

Handout 11: Powder Methods

Beyond Simple Phase ID
Possibilities, Sample Preparation and Data Collection

Chem 6850/8850

X-ray Crystallography

Department of Chemistry & Biochemistry

cora.lind@utoledo.edu



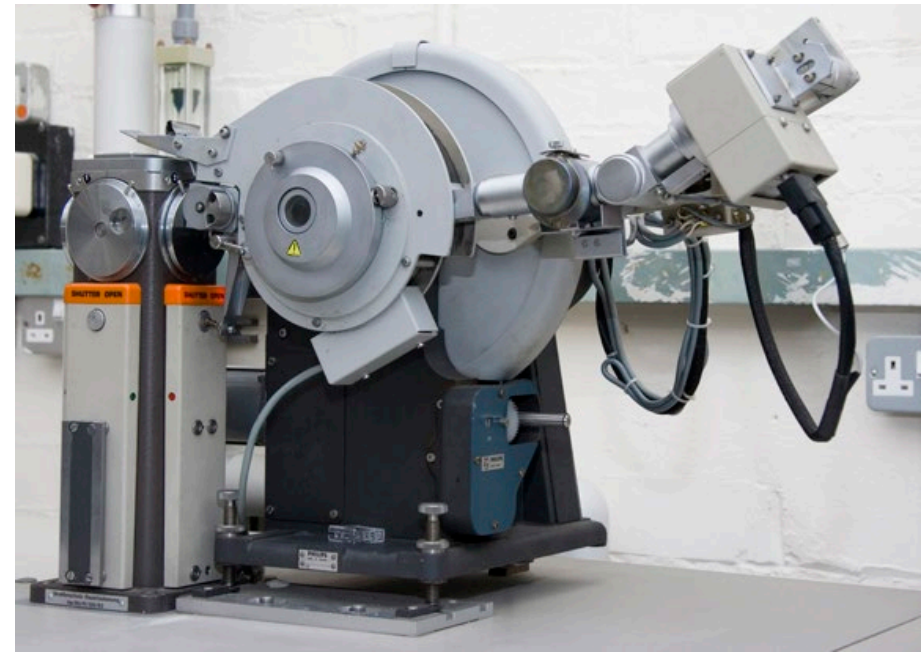
THE UNIVERSITY OF
TOLEDO

History of Powder Diffraction

- **Discovery of X-rays: Roentgen, 1895 (Nobel Prize 1901)**
- **Diffraction of X-rays: von Laue, 1912 (Nobel Prize 1914)**
- **Diffraction laws: Bragg & Bragg, 1912-1913 (Nobel Prize 1915)**
- **Powder diffraction: Developed independently in two countries:**
 - Debye and Scherrer in Germany, 1916
 - Hull in the United States, 1917
- **Original methods: Film based**
- **First commercial diffractometer:**

Philips, 1947 (PW1050)

<http://www.msm.cam.ac.uk/xray/images/pdiff3.jpg>



Original Powder Setups

- Oldest method: Debye-Scherrer camera
 - Capillary sample surrounded by cylindrical film
 - Simple, cheap setup

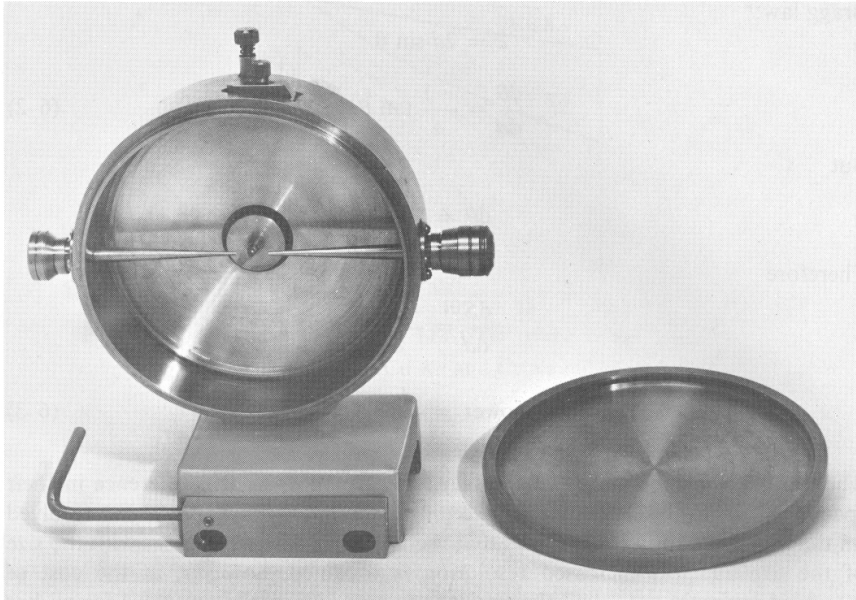


Fig. 6-1 Debye-Scherrer camera, with cover plate removed. (Courtesy of Philips Electronic Instruments, Inc.)

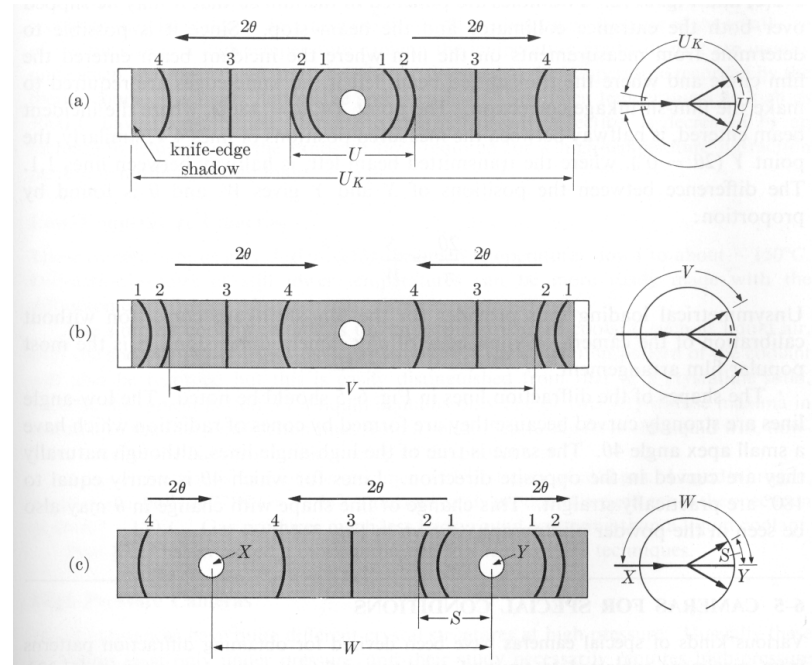


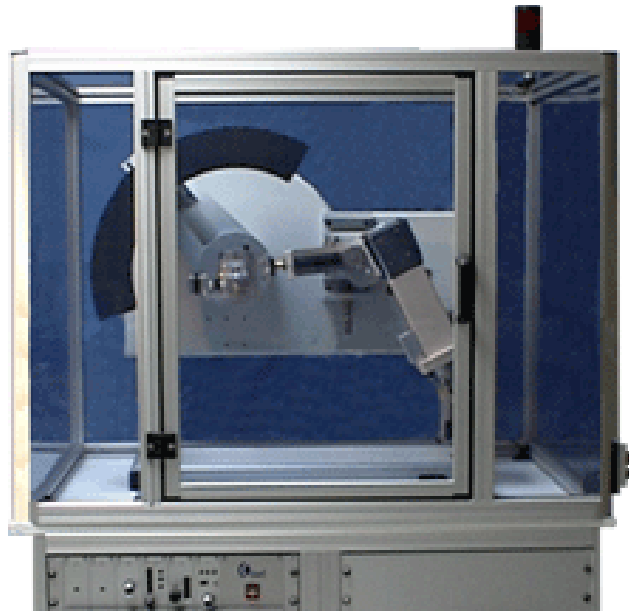
Fig. 6-5 Methods of film loading in Debye cameras. Corresponding lines have the same numbers in all films.

Cullity; "Elements of X-ray Diffraction"



Modern Powder Setups

- Powder diffractometers
 - theta-theta or theta-2theta
 - point or area detectors



Inel diffractometer with 120° PSD
(position sensitive detector)



Scintag theta-theta diffractometer with Peltier
cooled solid-state detector



Physical Basis of Powder Diffraction

- Powder diffraction obeys the same laws of physics as single crystal diffraction
- Location of diffraction peaks is given by Bragg's law
 - $2d \sin\theta = n\lambda$
- Intensity of diffraction peaks is proportional to square of structure factor amplitude

$$F(hkl) = \sum_{j=1}^N f_j \exp(2\pi i(hx_j + ky_j + lz_j)) \cdot \exp[-8\pi^2\langle u^2 \rangle (\sin^2(\theta)/\lambda^2)]$$

Goal of crystallography: Get structure

- **Single crystal experiments**

- Grow crystals (often hardest step)
- Collect data (usually easy, both access and setup)
- Determine unit cell (very easy for good quality single crystal)
- Reduce data and solve (=determine approximate structure) (often easy)
- Optimize structure (=refinement) (requires some care)

- **Powder experiments**

- Prepare powder sample (often easy)
- Collect data (usually easy, but easy to make mistakes, too!)
- Determine unit cell (can be very hard)
- “Solve structure” (can be even harder – requires expert knowledge!)
- Optimize structure – Rietveld refinement (requires considerable care)

Why Use Powder Diffraction?

- **Originally, powder diffraction was mainly used for phase identification**
- **Advantages over single crystal methods: Can be used on ANY sample**
 - If you can mount it, you can measure it!
- **For some materials, single crystal growth is difficult or impossible**
 - Powder methods are the only option
- **“Real life samples” rarely come as single crystals: Engineering materials, formulations etc.**
 - Powder diffraction can be used on mixtures of compounds
 - Peak shape analysis gives insights into size, stress and defects

Powder crystallography before Rietveld

- Primary strategy: AVOID when it comes to structure determination!
 - There was no straightforward way to deal with data
 - Had to manually integrate intensities
 - Overlapping reflections were a big problem
 - Usually discarded
 - Alternative: Rewriting of single crystal software to refine using sums of overlapped reflections
- Powder pattern simulation was more common
 - Relatively straightforward
 - Conclusions drawn based on similarities between patterns (e.g., isostructural compounds)
 - Visual comparison
- Main use of powder diffraction was for phase identification

Modern Use: What Information Can We Get From Powder Diffraction Data?

- **Phase identification (qualitative phase analysis)**
 - Most important/ frequent use of PXRD
 - Qualitative analysis tool
 - A powder pattern can be searched for the presence of known phases
 - Starting materials
 - Known target compounds
 - Likely impurities
 - A pattern can be compared to a database to identify phases present
 - Assumption: The material, or an isostructural material, is in the database

What Information Can We Get From Powder Diffraction Data? (2)

- **Phase fraction analysis (quantitative phase analysis)**
 - Applied to mixtures of two or more crystalline phases
 - Compare intensities of selected peaks of all phases
 - Theoretically only requires one peak per phase
 - Better values when using multiple peaks
- **Accurate analysis requires standardization**
 - Mix known quantities of two phases in several different ratios
- **Caution: Possibility of amorphous components**
 - No contribution to Bragg peaks, but contributes weight

What Information Can We Get From Powder Diffraction Data? (3)

- **Lattice parameters**
 - Two modes of analysis:
 - Accurate lattice parameters for a compound of known structure (example: solid solutions)
 - Lattice parameter/unit cell determination for an unknown compound through indexing
- **For this type of analysis, ACCURATE peak positions are crucial!**
 - Instrument needs to be well aligned, or data need to be corrected

What Information Can We Get From Powder Diffraction Data? (4)

- **Rietveld refinement (structural analysis)**
 - Least squares based minimization algorithm to obtain the best fit between a structural model and a powder pattern
 - You need a starting model to apply this method
 - Known compounds
 - Can be applied to isostructural compounds by substituting different atoms
 - Applicable to simple and complicated structures, single phase and multi-phase samples
 - Automatically gives you phase fractions and lattice parameters
 - Uses ALL peaks to determine this information!
 - Requires good data for meaningful results



What Information Can We Get From Powder Diffraction Data? (5)

- **Structure Determination from Powder Data (SDPD)**
 - Powder diffraction is subject to the same laws of physics as single crystal diffraction
 - However, data are “overlapping”, limiting the accessible information compared to single crystal experiments
 - 1D or 2D data
 - Careful analysis can allow determination of unknown structures
 - This type of analysis is non-trivial, requires excellent data quality, and sound crystallographic knowledge!

What Information Can We Get From Powder Diffraction Data? (6)

▪ Line shape analysis

- Width of Bragg peaks is inversely related to crystallite size
 - Often used for crystallite size estimates for nanoparticles
 - Requires use of a standard to determine instrument contribution first
- Microstrain (nonuniform strain) also results in peak broadening
 - Due to atomic disorder, dislocations, vacancies etc.
 - Different angular dependence than size effects
 - Residual stress can be determined
- Defects such as stacking faults and antiphase boundaries will also affect the line shape

What Information Can We Get From Powder Diffraction Data? (7)

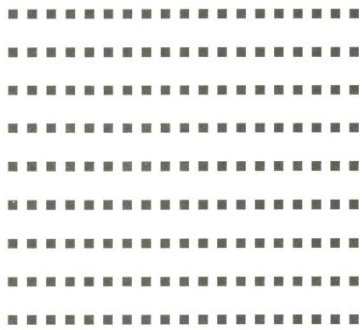
- **Texture analysis**
 - Epitaxial growth in thin films
 - Preferred orientation
 - Qualitative and quantitative measurements possible
- **Phase transition behavior**
 - *In situ* diffraction experiments
 - Temperature-induced phase transitions
 - Pressure-induced phase transitions
 - Kinetic studies
 - Requires specialized setups

What is a Powder?

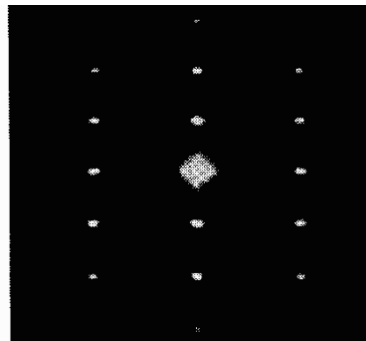
- **A perfect powder sample consists of an infinite number of small, randomly oriented crystallites**
 - Note that this is the underlying definition for many quantitative analysis methods!
- **“Powder samples” can come in many different forms:**
 - Loose powders
 - Films, sheets, blocks, wires...
 - Basically any “polycrystalline” sample can be used in PXRD – if it is not a single crystal, it is usually considered a “powder sample”

Observations from Single Crystals

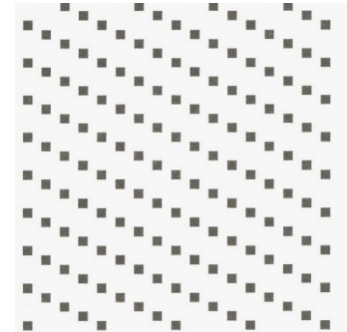
- For a single crystal, there is one orientation in real space, resulting in one orientation of the reciprocal lattice
 - reciprocal lattice points are resolved and will result in diffraction intensity when they touch the Ewald sphere
 - Rotating the crystal rotates the reciprocal lattice



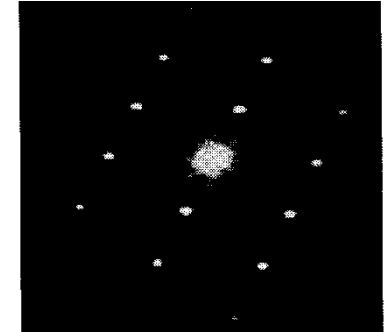
Real space



Reciprocal space



Real space

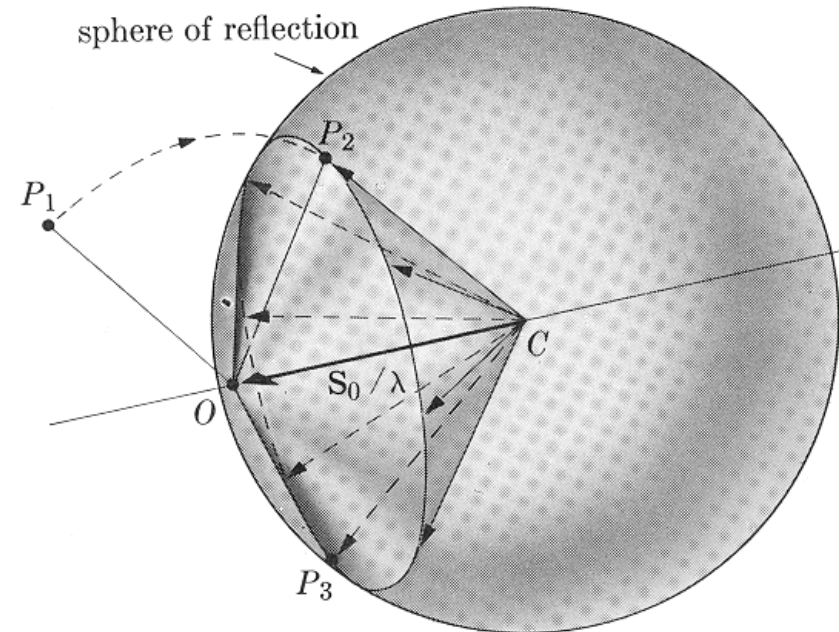


Reciprocal space



Observations from Powders

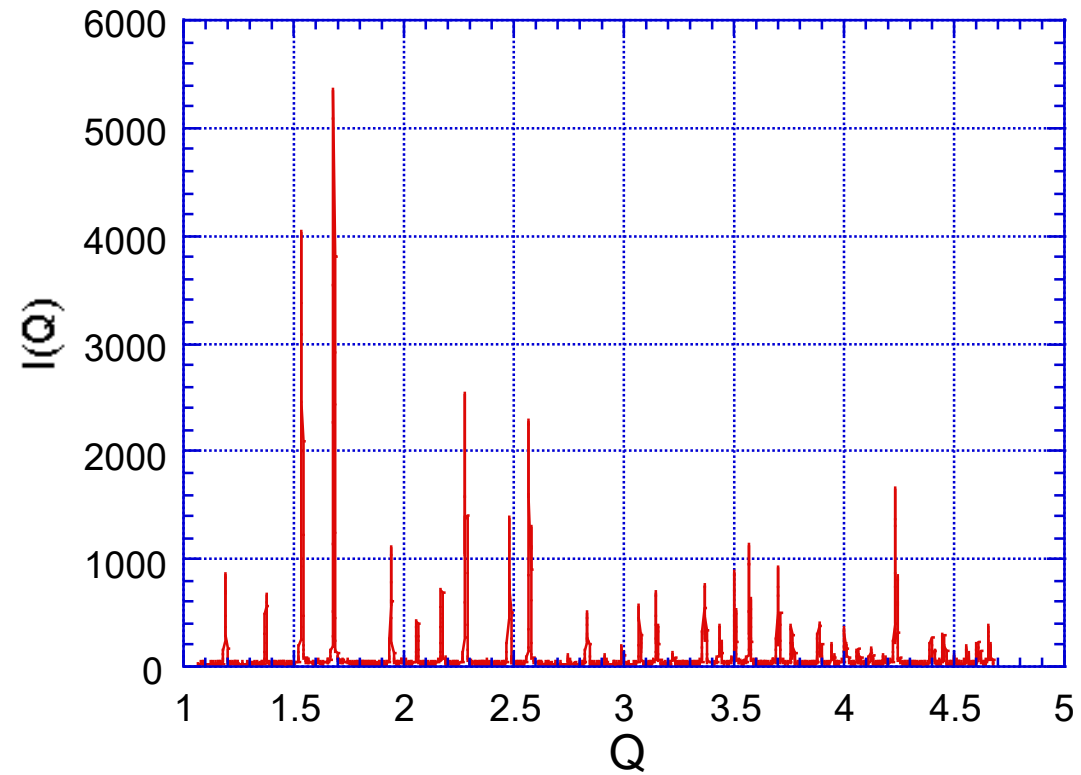
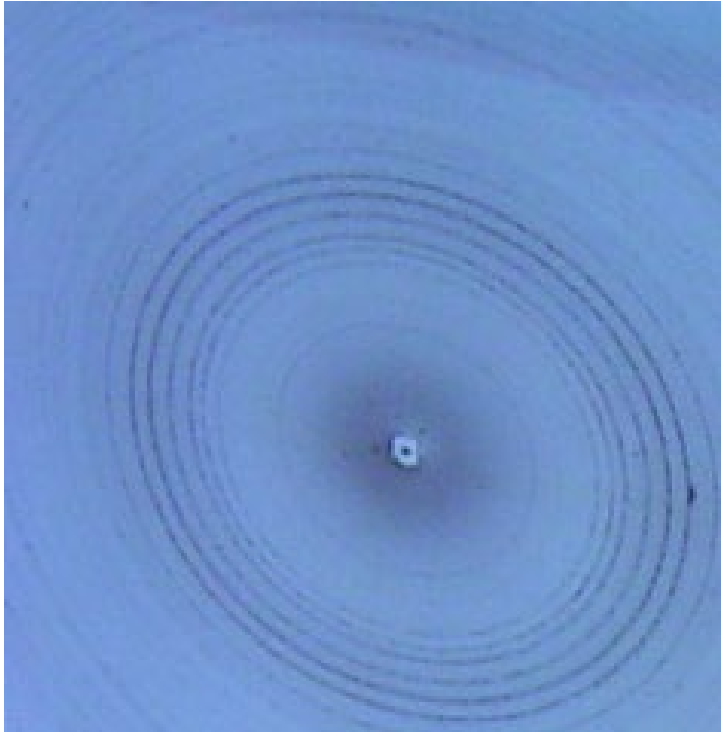
- **A powder sample consists of many crystallites with random orientations**
 - we get many overlapping reciprocal lattices, resulting in a “sphere” of reciprocal lattice points that fulfill the Bragg condition at a given 2θ
 - the sphere will intersect the Ewald sphere in a circle
 - we will observe “powder rings”



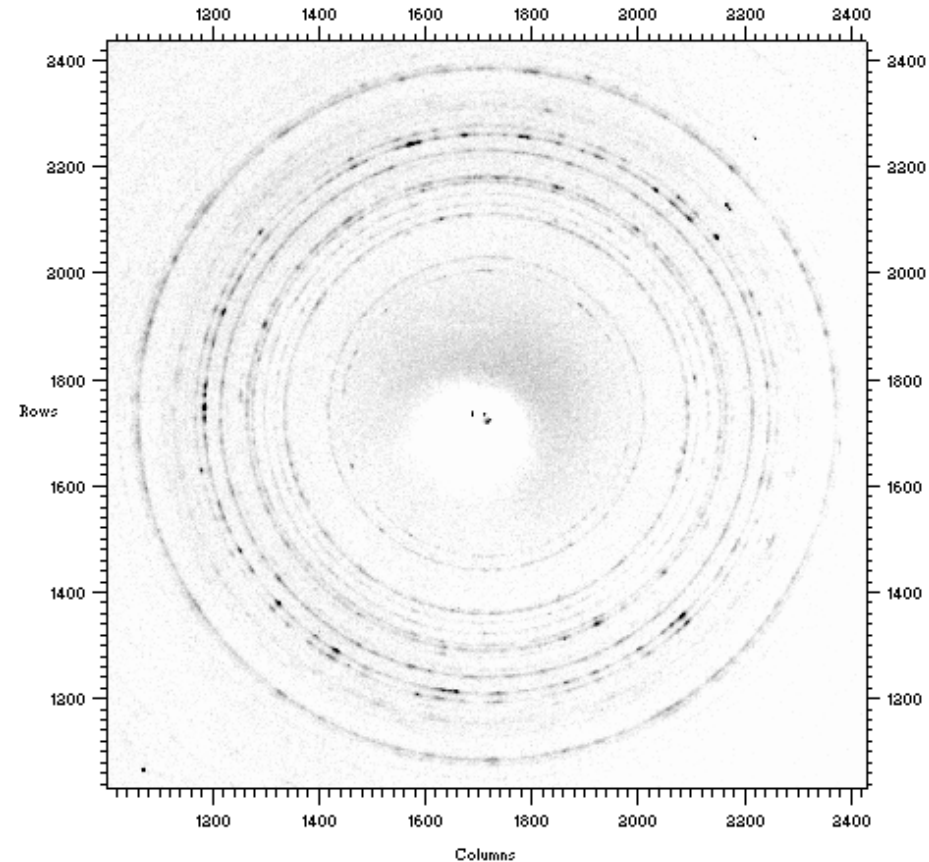
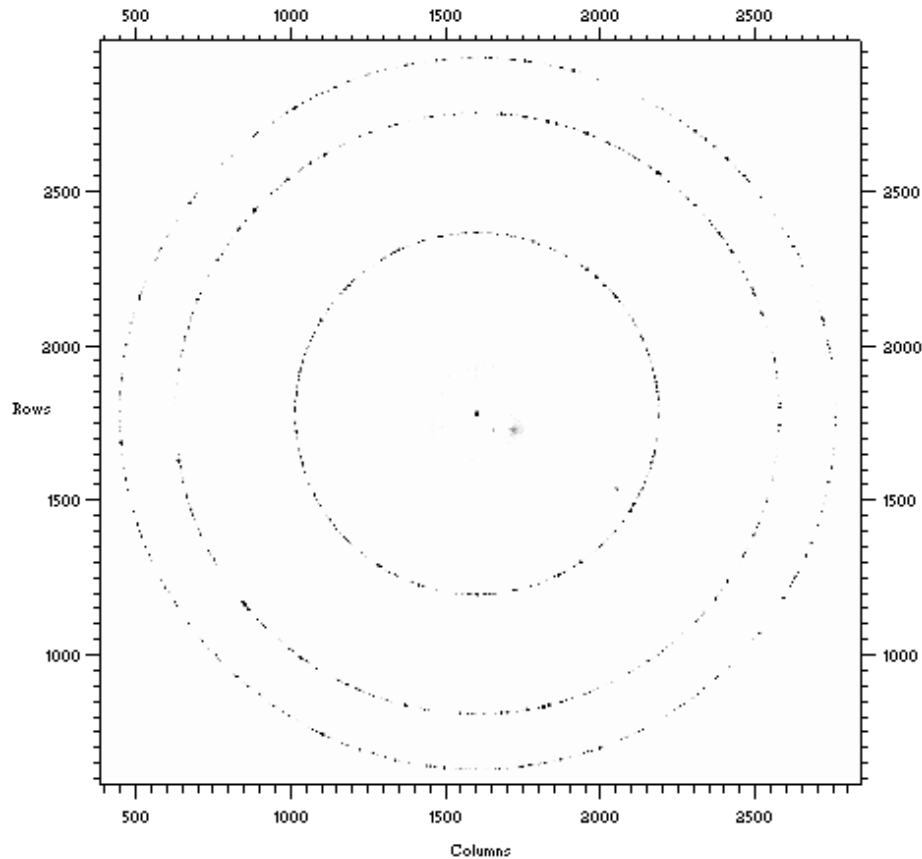
Cullity; “Elements of X-ray Diffraction”



Powder Data



Somewhere in Between



Anything from “several single crystals” to “almost homogeneous” is possible!
Often referred to as “graininess problem” (e.g., not enough grains in the beam).
Can result in non-random integrated intensities.



Extracting Information from the Diffractogram

- **All diffractograms contain three pieces of information:**
 - Peak positions – information about cell dimensions, space groups
 - Used for phase ID, indexing, accurate lattice parameters
 - Peak intensities – information about position, type, occupancy, ADP of atoms
 - Used in quantitative analysis, Rietveld analysis, structure solution
 - Peak shapes – information about crystallite size, strain, defect
 - Isotropic and anisotropic effects, also instrument contributions
- **Each of these can be used to extract qualitative or quantitative information from the data**
- **To extract quantitative data, errors must be avoided**

Peak Positions

- **Peak positions can be used to obtain the following pieces of information:**
 - Unit cell dimensions
 - d-spacing is related to unit cell constants
 - Could be a refinement of a known starting cell or a determination “from scratch” by indexing
 - Possible space groups
 - Look at systematic absences – “no peak” is information, too!
 - Qualitative phase analysis
 - What’s in the sample?
 - Approximate peak positions sometimes suffice for this

Sources of Error for Peak Positions

- **Zero point error**

- Constant offset in 2θ due to diffractometer misalignment
- You should not have to deal with this error, but you may not have the necessary privileges to fix it yourself

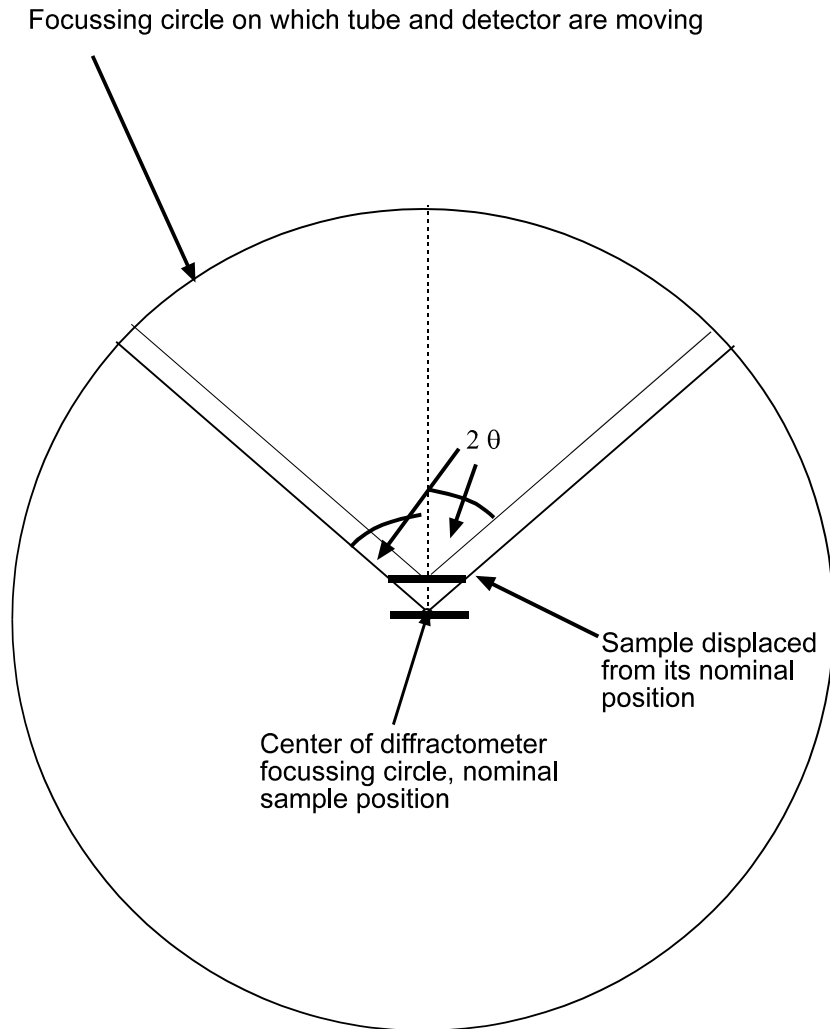
- **Sample displacement error**

- Incorrect sample height during a Bragg-Brentano setup experiment
- Most prominent at low angles
 - $\Delta 2\theta$ (in rad) = $2s \cos(\theta)/R$ s = displacement, R = goniometer radius
- Could be sample stage alignment issue, but in most cases, this is a user error!
- A height offset of 0.1 mm results in peak shifts of 0.04° at $20^\circ 2\theta$ when $R=250$ mm

- **Distinguishing zero point and sample displacement errors is tricky**

- Possible when large range of data is collected and used

Effects of sample height displacement



Standards

- **A standard can be used to check the alignment of a diffractometer**
 - Many different materials commercially available
 - SiO_2 , Si, CeO_2 , Al_2O_3 ...
 - Sold through independent vendors (e.g., NIST) or provided by diffractometer company
- **Easiest to use standards come as pressed solids**
 - Sample height is predefined this way
- **Experimentally determine peak positions of the standard, then compare to certified values to construct a calibration curve**
 - Allows for correction of data collected under same conditions

Internal Standards

- **A standard can also be mixed with your powder sample**
 - Called internal standard
- **You can use any material that is available as a powder and has well-established lattice constants**
- **If you are planning to refine a model for your data, a model for your internal standard can be refined at the same time**
 - Constrain standard to known lattice constants, refine sources of peak position errors, which also apply to your sample
- **Choose a standard with similar absorption properties as your sample**
 - This allows you to account best for ALL sources of error
 - e.g., sample transparency

Peak Intensities

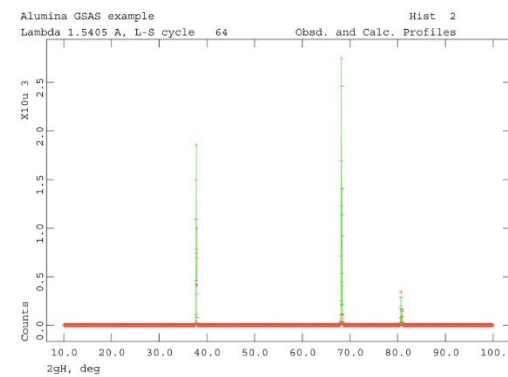
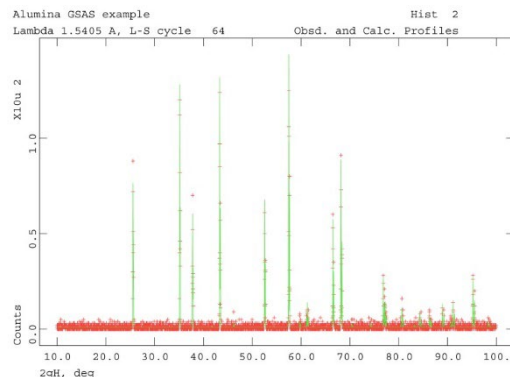
- **Peak intensities contain information about the following:**
 - Positions and types of atoms
 - Site occupancy of atoms
 - Atomic displacement parameters
 - Often referred to as “temperature factors”
- **Accurate intensities are necessary for:**
 - Quantitative phase analysis
 - Rietveld (structural) refinement
 - Structure solution from powder data
- **Use integrated peak intensities to eliminate line broadening effects!**
- **Experimental setup also influences peak intensities**
 - Lorentz-Polarization factor, absorption...
- **So does the sample itself**

Sources of Error for Peak Intensities

- **Preferred orientation**
- **Inhomogeneous samples and fixed slit setups**
 - Only for setups where the irradiated area changes
- **Graininess**
- **Beam not completely on the sample at low angles**
 - Only for setups where the irradiated area changes
- **Surface roughness for flat plate samples**
 - Results in reduced intensities at low angles
 - Really an absorption problem

Preferred Orientation

- **Some samples do not show random intensities**
 - Some orientations are over- or underrepresented
- **In severe cases, only some lines are observed, others are absent**
- **Preferred orientation can be desired**
 - e.g., epitaxial film
 - Certain engineering applications when materials have anisotropic properties
- **Can in special cases be used for structure solution**
 - High symmetry structures
- **Generally problematic and undesirable for powder data analysis**
 - Can be accounted for in Rietveld
 - but refinement is often unstable
 - For structure solution, correct
 - extracted intensities are required!



Avoiding Preferred Orientation

- **Run sample in a rotating capillary setup to reduce effects**
 - Notice that Bragg-Brentano spinning is completely useless!
 - Lab sources often suffer from absorption problems
- **Loosely pack the powder**
 - Can result in surface roughness problems or incorrect samples height
- **Side pack a sample holder**
 - Equivalent to “loose packing”, but surface remains smoother and at the correct height
- **Consult the literature**
 - Many specialized methods have been developed, e.g. spray drying with a polymer and packing the beads

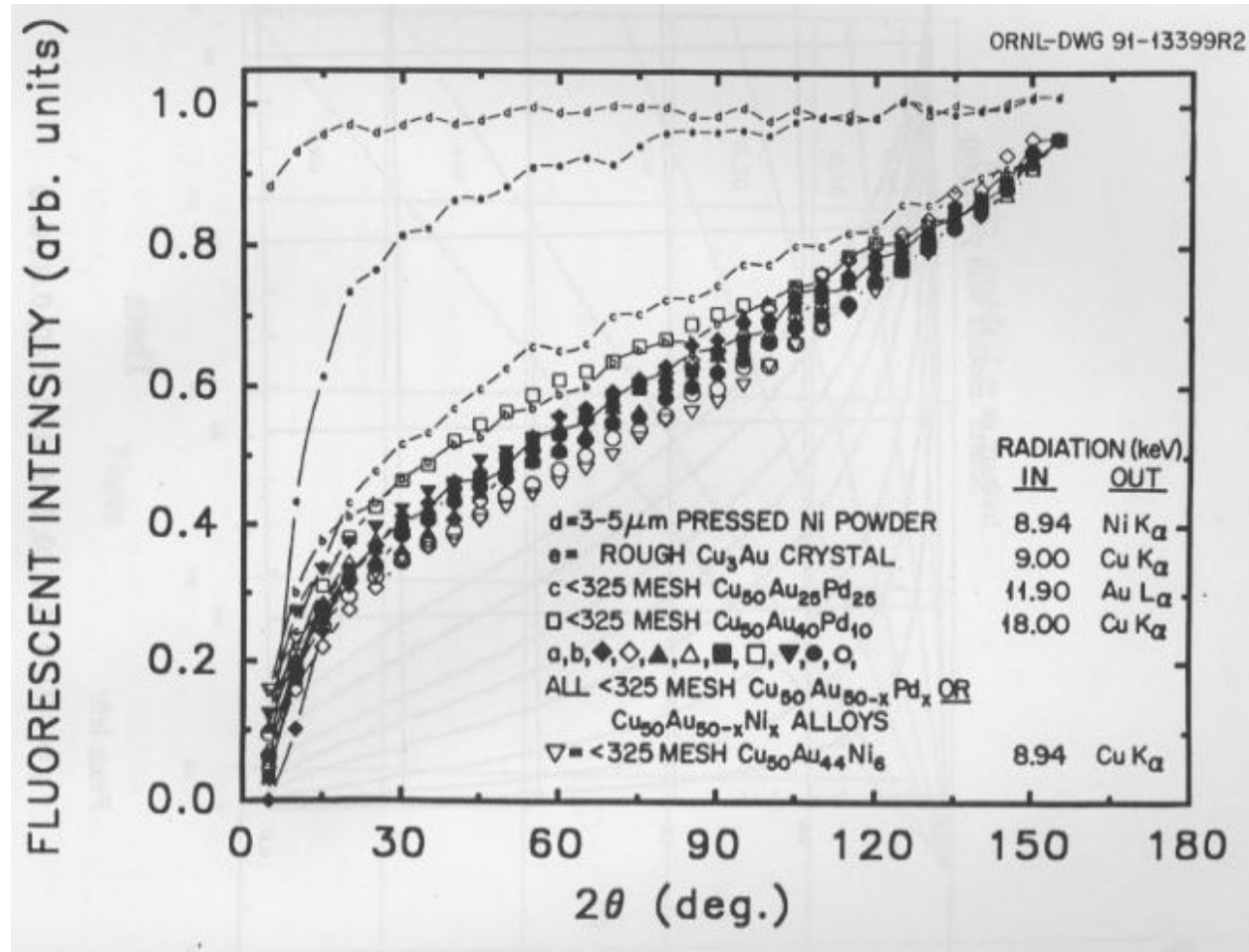
Surface Roughness Effects (Microabsorption Problem)

Smooth surface



Rough surface

Beam at low angled often must travel through material – absorption happens!

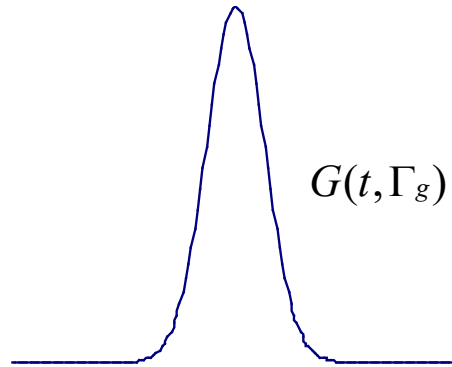


Peak Shapes

- **Peak shapes are affected by the following:**
 - Crystallite size
 - Significant effects for crystallites below 100 nm
 - Microstrain
 - Microstrain can lead to a “range” of lattice parameters due to strain
 - Ordered defects
 - Stacking faults, antiphase boundaries
 - Instrument
 - Finite source size
 - Axial divergence
 - Slits
 - Detector resolution
- **Isotropic or anisotropic peak broadening can result**
- **For quantitative analysis, a standard with no crystallite size or strain broadening must be used to determine the instrumental contribution**

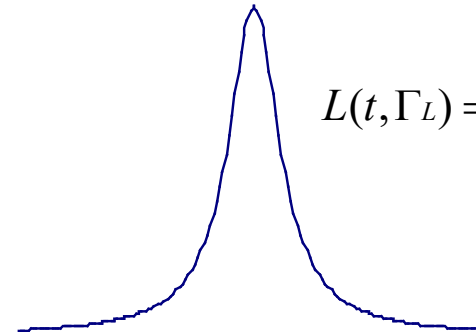
Examples of Peak Shapes

Gaussian peak shape



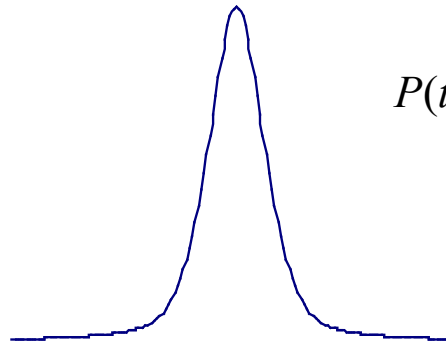
$$G(t, \Gamma_g) = \frac{1}{\sqrt{2\pi}\Gamma_g} \exp\left(\frac{-t^2}{2\Gamma_g^2}\right)$$

Lorentzian peak shape



$$L(t, \Gamma_L) = \frac{\Gamma_L}{2\pi} \frac{1}{(\Gamma_L/2)^2 + t^2}$$

Pseudo-Voigt peak shape



$$P(t) = \eta \cdot L(t, \Gamma) + (1 - \eta) \cdot G(t, \sigma)$$



Sample Related Peak Broadening

■ Crystallite size:

- Diffraction from an infinite crystal would give infinitely sharp peaks (delta function)
- Finite repeat leads to broadening
- Can be used to calculate crystallite size (Scherrer equation), $B = \text{FWHM in radians}$
 - For lab instrument: $B_{\text{size}} = 0.9 \lambda / (t \cos(\theta))$

- Instrument broadening must be accounted for to get meaningful, qualitative results!

- $B_{\text{measured}}^2 = B_{\text{instrument}}^2 + B_{\text{size}}^2$

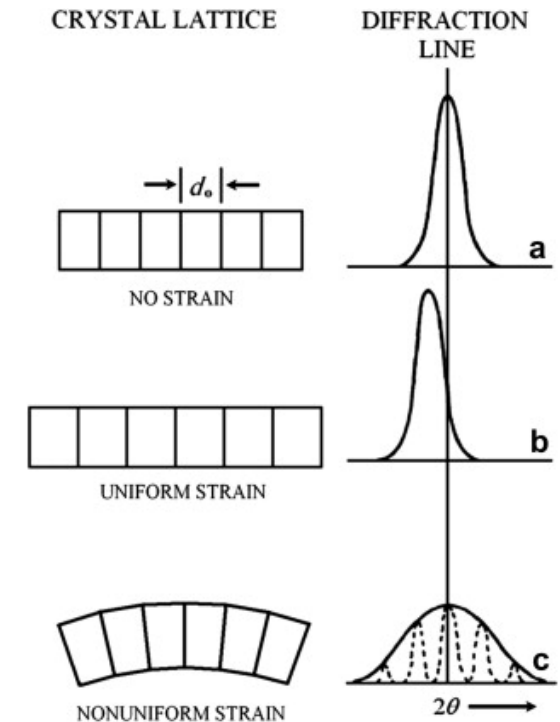
■ Strain broadening:

■ Results in distribution of lattice constants

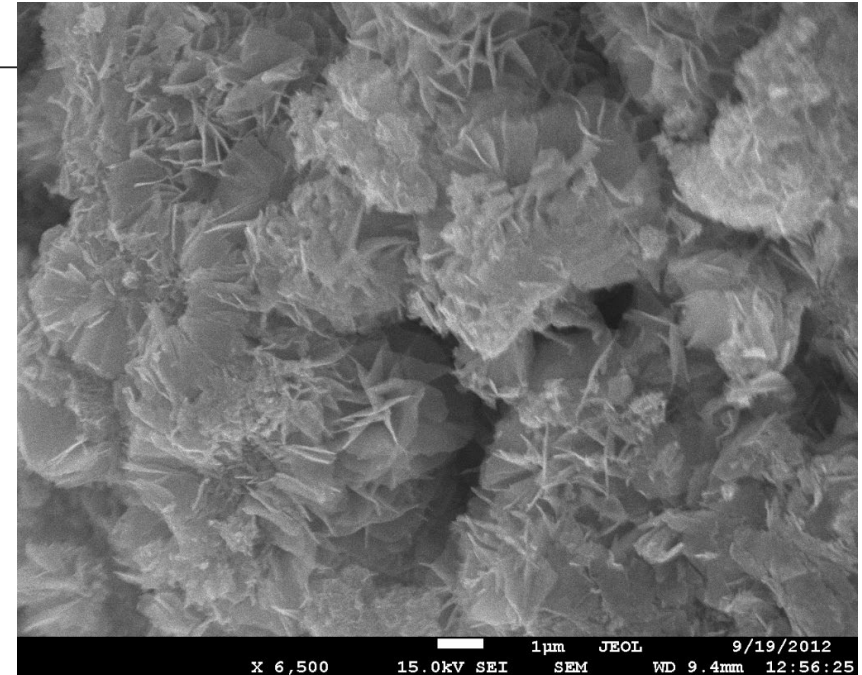
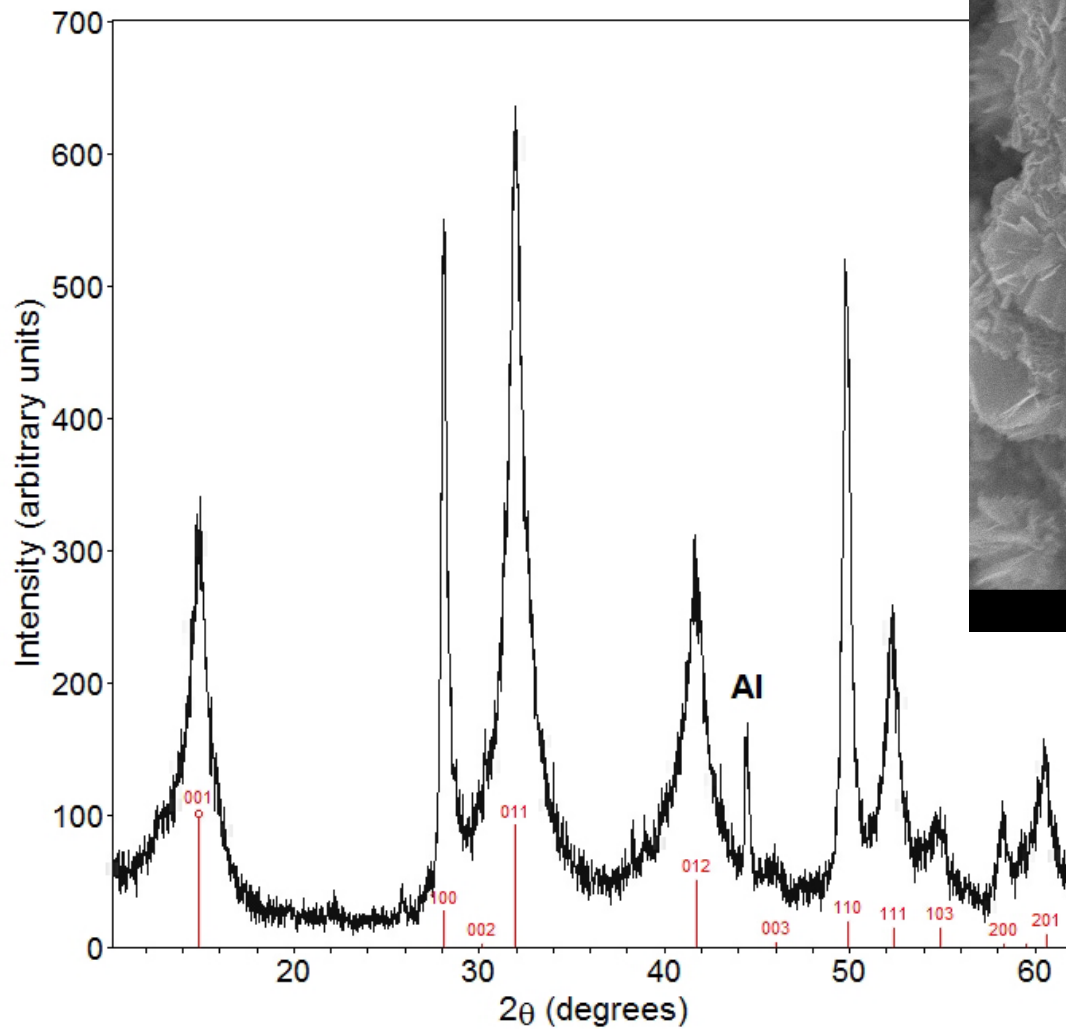
- More shift at higher angles – proportional to $\tan(\theta)$

■ Both effects can be isotropic or anisotropic!

- Anisotropic effects are generally hkl dependent



Sample related peak broadening



The most important part: Data collection!

- **Without high quality data, even the best program can't help you!**
- **Choice of instrument**
 - Resolution
 - Accessible angular range
 - "Tricks" you can play
- **Sample preparation**
 - Particle size
 - Surface roughness
 - Homogeneity
 - Preferred orientation
- **Instrument alignment, sample height and other errors**

Choice of instrument

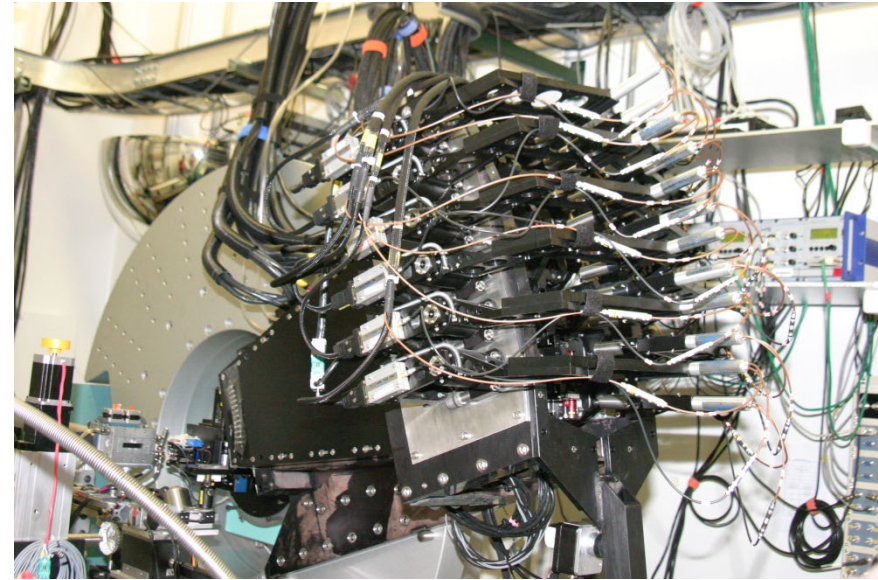
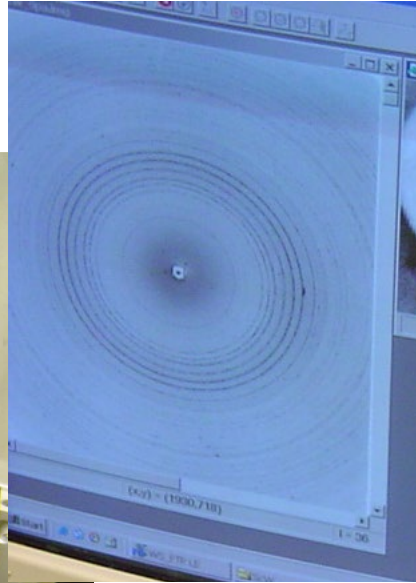
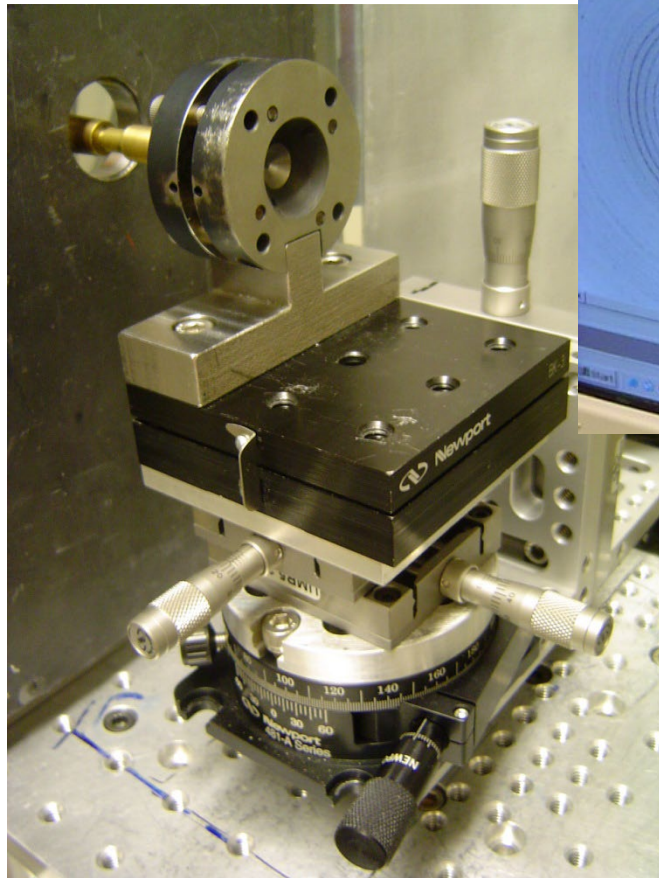
- **In many cases, a well-aligned laboratory x-ray will do**
 - Resolution is often sample limited (line broadening)
- **For samples with closely spaced lines (due to symmetry or large unit cell), it might be an advantage to use synchrotron radiation**
 - Tunable wavelength (lines can be spaced out)
 - Better instrument resolution
 - Larger accessible d-spacing range (commonly sample limited)
 - Absorption problems can be avoided
 - Methods like MAD (Multiple Anomalous Dispersion) phasing can help with locating atoms

Powder Diffraction Detector Options

- **Powder X-ray diffraction can use point, 1D or 2D detectors**
- **Area (2D) detectors allow for very fast data collection**
 - On high intensity synchrotron beamlines, a dataset can be collected in a fraction of a second!
 - Tradeoff with respect to resolution
 - Often used for parametric studies when speed of data collection is most important
- **Point detectors allow for very high-resolution data**
 - A single crystal analyzer can be mounted between the sample and the detector
 - Data collection speed can be improved by using multiple detectors
 - Example: 11-BM high resolution diffractometer at APS

Powder Diffraction Detector Options

- 2D detector (CHESS B2) and 1D detector array (APS 11-BM)



Sample Preparation – Particle Size

- **Particle size needs to be small enough to avoid graininess problems (e.g. < 10 microns, preferably 1-5 microns, some dependence on final sample size)**
 - Large grains can result in unpredictable intensity spikes when the diffraction condition of one of these grains is fulfilled
 - However, overgrinding should be avoided, as too small particles lead to line broadening!
 - Avoid “rocks” or “dust”
- **For flat plate samples, large grains can also result in surface roughness**
 - Intensity at low angles is reduced significantly

Sample Preparation

- **Choose a good sample setup for your particular sample**
 - Flat plate
 - Standard setup for most diffractometers
 - Requires smooth surface, which often results in preferred orientation
 - Sample transparency can be an issue
 - Capillary
 - Less problems with preferred orientation
 - Difficult for highly absorbing samples
 - Good for air-sensitive samples
 - Loose powder
 - Not for Bragg-Brentano parafocusing geometry
 - Surface roughness problems
- **The sample needs to be homogenous, so that every part is representative of the bulk sample (esp. if irradiated area changes with angle like in a fixed slit experiment)**



Experimental setup

- **Make sure that the instrument is well aligned before collecting data!**
 - Zero-point, footprint
- **Choose slits that will keep the full beam footprint on the sample at all angles (otherwise your low angle intensities will be off)!**
 - Programs will try to account for this through OTHER parameters!
- **The sample height needs to be correct to avoid peak shifts**
 - Height is a refinable parameter, but peak shape and intensity are also affected
- **Long counting times improve the signal to noise ratio and facilitate the extraction of integrated intensities**
- **Collect data to as high angles as possible (better resolution)**
 - However, there is no point in collecting data to 140° if you do not see peaks beyond 100°
- **Using an internal standard can be a smart decision**

Choices for Incident Beam Configurations

- **Most common lab diffractometer setup: Bragg-Brentano parafocusing geometry**
 - Watch for sample height errors
 - Very good resolution achievable
- **Parallel beam geometry (Goebel mirrors)**
 - Insensitive to sample height
 - Often a compromise with respect to resolution, as the beam is not re-focused into the detector
- **Incident beam double (or quadruple) bounce monochromator**
 - Eliminates $K\alpha_2$ radiation
 - Often paired with a mirror setup
- **Grazing incidence**
 - Powerful method for analyzing surface layers in samples or samples with strong preferred orientation

Choices for Diffracted Beam Configurations

- **Most lab diffractometers use a nickel filter to absorb unwanted radiation**
 - Works well to eliminate other lines from the Cu source
 - Can be less than ideal for fluorescent samples
- **A diffracted beam monochromator can be mounted in front of the detector**
 - Very useful when dealing with fluorescent samples
 - Disadvantage: Significant reduction in intensity
- **Parallel plate collimators can be used to focus the beam**
- **The most important piece of the diffracted beam configuration is the detector**