Introduction to Crystal Truncation Rod Diffraction

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Outline

• Introduction
• Diffraction
• Crystal Truncation Rod (CTR) Diffraction
  – Instrumentation
  – Measurement
• Diffractometer Geometry
• Data collection and reduction
• Sample Environments
• Example System
Advanced Photon Source (APS) – Argonne National Lab

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GSE CARS – Sector 13 Layout

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Surface & Interface Scattering – What can be measured?

- **Surface and interface structure**
  - Atomic level positions of atoms at a surface / interface
  - Growth and dissolution mechanisms (kinetics)
  - Structure and binding modes of adsorbates
  - Structure reactivity relationships

- **Interface electron density profiles @ the atomic scale**

- **Surface and interface roughness**
Why use x-rays to Study Surfaces and Interfaces

• **Advantages**
  – Large penetration depth allows for in-situ measurements
    • Liquid water, controlled atmospheres, growth chambers, hazardous materials (i.e. radioactive)
    • Provides access to buried interfaces
  – Kinematic scattering, simplifies the analysis

• **Disadvantages**
  – The generally weak signals requires a synchrotron source
  – Systems need to be well ordered and low roughness
  – Intense x-ray exposure can alter the system
Constructive interference when:

\[ n\lambda = 2d \sin \theta \]

Bragg's Law

Incident plan wave

\[ \lambda \]

\[ d \]

\[ \theta \]

\[ d \sin \theta \]
**Diffraction**

The scattered intensity is proportional to the square modulus of the Fourier transform of the electron density

\[ I_{\text{det}} = \mathbf{E} \mathbf{E}^* \propto \frac{E_0^2 r_e^2}{R^2} \left| \text{FT}[\rho(\mathbf{r})] \right|^2 \]

Where, \( r_e = \frac{e^2}{4\pi\varepsilon_0 mc^2} = 2.82 \times 10^{-5} \) angstroms

\[ \text{FT}[\rho(\mathbf{r})] \propto \int \rho(\mathbf{r}) e^{i\mathbf{Q} \cdot \mathbf{r}} dV \]

Where, \( \mathbf{Q} = \mathbf{k}_r - \mathbf{k}_i \)

\[ \text{FT}[\rho(\mathbf{r})] \propto \sum_n f_{a,n} e^{i\mathbf{Q} \cdot \mathbf{r}_n} \]

\[ f_{a,n} = \int \rho_n(\mathbf{r}) e^{i\mathbf{Q} \cdot \mathbf{r}} dV \]

The sum is over all \( n \) atoms at \( \mathbf{r}_n \) with atomic scattering factors \( f_{a,n} \)

**Master Equation for X-ray Scattering from a collection of atoms**

\[ I = \left| E(R) \right|^2 \propto \left| \sum_n f_{a,n} e^{i\mathbf{Q} \cdot \mathbf{r}_n} \right|^2 \]
Diffraction

The instrument measures $Q$ in the lab

Where, $|k_r| = |k_i| = \frac{2\pi}{\lambda}$

The scattering vector diagram gives:

$|Q| = \frac{4\pi}{\lambda} \sin \frac{2\theta}{2}$
**Single Crystal Diffraction**

**Real Space (BCC)**

- Fe
- \( \hat{z} \)
- \( \hat{y} \)
- \( \hat{x} \)
- \( (0 0 0) \)
- \( \frac{1}{2} \frac{1}{2} \frac{1}{2} \)
- \( a \)
- \( a^* \)

**Reciprocal Space (FCC)**

- \( \hat{z} \)
- \( \hat{y} \)
- \( \hat{x} \)
- \( (0 0 2) \)
- \( (1 0 1) \)
- \( (0 1 1) \)
- \( (1 1 2) \)
- \( (1 2 1) \)
- \( (2 1 1) \)
- \( (2 2 0) \)
- \( (2 2 2) \)

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Single Crystal Diffraction

Detector integrated signal during a wide angle rotation of the sample.

Location of directed (un-reflected) beam.
**CTR Diffraction**

**Crystal truncation rods (CTR)**

Rods of scattering intensity connect bulk Bragg peaks and are perpendicular to the surface. The rods are the result of a sharp termination of the crystal lattice (i.e. a surface) and their shape reflects the interface structure.

![CTR Diffraction Diagram](image)

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CTR Diffraction

Influence of surface structure:

Observe several orders of magnitude intensity variation with changes in surface:
- atomic site occupancy
- relaxation (position)
- presence of adatoms
- roughness
CTR Diffraction

Simulations of Pb/Fe$_2$O$_3$

A. Calculations as a function of surface coverage

B. Calculations as a function of the z-displacement (along the c-axis), the Pb occupation number is fixed at 0.3.
CTR Diffraction

Roughness “kills” rod intensity

Scattering between different height features cause destructive interference

\[ |B(L)|^2 = \frac{(1 - \beta)^2}{1 - \beta^2 - 2\beta \cos(\pi L)} \]

\[ \sigma_{rms} = \frac{\beta^2}{1 - \beta} d_\perp \]

Robinson \( \beta \) model

Distinguish roughness from structure because roughness is uniform decrease in intensity
CTR Diffraction

Real Space (BCC)

Reciprocal Space (FCC)
CTR Diffraction

Real Space (BCC)

Reciprocal Space (FCC)

With a surface

Fe

(0 0 0)

\(\frac{1}{2} \frac{1}{2} \frac{1}{2}\)

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Real Space (BCC)

Reciprocal Space (FCC) With a (001) Surface

\[ \hat{z} \]

\[ \hat{y} \]

\[ \hat{\chi} \]

\[ \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \]

\[ (0, 0, 0) \]

\[ a \]

\[ a^* \]

Fe

\[ a \]

\[ (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \]

\[ (0, 0, 0) \]

\[ (0, 2, 2) \]

\[ (0, 0, 2) \]

\[ (2, 2, 2) \]

\[ (2, 0, 0) \]

\[ (1, 1, 2) \]

\[ (1, 1, 0) \]

\[ (2, 1, 1) \]

\[ (1, 2, 1) \]

\[ (0, 2, 0) \]

\[ (2, 1, 0) \]

\[ (2, 2, 0) \]

\[ (0, 1, 1) \]

Real Space (BCC) Reciprocal Space (FCC)

With a (001) Surface

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Reciprocal Space (FCC)
With a (001) Surface

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CTR Diffraction – Instrumentation

GSECARS 13BMC Diffractometer
CTR Diffraction – Instrumentation

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CTR Diffraction – Instrumentation

- Sample Rotations (four)
- Sample Location and Center of all Rotations
- Detector Rotations (two)
- Pixel Array Area Detector
- X-ray In
- Flux Monitor, Instrument Shutter, Beam Slits and Filters
- Five Axis Instrument Centering Table

Reciprocal Space (FCC) With a (001) Surface

- (0 0 2)
- (2 0 2)
- (2 2 0)
- (0 2 2)
- (2 2 2)
- (0 0 0)
- (0 2 0)
- (2 0 0)
CTR Diffraction – Instrumentation

X-rays delivered from upstream optics

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CTR Diffraction – Instrumentation

\[ Q = k_r - k_i \]

Sample: bcc single crystal with a 001 surface

Reciprocal Space (FCC) With a (001) Surface
CTR Diffraction – Instrumentation

Reciprocal Space (FCC) With a (001) Surface

\[ \mathbf{Q} \]

\[ \mathbf{k}_i \]

\[ \mathbf{k}_r \]
CTR Diffraction – Measurement

Ewald Sphere

\[ Q, k_i, k_r \]

(0 0 1.3)

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CTR Diffraction – Measurement

\[ Q(0,0,1.3) \]

\[ |Q(0,0,1.3)| \]

Ewald Sphere
CTR Diffraction – Measurement

Ewald Sphere

Specular Rod:
- A rod that only probes the z direction of the crystal only
- Does not require order in x and y.

Off-Specular Rods:
- Rods that probe structure in z as well as x and y.
- Requires order in x and y.

\[ \mathbf{k}_i \]
\[ \mathbf{k}_r \]

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CTR Diffraction – Measurement – Off Specular Rod

$L = 0.3$

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CTR Diffraction – Measurement– Off Specular Rod

L = 0.6

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CTR Diffraction – Measurement– Off Specular Rod

L = 1.3

(1, 1, L)Rod

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CTR Diffraction – Measurement– Off Specular Rod

$L = 1.8$

$(1, 1, L)$

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CTR Diffraction – Measurement – Pixel Array Detector

FeOOH 00L Rod

PILATUS 100K detector
CTR Diffraction – Measurement – Specular Rod

$$(0, 0, L) \text{ or (Specular)Rod}$$

$L = 0.3$
CTR Diffraction – Measurement – Specular Rod

$(0, 0, L)$ or (Specular)Rod

$L = 0.6$
CTR Diffraction – Measurement – Specular Rod

(0, 0, L) or (Specular)Rod

$L = 1.3$
CTR Diffraction – Measurement – Specular Rod

$(0, 0, L)$ or (Specular)Rod

$L = 1.8$
For off-specular specify two diffraction geometry parameters:
1) Incidence angle \( \alpha \) that the \( k_i \) vector makes with the crystal surface
2) The angle \( \text{Naz} \) that the surface normal vector makes with the horizontal plane (a plan parallel to the floor in our lab)
Diffractometer Geometry – Specular Rod

For specular specify one diffraction geometry parameters:

1) The angle Naz that the surface normal vector makes with the horizontal plane (a plan parallel to the floor in our lab).

View from the source

View perpendicular to the source
Diffractometer Geometry – Finding the Surface Normal

Rotation Center of Eta

PHI

CHI
Diffractometer Geometry – Finding the Surface Normal

Laser Centered at: FLAT_CHI = -0.5 and FLAT_PHI = 10

Phi +10

Chi -0.25

Chi -0.25
Diffractometer Geometry: (1,1,1.6), Naz = 90°, alpha = 5°

Vertical Scattering Geometry
Diffractometer Geometry: (1,1,1.6), Naz = 0°, alpha = 5°

Horizontal Scattering Geometry
Data collection and reduction

Rod data set:

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Data collection and reduction

Data integration → Data Shell:

https://github.com/xraypy/tdl

Scan and point tree

Image view, ROI control, background subtraction and integration

Integration parameters

Correction factors

Point information

Corrected structure factor

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Sample Environments

In-situ liquid cells:

(a) Transmission and (b) thin film cells

(Fenter 2004)
Sample Environments

GSECARS \textit{in situ} liquid cell for radioactive material interface studies

\textit{Developed in collaboration with Moritz Schmidt, Paul Fenter and Lynda Soderholm (ANL)}

The radiological hazard must be mitigated at the beamline during the measurements

- Multiple containment required
- X-ray scattering compatible
- Remote liquid control

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Sample Environments

*In situ* gas cell for radioactive (or gas sensitive) material interface studies:
Sample Environments

Miniature electrochemistry cell

Collaboration with M. McBriarty, K. Rosso, PNNL

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Sample Environments

Adjustable gap thin membrane cell

- Humidity dome
- Check valve
- Solution syringe
- Gap Index ring
- Gap adjustment turn wheel
- ½"-20 Lead Screw
- PEEK sample cell
- Lead screw nut
- Radial bearing
- Solution inlet / outlet
- 300μm dia. X 25μm thick chalcophanite crystal
- Kapton solution capture membrane
- Thin flexible PEEK joint
- O-ring membrane Seal
- Quartz single crystal sample mount

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Electrochemistry at the (1-102) surface Hematite

Potential-Specific Structure at the Hematite–Electrolyte Interface


The atomic-scale structure of the interface between a transition metal oxide and aqueous electrolyte regulates the interfacial chemical reactions fundamental to (photo)electrochemical energy conversion and electrode degradation.
Electrochemistry at the (1-102) surface Hematite

The flux of current and ions across the interface are regulated by multiple electrolyte layers whose specific structure and polarization change in response to the applied potential.
References

Reference texts:

A few surface scattering methods papers:
Fenter P. A. (2002) Reviews in Mineralogy & Geochemistry 49, 149-220. (→ Excellent tech. review)

Reviews

Coordinate transformations, reciprocal space, diffractometry