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: 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- In these examples, 30% of atoms (blue dots) have been replaced by vacancies (green dots)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

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$_2$

Diffuse Scattering from Molecular Solids

Diffuse Scattering from Relaxor Ferroelectrics

Lead Magnesium-Niobate

Lead Zinc-Niobate


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**

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

- **Warren Size Effect**

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

- **Borie and Sparks Correlations**

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

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 $Q$

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

Some Rules of Thumb \textit{(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 $AlO_4$ 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: $Al_2(Al^{2+}_{2x}Si_{2-2x})O_{10+x}$

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
Data Reduction Workflows

Peak Search

Refinement and Orientation

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 $Q_l$
- 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

\[ E^{(1)} = \sum_\alpha J_\alpha \sigma_\alpha^{(1)} \]
\[ E^{(2)} = \sum_\alpha J_\alpha \sigma_\alpha^{(2)} \]

First-principles Calculations

Least Squares Fit

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

Peter Zapol & Anh Ngo

Lowest Energy 3:2 Mullite Structure from Kinetic Monte Carlo Calculation
Nearly-Commensurate Vacancy Stripes in Mullite

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

\(c = 0\)

\(c = 1.0\)
Case Study 1: Bilayer Manganites
Diffuse Scattering from Jahn-Teller Polarons

\[ T = 115 \text{ K} \]

\[ T = 300 \text{ K} \]

\[ d_{\text{Mn}} \]

\[ \Delta_{\text{CF}} \]

\[ t_{2g} \]

\[ e_g \]

4+

4+

3+

4+

\[ d(3x^2-r^2) \]

\[ d(3y^2-r^2) \]
Huang Scattering

\[ I(Q) = \sum_{m,n} e^{iQ \cdot (R_m - R_n)} f_m f_n e^{-W_m} e^{-W_n} \langle (Q \cdot u_m)(Q \cdot u_n) \rangle \]

\[ I_{POL}(Q) = N|F_G|^2 \sum_{\alpha,\beta,\gamma,\delta} Q_\beta Q_\delta \left( \sum_{j,j'} \frac{\epsilon_{\alpha,q,j}^* \epsilon_{\beta,q,j} \epsilon_{\gamma,q,j'}^* \epsilon_{\delta,q,j'}}{\omega_{q,j}^2 \omega_{q,j'}^2} \right) \sum_{m,n} \zeta_{m,\alpha} \zeta_{n,\gamma} e^{iQ(xR_m - R_n)} \]

\[ I_{TDS}(Q) = N|F_G|^2 \left( \frac{kT}{2M} \right) \sum_{\beta,\delta} Q_\beta Q_\delta \left( \sum_{j} \frac{\epsilon_{\beta,q,j}^* \epsilon_{\delta,q,j}}{\omega_{q,j}^2} \right) \sum_{m,n} \zeta_{n,\beta} e^{iQ(xR_m - R_n)} \]

\[ u_{m,\delta} = \int \frac{d^3 q}{(2\pi a)^3} \sum_{\beta} \left( \sum_{j} \frac{\epsilon_{\beta,q,j}^* \epsilon_{\delta,q,j}}{\omega_{q,j}^2} \right) \sum_{n} \zeta_{n,\beta} e^{iQ(xR_m - R_n)} \]

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

this allows us to subtract background from thermal diffuse scattering!
TDS + Huang scattering

neutrons

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TDS

polaron

d(3x^2 - r^2)
d(3y^2 - r^2)
Cooperative Jahn-Teller Distortions

\[ \xi \sim 6a \]

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

Bilayer Manganites Revisited
Huang Scattering as a Function of (Qh, Qk, Ql)
Expanding the Concept of a Data Set

Total Data: $S(Q, T, x)$

Correlated Data Analysis/Machine Learning

Phase Diagram
How do I look at static disorder?
Importance of Elastic Discrimination

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

Arcangelo Corelli (1653-1713)

Arcangelo Corelli was the greatest violinist of his age and an influential composer who became known as the "Father of the Concerto Grosso". This musical form contrasts music from a small ensemble of solo musicians with the full orchestra. Similarly, the properties of many materials are enriched by the interactions between both short and long-range ordering motifs that the Corelli instrument is designed to explore.
Corelli

Instrument Scientists
Feng Ye
Yaohua Liu
Cross Correlation in Action

Before cross-correlation

After cross-correlation
First Results
Benzil $C_{14}H_{10}O_2$

Acknowledgement: Richard Welberry (PI) and Christina Hoffmann
Does Cross Correlation Work?

Benzil $C_{14}H_{10}O_2$

Acknowledgement: Richard Welberry (PI) and Christina Hoffmann
First Results
Relaxor Ferroelectrics - \( \text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-30\%\text{PbTiO}_3 \)

Acknowledgement: Matt Krogstad, Daniel Phelan, Stephan Rosenkranz
Complementarity of Neutrons and X-rays

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

Corelli Neutrons

CHESS 55keV X-rays

Acknowledgement: Matt Krogstad, Daniel Phelan, Stephan Rosenkranz
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

*Disordered real space model
Compare to observed diffuse scattering
Atlas of Optical Transforms, Harburn, Taylor and Welberry (1975)*
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