Virtual Tutorial on Crystal Truncation Rod Diffraction for Atomic-Scale Surface Structure Measurement

Peter Eng – Beamline Scientist – eng@cars.uchicago.edu
Joanne Stubbs – Beamline Scientist – stubbs@cars.uchicago.edu
Anna Wanhala – Postdoctoral Scholar – wanhala@cars.uchicago.edu
Introduction to fitting CTR data

CTR suffers from same “phase problem” as all diffraction techniques
• Can’t directly invert data to find structure
• Build a model
• Calculate rods and compare to data
• Adjust structural parameters to optimize a figure-of-merit (chi-squared, R-factor, etc.)

Model construction
• Bulk lattice parameters and unit cell contents
• Surface lattice parameters and unit cell contents
• Roughness
• Scale factor

Fit algorithm
• Differential evolution (genetic algorithm)
• Non-linear least squares (e.g., Levenberg-Marquardt)
• Simplex
• Simulated annealing
Hematite bulk structure
Hexagonal - $a = 5.038$, $c = 13.772$
How is the surface terminated?

1 layer of Fe

2 layers of Fe

Oxygen

Adsorbates
Atomic positional relaxation due to presence of surface

Surface breaks 3-D space group symmetry
2-D plane group symmetry often remains intact (check with symmetry equivalent CTR’s)
Out-of-plane relaxation usually stronger than in-plane
Surface atoms may have different thermal/disorder displacement parameters from bulk.

Isotropic

Anisotropic

Fe Fe O
Surface roughness affects CTR’s

$\beta$–roughness model


$0 < \beta < 1$
Chemically identical, symmetry related terminations

Energetically equivalent
Polished surface – 50:50 ratio
GenX Fitting Software
http://genx.sourceforge.net/

Advantages
• Open-source, Python-based, modular – easily modified, customized
• Models available for x-ray and neutron reflectivity, CTR
• “Slab” (layer) based model construction
• Differential evolution (genetic algorithm) helps avoid local minima in which traditional downhill fits can get trapped
• Fit many parameters simultaneously

Disadvantages
• Individual fits are much slower than non-linear least squares (but time to structure solution is not necessarily longer)
• As currently implemented, error bar calculation does not consider covariance

Note about versions: Tutorial will use GenX2, but model has been tested with GenX3 (the latest version available on SourceForge)
CTR Data Fitting
Hematite bulk structure
Hexagonal - $a = 5.038$, $c = 13.772$

O6 Fe 11 Fe 10 O5 Fe 09 Fe 08 O4 Fe 07 Fe 06 O3 Fe 05 Fe 04 O2 Fe 03 Fe 02 O1 Fe 01
Fit results

L (Miller Index – reciprocal lattice units)
Fit results

L (Miller Index – reciprocal lattice units)
Fit results

$L$ (Miller Index – reciprocal lattice units)
Hematite bulk structure
Hexagonal - $a = 5.038$, $c = 13.772$
Fit results

$L$ (Miller Index – reciprocal lattice units)
Big improvement in fit quality with more dz’s deeper below surface – why?

**Fit 3:**
dz’s for top O and 2 Fe
FOM = 21

<table>
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<tr>
<th>Parameter</th>
<th>Value</th>
<th>Fit</th>
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<tr>
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</table>

The fit could only use the parameters we allowed to vary and did the best it could.

Letting additional dz’s vary results in smaller dz displacements from bulk positions (some with opposite signs) for the original 3 atoms.

**Fit 4:**
Add dz’s for next set of O and 2 Fe
FOM = 5.8

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</table>

Occupancies and roughness have also changed.
So far we have only considered out of plane relaxation (dz), not in-plane.

What about dx and dy? Before we turn these on, we need to decide whether this is allowed by symmetry.

- Hematite crystallizes in space group R -3 c, in which there are 3-fold axes parallel to c at
  \[
  \begin{align*}
  x &= 0 & y &= 0 \\
  x &= 1/3 & y &= 2/3 \\
  x &= 2/3 & y &= 1/3 
  \end{align*}
  \]
- All Fe atoms lie on these special positions in x, y
- To move them would split them into 3 separate positions, thus the Fe atoms cannot move in x, y
- O atoms do not lie on special positions in x, y and are three-fold in multiplicity. They can move so long as their three-fold symmetry is maintained, which is handled by the symmetry code in GenX.
Fit results

\[ |F_{HKL}| \text{(arb. units)} \]

L (Miller Index – reciprocal lattice units)
So far we have assumed surface atoms have the same disorder/thermal (Uiso) parameters as bulk atoms, but this is not always true.
Fit results

$L$ (Miller Index – reciprocal lattice units)
Dry surface under helium is a simple example
GSECARS users are generally interested in measuring more complicated systems

Good fit from simple model:
• Scale factor
• Roughness
• Occupancies for top 3 atomic layers
• Surface-normal displacements (dz’s) for top 6 atomic layers
• Effects of in-plane O displacements (dx, dy) and temperature factors are small for this system
Adsorption and incorporation of cations from aqueous solutions

Response of interfacial water to arsenate adsorption on corundum (001) surfaces: Effects of pH and adsorbate surface coverage

Pb Sorption at the Barite (001)-Water Interface
Economic geology problems

Mineral–Water Interface Structure of Xenotime (YPO₄) {100}

• Contains HREEs important to energy technologies
• Difficult to separate from “gangue” (waste minerals)
• Flotation is promising, but need to design ligands

Hydration Structure of the Barite (001)–Water Interface:
Comparison of X-ray Reflectivity with Molecular Dynamics Simulations

• Important in pipeline scale

Barite scale in offshore well pipe
http://hitcleanproject.co.uk/project/
Surface-mediated nucleation and growth

Epitaxial Growth of Gibbsite [Al(OH)₃] Sheets on the Basal Surface of Muscovite Mica

• Gibbsite sheets form 3 structurally related domains, one layer thick
• Total coverage < 70%, may be limited by charge balance and antiphase domain boundaries
• Implications for weathering, secondary minerals (clays, Al-oxyhydroxides)

Gibbsite and muscovite contain similar dioctahedral Al sheets
**Electrochemistry at the mineral-water interface**

Miniature electrochemistry cell designed and fabricated in house

Potential-Specific Structure at the Hematite-Electrolyte Interface

Reductive dissolution mechanisms at the hematite-electrolyte interface probed by in situ X-ray scattering

Water molecules flip in response to applied potential at pH 7

**Redox control for geochemical problems as well as energy technologies**

At pH 4 cathodic bias induces dissolution of high-energy interfacial species, effectively annealing surface. Removal of bias results in disordered Fe reprecipitation.
Ready to try fitting?

The following will be available after the tutorial (we’ll send an email with links for downloads)

- Slides from today’s presentations
- Data and model from today’s demonstration
- Step-by-step fitting instructions

If there is sufficient interest, we can hold a separate workshop in which participants run fits on their own computers with guidance from us
Applying for Beam Time

- The APS and GSECARS make beam time available to the international scientific community through the APS General User Program
  
- Proposals are submitted, peer-reviewed, and allocated beam time 3 times per year

- There is no charge to use the APS and GSECARS

- In addition to supporting measurements at the beamline (including remote measurements during the COVID-19 pandemic), we also help users with proposal writing and data analysis

- We welcome and enjoy working with novice users including students

Acknowledgments

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