Single Crystal Diffuse Scattering

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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: 3D-\Delta PDF in sodium-intercalated V_{2}O_{5}
‣ How do I look at static disorder? Hint: Corelli
  • Neutrons vs X-rays
  • Diffuse scattering with elastic discrimination
‣ Diffuse scattering - the musical
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- In these examples, 30% of atoms (blue dots) have been replaced by vacancies (green dots)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

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

Workshop on “Single-Crystal Diffuse Scattering at Pulsed Neutron Sources” June 16-17, 2003
Intense Pulsed Neutron Source
Argonne National Laboratory

<http://www.neutron.anl.gov/diffuse/>
Diffuse Scattering from Metallic Alloys

Short-range Order in Null Matrix $^{62}$Ni$_{0.52}$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$_2$

Diffuse Scattering from Molecular Solids

Diffuse Scattering from Relaxor Ferroelectrics

Lead Zinc-Niobate

Lead Magnesium-Niobate

E=0

E∥[111]


National School on Neutron & X-ray Scattering - 2019
Diffuse Scattering from Jahn-Teller Polarons

$\Delta_{\text{CF}}$ $\Delta_{\text{JT}}$

$\Delta_{\text{JT}}$

d$\Delta_{\text{CF}}$

dMn

t$_{2g}$
e$_{g}$

4+ 4+ 3+ 4+

$T = 115 \text{ K}$

$T = 300 \text{ K}$

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

$d(3y^2-r^2)$
Incommensurate Modulations in $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{NbO}_6$

Acknowledgements:
Bixia Wang and Daniel Phelan
Magnetic Diffuse Scattering from Geometric Frustration

ZnCr$_2$O$_4$

How do I model it?
A Few Equations

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

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

• **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**

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

• **Warren Size Effect**

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

• **Borie and Sparks Correlations**

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

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

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

**Reciprocal space**
- Only sharp Bragg reflections
- Sharp diffuse rods
- Sharp diffuse planes
- Diffuse clouds

**Direct space**
- 3D-periodic structure
  - no defects
- 2D-periodic structure
  - perpendicular to the streaks
  - disordered in streak directions
- 1D-periodic structure
  - perpendicular to the planes
  - disordered within the plane
- 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 $\text{AlO}_4$ and $\text{SiO}_4$ tetrahedra
  - Mullite has excess $\text{Al}^{3+}$ occupying $\text{Si}^{2+}$ sites for charge balance
- This results in strong vacancy-vacancy correlations

Sillimanite: $\text{Al}_2\text{SiO}_5$  
Mullite: $\text{Al}_2(\text{Al}_{2+2x}\text{Si}_{2-2x})\text{O}_{10-x}$

Measuring X-ray Diffuse Scattering with Continuous Rotation Method
Measuring X-ray Diffuse Scattering with Continuous Rotation Method

- The sample is continuously rotated in shutterless mode at 1° per second
- A fast area detector (e.g., a Pilatus 2M) acquires images at 10 frames per second
  - *i.e.*, 3600 x 8MB frames ~ 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
Experiment Workflow

- Powder calibration to determine detector distance, centers, and tilts
- Bragg peak search to optimize the sample/detector geometry
- Determine the orientation matrix
- Perform coordinate transformation at each detector position
- Merge the three transforms
Diffuse Scattering in the Relaxor PbMg$_{1/3}$Nb$_{2/3}$O$_3$
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 $Q_l$.
- There are incipient superlattice peaks at $Q = 0.5 \, c^* + 0.31 \, a^*$.
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,

\[ V_i = \frac{\sum E_{ij}}{kT} \frac{(N_v - N_v^0)^2}{N_v^0} \text{ sgn}(N_v - N_v^0) . \]

Monte Carlo Analysis Results
Vacancy Short-Range Order in Mullite
A First-Principles Approach (\textit{ab initio} HRMC)

\[ E(\sigma) = J_0 + \sum_i \sigma_i J_i + \sum_{i,j} J_{ij} \sigma_i \sigma_j + \sum_{i,j,k} J_{ijk} \sigma_i \sigma_j \sigma_k + \ldots \]
Nearly-Commensurate Vacancy Stripes in Mullite

\[ \mathbf{c} = 0 \]

\[ \mathbf{q} = \pm \frac{1}{2} \mathbf{c}^* \pm \frac{1}{3} \mathbf{a}^* \]

\[ \zeta \approx 20 \text{Å} \]
Case Study 2: Sodium-Intercalated V$_2$O$_5$
3D-$\Delta$PDF
Pair Distribution Function Analysis

Radial atomic pair distribution function (PDF) gives the interatomic distance distribution, or “probability” of finding atomic pairs distance $r$ apart.

$$G(r) = 4\pi r [\rho(r) - \rho_o] = \frac{2}{\pi} \int_{Q=Q_{\text{min}}}^{Q_{\text{max}}} Q[S(Q) - 1]\sin(Qr) dQ$$

Emil Bozin (ADD 2013)
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.
“Punch and Fill”

\[ P_{\text{tot}}(r) = FT[I(u)] = FT[|\bar{F}(u)|^2] + FT[|\Delta F(u)|^2] = P_{hkl}(r) + \Delta P(r) \]
Sodium-Intercalated V$_2$O$_5$

Diffuse Scattering in Na$_{0.2}$V$_2$O$_5$ and Na$_{0.4}$V$_2$O$_5$

$Q_k=0.5$

Na$_{0.4}$V$_2$O$_5$

300K

Na$_{0.4}$V$_2$O$_5$

100K
Sublattice Melting

- $x = 0.4 \ 100K$
- $x = 0.4 \ 300K$
- $x = 0.2 \ 100K$
3D-ΔPDF Analysis of \(\text{Na}_x\text{V}_2\text{O}_5\)
Real Space vs 3D-ΔPDF
Order-Disorder Transition
Viewed in Reciprocal and Real Space

40% Na-intercalation

50K 150K 250K
3D-ΔPDF: Importance of High Energy

- Expanding the Q-range enhances the real-space resolution
Back to Mullite

c = 0
How do I look at static disorder?
Comparison of Elastic Scattering and the Static Approximation

\[
\left( \frac{d^2\sigma}{d\Omega dE'} \right)_{\text{coh}} = b^2_{\text{coh}} \frac{k'}{k} N \frac{1}{2\pi\hbar} \int G(\vec{r}, t) e^{i(\vec{Q}.\vec{r} - \omega t)} d\vec{r}.dt
\]

where \( G(\vec{r}, t) = \frac{1}{(2\pi)^3} \frac{1}{N} \int e^{-i\vec{Q}.\vec{r}} \sum_{i,i'} \left( e^{-i\vec{Q}.\vec{R}_j(0)} e^{i\vec{Q}.\vec{R}_j(t)} \right) \)

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{static}} = b^2_{\text{coh}} N \int G(\vec{r}, 0) e^{i\vec{Q}.\vec{r}} d\vec{r}
\]

since \( \hbar\delta(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega} d(\hbar\omega) \)

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{elastic}} = b^2_{\text{coh}} N \int G(\vec{r}, \infty) e^{i\vec{Q}.\vec{r}} d\vec{r}
\]

› Reference: Roger Pynn, National School of Neutron and X-ray Scattering, 2018
Importance of Elastic Discrimination

\[ Q = 4\pi \frac{\sin \theta}{\lambda} \]

Detector 1
2\(\theta\) \(\sim\) 142.5°

Detector 2
2\(\theta\) \(\sim\) 90.0°

Detector 3
2\(\theta\) \(\sim\) 37.5°

Measuring Large Volumes of Reciprocal Space
Conventional Time-of-Flight Neutron Methods

White Beam: efficient

Fixed $k_i$: energy resolved

NO energy discrimination

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
\[ \hbar \omega = +E_0 \]
\[ \hbar \omega = -E_0 \]

Corelli

Instrument Scientists
Feng Ye
Yaohua Liu

Instrument Proposers
Stephan Rosenkranz
Ray Osborn
Cross Correlation in Action

Before cross-correlation

After cross-correlation

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Elastic Discrimination with Cross Correlation

Benzil C_{14}H_{10}O_{2}

Complementarity of Neutrons and X-rays

Pb\((\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\)-30\%\(\text{PbTiO}_3\)

Corelli Neutrons

CHESS 55keV X-rays
Sublattice Melting in Superionic Cu$_{1.8}$Se

- It has been proposed that Cu$_{2-x}$Se is a Phonon Liquid-Electron Crystal thermoelectric
  - $zT > 1.5$ at high temperature

![Image](image-url)

**Copper ion liquid-like thermoelectrics**

Huili Liu$^{1,2}$, Xun Shi$^{1,3,*}$, Fangfang Xu$^3$, Linlin Zhang$^3$, Wenqing Zhang$^3$, Lidong Chen$^{1,*}$, Qiang Li$^4$, Ctirad Uher$^5$, Tristan Day$^6$ and G. Jeffrey Snyder$^6
3D-ΔPDF from Cu$_{1.8}$Se
Corelli Data

Symmetrized Corelli Data

z=1/2c
The Future

› High-Energy X-rays
  • Absorption lengths similar to neutrons
  • Detectors now have sensors optimized for high energies, e.g. Pilatus 2M 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
A Few References

**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**

- No defects
- Defects of 1st kind
- Defects of 2nd kind

Krivoglaz Classifications