SINGLE CRYSTAL DIFFUSE SCATTERING

RAYMOND OSBORN
Neutron & X-ray Scattering Group
Materials Science Division

Acknowledgements: Stephan Rosenkranz and Matthew Krogstad

Work supported by the U.S. Department of Energy,
Office of Science, Materials Sciences and Engineering Division.

Neutron & X-ray School
July 21, 2022
OUTLINE

- What is diffuse scattering?
  - What causes it?
- What is it good for?
  - A random walk through disordered materials
- How do I model it?
  - A few equations
- How do I measure it?
- Case Study 1: Diffuse scattering from vacancies in mullite
- Case Study 2: 3D-ΔPDF in sodium-intercalated V$_2$O$_5$
- How do I look at static disorder?
  - Diffuse scattering with elastic discrimination
WHAT IS DIFFUSE SCATTERING?
DIFFUSE SCATTERING

Bragg Scattering
Average Structure

Diffuse Scattering
Deviations from the Average Structure
SIMPLE EXAMPLE OF DISORDER
Replace 30% of atoms (blue dots) by vacancies (green dots)

Random Vacancies

Vacancy Clusters

Model due to Thomas Proffen
BRAGG SCATTERING

The average occupancy is unchanged \(\Rightarrow\) Bragg peaks are identical

Random Vacancies

Vacancy Clusters
DIFFUSE SCATTERING

The diffuse scattering is quite different.

Random Vacancies

Laue Monotonic Scattering

Vacancy Clusters

Substitutional Diffuse Scattering
WHAT IS IT GOOD FOR?
DIFFUSE SCATTERING FROM METALLIC ALLOYS

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

DIFFUSE SCATTERING FROM A FAST-ION CONDUCTOR
Sublattice Melting in Fluorite Compounds

CaF$_2$

M. T. Hutchings et al
DIFFUSE SCATTERING FROM MOLECULAR SOLIDS

Molecular Flexibility in Benzil

1941 BENZIL
1997
2001

X-RAY

DIFFUSE SCATTERING FROM JAHN-TELLER POLARONS

INCOMMENSURATE MODULATIONS IN Sr$_{0.5}$Ba$_{0.5}$NbO$_6$

Acknowledgements:
Bixia Wang and Daniel Phelan
MAGNETIC MONOPOLES IN SPIN ICE

Diffuse Magnetic Scattering in Dy$_2$Ti$_2$O$_7$

HOW DO I MODEL IT?
DIFFUSE SCATTERING THEORY

A Few Equations

\[ I = \sum_i \sum_j b_i b_j \exp(iQ \cdot r_{ij}) \]

- Laue Monotonic Diffuse Scattering

\[ I = \bar{b}^2 \sum_{ij} \exp(iQ \cdot r_{ij}) + N(\bar{b}^2 - \bar{b}^2); \quad \bar{b}^2 = (c_A b_A + c_B b_B)^2; \quad \bar{b}^2 = c_A c_B (b_B - b_A)^2 \]

- Cowley Short-Range Order

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

- Warren Size Effect

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

- Borie and Sparks Correlations

\[ I = \sum_i \sum_j b_i b_j \exp(iQ \cdot (R_i - R_j)) \left[1 + iQ \cdot (u_i - u_j) - \frac{1}{2} (Q \cdot (u_i - u_j))^2 + \ldots \right] \]


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 (2022)
SOME RULES OF THUMB

Acknowledge: Hans Beat Bürgi

Reciprocal space

- Sharp Bragg reflections
  - no defects
- Sharp diffuse rods
  - no defects
- Sharp diffuse planes
  - no defects
- Diffuse clouds
  - no defects

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
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 $Q$

\[
I_0 \propto f^2 e^{-2M} \sum_{j=1}^{6} \frac{|\mathbf{q} \cdot \hat{e}_j|^2}{\omega_j} \coth\left( \frac{\hbar \omega_j}{2k_B T} \right).
\]
HOW DO I MEASURE IT?
MEASURING X-RAY DIFFUSE SCATTERING

Continuous Rotation Method

Sector 6 - APS

Incident Beam

Detector

Cryocooler

Sample
X-RAY SCATTERING GEOMETRY

Continuous Rotation Method

- The sample is continuously rotated at $1^\circ \text{s}^{-1}$
- Frames are collected at 10Hz
  - 3600 x 8MB frames
  - 30GB every 6 minutes
  - 3TB per day
Q-RANGE IN ROTATION METHOD ON SECTOR 6

- With the following parameters, we cover \(-15\,\text{Å}^{-1}<Q<15\,\text{Å}^{-1}\)
  - $E_i \approx 87$ keV
  - $\lambda \approx 0.14$ Å
  - Detector distance $\approx 650$ mm
  - Pilatus 2M CdTe: 1679x1475 pixels
  - Pixel size $\approx 170$ µm
- This Q-range includes thousands of Brillouin zones.
  - e.g., for $a \approx 10$ Å, $\approx 60,000$ Bragg peaks
MANAGING THE FLOOD
EXPERIMENT WORKFLOW
DIFFUSE SCATTERING IN 3D
THE RELAXOR PbMg$_{1/3}$Nb$_{2/3}$O$_3$

DIFFUSE GALLERY
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: $Al_2(Al_{2+2x}Si_{2-2x})O_{10-x}$
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 L
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
MONTE CARLO ANALYSIS RESULTS
VACANCY ORDERING IN MULLITE

\[ c = 0 \]

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

\[ c = 1.0 \]

\[ \xi \sim 29 \text{Å} \]
CASE STUDY 2: SODIUM-INTERCALATED $\text{V}_2\text{O}_5$
3D-ΔPDF
PAIR DISTRIBUTION FUNCTION ANALYSIS

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

$$G(r) = 4\pi r [\rho(r) - \rho_o] = \frac{2}{\pi} \int_{\mathbf{G} = \mathbf{G}_{\text{min}}}^{\mathbf{G}_{\text{max}}} [S(\mathbf{G}) - 1] \sin(\mathbf{G} r) d\mathbf{G}$$

Emil Bozin (ADD 2013)
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

- The 3D PDF technique was pioneered by Thomas Weber and colleagues at ETH
  - Philippe Schaub, Walter Steurer, Arkadiy Simonov
- The ability to measure three-dimensional S(Q) over a large volume of reciprocal space provides the 3D analog of PDF measurements.
  - Total PDFs if Bragg peaks and diffuse scattering can be measured simultaneously
  - ΔPDFs if the Bragg peaks are eliminated
- This allows a model-independent view of the measurements in real space.
I = \sum_i \sum_j b_i b_j \exp(iQ \cdot r_{ij})

P_{tot}(r) = FT[I(Q)] = FT[|\bar{F}(Q)|^2] + FT[|\Delta F(Q)|^2] = P_{hkl}(r) + \Delta P(r)

SODIUM-INTERCALATED V$_2$O$_5$

SUBLATTICE MELTING IN Na$_{0.45}$V$_2$O$_5$

Order-Disorder Transition in the Half-Filled Sodium Sublattice

$K=0.5$

50K  200K  250K
3D-$\Delta$PDF ANALYSIS OF Na$_{0.45}$V$_2$O$_5$

50K  200K  250K
3D-ΔPDF ANALYSIS OF Na$_{0.45}$V$_2$O$_5$
REAL SPACE vs 3D-ΔPDF
ORDER-DISORDER TRANSITION VIEWED IN REAL SPACE

$\text{Na}_{0.45}\text{V}_2\text{O}_5$
EFFECT OF Q-RESOLUTION

- Finite Q-resolution → Gaussian envelope in real space.
- The width can be determined from the total PDF
  - *i.e.*, the transform of the long-range crystal structure.
FITTING CORRELATION LENGTHS IN REAL SPACE

\[ f(r) = A \times G(r) \times \exp(-|r|/\xi) \]
24.3.3 Ordering of Na within the two-leg ladders.

Fig. 24.10(a) shows a small region near the origin of the x = 0 plane of the APDF map obtained from the 50K X-ray data. The strong white origin peak indicates perfect positive correlation for an atom with itself. Other white peaks also indicate a positive correlation between an atom at the origin with another at a position given by the vectors A, B or C (and the reverse vectors A+, B- and C-). Conversely, the dark peaks indicate strong negative correlations. It is quite straightforward to deduce from the observed pattern of white and dark peaks that the local arrangement of the Na ions must follow a pattern like that shown in Fig. 24.10(b), where the occupancy of the two Na sites on each rung of the two-leg ladders tends to alternate between (Na+) and (CNa) producing a zig-zag chain of occupied sites. Neighbouring ladders at z = ±1/10 have the same occupancy pattern which is in phase with the ladder at z = 0.

![Diagram](image)

24.3.4 APDF peak intensities in the z = 0 plane.

Fig. 24.12 shows the z = 0 plane of the APDF map observed at three different temperatures. Fig. 24.11(b) shows an enlargement of part of Fig. 24.11(a) where white arrows (labelled A–F) have been used to identify different interatomic vectors. The same set of vectors is shown in Fig. 24.11(c) which is a plot of the z = 0 plane of the average structure. The maps are dominated by the same alternating correlations of Na occupancy along the ladder direction parallel to y. Similarly, neighbouring chains at z = ±1 are in phase with each other for temperatures 50K and 150K but at 250K these correlations have been lost.

Although the maps are dominated by the correlations in the Na ladders there are numerous weaker peaks that correspond to correlations between the ladder Na+ ions and the interstitial Na- ions. These correspond to vectors A, B, C and E in Fig. 24.11(c) and involve one Na+ and one Na- ion. These peaks are clearly evident in the 50K map, somewhat less evident at 150K and even less evident at 250K. They are weak relative to those involving Na+ ions alone simply because of the low occupancy of the Na- sites.

"Site 0" is used to represent a vacant site.
BACK TO MULLITE
HOW DO I LOOK AT STATIC DISORDER?
COMPARISON OF ELASTIC SCATTERING AND THE STATIC APPROXIMATION

\[ G(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i(t) + \mathbf{r}_j(0)) \right\rangle \]

\[ S(Q, \omega) = \frac{1}{N} \frac{1}{2\pi\hbar} \int_\infty^\infty e^{-i\omega t} dt \int G(\mathbf{r}, t) e^{-iQ\cdot\mathbf{r}} d\mathbf{r} \]

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

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

\[ \left( \frac{d\sigma}{d\Omega} \right)_{\text{elastic}}^{\text{coh}} = b_{\text{coh}}^2 N \int G(\mathbf{r}, \infty) e^{i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{r} \]
MEASURING LARGE VOLUMES OF RECIPROCAL SPACE

Conventional Time-of-Flight Neutron Methods

White Beam: efficient

Fixed ki: 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

Elastic scattering: \( \hbar \omega = 0 \)

Inelastic scattering: \( \hbar \omega = +E_0 \), \( \hbar \omega = -E_0 \)
CORELLI

Instrument Scientists
Feng Ye
Yaohua Liu

Instrument Proposers
Stephan Rosenkranz
Ray Osborn
CROSS CORRELATION IN ACTION

Raw Data

Cross Correlation

Reconstructed Scattering Function

elastic

inelastic
ELASTIC DISCRIMINATION WITH CROSS CORRELATION

Benzil C$_{14}$H$_{10}$O$_{2}$

DIFFUSE SCATTERING FROM A FAST-ION CONDUCTOR

Sublattice Melting in SrCl$_2$

RELAXOR FERROELECTRICS - Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-xPbTiO$_3$

COMPLEMENTARITY OF NEUTRONS AND X-RAYS

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

Corelli Neutrons

CHESS 55keV X-rays
Advances in instrumentation have transformed our ability to measure single crystal total scattering over large volumes of reciprocal space.
- High-Energy X-rays
- Time-of-Flight Neutrons

This is enabling new ways of analyzing the data:
1. Unsupervised machine learning
2. \textit{ab initio} computational modeling
3. 3D-ΔPDF - real-space pair distributions

The results give unique insight into disordered materials
- Bridging the gap between diffraction and imaging
A FEW REFERENCES