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: 3D-ΔPDF in sodium-intercalated V₂O₅
‣ How do I look at static disorder? *Hint: Corelli*
  • Neutrons vs X-rays
  • Diffuse scattering with elastic discrimination
‣ Diffuse scattering - the musical
Diffuse Scattering

Diffuse Scattering: Deviations from the Average Structure

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- In these examples, 30% of atoms (blue dots) have been replaced by vacancies (green dots)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

Lead Magnesium-Niobate

E=0

E\|[111]


Diffuse Scattering from Jahn-Teller Polarons

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

\[ \Delta_{\text{JT}} \]

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

\[ t_{2g} \]

\[ e_g \]

\[ 4+ \]

\[ 4+ \]

\[ 3+ \]

\[ 4+ \]

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

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

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

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

Acknowledgements:
Bixia Wang
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

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

- Warren Size Effect

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

- Borie and Sparks Correlations

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

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

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

- 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,

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

Monte Carlo Analysis Results
Vacancy Short-Range Order in Mullite
A First-Principles Approach (*ab initio* HRMC)
Nearly-Commensurate Vacancy Stripes in Mullite

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

\( c = 0 \)

\( c = 1.0 \)

\( \xi \sim 20 \text{Å} \)
Case Study 2: Sodium-Intercalated $V_2O_5$
3D-$\Delta$PDF
Pair Distribution Function Analysis

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

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
  - \( \Delta \)-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.
“Punch and Fill”

\[
P_{\text{tot}}(r) = FT[I(u)] = FT[|\tilde{F}(u)|^2] + FT[|\Delta F(u)|^2] = P_{hkl}(r) + \Delta P(r)
\]
Sodium-Intercalated $V_2O_5$
Diffuse Scattering in $\text{Na}_{0.2}\text{V}_2\text{O}_5$ and $\text{Na}_{0.4}\text{V}_2\text{O}_5$

$Qk=0.5$

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

300K

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

100K
Sublattice Melting

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

300K

40% Na-intercalation

200K
3D-ΔPDF: Importance of High Energy

- Expanding the Q-range enhances the real-space resolution

CHESS – A2 – 55keV

APS – 11-ID-D – 18.5keV
How do I look at static disorder?
Comparison of Elastic Scattering and the Static Approximation

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

where \( G(\vec{r}, t) = \frac{1}{(2\pi)^3} \frac{1}{N} \int e^{-i\vec{Q} \cdot \vec{r}} \sum_{i,l} \left( e^{-i\vec{Q} \cdot \vec{R}_i(0)} e^{i\vec{Q} \cdot \vec{R}_j(t)} \right) \)

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

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

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

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

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

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
\(\hbar \omega = +E_0\)
\(\hbar \omega = -E_0\)

Corelli

Instrument Scientists
Feng Ye
Yaohua Liu

Instrument Proposers
Stephan Rosenkranz
Ray Osborn
Cross Correlation in Action

Before cross-correlation:
- $f=91.5294 \text{ Hz}$
- $f=176.7059 \text{ Hz}$
- $f=269.8823 \text{ Hz}$

After cross-correlation:
- $f=91.5294 \text{ Hz}$
- $f=176.7059 \text{ Hz}$
- $f=269.8823 \text{ Hz}$
Elastic Discrimination with Cross Correlation
Benzil C$_{14}$H$_{10}$O$_{2}$

Relaxor Ferroelectrics - Pb\((\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3\) PMN

PMN-20PT

PMN-30PT

PMN-35PT

PMN-40PT

PMN-50PT

Complementarity of Neutrons and X-rays

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

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

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

Alex Rettie
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

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

\[ \theta \]

Defects of 1st kind

Defects of 2nd kind

Krivoglaz Classifications