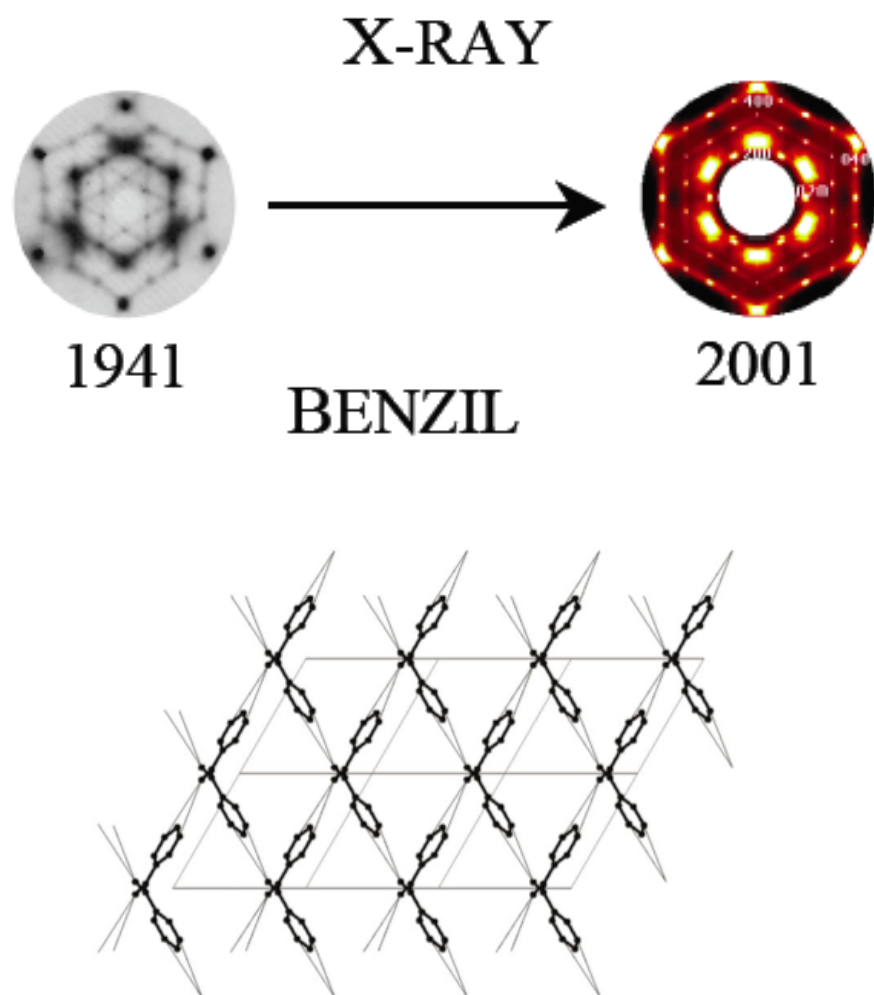
Frenkel pair  
○ vacancy  
⊗ interstitial

Relaxed anion  
□ vacancy  
⊗ interstitial



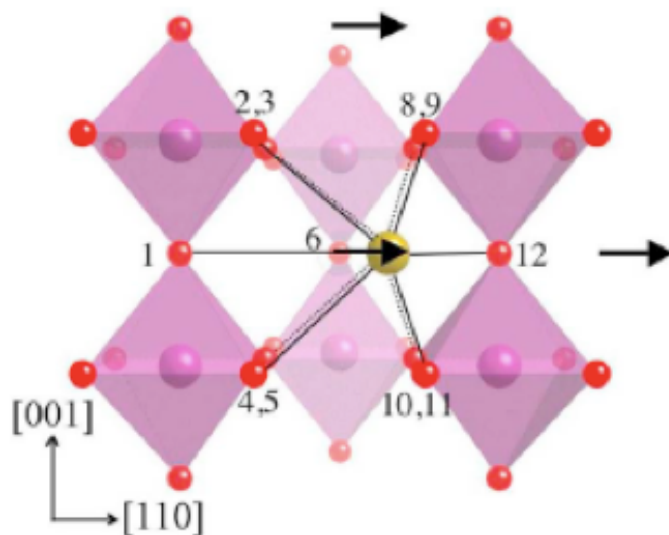
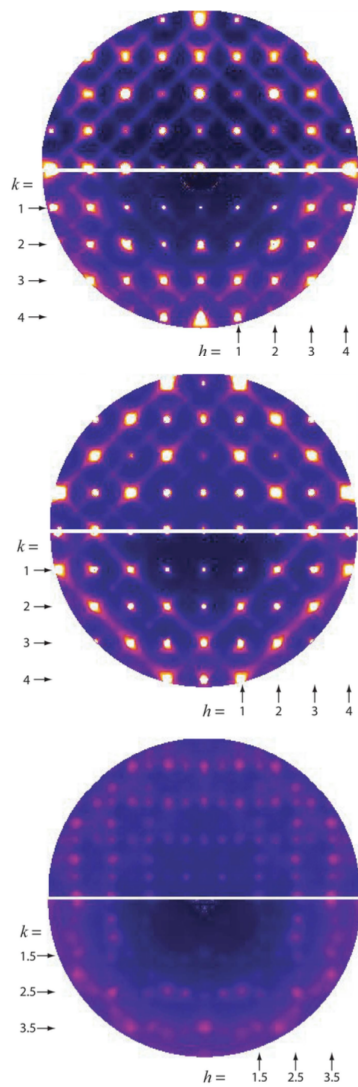
M. T. Hutchings et al J. Phys. C 17, 3903 (1984)

# Diffuse Scattering from Molecular Solids

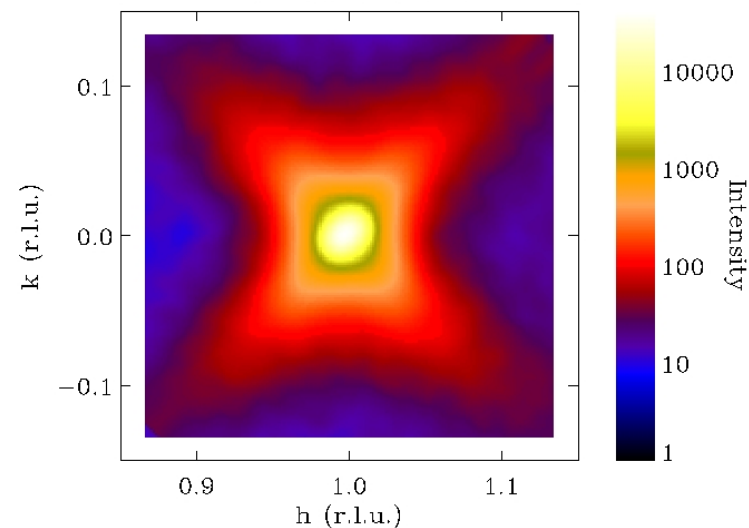


T. R. Welberry *et al* J. Appl. Cryst. **36**, 1400 (2003)

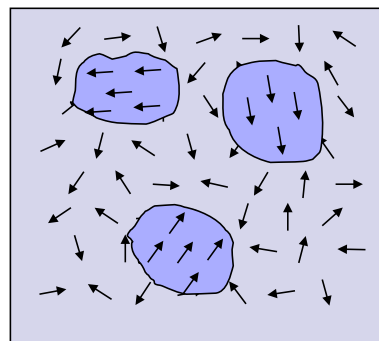
# Diffuse Scattering from Relaxor Ferroelectrics



## Lead Magnesium-Niobate

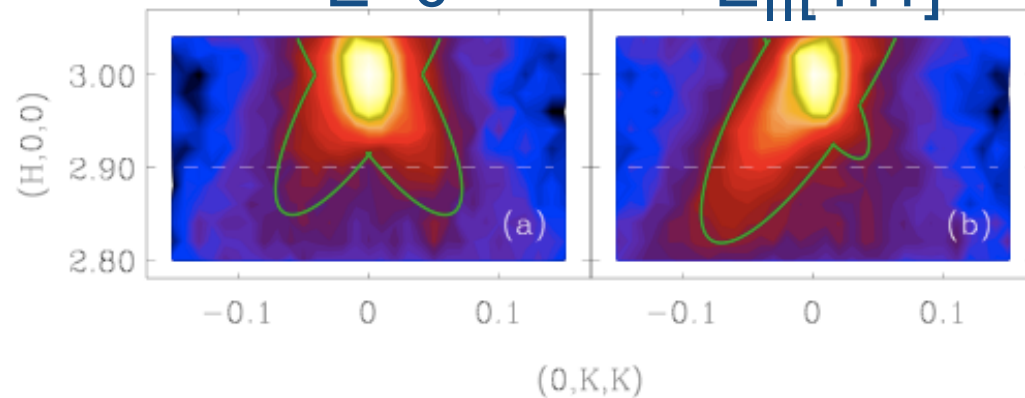


## Lead Zinc-Niobate



$E=0$

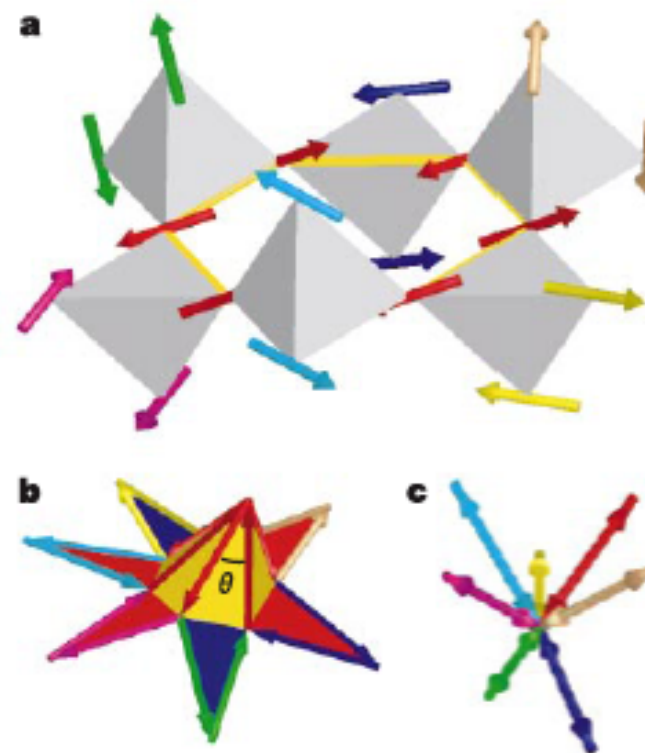
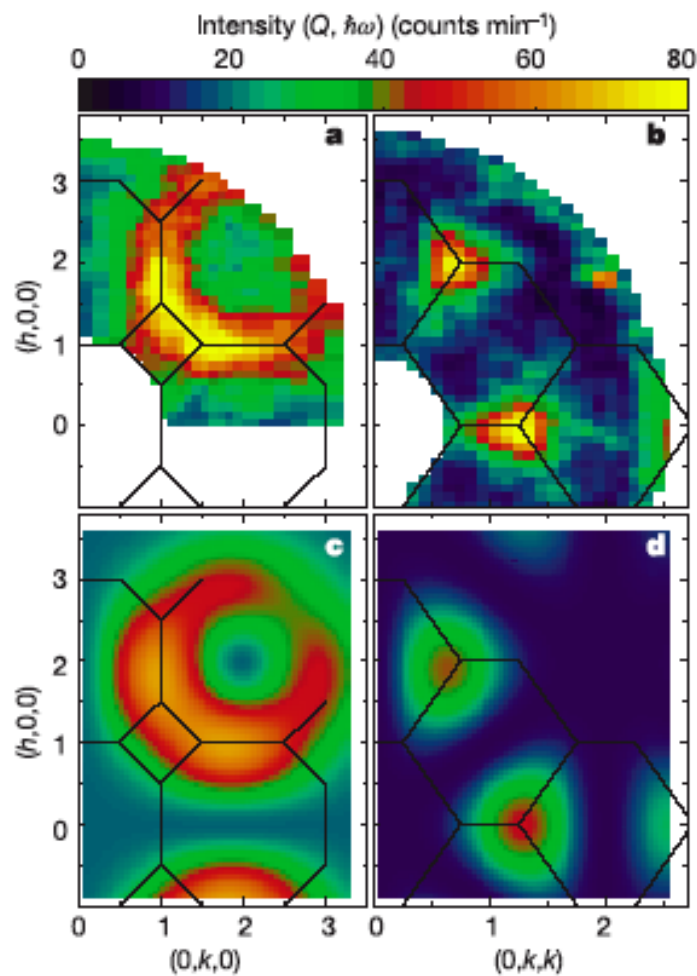
$E \parallel [111]$



T. R. Welberry *et al* J. Appl. Cryst. **38**, 639 (2005)

G. Xu, P. M. Gehring, G. Shirane, Phys. Rev. B **72**, 214106 (2005).

# Magnetic Diffuse Scattering from Geometric Frustration



S.-H. Lee *et al* Nature **418**, 856 (2002)

How do I model it?



# A Few Equations

V. M. Nield and D. A. Keen *Diffuse Neutron Scattering From Crystalline Materials* (2001)

T. R. Welberry *Diffuse X-ray Scattering and Models of Disorder* (2004)

$$I = \sum_i \sum_j b_i b_j \exp(i\mathbf{Q} \cdot \mathbf{r}_{ij})$$

## ► Laue Monotonic Diffuse Scattering

$$I = \bar{b}^2 \sum_{ij} \exp(i\mathbf{Q} \cdot \mathbf{r}_{ij}) + N(\bar{b}^2 - \bar{b}^2); \quad \bar{b}^2 = (c_A b_A + c_B b_B)^2; \quad \bar{b}^2 = c_A c_B (b_B - b_A)^2$$

## ► Cowley Short-Range Order

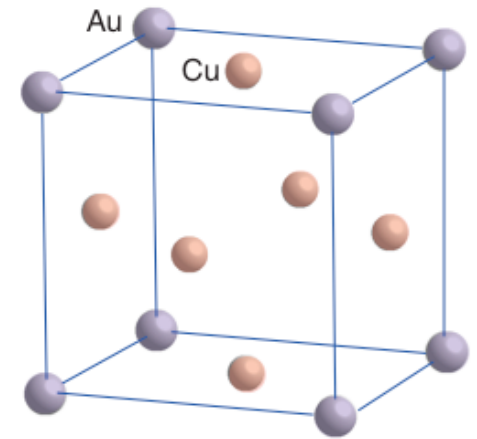
$$I_{diffuse} = N c_A c_B (b_B - b_A)^2 + \sum_{ij} \alpha_i c_B c_A (b_B - b_A)^2 \exp(i\mathbf{Q} \cdot \mathbf{r}_{ij}); \quad \alpha_i = \left(1 - \frac{p_i}{c_A}\right)$$

## ► Warren Size Effect

$$I_{diffuse} = N c_A c_B (b_B - b_A)^2 \left(1 + \sum_{ij} \alpha_i \exp(i\mathbf{Q} \cdot \mathbf{r}_{ij}) + \sum_{ij} \beta_i \exp(i\mathbf{Q} \cdot \mathbf{r}_{ij})\right); \quad \beta_i = f(\epsilon_{AA}^i, \epsilon_{BB}^i)$$

## ► Borie and Sparks Correlations

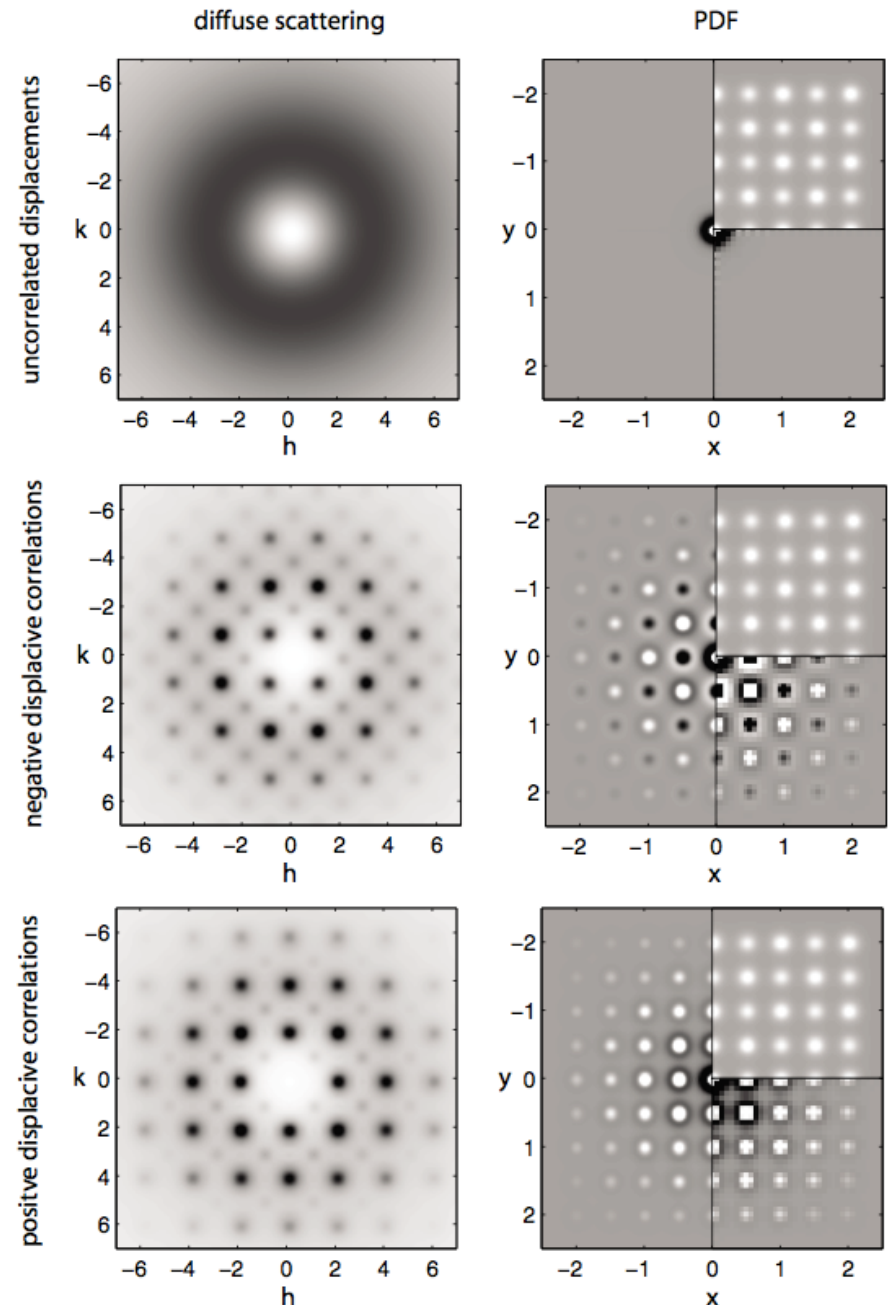
$$I = \sum_i \sum_j b_i b_j \exp(i\mathbf{Q} \cdot (\mathbf{R}_i - \mathbf{R}_j)) \left[1 + i\mathbf{Q} \cdot (\mathbf{u}_i - \mathbf{u}_j) - \frac{1}{2} (\mathbf{Q} \cdot (\mathbf{u}_i - \mathbf{u}_j))^2 + \dots\right]$$



J. M. Cowley, J. Appl. Phys. **21**, 24 (1950)

# Three-Dimensional Pair Distribution Functions

- ▶ The ability to measure three-dimensional  $S(\mathbf{Q})$  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
  - $\Delta$ -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.



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Z. Kristallogr. **2012**, 227, 238–247 / DOI 10.1524/zkri.2012.1504

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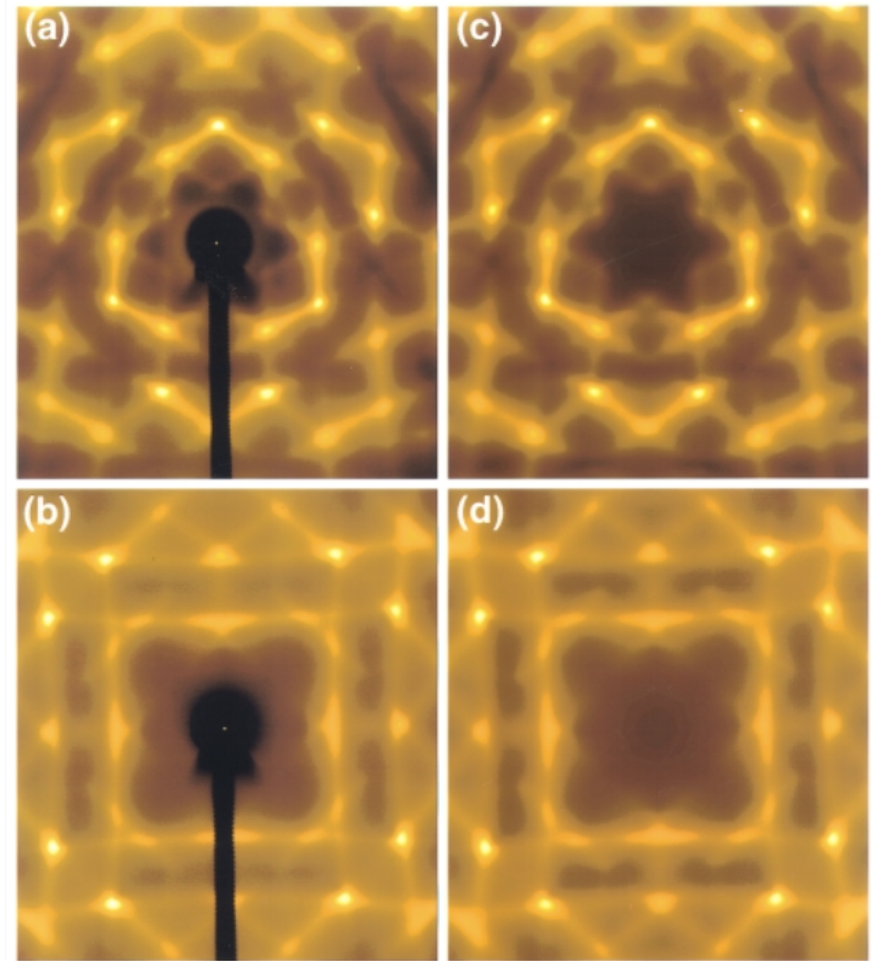
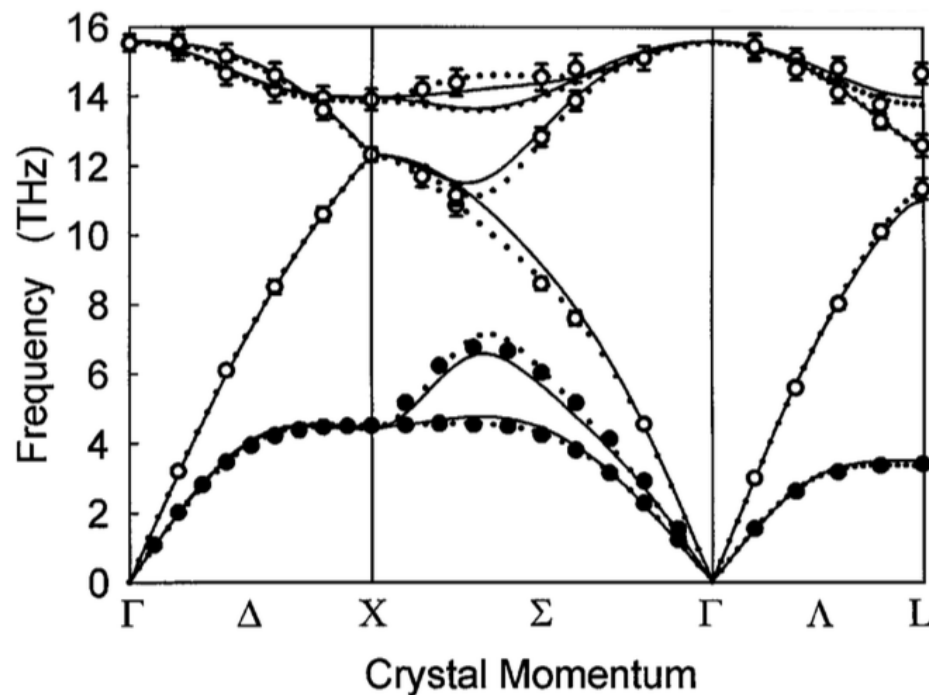
## The three-dimensional pair distribution function analysis of disordered single crystals: basic concepts

Thomas Weber\* and Arkadiy Simonov

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

# Thermal Diffuse Scattering

- ▶ Lattice vibrations produce deviations from the average structure even in perfect crystals
- ▶ X-ray scattering intensity is given by the integral over all the phonon branches at each  $\mathbf{Q}$



$$I_0 \propto f^2 e^{-2M} \sum_{j=1}^6 \frac{|\mathbf{q} \cdot \hat{\mathbf{e}}_j|^2}{\omega_j} \coth\left(\frac{\hbar \omega_j}{2k_B T}\right).$$

M. Holt, *et al*, Phys Rev Lett **83**, 3317 (1999).

## Some Rules of Thumb (*thanks to* Hans Beat Bürgi)

### Reciprocal space

### Direct space

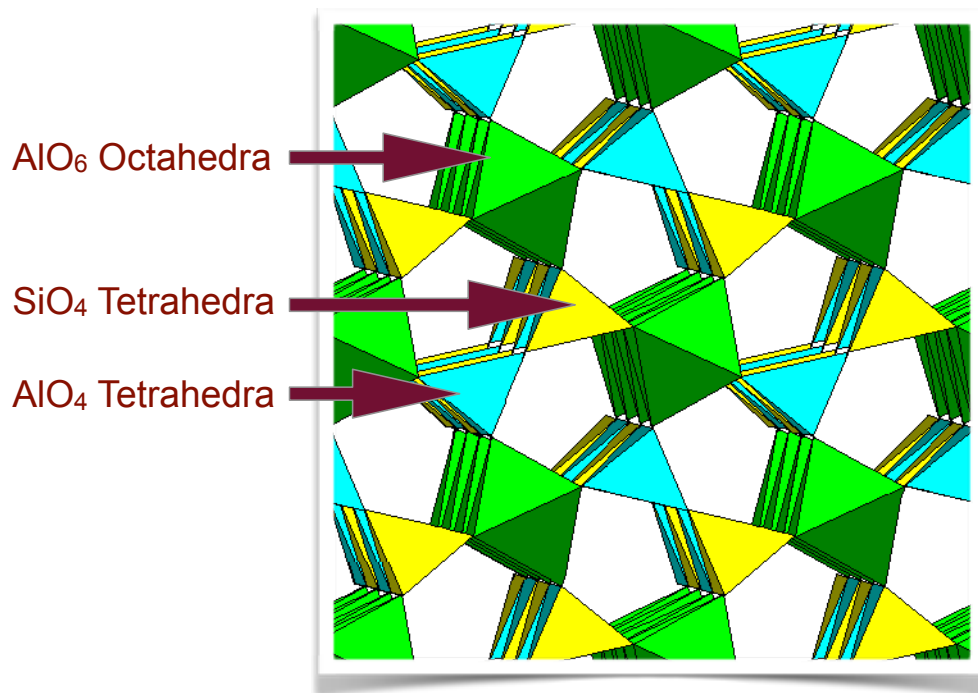
- |                                |   |                         |   |
|--------------------------------|---|-------------------------|---|
| ▶ Only sharp Bragg reflections | ➔ | ▶ 3D-periodic structure | ▶ no defects  |
| ▶ Sharp diffuse rods           | ➔ | ▶ 2D-periodic structure | ▶ perpendicular to the streaks<br>▶ disordered in streak directions |
| ▶ Sharp diffuse planes         | ➔ | ▶ 1D-periodic structure | ▶ perpendicular to the planes<br>▶ disordered within the plane      |
| ▶ Diffuse clouds               | ➔ | ▶ 0D-periodic structure | ▶ no fully ordered direction  |

# Case Study 1: Mullite

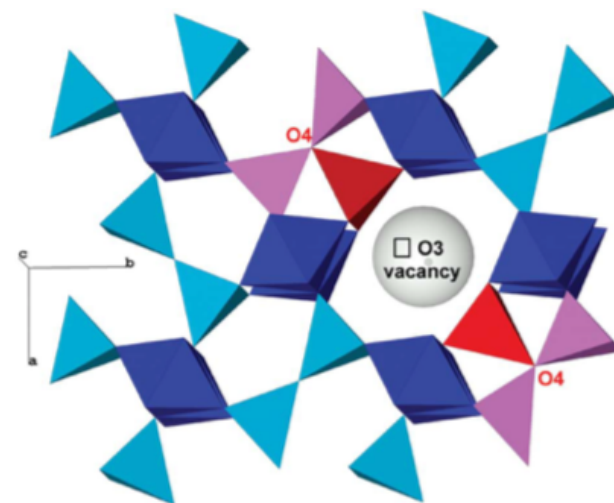


# Mullite - A Case Study

- ▶ Mullite is a ceramic that is formed by adding  $O^{2+}$  vacancies to Sillimanite
  - Sillimanite has alternating  $AlO_4$  and  $SiO_4$  tetrahedra
  - Mullite has excess  $Al^{3+}$  occupying  $Si^{2+}$  sites for charge balance
- ▶ This results in strong vacancy-vacancy correlations



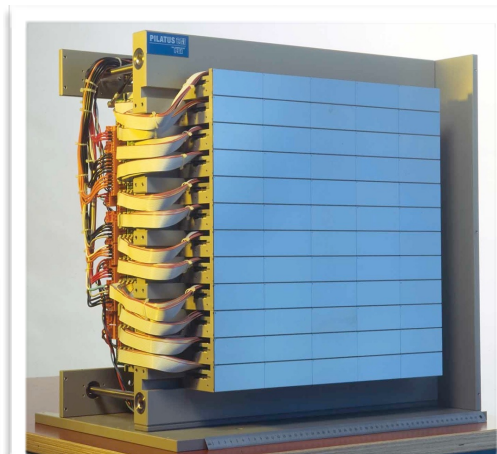
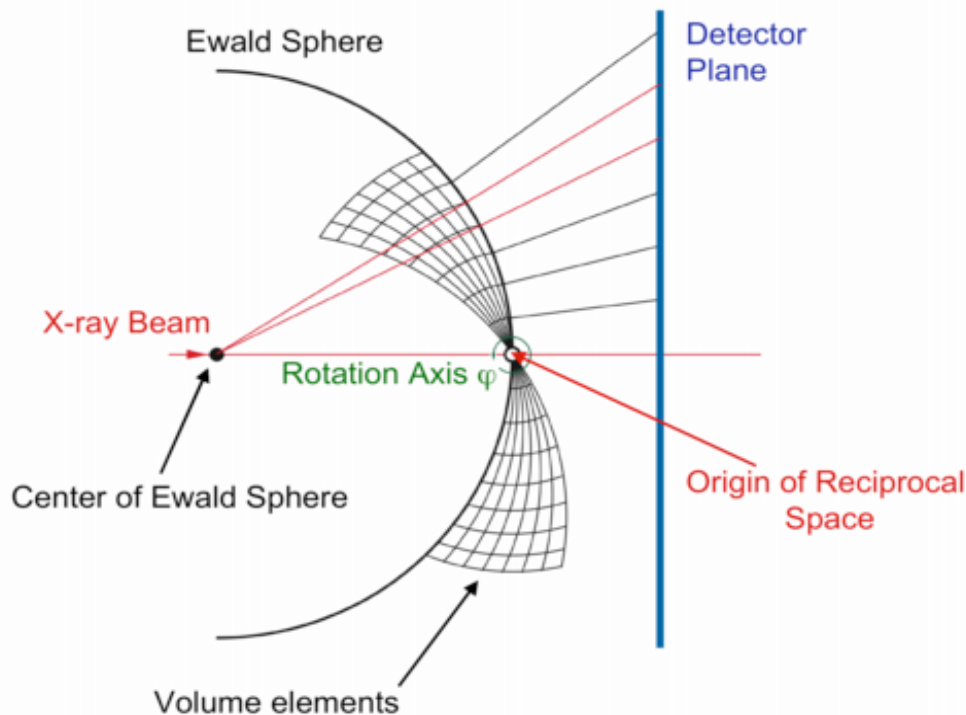
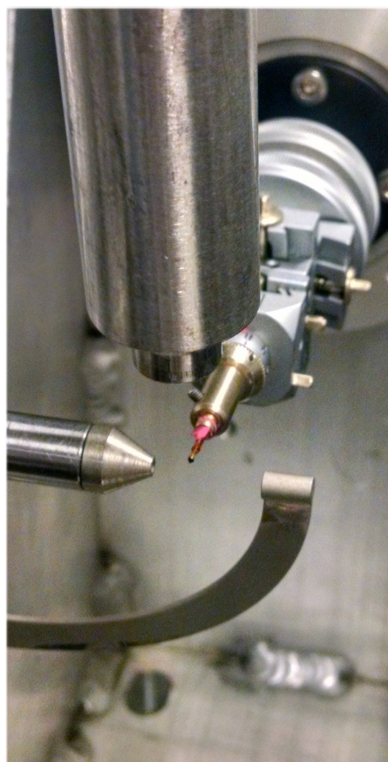
Sillimanite:  $Al_2SiO_5$



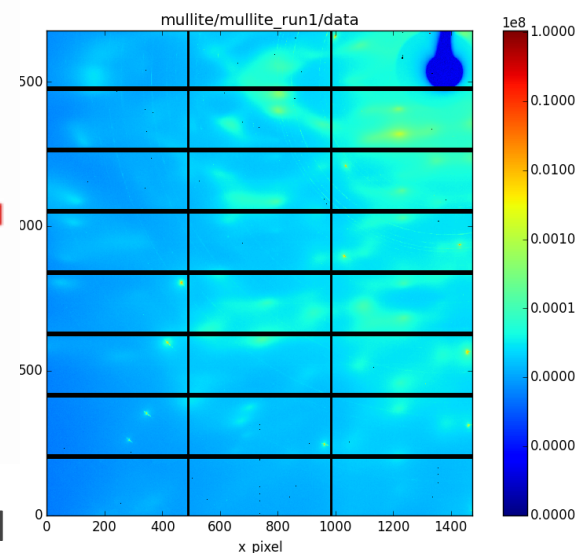
Mullite:  $Al_2(Al_{2+2x}Si_{2-2x})O_{10+x}$

B. D. Butler, T. R. Welberry, & R. L. Withers, Phys Chem Minerals **20**, 323 (1993)

# Measuring X-ray Diffuse Scattering with Continuous Rotation Method

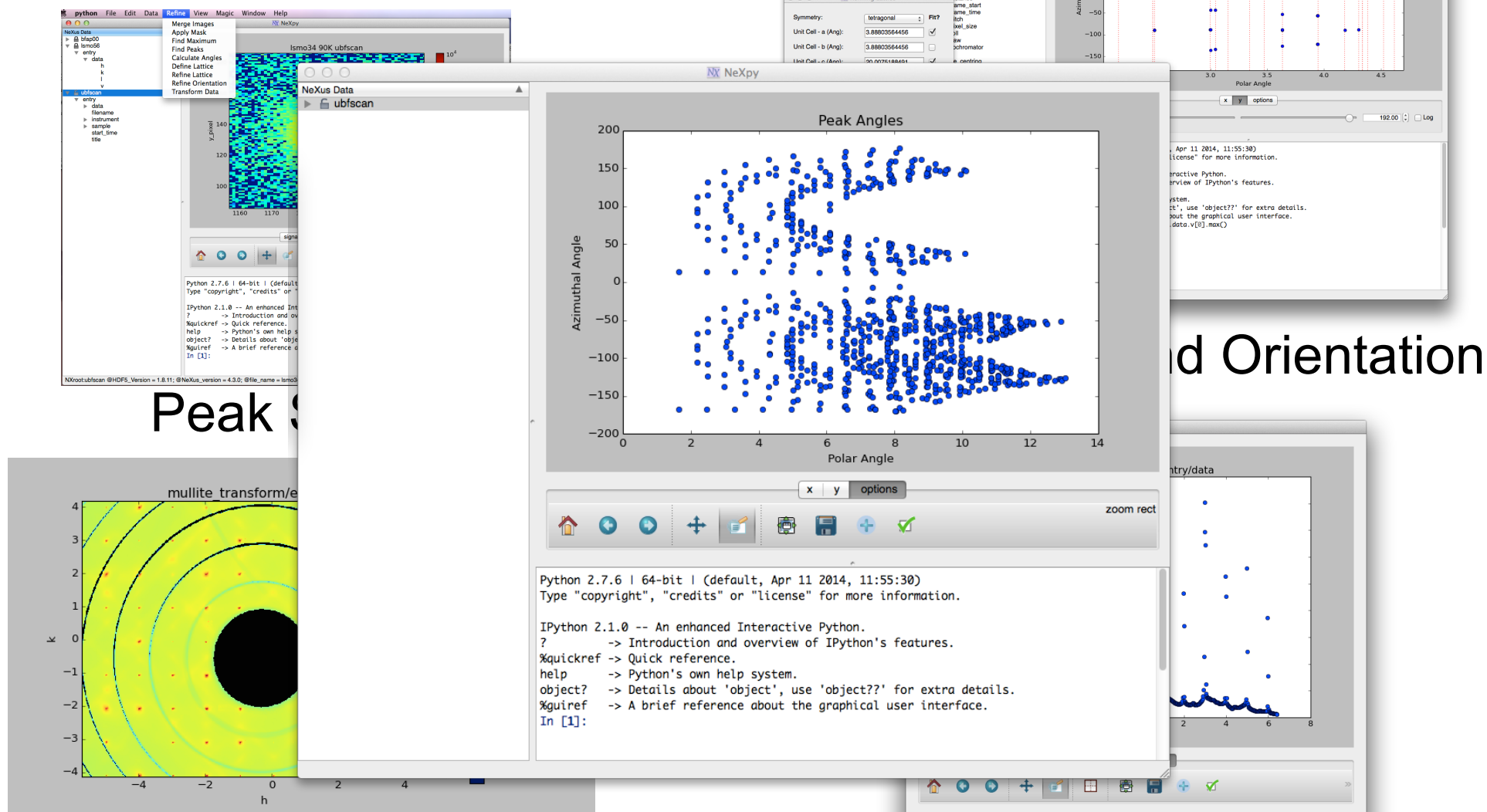


Pilatus 2M Detector



- ▶ The sample is continuously rotated in shutterless mode at  $1^\circ$  per second
- ▶ A fast area detector (e.g., a Pilatus 2M) acquires images at 10 frames per second
  - i.e., 3600 x 8MB frames  $\sim$  30GB every 6 minutes
- ▶ The detector needs low background, high dynamic range, and energy discrimination
  - Ideally, this is performed with high-energy x-rays, e.g., 80 to 100 keV

# Data Reduction Workflows

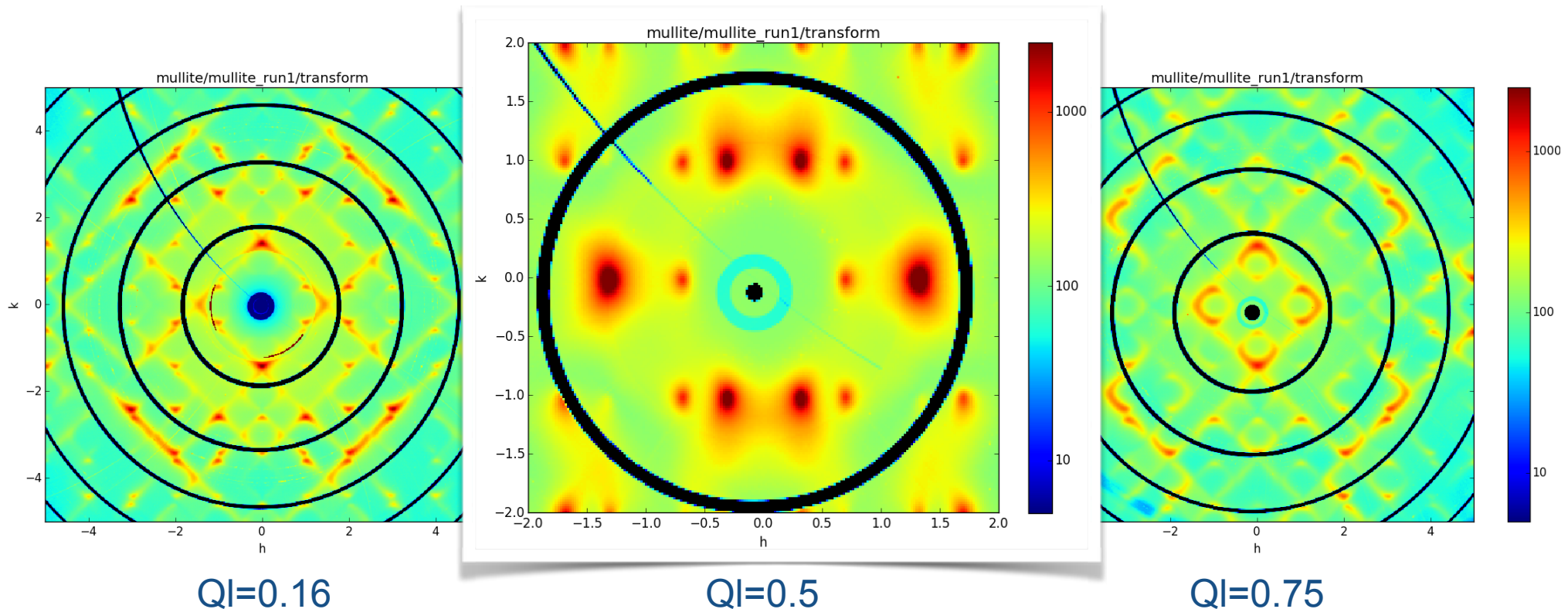


Coordinate Transformation

Data Projections

# 3D Diffuse Scattering in Mullite

- ▶ There is strong diffuse scattering throughout reciprocal space
- ▶ The shape of the diffuse scattering is strongly dependent on the value of  $QI$
- ▶ There are incipient superlattice peaks at  $\mathbf{Q} = 0.5 \mathbf{c}^* + 0.31 \mathbf{a}^*$



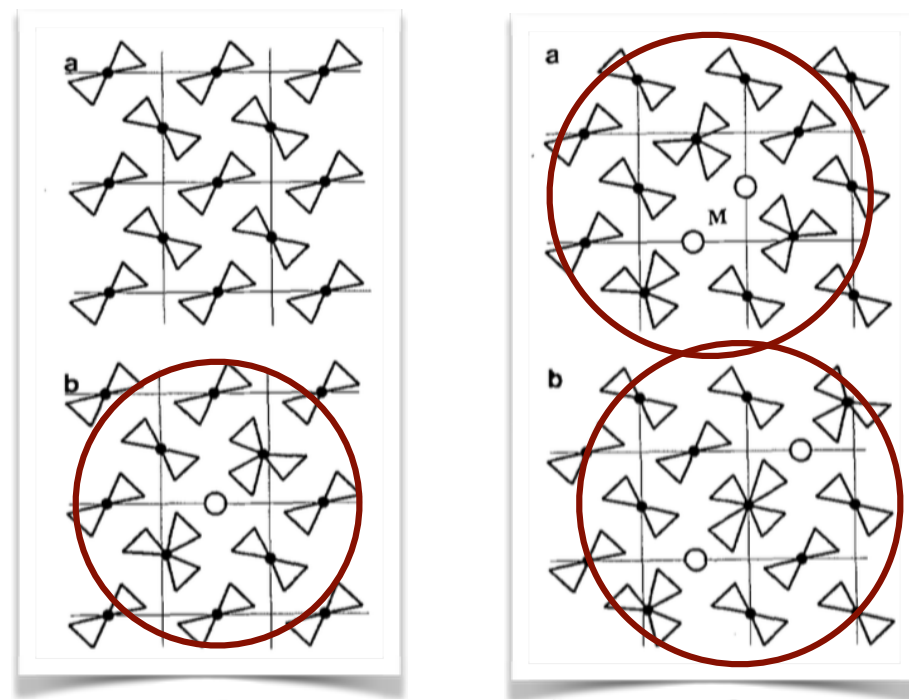
# Monte Carlo Analysis

- ▶ In a classic analysis, Richard Welberry and colleagues developed a set of interaction energies to model mullite disorder
- ▶ Interaction energies were initialized:
  - ▶ insights from chemical intuition
  - ▶ insights from the measured diffuse scattering
- ▶ The diffuse scattering was calculated using a Monte Carlo algorithm to generate vacancy distributions first in 2D slices and then in 3D

$$P_i = \frac{e^{-V_i}}{1 + e^{-V_i}},$$

where,

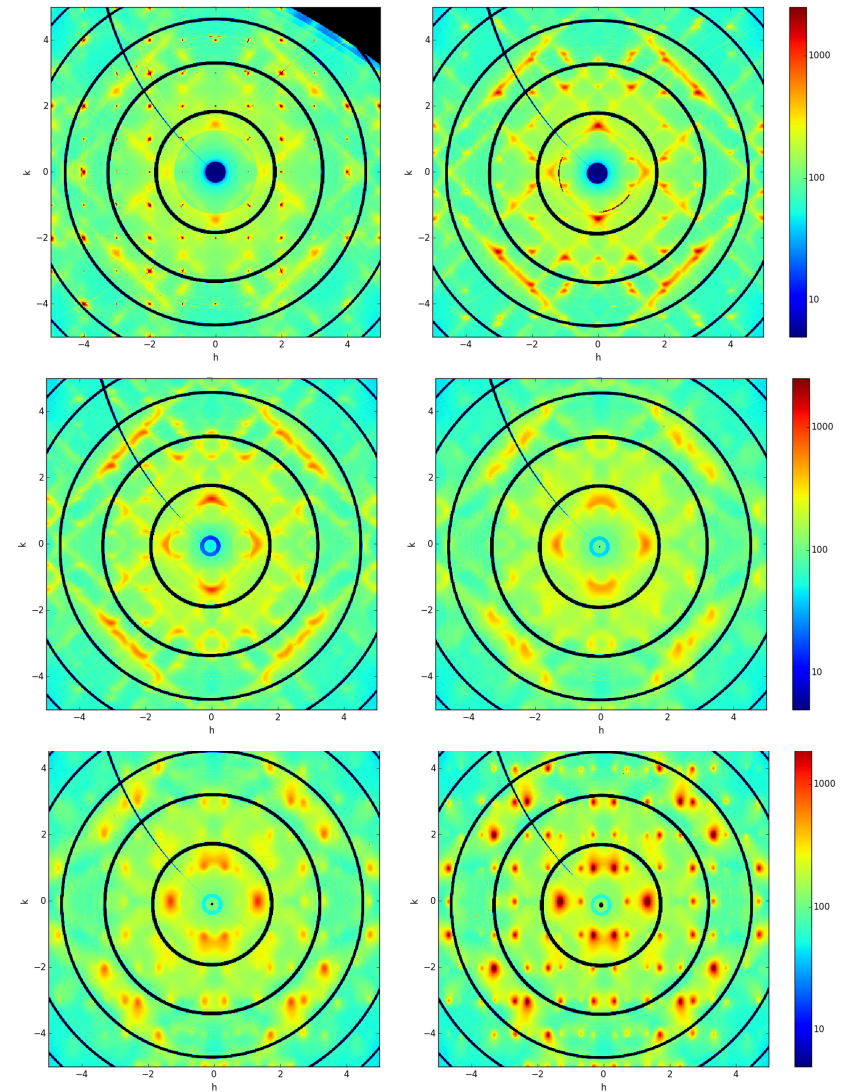
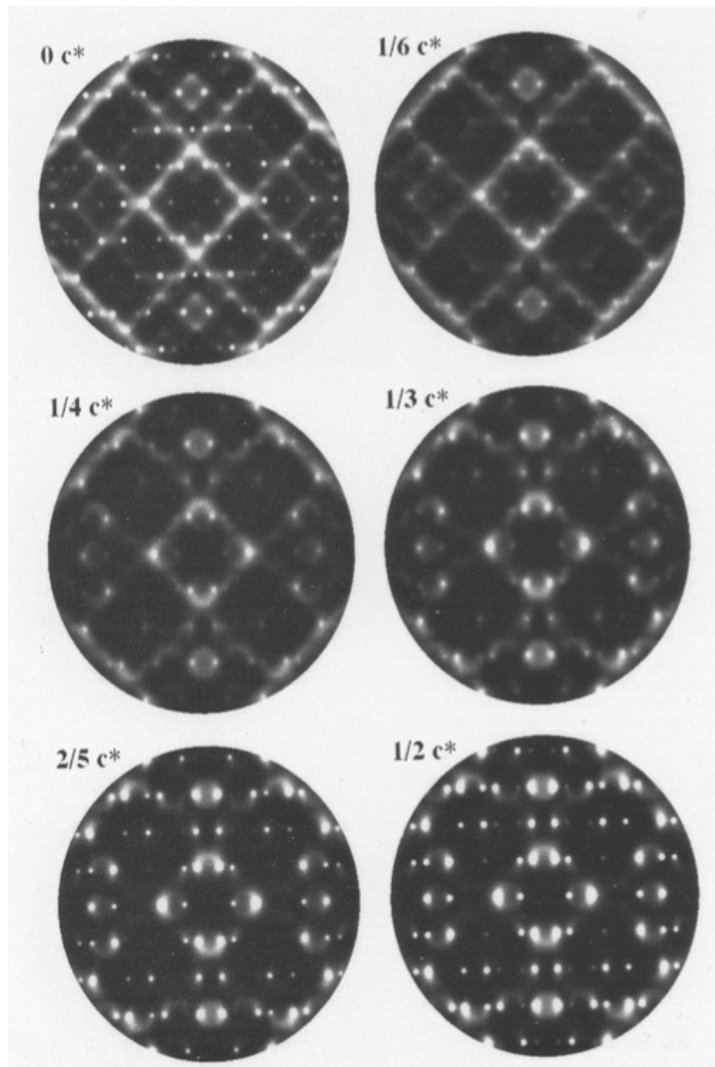
$$V_i = \frac{\sum_j E_{ij}}{kT} + \frac{(N_v - N_v^o)^2}{N_v^o} \text{sgn}(N_v - N_v^o).$$



Interatomic vector	$\alpha_{lmn}$	Interatomic vector	$\alpha_{lmn}$
$\frac{1}{2}\langle 1\ 1\ 0 \rangle$	-0.24	$\langle 0\ 2\ 0 \rangle$	+0.13
$[1\ 1\ 0]$	-0.23	$\frac{1}{2}\langle 3\ 1\ 0 \rangle$	+0.22
$[1\ -1\ 0]$	-0.05	$\frac{1}{2}\langle 1\ 3\ 0 \rangle$	-0.01
$\langle 1\ 0\ 0 \rangle$	-0.06	$\langle 1\ 0\ 1 \rangle$	+0.07
$\langle 0\ 1\ 0 \rangle$	+0.22	$\langle 0\ 1\ 1 \rangle$	-0.12
$\langle 0\ 0\ 1 \rangle$	-0.03	$\frac{1}{2}\langle 3\ 3\ 0 \rangle$	+0.17
$\frac{1}{2}[1\ -1\ 2]$	+0.12	$\langle 1\ 1\ 1 \rangle$	-0.01
$\frac{1}{2}[1\ 1\ 2]$	+0.12	$\frac{1}{2}\langle 3\ 1\ 2 \rangle$	-0.11
$\langle 2\ 0\ 0 \rangle$	-0.12	$\frac{1}{2}\langle 3\ 3\ 2 \rangle$	-0.07

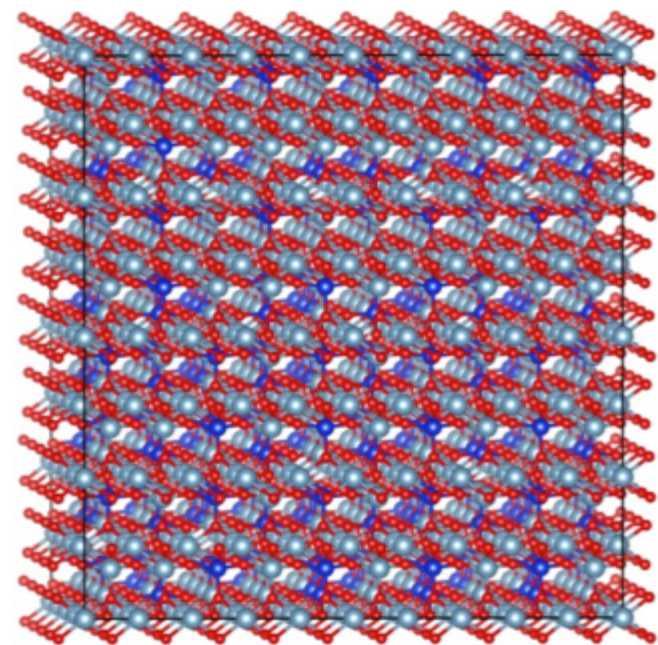
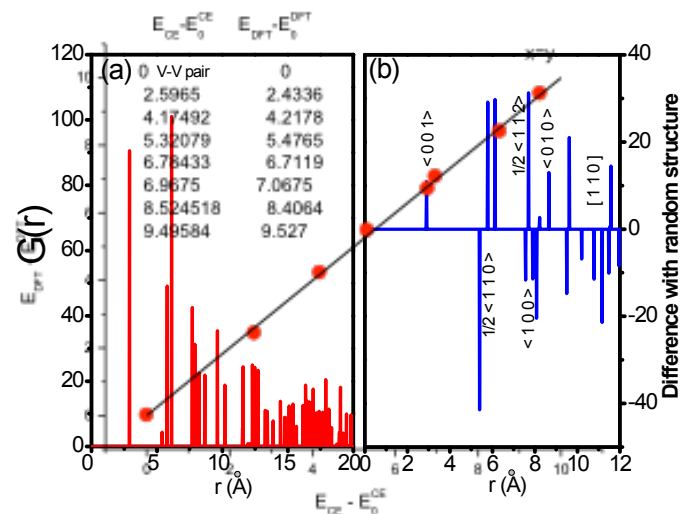
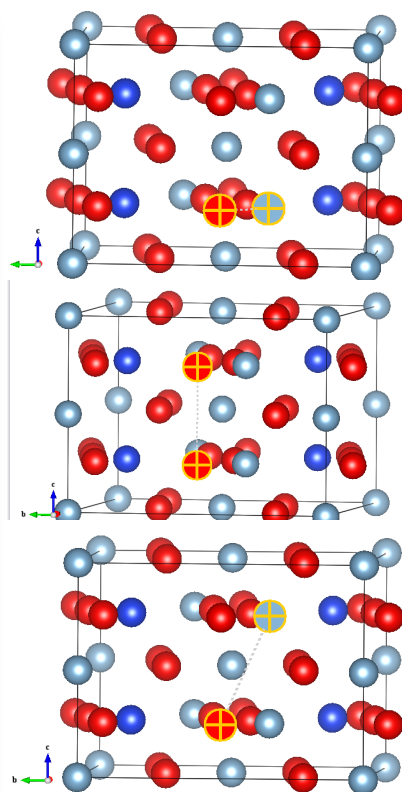
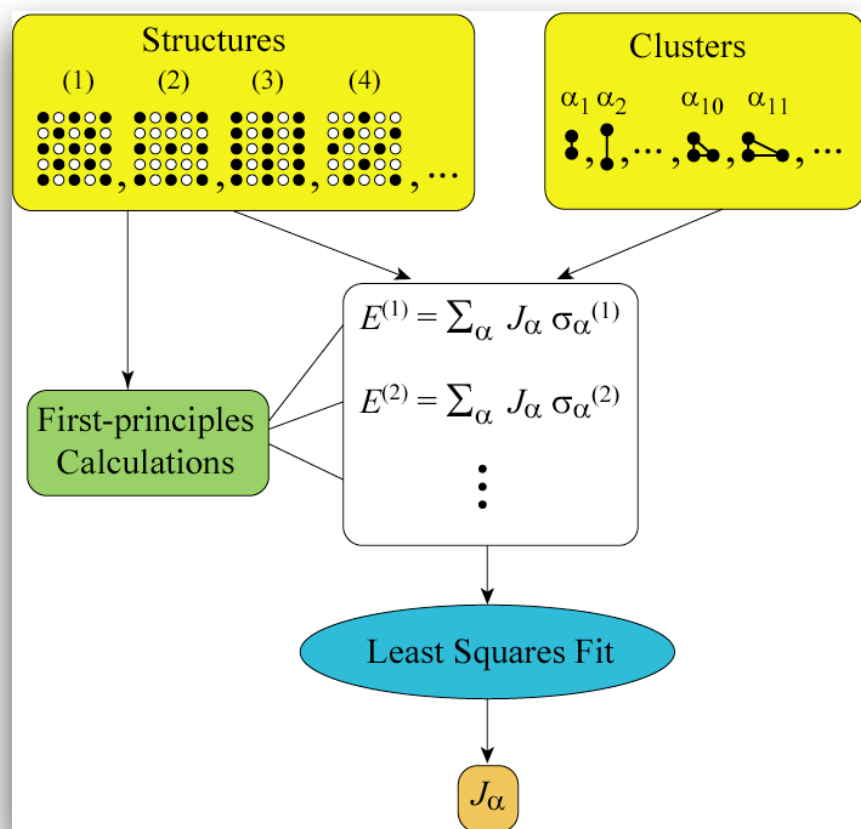
B. D. Butler, T. R. Welberry, & R. L. Withers, Phys Chem Minerals **20**, 323 (1993)

# Monte Carlo Analysis Results



# Vacancy Short-Range Order in Mullite

## A First-Principles Approach



$$E(\sigma) = J_0 + \sum_i \sigma_i J_i + \sum_{i,j} J_{ij} \sigma_i \sigma_j + \sum_{i,j,k} J_{ijk} \sigma_i \sigma_j \sigma_k + \dots$$

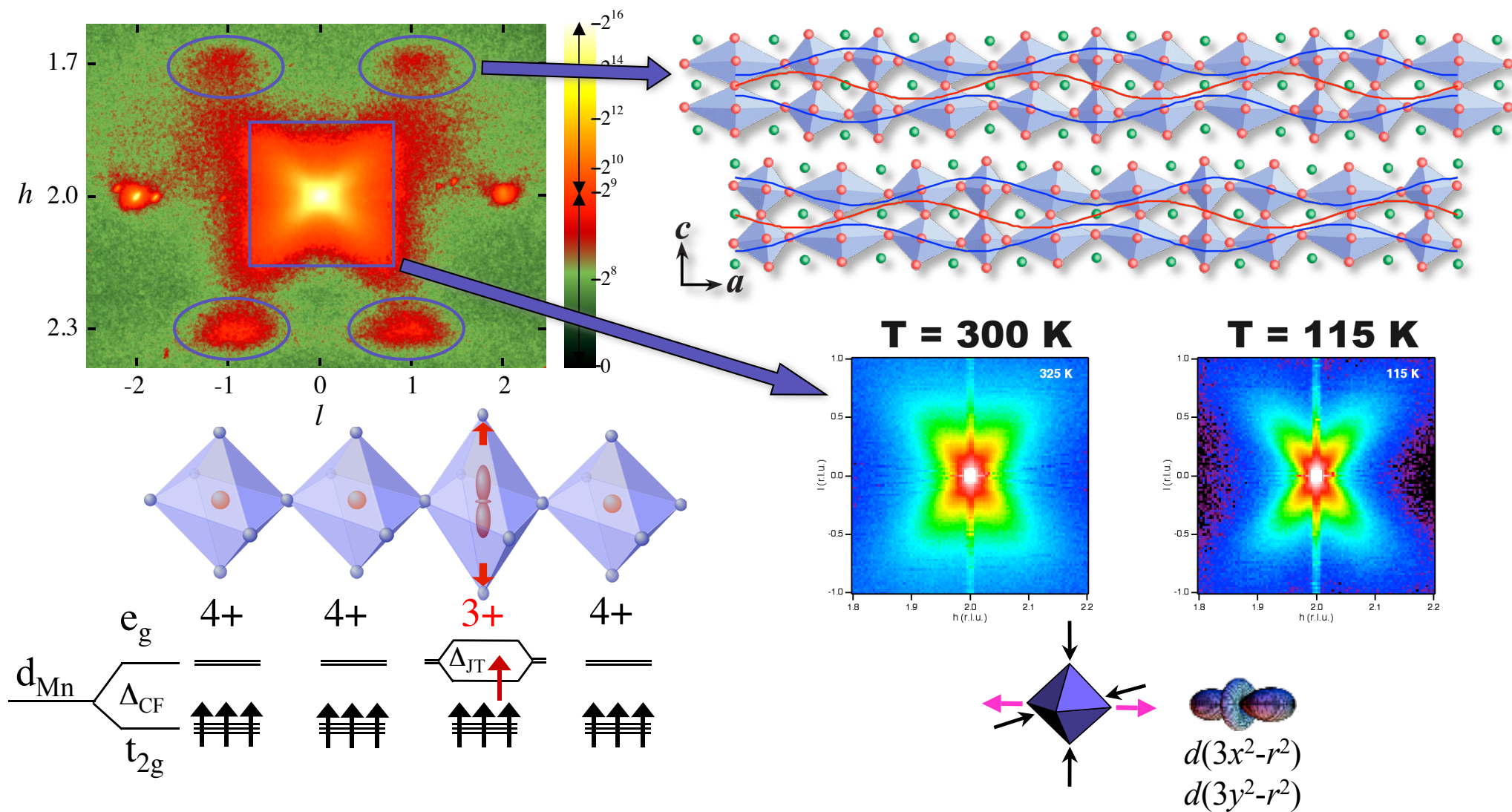
Peter Zapol & Anh Ngo

Lowest Energy 3:2 Mullite Structure  
from Kinetic Monte Carlo Calculation

# Case Study 1: Bilayer Manganites



# Diffuse Scattering from Jahn-Teller Polarons



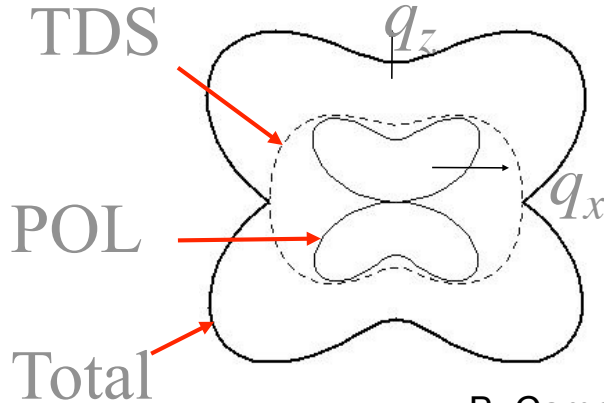
# Huang Scattering

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

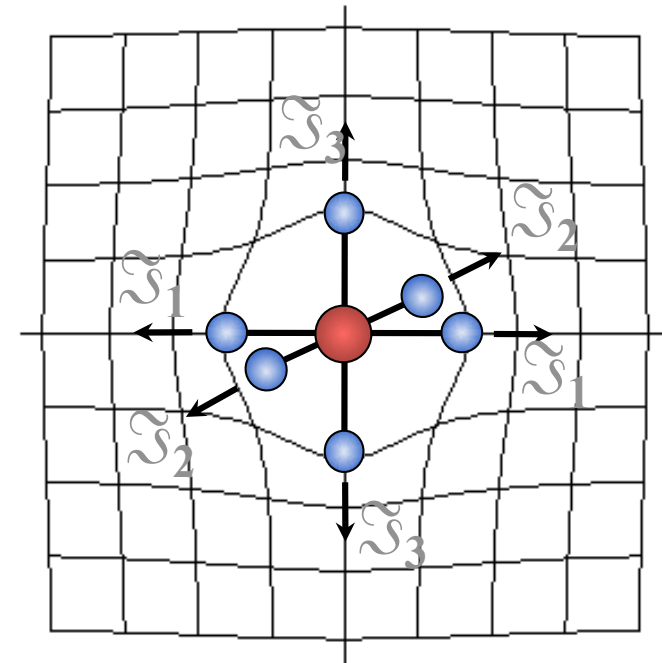
$$I_{POL}(\mathbf{Q}) = N |F_G|^2 \sum_{\alpha,\beta,\gamma,\delta} Q_\beta Q_\delta \left( \sum_{j,j'} \frac{\epsilon_{\alpha,\mathbf{q},j} \epsilon_{\beta,\mathbf{q},j}^* \epsilon_{\gamma,\mathbf{q},j'}^* \epsilon_{\delta,\mathbf{q},j'}}{\omega_{\mathbf{q},j}^2 \omega_{\mathbf{q},j'}^2} \right) \sum_{m,n} \mathfrak{S}_{m,\alpha} \mathfrak{S}_{n,\gamma} e^{i\mathbf{q} \cdot (\mathbf{R}_m - \mathbf{R}_n)}$$

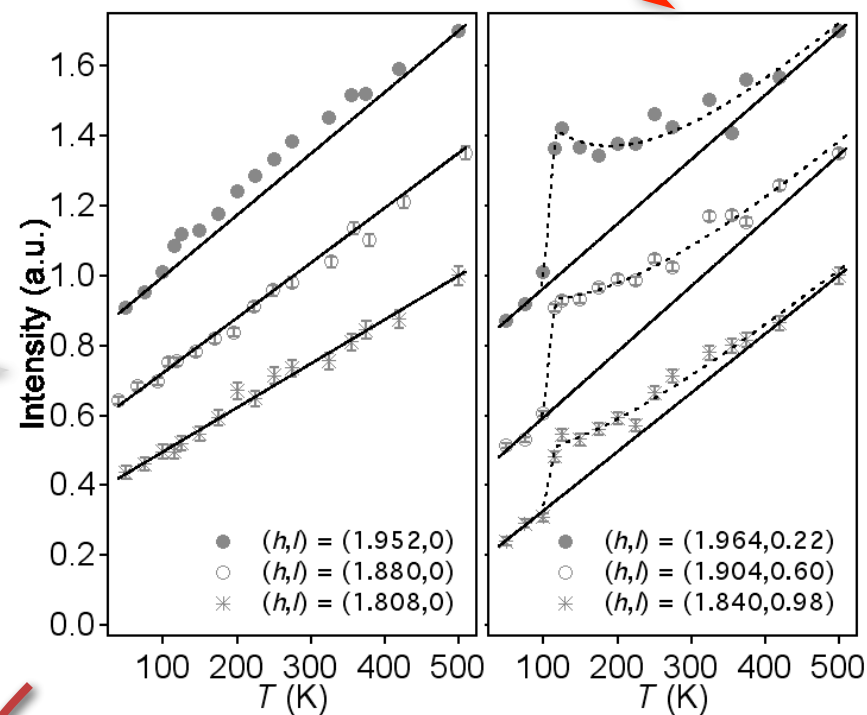
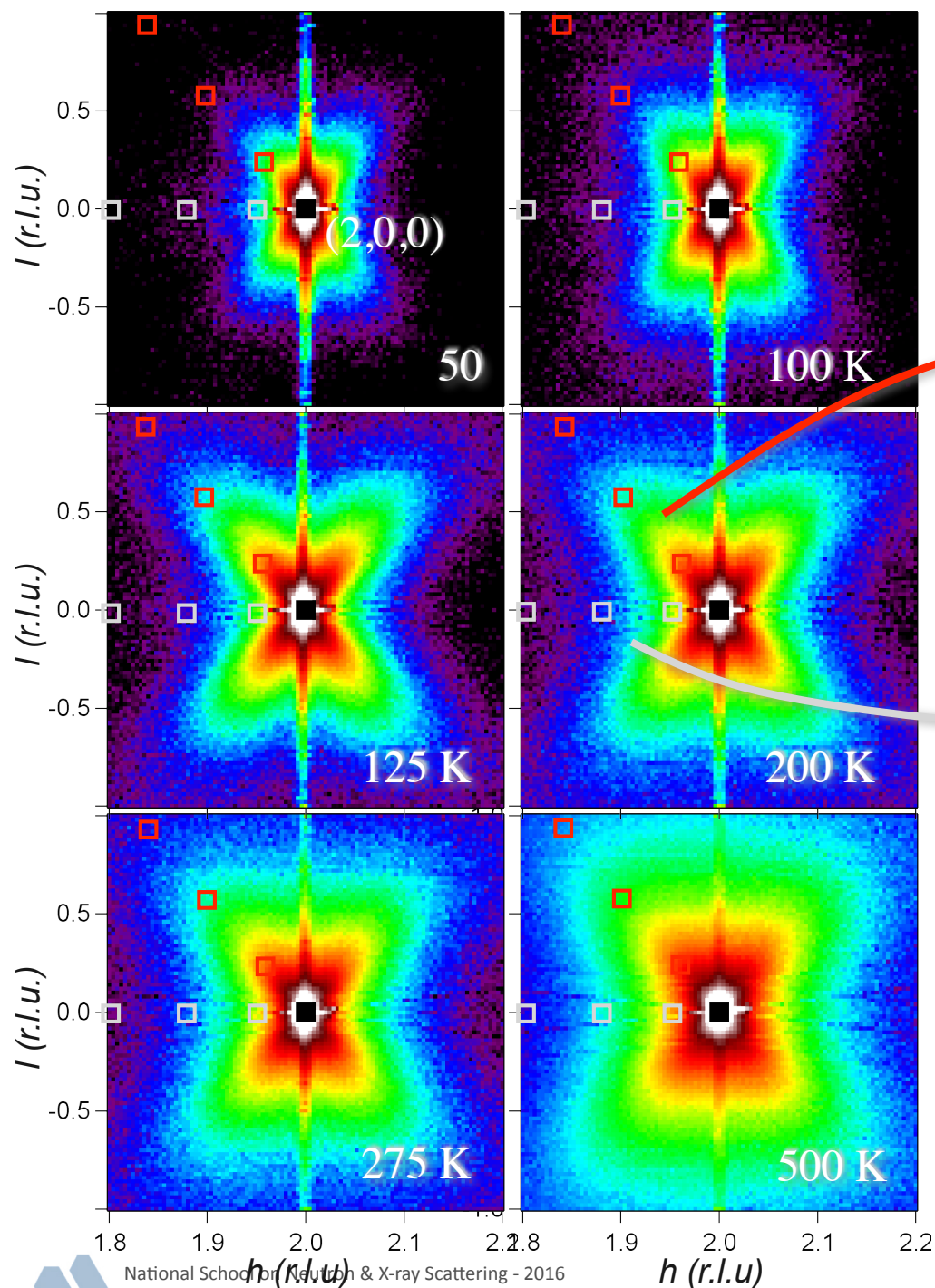
$$I_{TDS}(\mathbf{Q}) = N |F_G|^2 \left( \frac{kT}{2M} \right) \sum_{\beta,\delta} Q_\beta Q_\delta \left( \sum_j \frac{\epsilon_{\beta,\mathbf{q},j}^* \epsilon_{\delta,\mathbf{q},j}}{\omega_{\mathbf{q},j}^2} \right) \sum_n \mathfrak{S}_{n,\beta} e^{i\mathbf{q} \cdot (\mathbf{R}_m - \mathbf{R}_n)}$$

$$u_{m,\delta} = \int \frac{d^3 q}{(2\pi)^3} \sum_{\beta} \left( \sum_j \frac{\epsilon_{\beta,\mathbf{q},j}^* \epsilon_{\delta,\mathbf{q},j}}{\omega_{\mathbf{q},j}^2} \right) \sum_n \mathfrak{S}_{n,\beta} e^{i\mathbf{q} \cdot (\mathbf{R}_m - \mathbf{R}_n)}$$



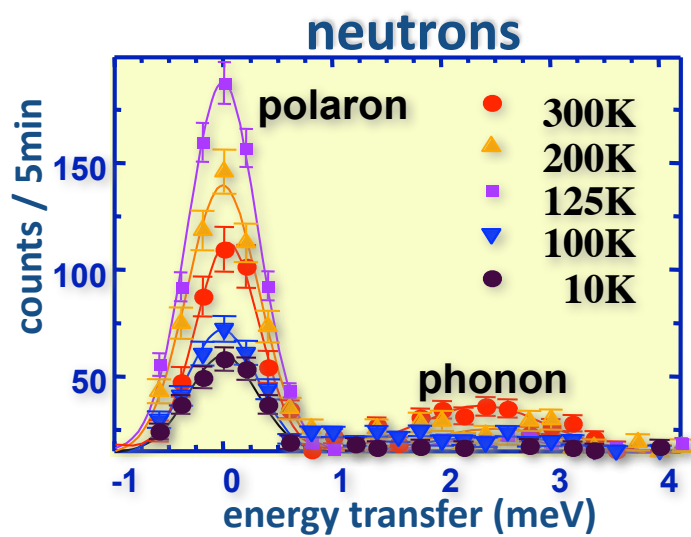
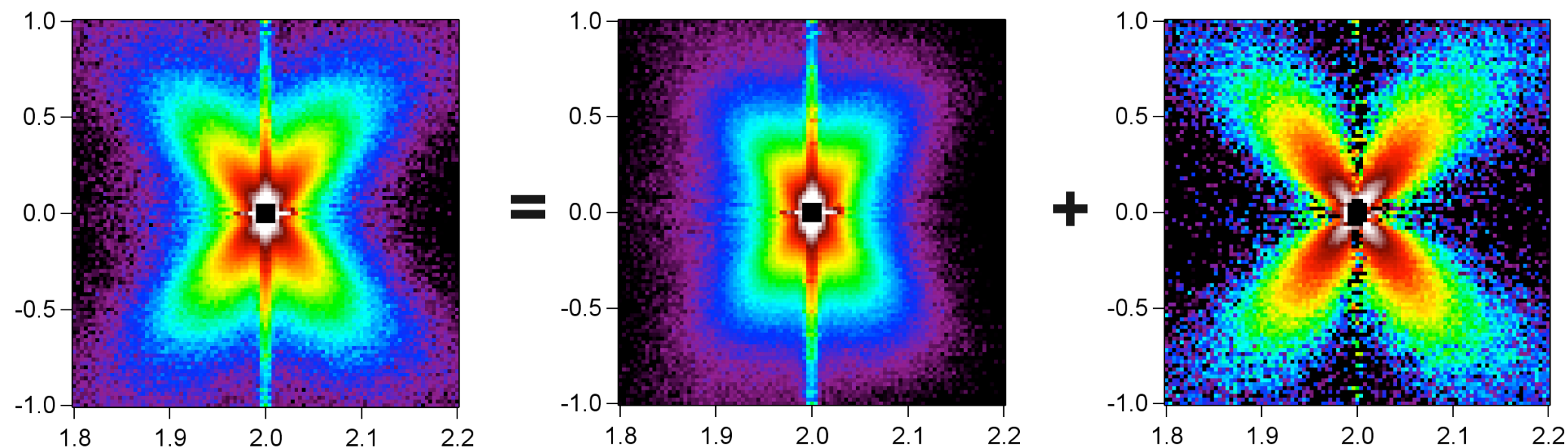
B. Campbell et al Phys. Rev. B. **67**, 020409 (2003)





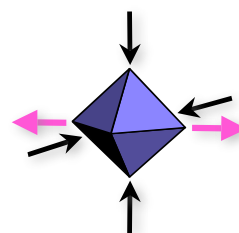
this allows us to subtract  
background from thermal  
diffuse scattering!

# TDS + Huang scattering



*TDS*

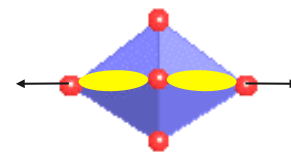
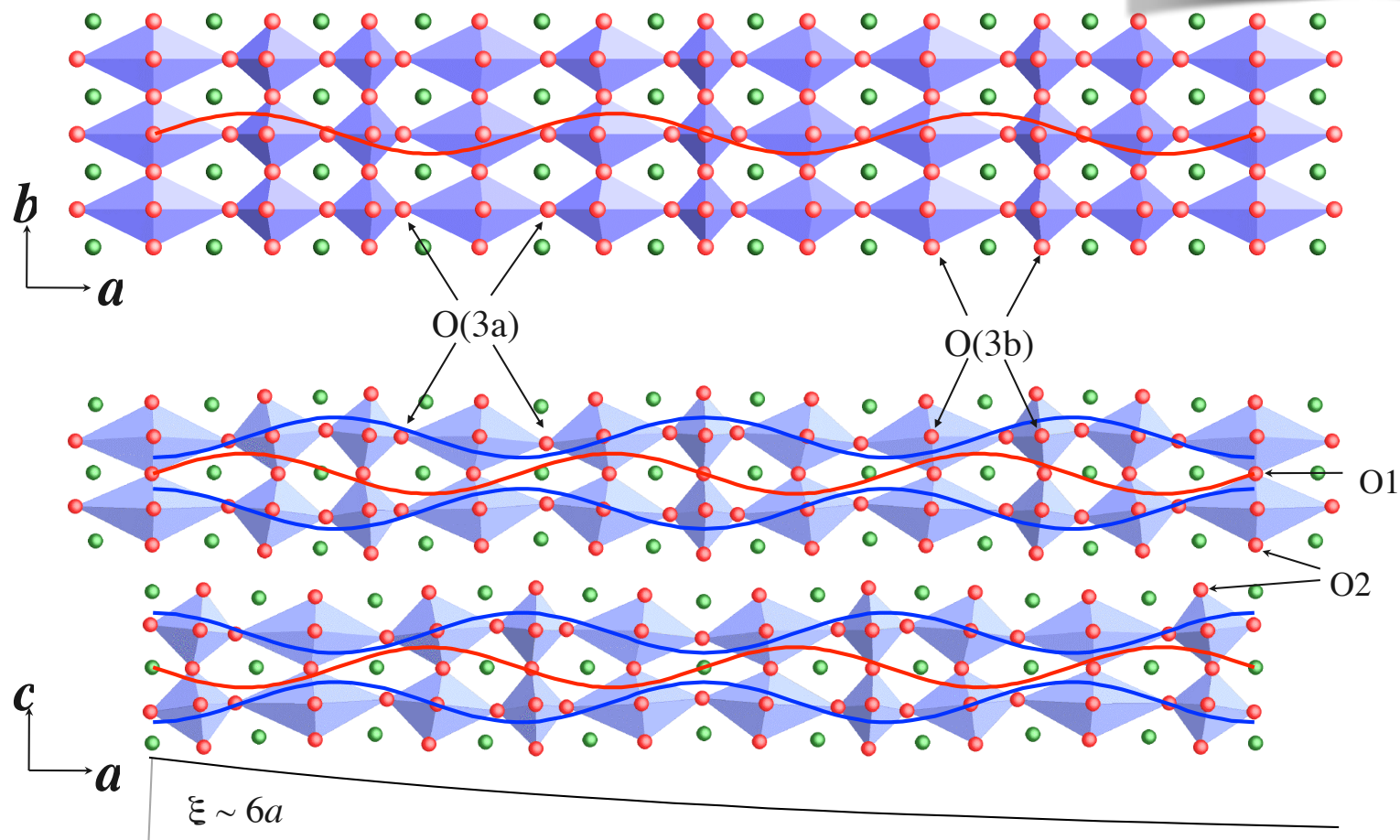
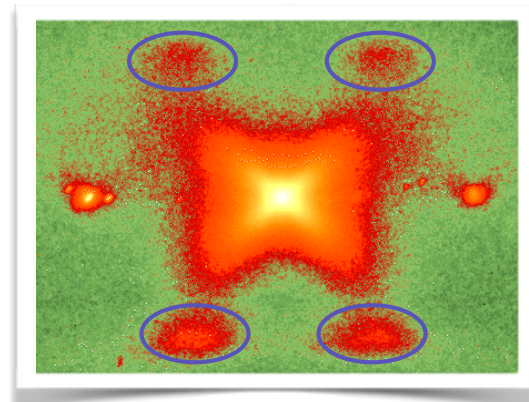
*polaron*



$$d(3x^2 - r^2)$$

$$d(3y^2 - r^2)$$

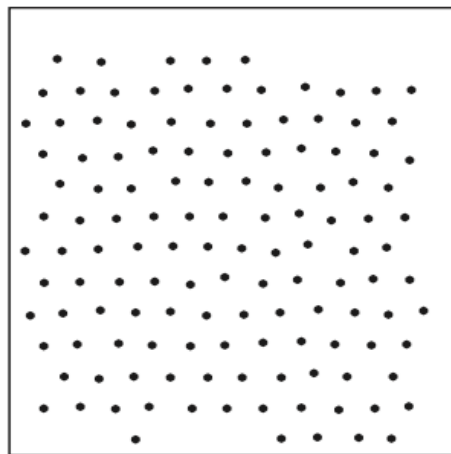
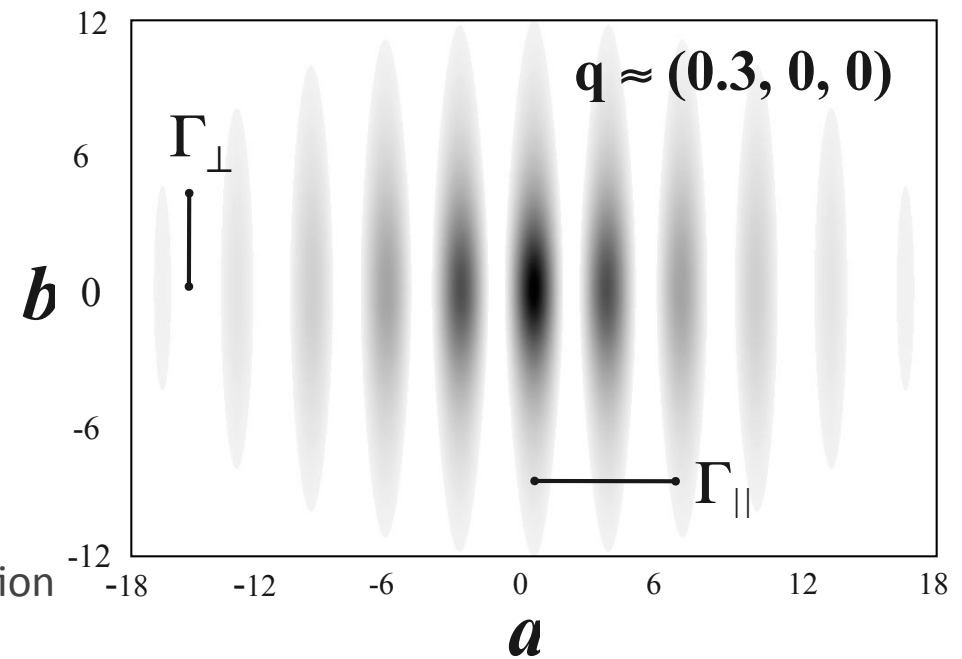
# Cooperative Jahn-Teller Distortions



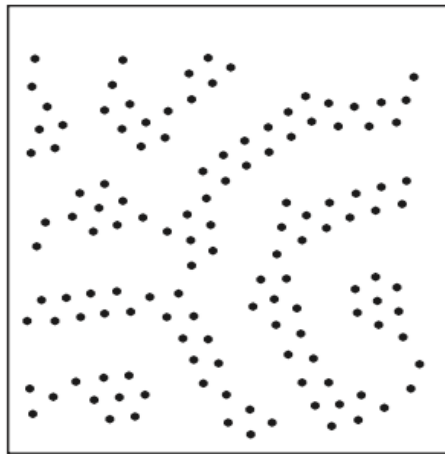
B. J. Campbell, R. Osborn, D. N. Argyriou, L. Vasiliu-Doloc, J. F. Mitchell, S. K. Sinha, U. Ruett, C. D. Ling, Z. Islam, and J. W. Lynn, *Physical Review B* **65**, 014427 (2001)

# Origins of Stripe Formation

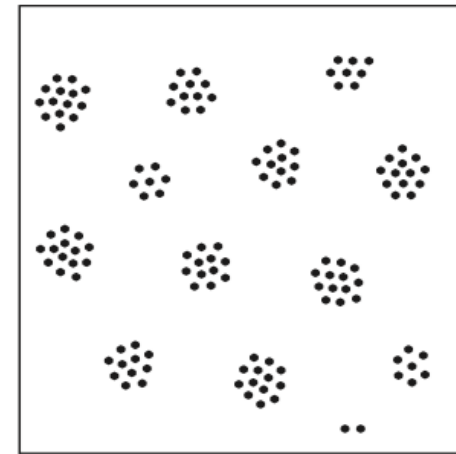
- ▶ Stripe formation is a very common motif of disordered systems
- ▶ It is the response of a system with interactions that compete on different length scales
  - *e.g.*, long-range repulsion vs short-range attraction



a  
Wigner Lattice



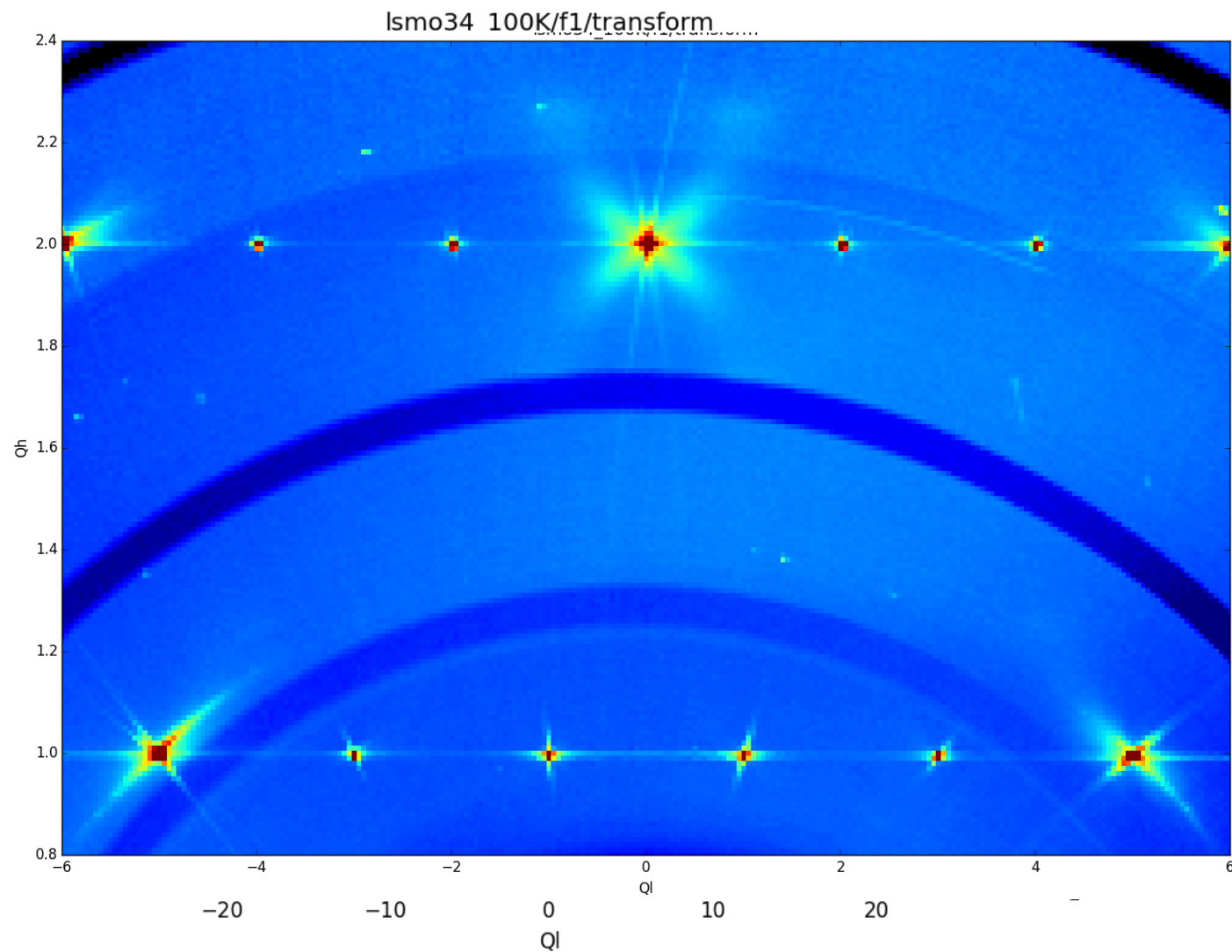
b  
Stripes



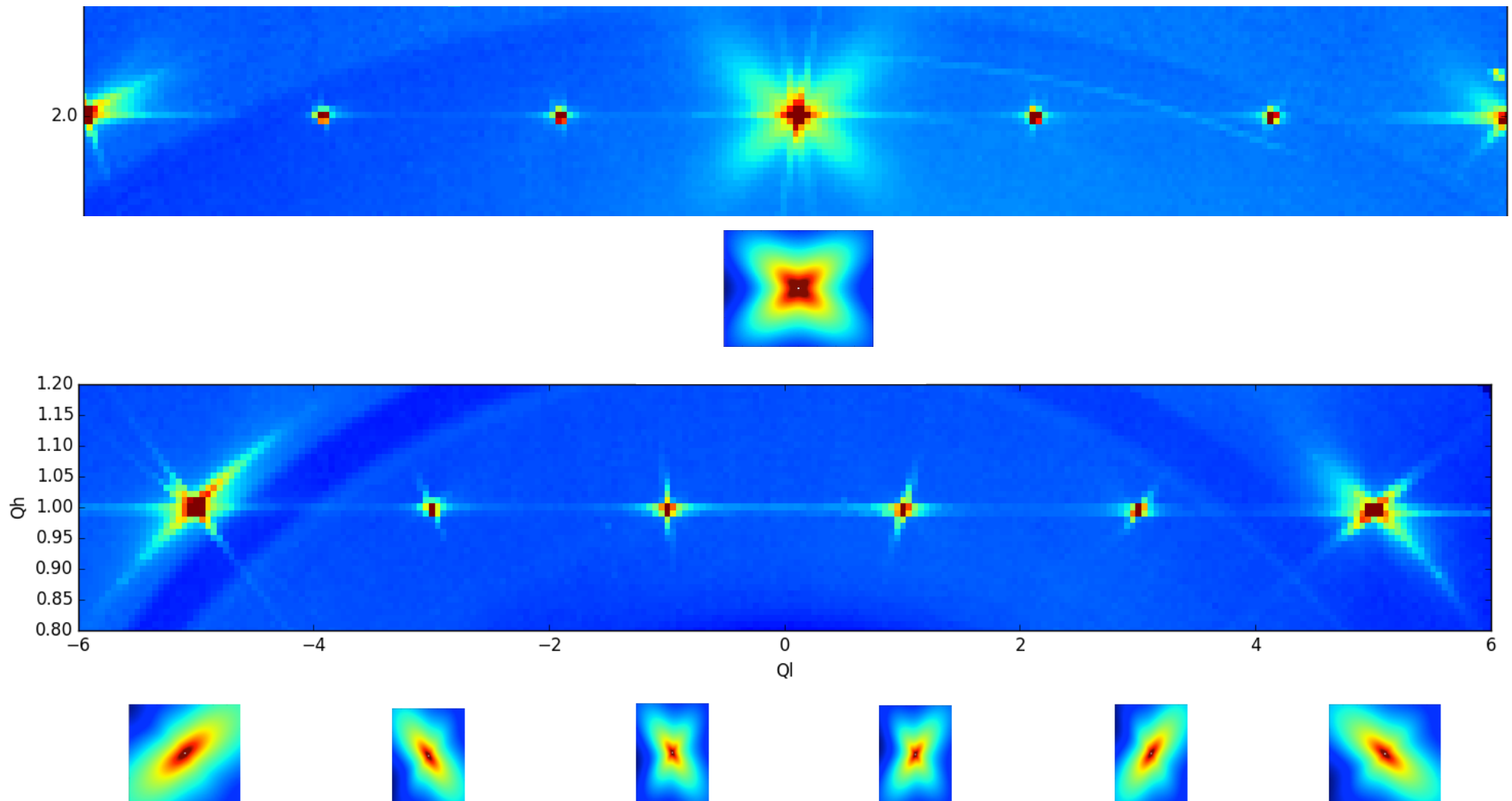
c  
Phase Separation

C. Reichhardt, C. J. Olsen, I. Martin & A. Bishop, EPL **61**, 221–227 (2003).

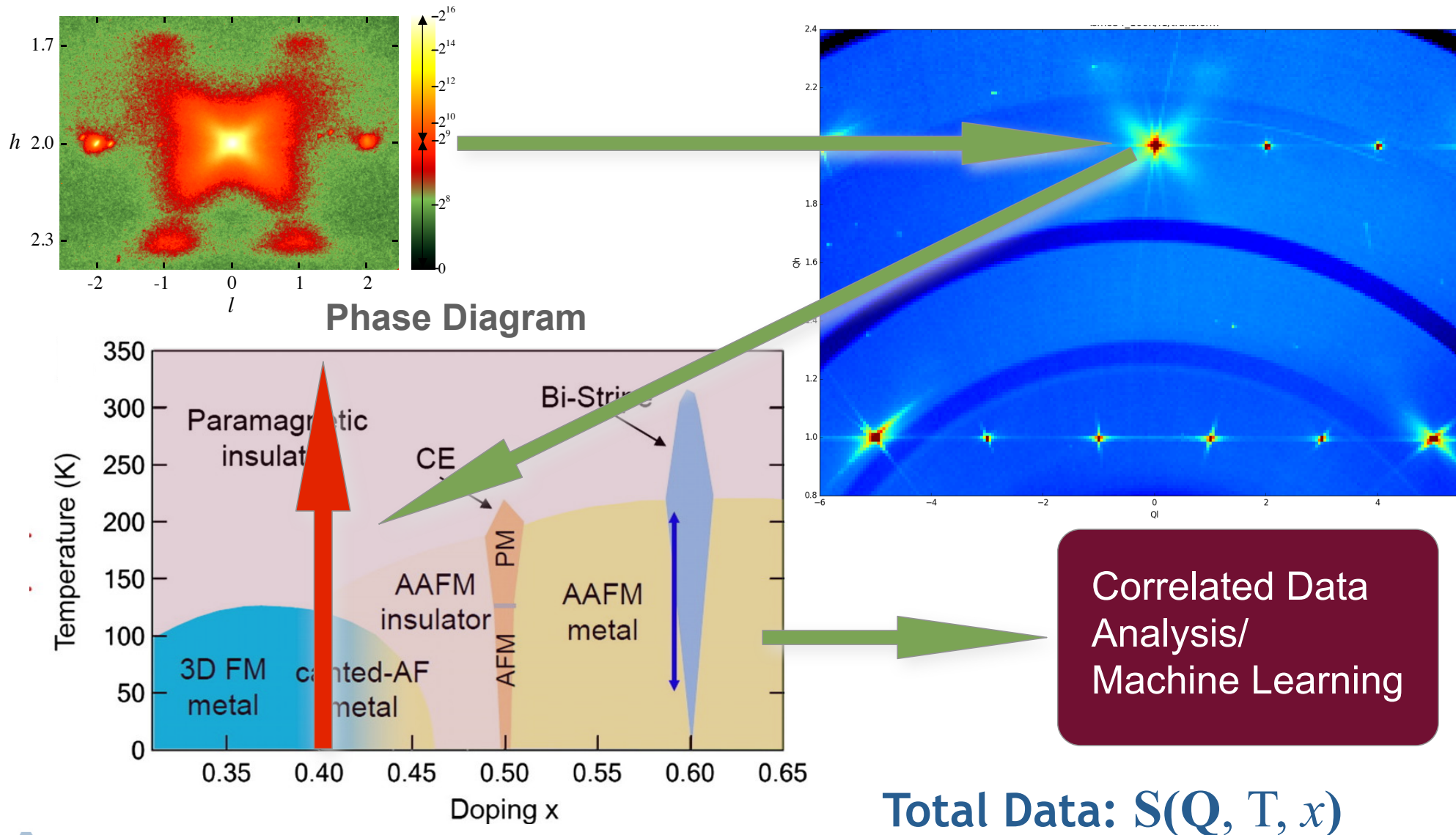
# Bilayer Manganites Revisited



# Huang Scattering as a Function of ( $Q_h$ , $Q_k$ , $Q_l$ )



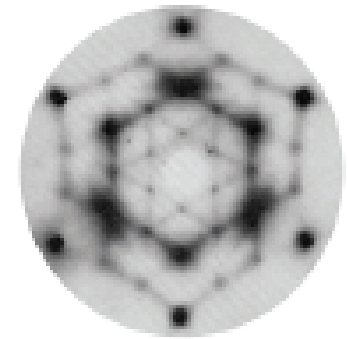
# Expanding the Concept of a Data Set



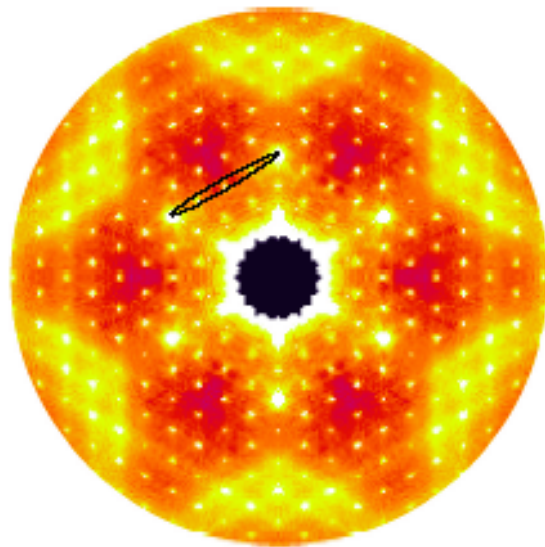
# How do I look at static disorder?



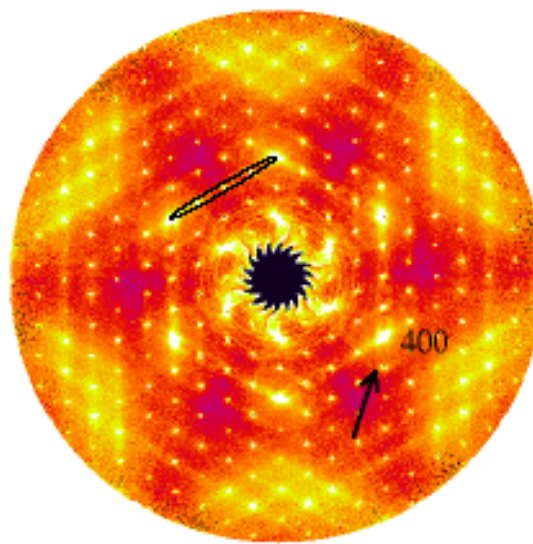
# Importance of Elastic Discrimination



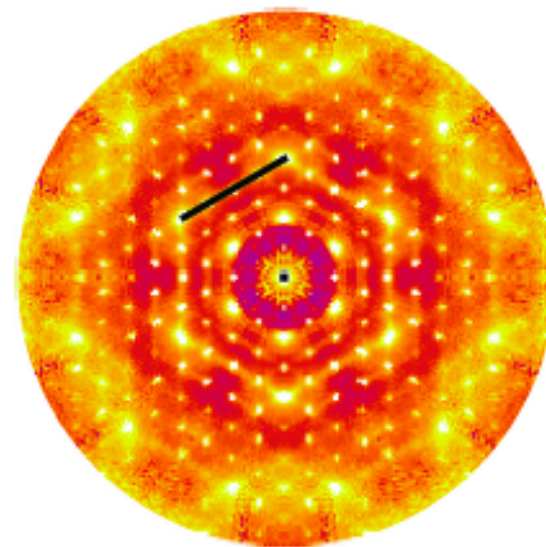
BENZIL



Detector 1  
 $2\theta \sim 142.5^\circ$



Detector 2  
 $2\theta \sim 90.0^\circ$



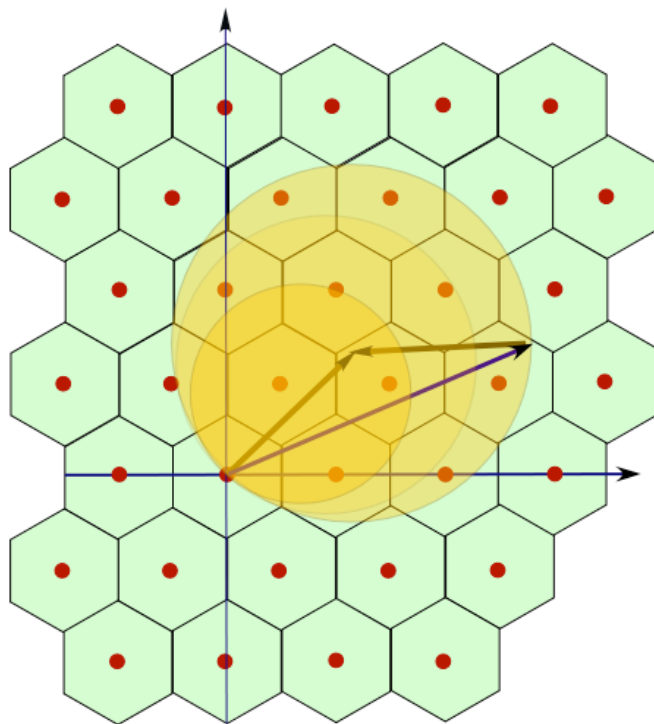
Detector 3  
 $2\theta \sim 37.5^\circ$

T. R. Welberry *et al* J. Appl. Cryst. **36**, 1400 (2003)

# Measuring Large Volumes of Reciprocal Space

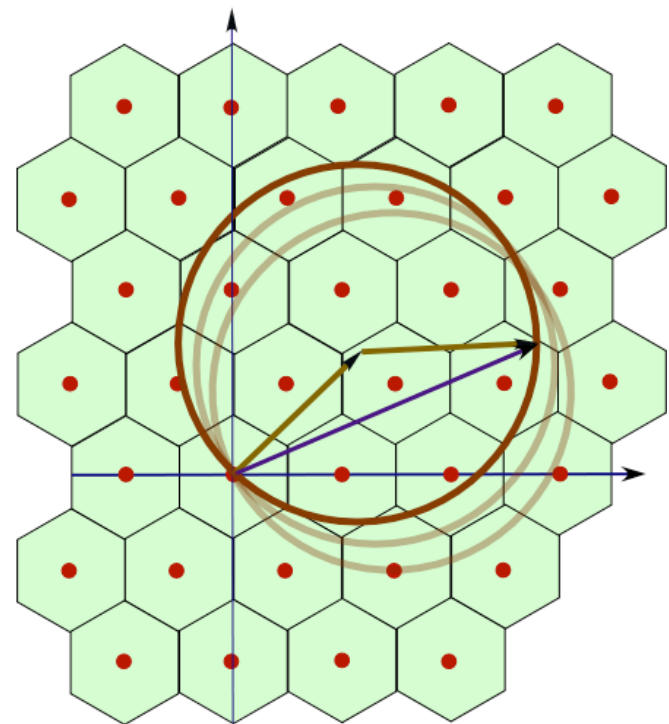
Conventional Time-of-Flight Neutron Methods

**White Beam:**  
*efficient*



**NO energy  
discrimination**

**Fixed  $k_i$ :**  
*energy resolved*



**NOT  
efficient**

# Cross Correlation Chopper

## TOF Laue Diffractometer

- highly efficient data collection
- wide dynamic range in Q

## Statistical Chopper

- elastic energy discrimination
- optimum use of white beam

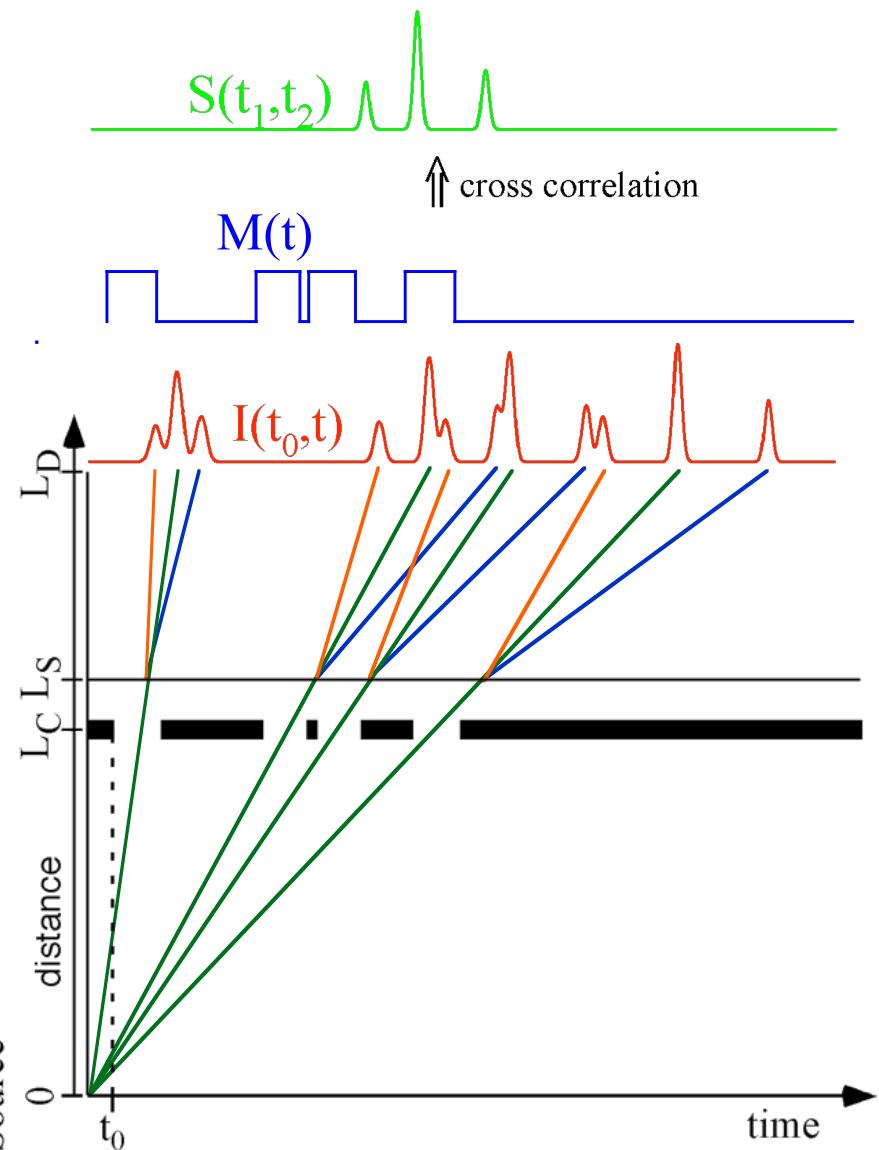
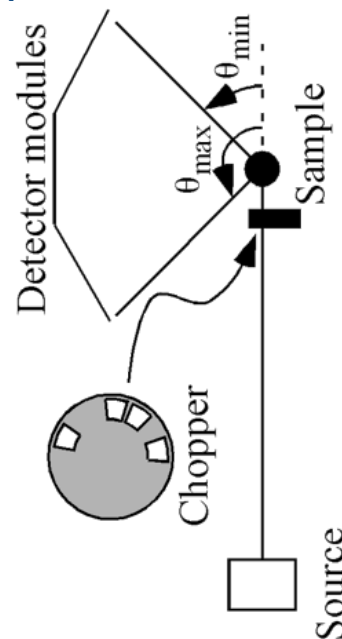
Sample with :  
elastic scattering

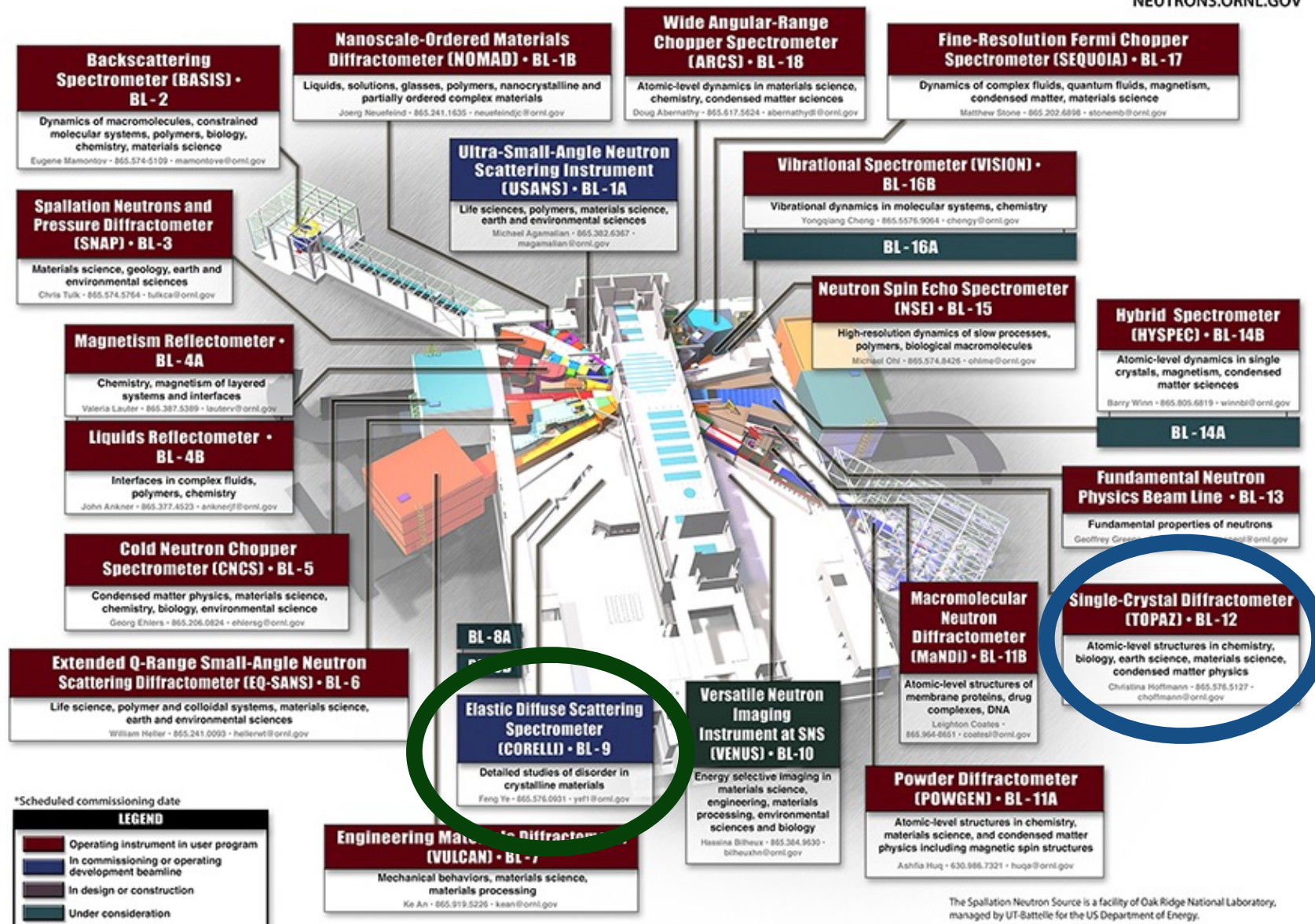
$$\hbar\omega = 0$$

inelastic excitations

$$\hbar\omega = +E_0$$

$$\hbar\omega = -E_0$$

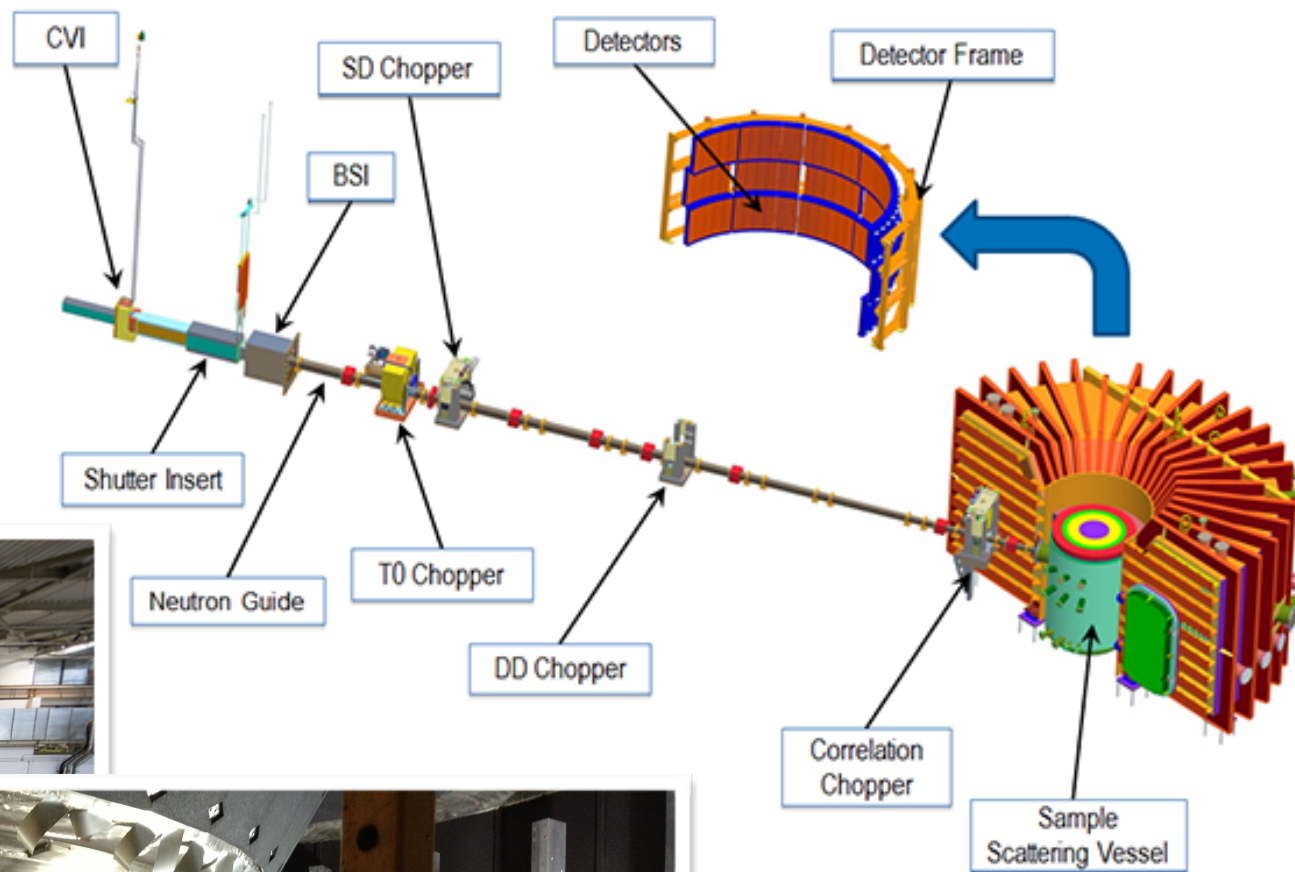




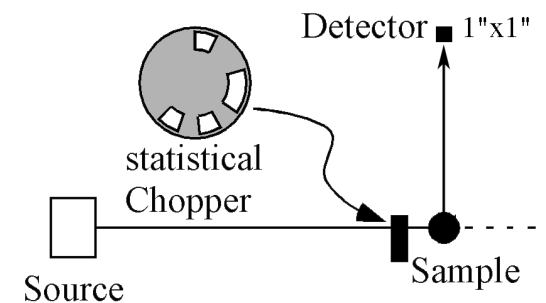
14-G00875A/gim

The Spallation Neutron Source is a facility of Oak Ridge National Laboratory, managed by UT-Battelle for the US Department of Energy.

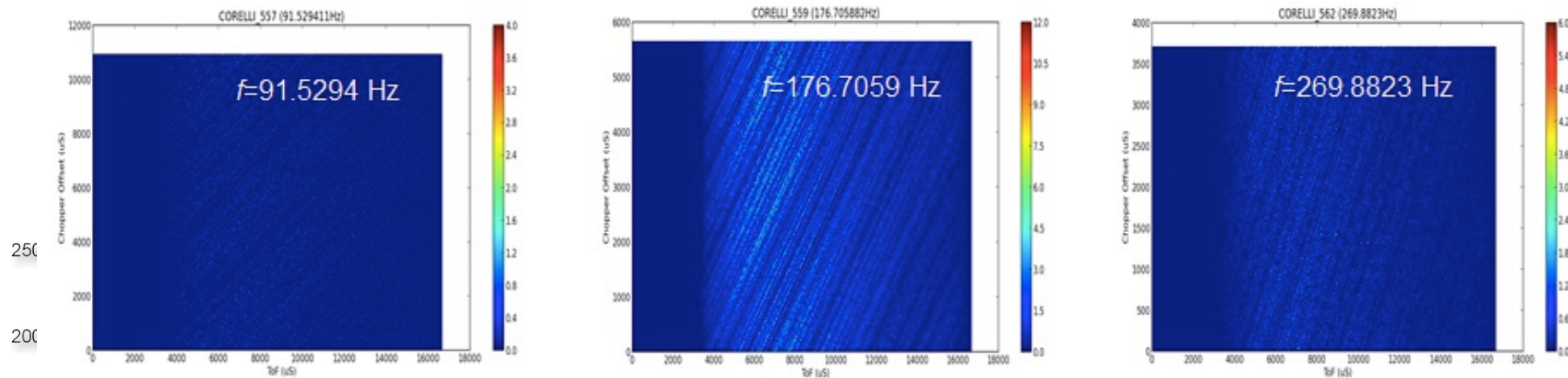
# Corelli



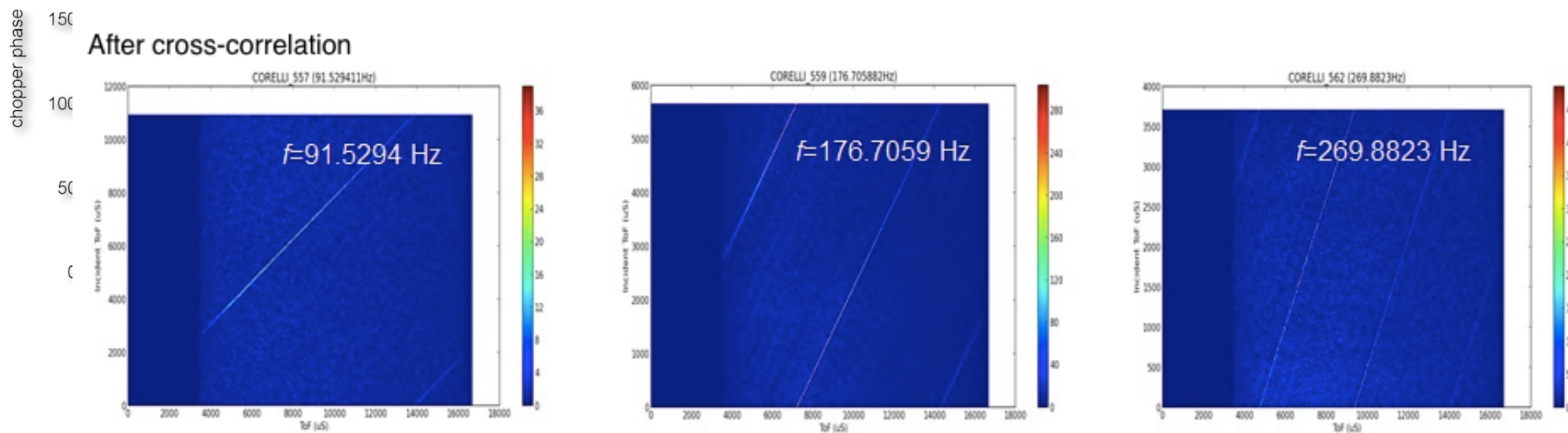
# Cross Correlation in Action



Before cross-correlation

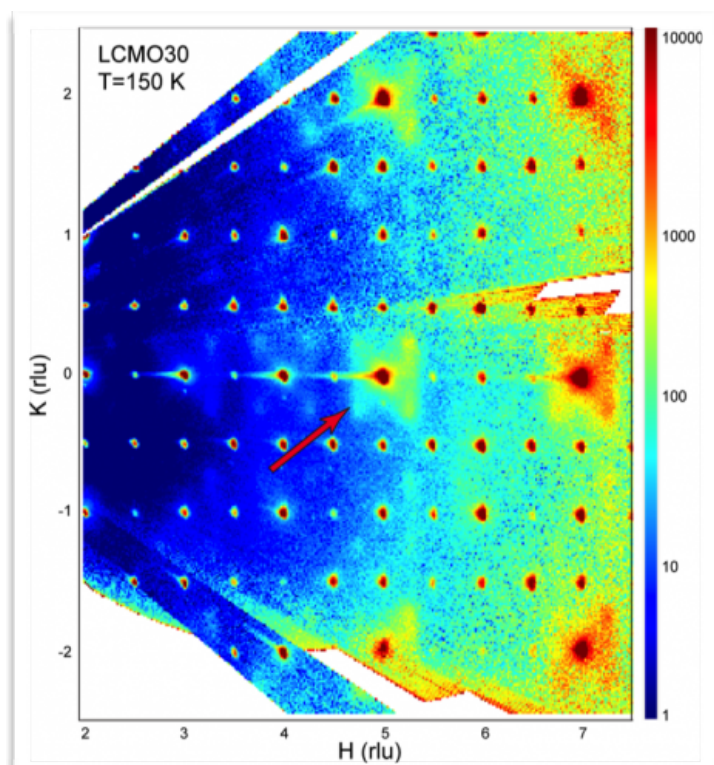


After cross-correlation

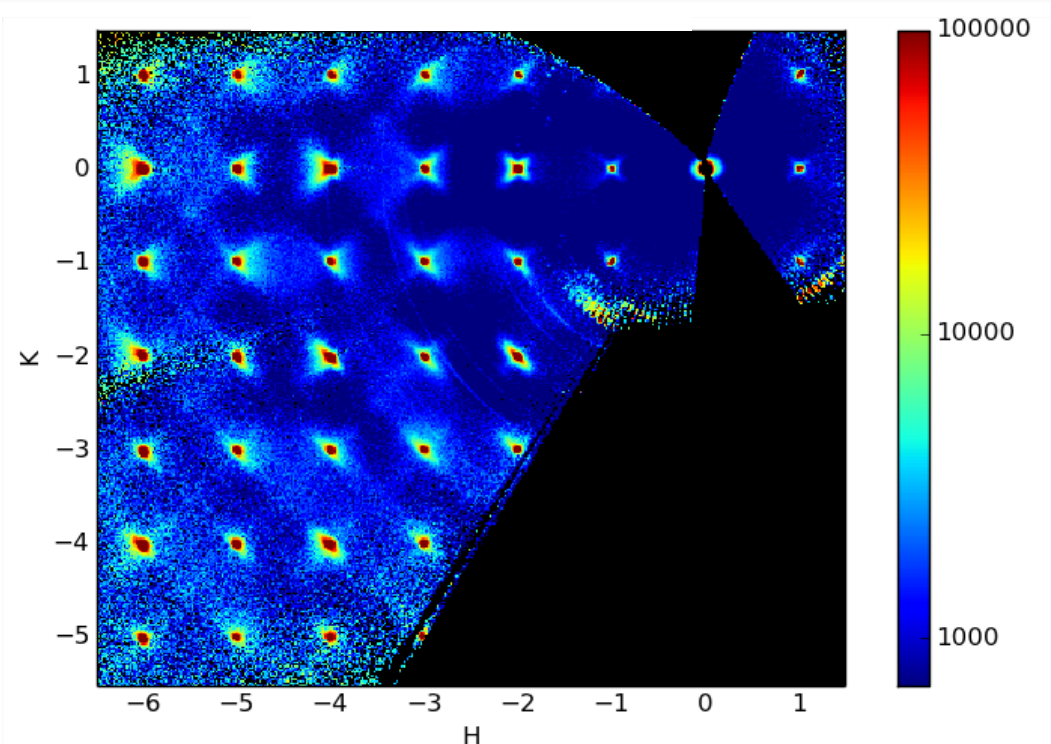


# First Results

## ► $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$

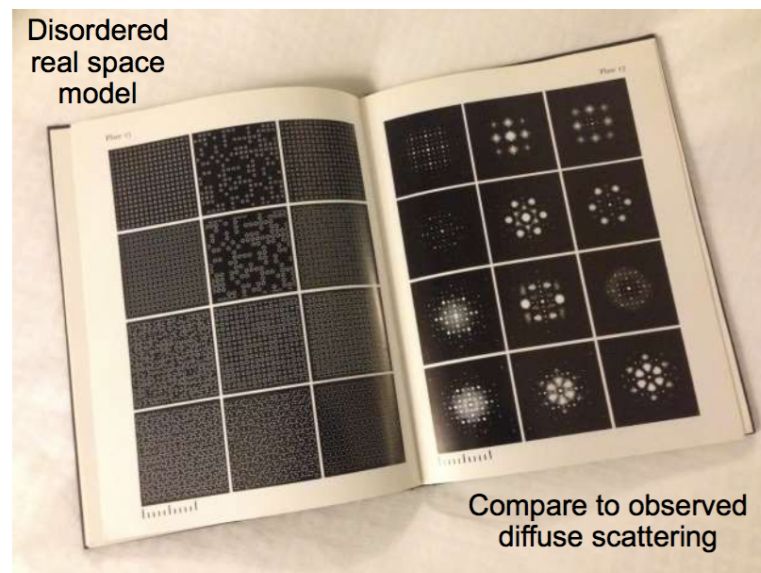
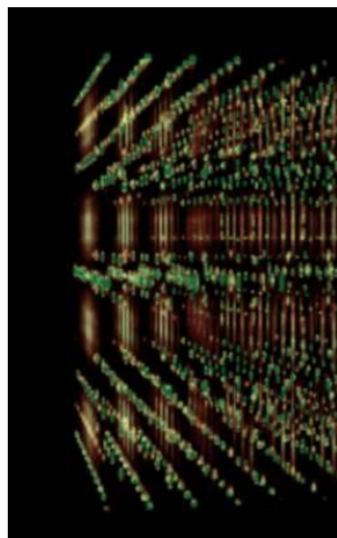


## ► $\text{PbMn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ -30% $\text{PbTiO}_3$



# The Future

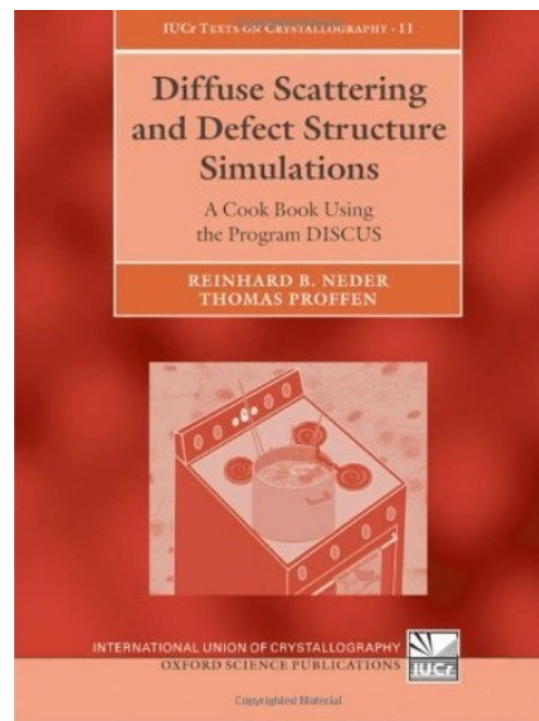
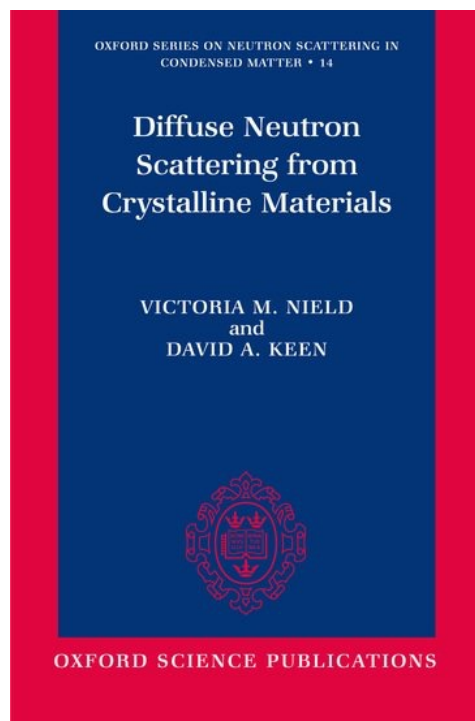
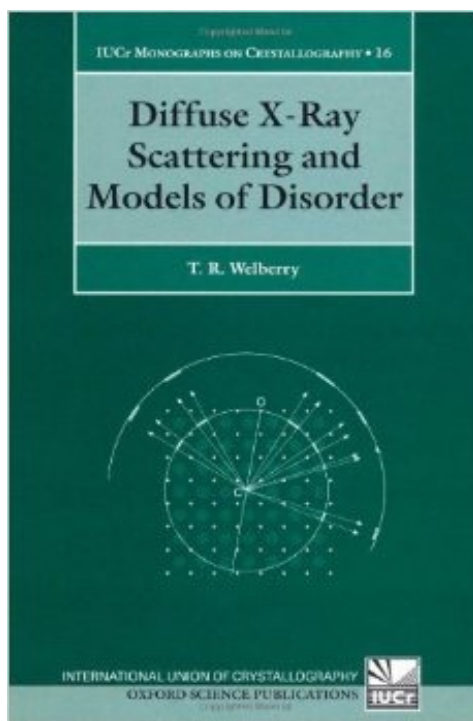
- ▶ High-Energy X-rays
  - Absorption lengths similar to neutrons
  - Most existing detectors have low efficiency but alternatives exist, *e.g.* CdTe
- ▶ Micro-diffuse scattering
  - Benefiting from increased brightness of, *e.g.*, APS Upgrade
- ▶ Increasing use of *ab initio* computational modeling
  - Allowing more complex systems to be investigated
  - Less dependence on intuition in modeling
- ▶ Enhanced analysis tools
  - Machine learning
  - Correlated data analysis
  - Easier co-refinement of neutrons and x-rays



Atlas of Optical Transforms, Harburn, Taylor and Welberry (1975)

## A Few References

- ▶ T. R. Welberry & B. Butler, Chem Rev **95**, 2369–2403 (1995).
- ▶ F. Frey, Acta Cryst B **51**, 592–603 (1995).
- ▶ T. R. Welberry & D. J. Goossens, Acta Cryst A **64**, 23–32 (2007).
- ▶ D. A. Keen & A. L. Goodwin, Nature News **521**, 303–309 (2015).

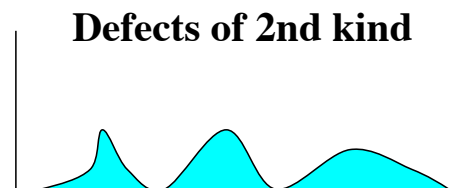
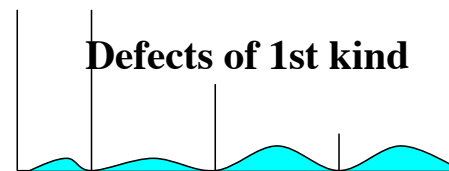
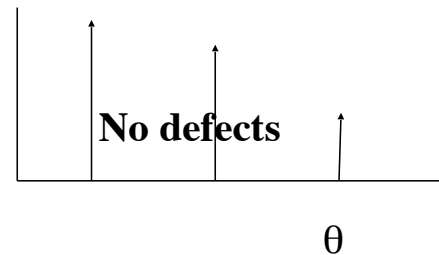


# Diffuse Scattering Song

- ▶ Come eager young scholars - so tender and new  
I'll teach you diffraction - what I says mostly true  
Between the Bragg Peaks lies a world where you see  
Fluctuations and defects- they stand out plane-ly
- ▶ *Chorus*  
For its dark as a dungeon between the Bragg peaks  
But here in the darkness - each defect speaks  
It gathers- from throughout- reciprocal space  
And re-distributes all over the place.
- ▶ Between the Bragg peaks - one thing that we see  
Is TDS on our CCD  
Intensity totals are conserved- you can't win  
It steals from the Bragg peaks that stay very thin
- ▶ Substitutional alloys can cause quite a stir  
The shorter the length scale the greater the blur  
With care you can find out the bond length between  
Each atom pair type-the measurements clean
- ▶ Dislocations and other- type 2 defects  
Destroy the Bragg peaks -they turn them to wrecks  
But near the Bragg peaks- you still can see  
Intense diffraction continuously
- ▶ Many -are- the defects you find  
Between the Bragg peaks where others are blind  
So go tell your friends and impress your boss  
You've new understanding -with one hours loss



Gene Ice



Krivoglaz Classifications

