Non-Ideal Data

_Diffraction in the Real World_

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http://prism.mit.edu/xray
The calculated diffraction pattern represents the ideal X-ray powder sample

- The ideal powder sample
  - Millions of grains
  - Randomly oriented grains
  - Flat
  - Smooth surface
  - Densely packed
  - Homogeneous
  - Small grain size (less than 10 microns)
  - Infinitely thick
Preferred Orientation (aka Texture): non-random orientation of crystallites

- If the crystallites in a powder sample have plate or needle like shapes it can be very difficult to get them to adopt random orientations
  - top-loading, where you press the powder into a holder, can cause problems with preferred orientation
- in samples such as metal sheets or wires there is almost always preferred orientation due to the manufacturing process
- for samples with systematic orientation, XRD can be used to quantify the texture in the specimen
- Preferred orientation causes a systematic error in peak intensities
Phase ID of samples with Preferred Orientation

- Preferred Orientation causes a systematic error in peak intensities
- When executing a Search & Match for phase ID, you can no longer use peak intensities to help identify the phases that are present
  - Uncheck “Match Intensity” and “Demote unmatched strong”
- It becomes more necessary that you know the chemistry and origin of the sample that you are analyzing
Practice Phase ID

- Open Steel_Original_C1.xrdml
- Fit background and search peaks
- Run Search & Match
  - Search with “Match Intensity” and “Demote unmatched strong”; do not constrain chemistry
  - Search with restrictions: EDXRF showed that Fe was the majority element (above Mg), along with small amounts of Cr.
  - Search with restrictions and with “Match Intensity” and “Demote Unmatched Strong” unchecked
Figure out what crystallographic directions are preferred

• Accept Fe as a match
  – Ferrite and austenite

• Determine the texture component for Austenite first

• To see peak (hkl)’s
  – In the Accepted Pattern List, right-click
  – Select Analyze Pattern Lines

• This table makes it easy to see what major peaks are missing peaks of the preferred orientation
Figure out what crystallographic directions are preferred

- To label the peak markers
  - Select menu Customize > Document Settings
  - Go to the Legends & Grids tab
  - Click on the button Pattern View Legend
  - Check Line hkl
  - Click OK
  - Check “Label pattern lines with pattern view legend”
  - Click OK
The table shows us the (hkl) of peaks that are missing; the main graphics shows us the (hkl) of peaks that are stronger than expected.

- (022) peak of austenite is stronger than expected
- Suggests [011] texture
To Refine the Preferred Orientation

• Add the reference pattern to the Refinement Control
  – Go to the Pattern List
  – Right-click on the both Fe entries and select *Convert pattern to phase*

• To set the preferred orientation
  – In the Refinement Control list, click on the second Fe phase
    • Make sure the symmetry is FCC
  – Change the title to Austenite
  – In the Object Inspector, find the Preferred Orientation section
  – Set the Direction h, k, and l
  – The Parameter (March/Dollase) is the amount to preferred orientation
    • 1 indicates random orientation
    • <1 indicates preferred platy orientation
    • >1 indicates preferred needle orientation
We will use Automatic Refinement

• The Preferred orientation setting is turned on
• It contains a “Toggle Directions” option so that the computer will try to figure out what the preferred orientation is
  – We made an educated guess, so we turn this off
The austenite is well refined, so we need to determine the orientation of the ferrite.
Refining 21 parameters to get a 6.3% weighted R profile

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</tbody>
</table>
The residual is good, but the fit still has areas of mismatch.
Finishing steel

- How I finished the refinement of steel
  - Refine all background parameters
  - Refine specimen displacement
  - Refine \( W \), then \( V \), then \( U \) one at a time
  - Turn off specimen displacement, turn on lattice parameters (cells)
  - Turn on specimen displacement
  - Refine \( W \)
  - Refine Peak Shape 1
  - Weighted R Profile= 6.3%
Another preferred orientation example

- Open snail_texture-small section.raw
- Fit background and search peaks
- Run Search & Match
  - Search with “Match Intensity” and “Demote unmatched strong”; do not constrain chemistry
  - Search with restrictions: EDXRF showed that Ca was the only element above Mg that was present
  - Search with restrictions and with “Match Intensity” and “Demote Unmatched Strong” unchecked
Figure out what crystallographic directions are preferred

• Accept calcite as a match
• To see peak (hkl)’s
  – In the Accepted Pattern List, right-click
  – Select Analyze Pattern Lines
• This table makes it easy to see what major peaks are missing peaks of the preferred orientation
The table shows us the (hkl) of peaks that are missing; the main graphics shows us the (hkl) of peaks that are stronger than expected.

- (hh0) and (hhk) peaks tend to be stronger and (00l) peaks weaker
- Suggests (110) texture
To Refine the Preferred Orientation

• Add the reference pattern to the Refinement Control
  – Go to the Pattern List
  – Right-click on the calcite entry and select *Convert pattern to phase*

• To set the preferred orientation
  – In the *Refinement Control* list, click on the Calcite phase
  – In the Object Inspector, find the Preferred Orientation section
  – Set the Direction h, k, and l
  – The Parameter (March/Dollase) is the amount to preferred orientation
    • 1 indicates random orientation
    • <1 indicates preferred orientation
    • >1 indicates avoided orientation
Correlation matrix shows correlation between:
- Specimen displacement and lattice parameters
- Peak width and preferred orientation
Undo and Try Again

- Change the Automatic Rietveld steps
  - Do not refine Lattice Parameters and \( W \) (Halfwidth)
  - Refine Preferred orientation before refining peak positions (specimen displacement)
    - After scale factor adjusts, there is not enough intensity for different peaks to refined the peak positions
The low angle data fits well with this preferred orientation model.
This is an example of strong preferred orientation

- The March-Dollase function can only work for limited cases of preferred orientation
- A program with spherical harmonics can model more pronounced types of preferred orientation
- In a case like this, the texture needs to be studied using pole figure analysis; Rietveld can provide only limited results
• More preferred orientation with J Kaduk “Dealing with Difficult Samples”
Other complications: fluorescence

- We are studying Fe-bearing steel with a diffractometer that used Cu wavelength radiation.
- Fe and Co absorb the Cu wavelength radiation, and then fluoresce that energy as their characteristic X-rays.
  - These fluoresced X-rays become background noise.
  - The absorption of X-rays also decreases the depth of penetration of the X-rays, which limits the irradiated volume of the sample and makes it more probable that you will have problems with particle statistics.
How to calculate the depth of penetration

• \( t = 0.5L \sin \theta \)
  – \( t \) is the thickness of the sample contributing to 99% of the diffracted intensity
  – \( L \) is the path length calculated based on the formula:
    • \( I_L = I_0 \times \exp^{-\left(\frac{\mu}{\rho}\right)\rho L} \)
  – *but all that math is hard ... so let Thomas Degen do it for you*
  – go to menu *Tools > MAC Calculator*

• Penetration depth is 6 microns with Cu wavelength radiation and 31 microns with Co wavelength radiation
Problems with Fluorescence

- Increases background noise
- Decreases irradiated volume
- Decreases the diffraction signal
  - Decreases the fraction of X-rays scattered by the sample
  - Every X-ray that is absorbed is an X-ray that was not diffracted
- Best solution is to change the X-ray anode
  - This is not always practical
- A diffracted-beam monochromator can eliminate the fluoresced X-rays, decreasing the background noise
  - This also decreases the overall signal

<table>
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<tr>
<th></th>
<th>Peak Ht:Bkg</th>
<th>Ratio</th>
<th>Peak Area</th>
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</thead>
<tbody>
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<td>Without monochromator</td>
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<td>1.98</td>
<td>1565</td>
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<tr>
<td>With monochromator</td>
<td>1157:45</td>
<td>25.7</td>
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</table>
Anistropic Peak Broadening

- Small crystallite sizes produce peak broadening
- If the nanocrystals in a sample have an anistropic shape, then different peaks will be broadened differently
  - Example: nanorod in which the axial direction of the rod corresponds to the c-axis of the crystal
    - The crystal dimension in the c direction is much larger than the direction in the a or b directions
    - The (00l) peaks, which correspond to planes stacked along the c-axis, will be sharper—corresponding to the larger dimension
    - The (h00), (0k0), and (hk0) peaks, which correspond to planes stacked along the diameter of the nanorod, will be broader—due to the smaller dimension.
Anisotropic broadening can also change peak heights, giving the appearance of preferred orientation along the c-axis.
The anisotropic broadening model in HSP can deal with many simple cases.
More complex cases may require using multiple models of the phase

- In the **Refinement Control**, right-click on phase and select *Duplicate Phase*
- One phase may model anisotropic broadening in the [100] direction and the second phase may model anisotropic broadening in the [110] direction
- This approach also works for modeling more complex types of preferred orientation—create two phases with different preferred orientation functions
Anisotropic Peak Broadening may also be due to complex defect structures in layered materials

- In this case, \((h0h)\) peaks are broadened and asymmetric
- this is due to a lack of correlation between well-formed \((h0h)\) planes
- This cannot be modeled in current Rietveld codes
Dealing with Peak Asymmetry

- Peak asymmetry is produced by:
  - Axial divergence
  - Sample transparency
- Axial divergence can be reduced by using Soller slits
Sample Transparency Error

• X Rays penetrate into your sample
  – the depth of penetration depends on:
    • the mass absorption coefficient of your sample
    • the incident angle of the X-ray beam
• This produces errors because not all X rays are diffracting from the same location
  – Angular errors and peak asymmetry
  – Greatest for organic and low absorbing (low atomic number) samples
• Can be eliminated by using parallel-beam optics
• Can be reduced by using a thin sample

\[ \Delta 2\theta = \frac{\sin 2\theta}{2\mu R} \]

\( \mu \) is the linear mass absorption coefficient for a specific sample
Modeling peak asymmetry in HighScore Plus

- The asymmetry correction that works with the pseudo-Voigt function only offers limited adjustment

![Graph showing no asymmetry correction and full asymmetry correction.](image)
The Pseudo Voigt 3 (FJC Asymmetry) correction can be manually adjusted to model more pronounced asymmetry.

- S/L Asymmetry and D/L Asymmetry cannot be refined.

Procedure:
- Run a simple low angle standard such as mica or silver behenate.
- Manually adjust S/L and D/L to fit your data.
- Use those values in the refinement of your sample of interest.
  - This only works if your sample does not contribute additional asymmetry due to transparency.
Exercise: modeling asymmetry

• Open the file “Silver Behenate.hpf”
  – We have modeled the silver behenate as an orthorhombic unit cell
  – The most important parameter is the $c \approx 58.06\text{Å}$
  – We are using a LeBail fit because the crystal structure of silver behenate is not known

• Change the peak profile to Pseudo Voigt 3(FJC Asymmetry)
  – This is found in the Refinement section of the Object Inspector for Global Parameters

• Start a refinement

• Begin to manually vary S/L and D/L Asymmetry in the Profile Variables for the phase, running the refinement again each time

• You may be able to try refining S/L or D/L with no other variables
- $S/L = 0.025$
- $D/L = 0.025$
• J Kaduk follow up comments on transparency
• J Kaduk slides on Absorption, Surface Roughness, and Particle Statistics
• Skip to Speakman constant volume assumption, thin samples, inhomogeneous samples
Particle Statistics

- XRPD Methods are based on the irradiation of millions of crystallites in a polycrystalline sample
- If there are not enough crystallites contributing to the diffraction pattern, then the observed peak intensities will be erroneous
- Poor particle statistics may be created if:
  - The average grain size is too large
  - The irradiated volume is too small
    - Either because the X-ray beam is too small or because there is not enough material in the sample
  - The collimation of the X-ray beam is too tight
  - These factors interrelate- the grain size that is acceptable for a loosely collimated X-ray beam might be too large for a tightly collimated X-ray beam
Only a small fraction of the crystallites irradiated contribute to the diffraction pattern

- A diffraction peak is observed when the crystallographic direction is parallel to the diffraction vector
  - The crystallographic direction is the vector normal to the family of atomic planes that produce the diffraction peak
  - The diffraction vector is the vector that bisects the angle between the incident and scattered X-ray beam

The crystallographic direction (black arrow) is parallel to the diffraction vector (blue arrow), so the illustrated planes will diffract.

The crystallite is now tilted so that the crystallographic direction (black arrow) is NOT parallel to the diffraction vector (blue arrow), so the illustrated planes will NOT diffract.
Only a small fraction of the crystallites irradiated contribute to the diffraction pattern

- A small fraction of crystallites will be properly oriented to diffract for each observable

A small fraction of grains (shaded blue) in this sample are properly oriented to produce the (100) diffraction peak

A different fraction of grains (shaded blue) are properly oriented to produce the (110) diffraction peak

Some grains (shaded blue) are oriented in such a way that they do not contribute to any diffraction peak
Particle Statistics are determined by

• The number of crystallites that are irradiated
  – The irradiated volume
    • The irradiated area (width and length of the X-ray beam)
    • The depth of penetration of the X-rays
  – The average crystallite size
  – The particle packing factor (porosity)

• The fraction of irradiated crystallites that contribute to the diffraction peak
  – Vertical divergence of the X-ray beam
  – Detector size and aperture (receiving slit)
The Number of Irradiated Crystallites

• The Irradiated Volume will be discussed in the next section (the constant volume assumption)
  – The X-ray beam width and length are determined by the instrument configuration
  – The depth of penetration depends on $\mu$, the linear mass absorption coefficient, of the specimen
  – For now, the irradiated volume will be treated as a value $V_i$

• The number of irradiated crystallites ($N_i$) is: 
  
  \[ N_i = \frac{V_i}{a^3} \]

  – $a$ is the average crystallite size
    • Assumes a cubic crystallite shape where the length of the side of the cube is $a$
    • Empirical testing has shown that $a < 5 \, \mu m$ gives the best statistically valid results
    • A 20 mm crystallite size will produce 64times fewer irradiated grains
Preparing a powder specimen

• An ideal powder sample should have many crystallites in random orientations
  – the distribution of orientations should be smooth and equally distributed amongst all orientations
• If the crystallites in a sample are very large, there will not be a smooth distribution of crystal orientations. You will not get a powder average diffraction pattern.
  – crystallites should be <10µm in size to get good powder statistics
• Large crystallite sizes and non-random crystallite orientations (preferred orientation) both lead to peak intensity variation
  – the measured diffraction pattern will not agree with that expected from an ideal powder
  – the measured diffraction pattern will not agree with reference patterns in the Powder Diffraction File (PDF) database
Spotty Debye diffraction rings from a coarse grained material

Polycrystalline thin film on a single crystal substrate

Mixture of fine and coarse grains in a metallic alloy

Conventional linear diffraction patterns would miss information about single crystal or coarse grained materials
Working with large grain size materials

• We talked about ways to prepare and collect data from large grain size materials on Tuesday morning

• If you have spotty data from a sample with large grain sizes
  – you cannot determine quantitative weight fraction of that material
    • you can determine the quantities of the other phases in the mixture
    • fit the large grain size material as a ‘dummy’ phase
  – you cannot refine the crystal structure
  – you can determine unit cell lattice parameters
  – you can determine crystallite size and microstrain

• Large grain size may produce irregular peak shapes
Large grain sizes can create irregular peak shapes

- The Si powder in this sample was much too coarse
- This data is unusable for refinement
  - No data treatment tricks can save this data
- Better data is needed
  - Pulverize & grind the powder
  - Spin the sample
  - Oscillate the sample
  - Use a Wobble scan
  - Use a larger beam size
  - Use a larger detector
The constant volume assumption

• In a polycrystalline sample of ‘infinite’ thickness, the change in the irradiated area as the incident angle varies is compensated for by the change in the penetration depth
• These two factors result in a constant irradiated volume
  – (as area decreases, depth increase; and vice versa)
• This assumption is important for many aspects of XRPD
  – Matching intensities to those in the PDF reference database
  – Crystal structure refinements
  – Quantitative phase analysis
• This assumption is not necessarily valid for thin films or small quantities of sample on a ZBH
Varying Irradiated area of the sample

- the area of your sample that is illuminated by the X-ray beam varies as a function of:
  - incident angle of X rays
  - divergence angle of the X rays
- at low angles, the beam might be wider than your sample
  - “beam spill-off”
Varying Length of X-Ray Beam

- Length (mm) = $R \frac{\alpha}{\sin \theta}$
  - $R$ is goniometer radius in mm
  - $\alpha$ is the divergence angle of the beam in radians
Deviations from the constant volume assumption: Beam Overflow

- Beam Overflow, aka beam spill-off
- At low angles, the X-ray beam might be larger than the sample
  - example: a ½ deg divergence slit will produce a 48.5mm long X-ray beam at 5deg 2theta
    - this might be a bit larger than your 5mm x 5mm sample
- Corrections
  - use a smaller divergence slit for low angle data
    - this will yield weaker peak intensities at high angles of 2theta
  - use Treatment > Corrections > Correct Beam Overflow option in HSP
  - throw away (clip or exclude) low angle data where beam was larger than sample
  - use automatic divergence slits
Deviations from the constant volume assumption: Automatic Divergence Slits

• Automatic Divergence Slits (ADS) is possible with computer-controlled variable divergence slits
  – the divergence slit is changed during the scan to maintain a constant X-ray beam length
  – advantage: get better intensity at high angles without risking beam overflow at low angles
  – disadvantage:
    • at higher angles, the background is noisier and the peaks are broader because of the larger divergence slit
    • constant volume assumption not preserved
      – as penetration depth increases, the X-ray beam length does not shorten
      – have more irradiated volume at higher angles
Deviations from the constant volume assumption: Automatic Divergence Slits

• How to correct for increasing irradiated volume due to automatic divergence slits
• Correct with HSP
  – use Treatment > Corrections > Convert Divergence Slit

  – a round-robin led by Armel LeBail showed that converted ADS data works as well as data collected with fixed divergence slits
Deviations from the constant volume assumption: Thin Samples

- If the thickness of a sample is not greater than the maximum penetration depth of the X-ray beam, then the constant volume assumption will not be preserved
  - when the penetration depth exceeds the thickness of the sample, intensity will begin to decrease as $1/\sin \theta$
- A sample may be thin because of
  - preparation as a monolayer of powder on a ZBH
  - a thin film on a substrate
  - it is just a wafer thin sample
Dealing with Thin Samples

• Use automatic divergence slits
  – useful only for very thin samples, when the penetration depth of the X-ray beam exceeds the sample thickness over the entire measurement range
  – maintains a constant irradiated length, and the thinness of the sample enforces a constant penetration depth
    • consequently, the irradiated volume is constant
  – when you collect data from a thin sample using ADS, you need to lie to HSP and tell it that you used fixed slits
    • HSP takes ‘fixed slits’ to mean that the constant volume assumption was observed
    • select the pattern in the Scan List
    • in the object inspector, find instrument settings > divergence slit type
      – change from automatic to fixed
Dealing with Thin Samples

• If data were collected with a fixed slit, apply a divergence slit correction
  – Then, lie to HSP and tell it that the data are from automatic slits
    • select the pattern in the Scan List
    • in the object inspector, find instrument settings > divergence slit type
  – change from automatic to fixed use Treatment > Corrections > Convert Divergence Slit
    • convert data from fixed to automatic slit
    • applies a sin $\theta$ correction to the peak intensities

• This has limited effectiveness in my experience
  – this approach greatly increases noise at high angles
Dealing with Thin Samples

• Use grazing incidence angle X-ray diffraction
  – only if you are using parallel-beam optics
    • loss of angular resolution- peaks are broadened
  – use a fixed incident angle, so that the irradiated area does not change
    • the incident angle is fixed at a small value to limit the depth of
      penetration of the X-rays, favoring scattering from the upper layers of the
      thin film

• GIXD used to be the standard for thin film analysis
  – when given the choice between GIXD with a point detector or Bragg-
    Brentano geometry with the X’Celerator, the choice is harder
    • often get more intensity from thin film peaks using the more efficient
      detector rather than the grazing incident angle
What if we cannot compensate for a thin sample?

• There will be errors in the refined model—especially thermal parameters
  – the model will try to compensate for the intensity being too low at higher angles of 2theta

• We can still use Rietveld refinement to quantify parameters that are independent of intensity
  – unit cell lattice parameters
  – nanocrystallite size and microstrain

• We can do semi-quantitative phase composition analysis
  – use the RIR method with peaks that are close to each other
  – over a narrow range of 2theta, we can approximate the irradiated volume as nearly constant
Inhomogeneous Samples

- The changing size of the X-ray beam can be problematic if the sample is inhomogeneous
  - Poorly mixed powder
  - Layered microstructure, such as coatings on a substrate
- To collect refinable data, do not allow the X-ray beam size to change during the data collection
  - Use GIXD technique (fixed incident beam)
  - Use automatic divergence slits if the sample is thin
    - The penetration depth will change during the scan, even if the X-ray beam length is held constant—so there must not be any thickness to allow the changing penetration depth.