Single Crystal Diffuse Scattering

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ADD 2019, March 18, 2019
Disordered Structures

Partial cross section of 200x200 unit cell model crystals
Composition 75% A  25% B

Random position of A B atoms  Non-random position of A B atoms

Properties of the two crystals will differ
Effect on Bragg Reflections

Bragg reflections see the global picture, the **average** structure, i.e. just one **averaged unit cell**.
Diffuse scattering to the rescue ...

Diffuse scattering sees the local picture, the **deviations** from the average structure, the local (approximate) periodicity on a short scale

Continuous unstructured scattering

Modulated diffuse scattering
Structure factor

\[ F(hkl) = \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j)} \]  
Sum over all N atoms in one unit cell

In the experiment this is really:

\[ F(hkl) = \sum_{Ra=-\infty}^{\infty} \sum_{Rb=-\infty}^{\infty} \sum_{Rc=-\infty}^{\infty} \sum_{j(abc)=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j + hRa + kRb + lRc)} \]  
Sum over all N atoms in all unit cells \( R_a, R_b, R_c \)

If all unit cells are identical and strictly periodic to \( \pm \infty \):

\[ F(hkl) = 0 \quad \text{unless} \quad hkl \text{ are whole numbers} \]

Bragg reflections only

J. Cowley: Diffraction Physics
Structure factor

\[ F(hkl) = \sum_{R_a=-\infty}^{\infty} \sum_{R_b=-\infty}^{\infty} \sum_{R_c=-\infty}^{\infty} \sum_{j(abc)=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j + hR_a + kR_b + lR_c)} \]

Sum over all N atoms in all unit cells \( R_a, R_b, R_c \)

If all unit cells are identical and strictly periodic to \( \pm \infty \):

\[ F(hkl) = 0 \quad \text{unless} \quad hkl \text{ are whole numbers} \]

Diffuse scattering is observed if:

- crystal is truncated by surfaces
  
  truncation rod   surface diffraction, surface crystallography, LEED, RHEED

- atoms move within the crystal
  
  Vibrations:  Thermal diffuse scattering
  Diffusion: Quasielastic neutron scattering

- individual unit cells differ throughout the crystal

  Disorder:  diffuse scattering between Bragg reflections
  
  \[ \Rightarrow \]  This talk; W. Paulus, P. Welch, N. Roth
  
  \[ \Rightarrow \]  E.M. Schmidt

  Real structures:  diffuse scattering predominantly close to Bragg reflections
Defect types

**Point defects**
- individual missing, wrong, additional atoms
- small clusters
- missing atoms
- Interstitials
- small clusters
- with overall charge neutrality

Predominantly in inorganic materials

- Metal Alloys, non-stoichiometric oxides and halides
Defect types

**Point defects**
- individual missing, wrong, additional atoms
- small clusters

Predominantly in inorganic materials
- Metal Alloys, non-stoichiometric oxides and halides

Neder, PhD Munich 1990
Defect types

**Point defects**
- individual missing, wrong, additional atoms
- small clusters
- Different molecular conformation

Perfect structure model

Disorder:
- Rotate molecule around [100]

Stacks with perfect periodicity along c
- Either up or down

Diffuse scattering in Trisamides
Defect types

**Point defects**
- individual missing, wrong, additional atoms
- small clusters

**Linear defects**
- embedded molecules in channels of host structure

Th Weber PhD München 1994

Alcane chains in Urea
Defect types

Point defects
- individual missing, wrong, additional atoms
- small clusters

Linear defects
- embedded molecules in channels of host structure

Planar defects
- stacking faults, wrong layer types, missing layers
- surfaces, boundaries, dislocations

Predominantly in layered materials
- Clays, mica, closed packed structures (Co, Cu, ZnS, SiC)
Defect types

**Point defects**
- individual missing, wrong, additional atoms
- small clusters

**Linear defects**
- embedded molecules in channels of host structure

**Planar defects**
- stacking faults, wrong layer types, missing layers
- surfaces, boundaries, dislocations

**3-D defects**
- dissolutions, twins, anti phase domains
- surfaces, boundaries
Defect types

**Point defects**
- individual missing, wrong, additional atoms
- small clusters

**Linear defects**
- embedded molecules in channels of host structure

**Planar defects**
- stacking faults, wrong layer types, missing layers
- surfaces, boundaries, dislocations

**3-D defects**
- dissolutions, twins, anti phase domains
- surfaces, boundaries

**Waves**
- periodic modifications of the crystal
- position, composition, valence

La$_{1.2}$ Sr$_{1.8}$ Mn$_2$ O$_7$

R. Osborn et al.
Defect correlations

**uncorrelated defects**
Location of individual defects is independent of each other

randomly distributed point defects
diffuse scattering shows no features

**correlated defects**
Location of a defect influences the location of defects in the immediate vicinity

point defects along rows
diffuse scattering in planes normal to the lines

Concentration of defects is identical,
average structure is identical!
Bragg reflections are identical!
Disorder versus Diffraction

perfect crystal structure

rigid molecules in P4mm

Intensity at Bragg reflections only
Intensity varies with structure factor
Disorder versus Diffraction

Individual atoms removed, no correlations

Neutron scattering

rigid molecules in P4mm
Bonds destroyed

Intensity at Bragg reflections
and monotonic diffuse Laue scattering
no special structure
Disorder versus Diffraction

all atoms shifted randomly, thermal displacement

rigid molecules in P4mm
bonds destroyed

Intensity at Bragg reflections and isotropic diffuse scattering
weak close to reciprocal origin

Neutron scattering
Disorder versus Diffraction

25 % of all molecules removed, no correlations

Neutron scattering

rigid molecules in P4mm

isotropic diffuse intensity modulated by molecular structure factor
Disorder versus Diffraction

all molecules shifted randomly

rigid molecules in P4mm

isotropic diffuse intensity modulated by molecular structure factor weak close to reciprocal origin

Neutron scattering
Disorder versus Diffraction

diffraction pattern of a single molecule

rigid molecules in P4mm

Neutron scattering

intensity modulated by molecular structure factor
Disorder versus Diffraction

**Substitutional disorder**
- Whole molecules: Neutron; rem
- Intensity is homogeneous throughout reciprocal space

**Displacement disorder**
- Whole molecules: Neutron; therm
- Intensity is weak near reciprocal origin
Disorder versus Diffraction

\[ F(hkl) = \sum_{j=1}^{M} f_j e^{2\pi i (hx_j + ky_j + lz_j)} \]

\[ F(\vec{h}) = \sum_{j=1}^{M} f_j e^{2\pi i \vec{h} \cdot \vec{r}_j} \]

\( f \rightarrow \langle f \rangle + \Delta f \) \quad Form factor as average form factor plus local deviation

\( \vec{r} \rightarrow \langle \vec{r} \rangle + \Delta \vec{r} \) \quad Position as average position plus local deviation

\[ F(\vec{h}) = \sum_{j=1}^{M} \left( \langle f_j \rangle + \Delta f_j \right) e^{2\pi i \vec{h} \cdot \langle \vec{r}_j \rangle + \Delta \vec{r}_j} \]

Pure substitutional disorder \( \Delta \vec{r} = 0 \)

\[ F(\vec{h}) = \sum_{j=1}^{M} \langle f_j \rangle e^{2\pi i \vec{h} \cdot \langle \vec{r}_j \rangle} \]

\[ = \sum_{j=1}^{M} \langle f_j \rangle e^{2\pi i \vec{h} \langle \vec{r}_j \rangle} + \sum_{j=1}^{M} \Delta f_j e^{2\pi i \vec{h} \langle \vec{r}_j \rangle} \]

Identical to perfect structure

\[ \sum_{j=1}^{M} \Delta f_j e^{2\pi i \vec{h} \langle \vec{r}_j \rangle} \]

For neutrons independent of \( |\vec{h}| \)

For X-ray, e\(^{-}\) dependent on \( |\vec{h}| \)
Disorder versus Diffraction

\[ F(hkl) = \sum_{j=1}^{M} f_j e^{2\pi i (hx_j + ky_j + lz_j)} \]
\[ F(\vec{h}) = \sum_{j=1}^{M} f_j e^{2\pi i \vec{h} \cdot \vec{r}_j} \]

\[ f \rightarrow \langle f \rangle + \Delta f \quad \text{Form factor as average form factor plus local deviation} \]
\[ \vec{r} \rightarrow \langle \vec{r} \rangle + \Delta \vec{r} \quad \text{Position as average position plus local deviation} \]

\[ F(\vec{h}) = \sum_{j=1}^{M} \left( \langle f_j \rangle + \Delta f_j \right) e^{2\pi i \vec{h} \cdot \langle \vec{r}_j \rangle + \Delta \vec{r}_j} \]

Pure displacement disorder \( \Delta f = 0 \)

\[ F(\vec{h}) = \sum_{j=1}^{M} \langle f_j \rangle e^{2\pi i \vec{h} \langle \vec{r}_j \rangle + \Delta \vec{r}_j} \]
\[ = \sum_{j=1}^{M} \langle f_j \rangle e^{2\pi i \vec{h} \langle \vec{r}_j \rangle} e^{2\pi i \vec{h} \Delta \vec{r}_j} \]

If: \( \vec{h} \Delta \vec{r} = 0 \quad \rightarrow \quad \text{Sum identical to perfect crystal} \)

- \( |\vec{h}| \) small \( \Rightarrow \) diffuse scattering weak near reciprocal origin
- All \( \Delta \vec{r} \) similar \( \Rightarrow \) extinction rules for diffuse scattering
Short range order versus Diffraction

Short Range Order  SRO

local structure shows tendency to preferred neighbors like AAAAA  or  ABABAB

often just the immediate or next few neighbors

unstructured diffuse scattering  random position
Short range order versus Diffraction

Short Range Order  SRO

local structure shows tendency to preferred neighbors like AAAAA  or  ABABAB

often just the immediate or next few neighbors

diffuse scattering below Bragg reflections

width indicates SRO range
tendency to equal next neighbors
Short range order versus Diffraction

Short Range Order     SRO

local structure shows tendency to preferred neighbors like AAAAA or ABABAB

often just the immediate or next few neighbors

diffuse scattering planes at Bragg reflections normal to [100]
width indicates SRO range

[100] equal neighbors

[010] random neighbors
Short range order versus Diffraction

Negative correlations in hexagonal structures

Frustrated systems

Diffuse scattering *ring* like around Bragg

Diffuse scattering with molecules
Size effect versus Diffraction

Radii: \( r_A > r_B \)

Form factors \( f_A > f_B \)

Asymmetrically shaped diffuse scattering
Higher intensity at smaller values of \( h \)
“size effect”
Initial interpretation / Model building

Very broad diffuse scattering, no regularity in reciprocal space

Diffuse layers fade away from Reciprocal origin

Predominantly substitutional disorder: Orientation in channels

No diffuse layer at L = 0!

\[ F(hk0) = \sum_{j=1}^{M} f_j e^{2\pi i (h x_j + k y_j + 0 z_j)} \]

Independent of z coordinates

\[ \Rightarrow hk0 \text{ sees projected structure} \]

No diffuse: projected structure is periodic

Th Weber PhD München 1994
Initial interpretation / Model building

Single crystal diffraction by stacking faults

Diffuse rods parallel 00L through all Bragg reflections

No diffuse rod at H = 0!

\[ F(00l) = \sum_{j=1}^{M} f_j e^{2\pi i(0x_j + 0y_j + l z_j)} \]

Independent of x,y coordinates

\[ \Rightarrow 00L \text{ sees projected structure} \]

No diffuse: projected structure is periodic along c, all layers are identical
Initial interpretation / Model building

Single crystal diffraction by stacking faults

Diffuse rods parallel 00L through all Bragg reflections

No diffuse rod at H = 3n!

\[ F(30l) = \sum_{j=1}^{M} f_j e^{2\pi i (3x_j + \Delta x_j) + 0y_j + lz_j} \]

\[ F(30l) = \sum_{j=1}^{M} f_j e^{2\pi i (3x_j + 0y_j + lz_j)} e^{2\pi i 3\Delta x_j} \]

If \( 3\Delta x = n \), exponential factor is equal to 1

\[ \implies \] structure factor is equal to that of perfect structure

No diffuse: \( \Delta x = 1/3 \)

Layers are shifted by \( 1/3 \)! 
Initial interpretation / Model building

Single crystal diffraction by stacking faults

Diffuse rods parallel 00L through all Bragg reflections

No diffuse rod at $H = 3n$!

Layers are shifted by $1/3$!

Diffuse extinction rules give insight into shifts in the structure

$\Delta x = 1/3$

Layers are shifted by $1/3$!
Disorder versus Diffraction

Large variety of defect types

Large variety of defect placement / correlation

no unified theory of diffuse scattering

Generally:

Dimension direct space $\iff$ 3 – dimension reciprocal space

0-D point defects $\implies$ 3D (unstructured) diffuse scattering

1-D linear defects $\implies$ 2D planes normal to lines in direct

2-D planar defects $\implies$ 1-D rods normal to planes in direct

3-D defects $\implies$ 0-D maxima / satellites
Disorder versus Diffraction

Large variety of defect types

Large variety of defect placement / correlation

\{ \text{independent of each other!} \}

No unified theory of diffuse scattering

No periodicity: \quad \text{Dimension direct space} <== \quad 3 – dimension reciprocal space

All 3 directions \quad 0-D point defects \quad 3D (unstructured) diffuse scattering

2 directions \quad 1-D linear defects \quad 2D planes normal to lines in direct

1 direction \quad 2-D planar defects \quad 1-D rods normal to planes in direct

0 directions \quad 3-D defects \quad 0-D maxima / satellites
## Disorder versus Diffraction

Large variety of defect types

Large variety of defect placement / correlation

no unified theory of diffuse scattering

Generally: substitutional defects $\leftrightarrow$ neutron: no systematic trend

X-ray: diffuse scattering stronger close to origin

displacement defects $\leftrightarrow$ diffuse scattering weaker close to origin

No diffuse scattering defects in layer of plane through reciprocal origin $\leftrightarrow$ Projected structure is periodic on average:

1D channels alike

Stack of identical layers

diffuse extinction rules $\leftrightarrow$ Restrict shifts with structure

diffuse scattering defects consists of: $\leftrightarrow$ Distribution of defects multiplied by molecular form factor
Literature

  100 Years of Diffuse Scattering
  Review of diffuse scattering and disordered structures

  Diffuse Scattering and Defect Structure Simulation
  Simulation and refinement of disordered structures, cook book

  Diffuse X-ray Scattering and Models of Disorder
  Limited to X-ray diffraction, short experimental part,
  otherwise extensive theory, many examples

V.M. Nield & D.A. Keen (Oxford, 2001)
  Diffuse Neutron Scattering from Crystalline Materials
  Limited to neutronen diffraction, otherwise extensive theory,
  experimental methodse, some simulations, many examples
A word of caution

Essentially identical diffuse scattering
A word of caution

Analyze single crystal refinement
Obtain complementary information:
HRTEM, SAXS, SANS, PDF, Chemistry Spectroscopy (NMR, EXAFS, ...)
Helps to define correct starting model

Identical Correlations
What is a single crystal?  Kaolinite $1 \times 2 \times 0.2 \, \mu m$

Figure 1. Section of the diffraction pattern of the $8 \, \mu m^3$ crystal. (a) The enlarged section shows the diffuse scattering parallel to [001]* through the 02l reflections. (b) The reflection at the bottom of this enlargement is the 021.

Clays and Clay Minerals, (1999), 47, 487
And finally

$\mathcal{F}^{-1}$

THANK YOU