X-ray, Synchrotron, and Neutron Diffraction Phase Purity and Structure Determination

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X-Ray Diffraction

How it works and what it can and cannot tell us

Some Useful References

APS lectures on powder diffraction crystallography:

https://www.aps.anl.gov/Education/Powder-Diffraction-Educational-Materials

Intended to introduce Crystallography and introduce Rietveld refinement techniques with GSAS & EXPGUI

X-ray

- X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science.
- Discovery of X-rays in 1895
- Structural Analysis
- X-ray diffraction provides most definitive structural information
- We can determine the size and the shape of the unit cell for any compound most easily using X-ray diffraction
- Interatomic distances and bond angles

- To provide information about structures we need to probe atomic distances - this requires a probe wavelength of 1×10^{-10} m ~Angstroms i.e. X-rays (and appropriate neutrons)

Production of X-rays

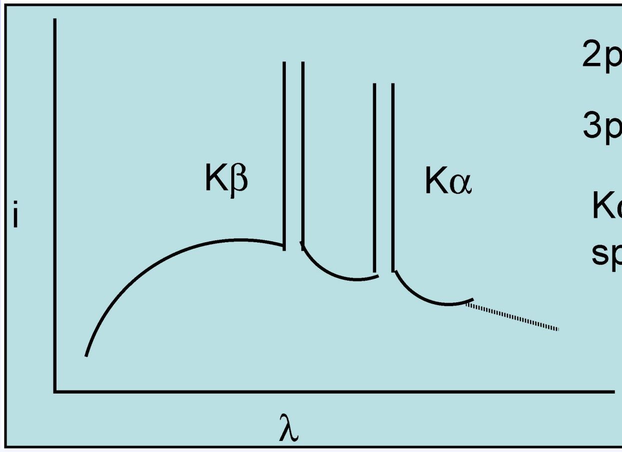
- X-rays are produced by bombarding a metal target (Cu, Mo usually) with electrons emitted from a hot filament (often tungsten).

- The incident beam will ionize electrons from the K-shell (1s) of the target atom and X-rays are emitted as the resultant vacancies are filled by electrons dropping down from the L (2P) or M (3p) levels.

- This gives rise to Kα and Kβ lines.

X-ray Diffraction Methods

- Laboratory X-rays
  - Affordable, excellent detectors and X-ray sources these days
- Synchrotron X-rays
  - Need synchrotron access, extremely high brightness, extremely high resolution



2p -- 1s = Kα

3p -- 1s = Kβ

Kα1 vs. Kα2
spin up vs. spin down

The broad background is called Bremsstrahlung – electrons are slowed down by collisions and lose their kinetic energy.

As the atomic #Z of the target element increases, the energy of the characteristic emission increases and the wavelength decreases

Moseley's Law: $(c/\lambda)^{1/2} \propto Z$

Cu Kα = 1.54178 Å Mo Kα = 0.71069 Å

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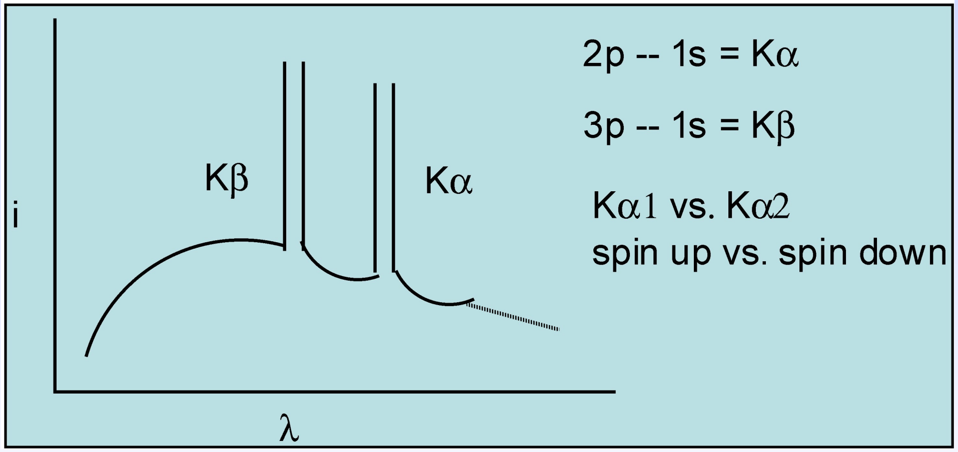


2p -- 1s = Kα

3p -- 1s = Kβ

Kα1 vs. Kα2
spin up vs. spin down

We can select a monochromatic beam of one wavelength by

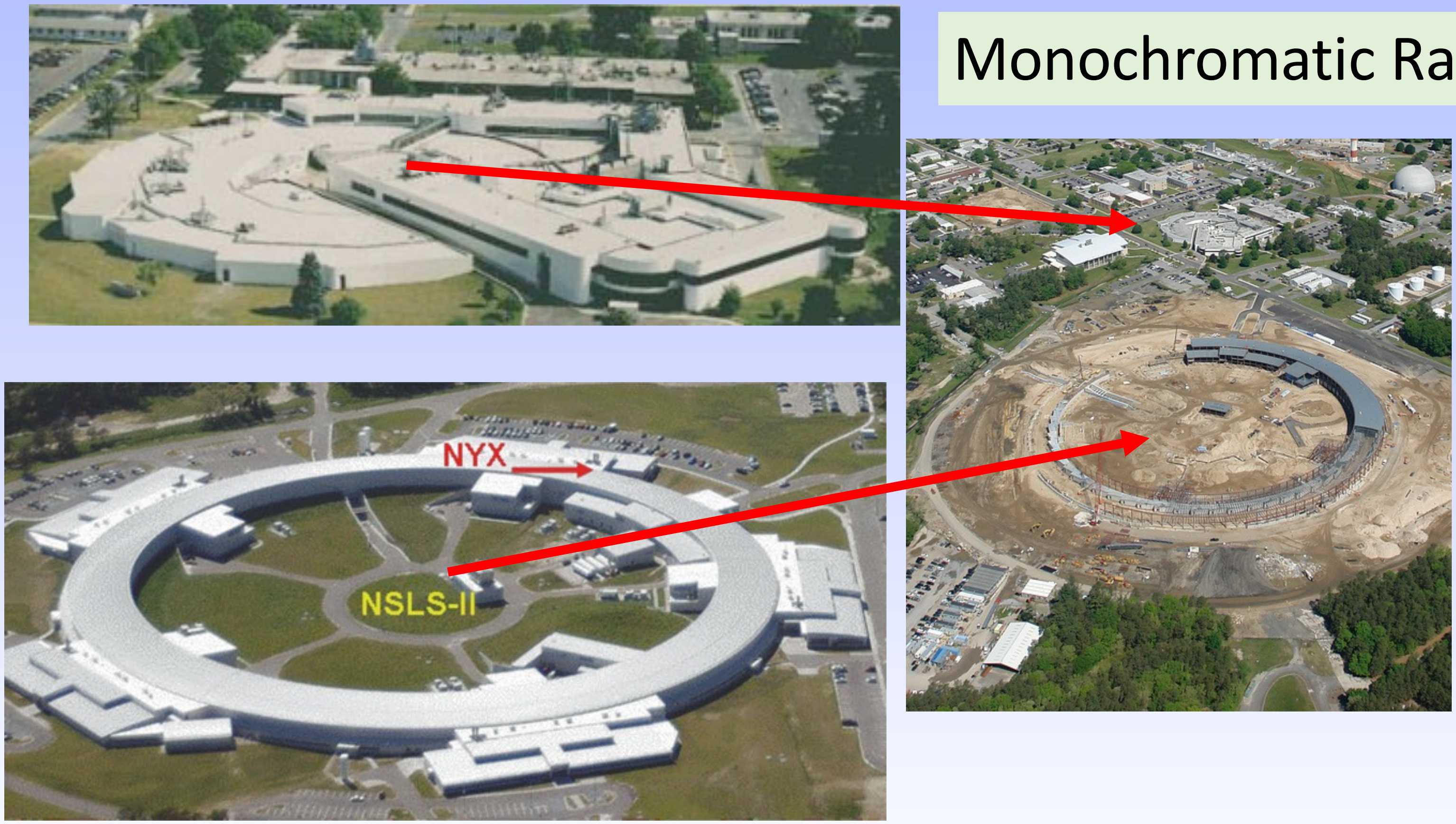
a) Crystal monochromator
$n\lambda = 2d\sin\theta$ (Bragg equation)

b) Filter – use element (Z-1) or (Z-2), Ni for Cu, and Zr for Mo. Absorption edge at the correct energy for filtering

c) Energy discriminating detector – state of the art

Brookhaven National Synchrotron Light Source

Monochromatic Radiation



X-ray and Neutron Diffraction Methods

- Radiation which scatters off atoms leads to interference patterns (diffraction) which can be used to probe how the atoms are arranged in a material.
- There are three types of radiation which are used for this purpose: Photons (X-rays), neutrons, and electrons
- These methods have different sensitivities, advantages/disadvantages, and much different instrumentation
- The best method depends on the specific problem. The methods are complementary and often two or all three methods are needed to gain a complete structural understanding.

X-ray Diffraction Methods

- Unit Cell – The smallest repeating unit that shows the full symmetry of the crystal structure.

- Crystal Systems – 6 (7) independent unit cell shapes that are possible in a three-dimensional crystal structure.

		Axis	Axis Angles
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90$
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90$
3	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90$
4a	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90, \gamma = 120$
4b	Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90 < 120$
5	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90, \beta > 90$
6	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90$

X-ray Diffraction

- X-rays scatter off the electrons, hence they tell you about the electron density
- As electrons density is diffuse, X-ray scattering has a form factor (the intensity falls off at large Q from destructive interference within an atom)
- X-rays can be easily produced by laboratory machines
- X-ray scattering factor proportional to atomic number Z.
- Heavy atoms scatter better
- Light elements can be difficult to locate in the presence of heavy elements

Neutron Diffraction

- Neutrons have no charge
  - Highly penetrating
  - Nondestructive
- Neutrons have a magnetic moment
  - Magnetic structure
- Neutrons have Spin
  - Polarized beams
  - Coherent and incoherent scatter

- Some elements absorb neutrons so strongly that they cannot be used – Gd, Sm, Eu, B
- Of course, sometimes specific isotopes are better and can be used, but of course, they are also typically quite expensive.

Neutron Scattering

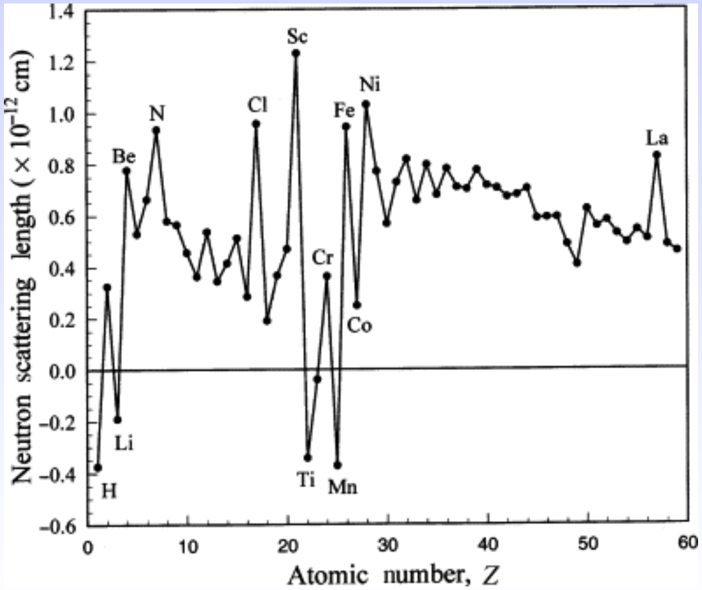
- Coherent elastic
  - Gives rise to diffraction – structural information
- Incoherent Elastic
  - No structure information
- Coherent Inelastic
  - Information on atom dynamics
- Incoherent Inelastic
  - Measures self-correlation

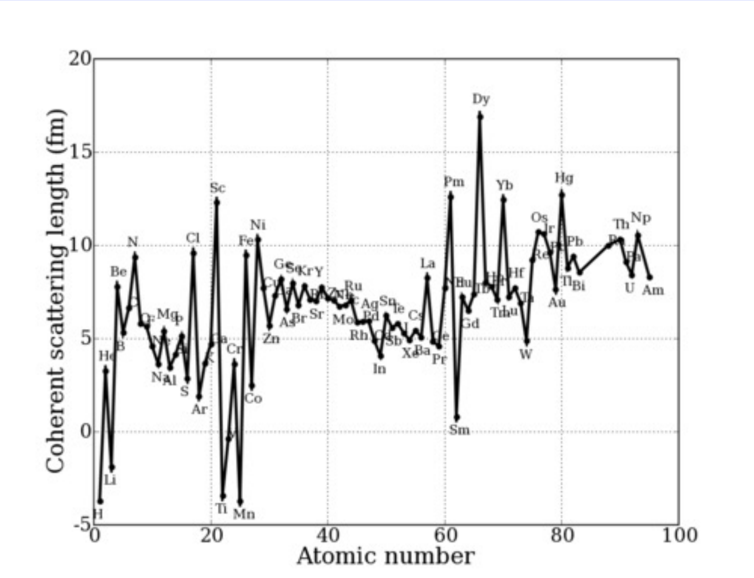
Coherent: the phase of the wave is preserved after scattering

Elastic: no energy is transferred; the scattered wave has the same energy as the incident wave

Neutron Scattering vs. Element

- ❖Neutron scattering length does not have any periodic trends – unlike X-ray scattering – and thus can complement X-rays and can sometimes differentiate atoms adjacent in the periodic table, which X-rays don't do very well. W and O Co and Ni

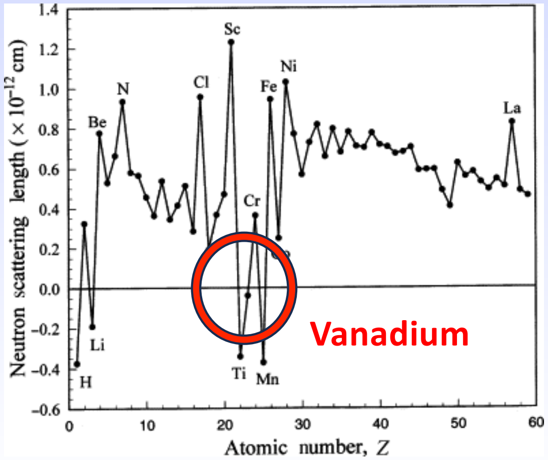




Negative Scattering Length

- When X-rays scatter there is always a phase shift. When neutrons scatter there is usually a phase shift, but for some elements there is not. This makes these waves have opposite phase (negative scattering length)
- This can lead to very strong contrast between some elements
- Some elements like vanadium have essentially zero scatting length – they are "invisible to neutrons". Often used as sample holder – vanadium cans.

Mn -3.74 Fe +9.45



X-ray and Neutron Diffraction Methods

- Need high quality data – without that even the best software cannot save you
- Choice of instrument
  - Resolution
  - Accessible angular range
- Sample Preparation
  - Particle size
  - Homogeneity
  - Preferred orientation
- Instrument alignment, sample height and other errors.

X-ray and Neutron Diffraction Methods

Sample Size as in Quantity Needed

- X-rays mg for capillary, 100 mg for flat plate

- Neutron 3-8 g of sample

Lattice Planes, Miller Indices and Directions

- Lattice Plane – are a concept introduced by Bragg's law, are defined as purely from the shape and dimensions of the unit cell.

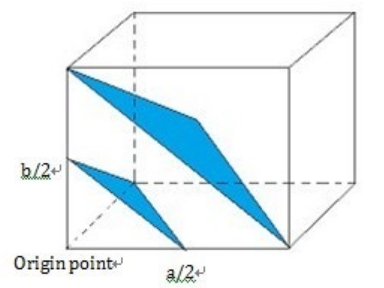
- Lattice Planes are entirely imaginary and simply provide a reference grid to which the atoms in the crystal structure may be referred.

- Sometimes a given set of lattice planes coincides with layers of atoms, but not usually.

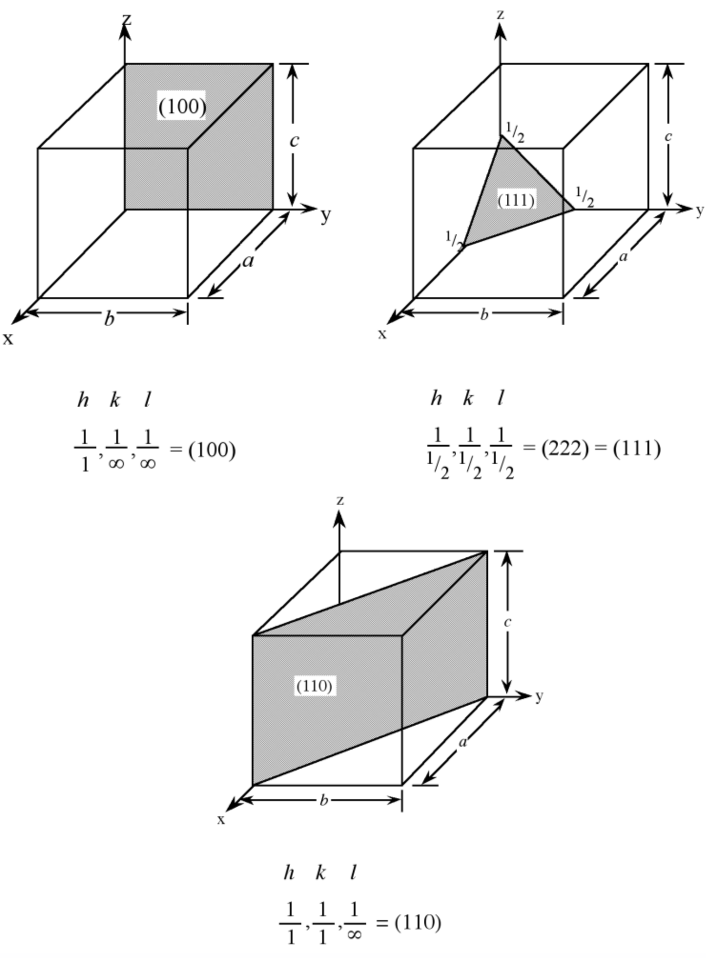
- Lattice planes are labeled by assigning three numbers known as Miller Indices to each set.

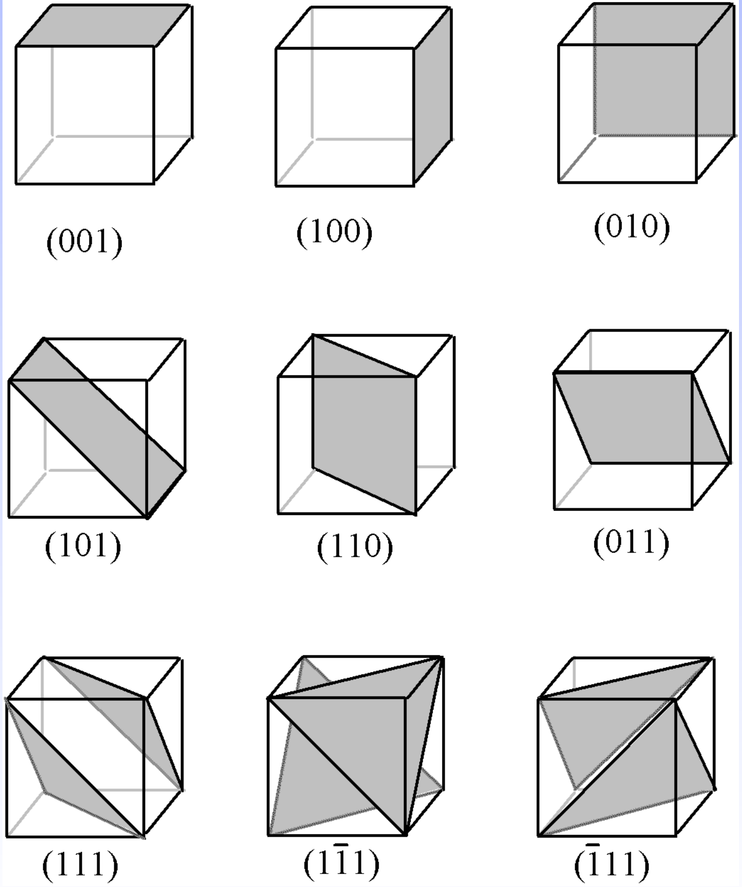
Lattice Planes, Miller Indices and Directions

- There are many equidistant parallel planes.
- Consider the plane that is adjacent to the one that passes through the origin.
- Find the intersection of this plane on the three axes of the cell.
- Write the intercepts as fractions of the cell edge.
- The plane cuts the x-axis at **a/2**, the y-axis at **b/2** and the z-axis at **c**, the fractional intersections are **1/2, 1/2, 1**
- Take the reciprocals of these fractions and it gives **(2 2 1)** – the parenthesis indicate Miller Indices.

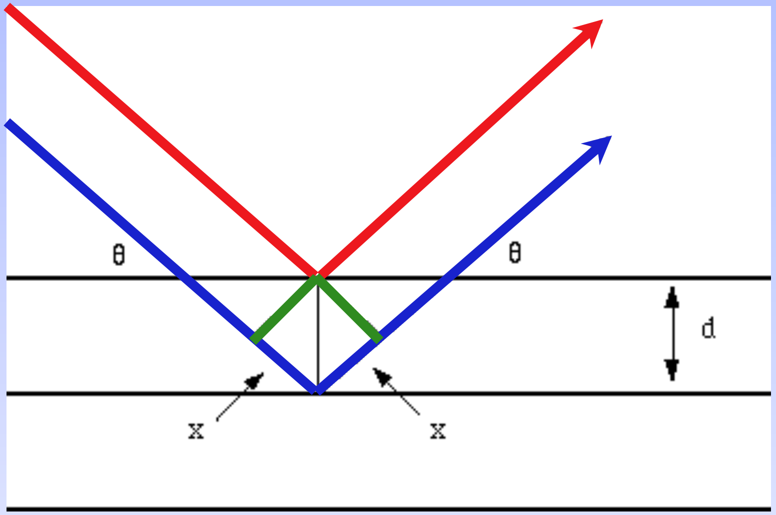


Lattice Planes, Miller Indices and Directions





The Bragg Equation



Reflection of X-rays from two planes of atoms in a solid.

$x = d\sin\theta$

The path difference between two waves: 2 x wavelength = 2dsin(theta)

Bragg Equation: $\mathbf{n\lambda = 2d\sin\theta}$

Relationship Between Diffraction Peaks, Miller Indices and Lattice Spacings

Simple cubic material **a** = 5.0 Å

hkl	d(Å)	2Θ
100	5.00	17.72
110	3.54	25.15
111	2.89	30.94

$$\boxed{\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}}$$

Bragg Equation: **nλ = 2dsinθ**

- How many lattice planes are possible?
  How many d-spacings? The number is large but finite.
- **nλ = 2dsinθ** If theta = 180, then d = λ/2. For Cu radiation that means that we can only see d-spacings down to 0.77 Å. For Mo radiation, down to about 0.35 Å

d-spacing in Different Crystal Systems

- Cubic

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

- Tetragonal

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

- Orthorhombic

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

- Hexagonal

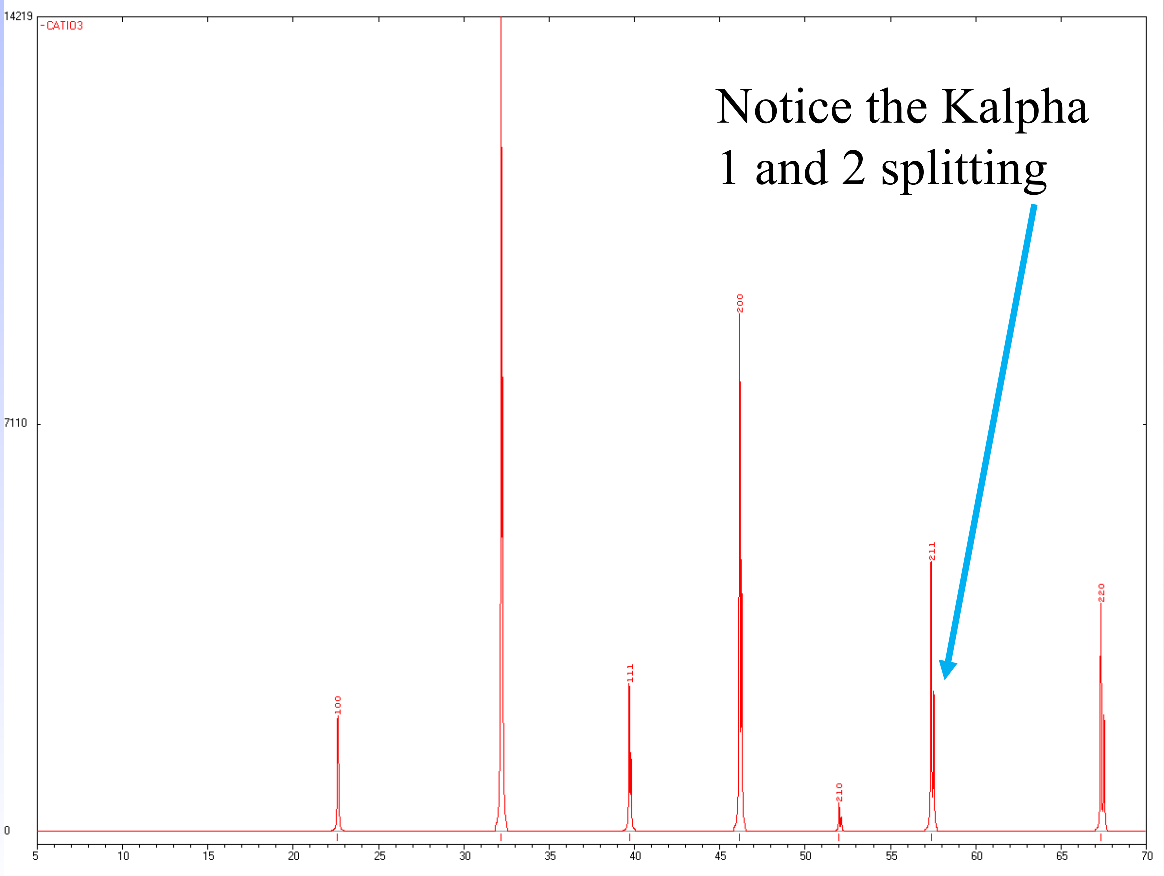
$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

- Monoclinic

$$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

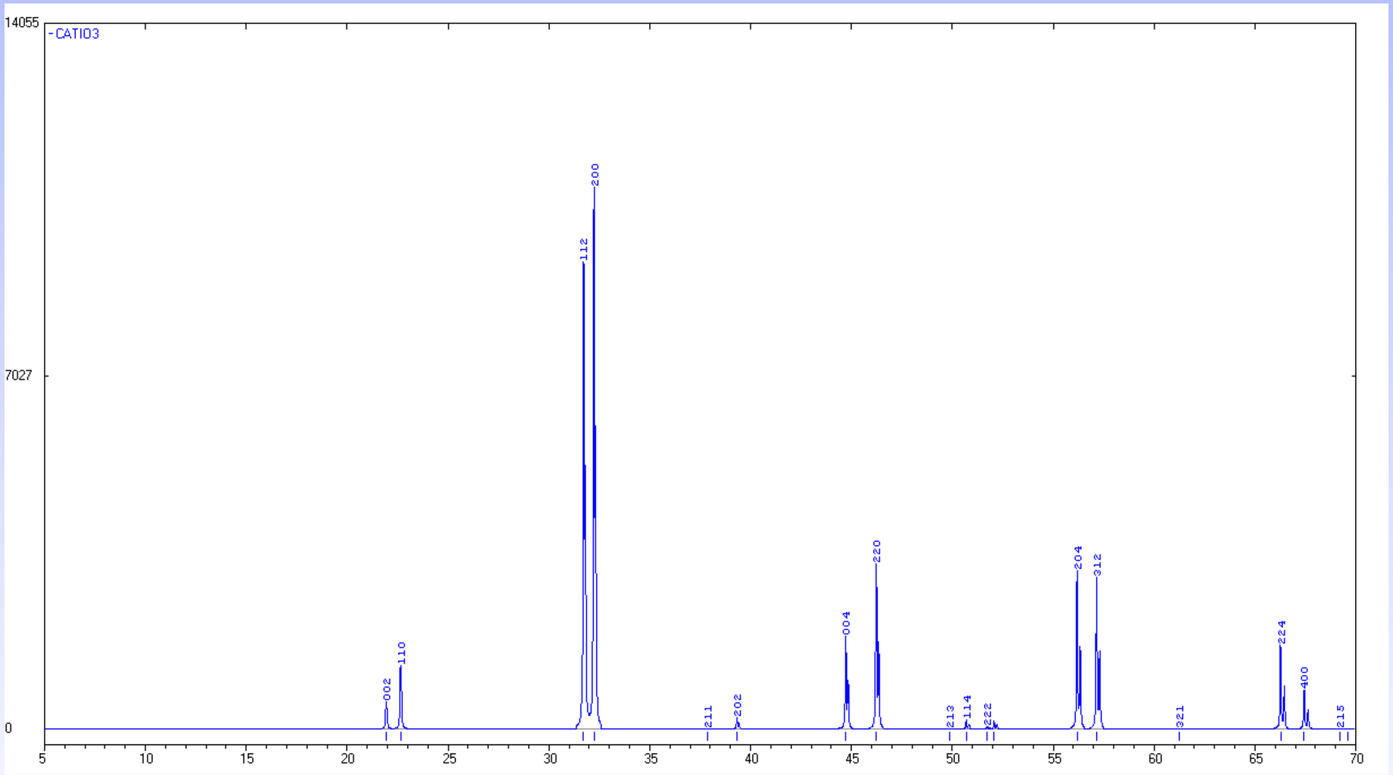
- Triclinic - ☹

Cubic Pattern



Notice the Kalpha 1 and 2 splitting

Tetragonal Pattern



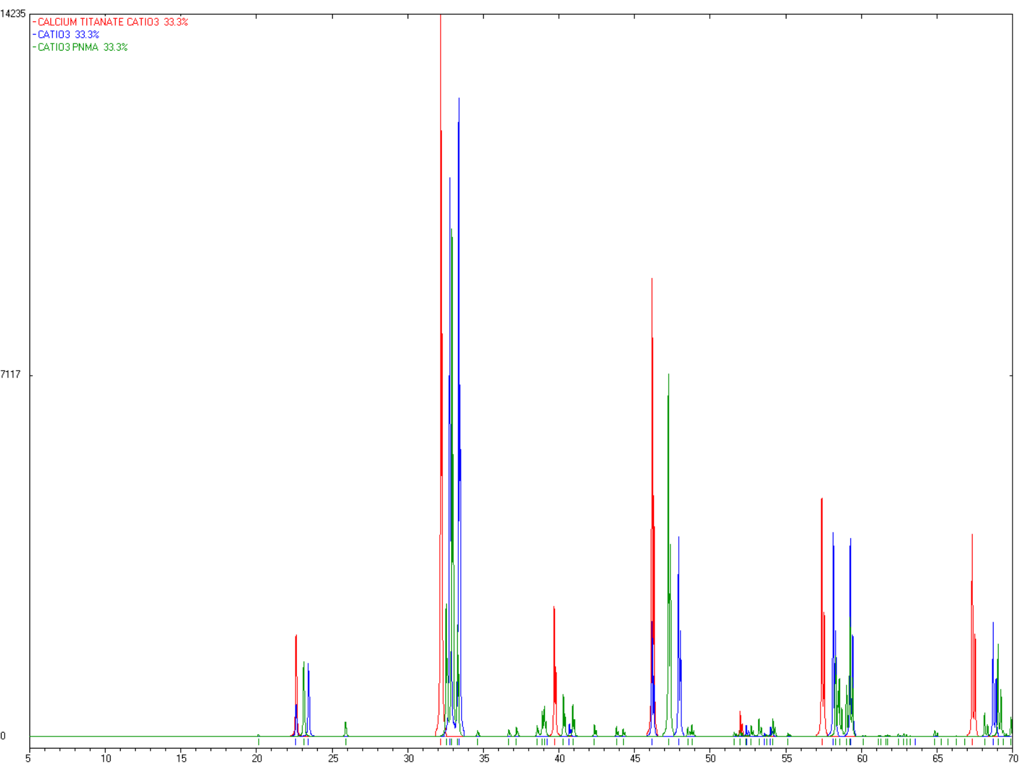
$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

$$\sin^2\theta = \frac{\lambda^2}{4}\left[\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}\right]$$

Orthorhombic Pattern

a ≠ b ≠ c, all angles are 90°

Multiplicity is further decreased as the symmetry decreases.



$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

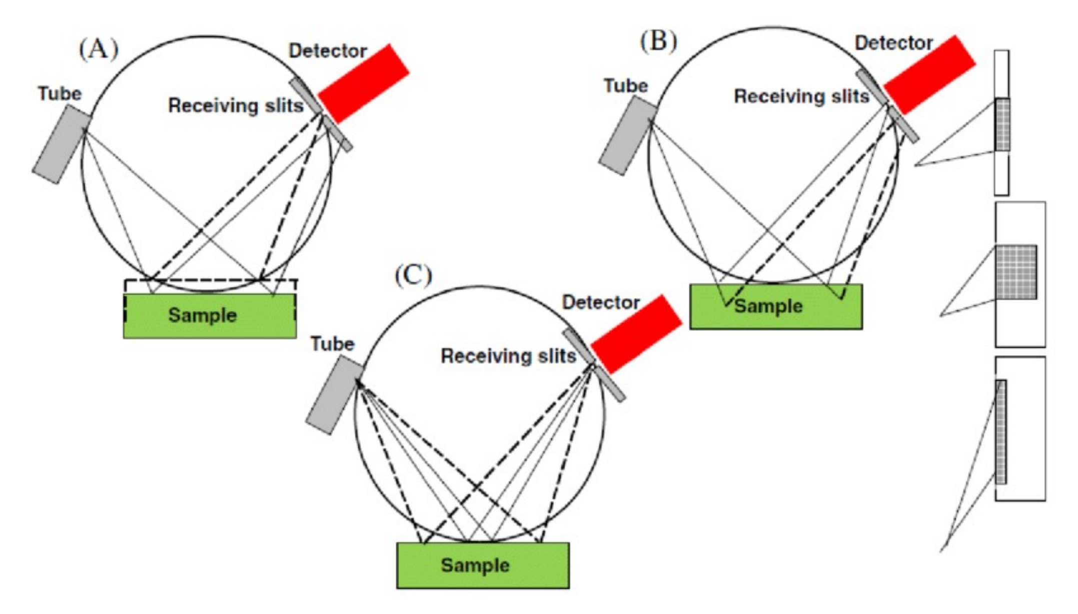
$$\sin^2\theta = \frac{\lambda^2}{4}\left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right]$$

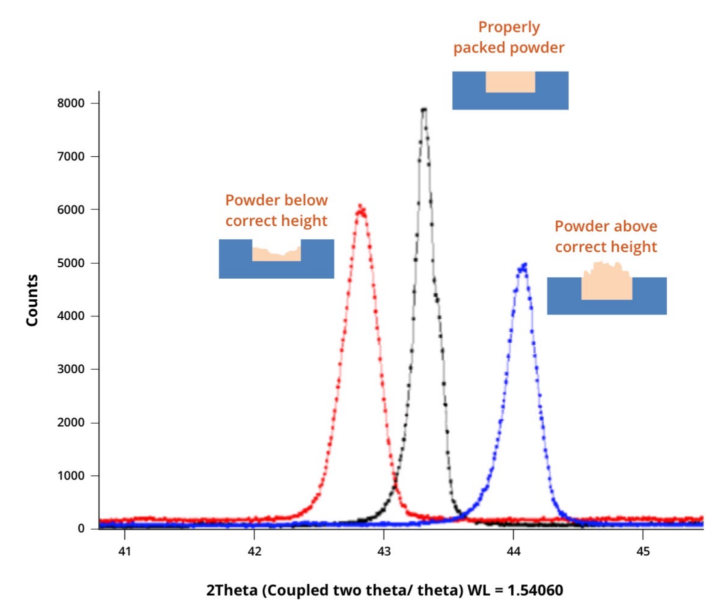
X-ray and Neutron Diffraction Methods

- Make sure instrument is well aligned before starting to collect data
- Chose the correct slit size
- Make sure sample height is correct – proper sample loading into sample holder is important
- Long counting times improve signal to noise ratio and lead to better refinement statistics and integrated intensities
- Chose a low background sample holder – ideally the sample holder will not be illuminated by X-ray beam
- Decide on step size

X-ray and Neutron Diffraction Methods

- ❖Sample height displacement





- ❖Loosely packing a sample into the sample holder, has the same effect as a negative displacement.

From: https://www.researchgate.net/figure/XRD-sample-based-errors-visualizing-a-sample-displacement-error-b-sample-transparency_fig7_357375472 and https://myscope.training/XRD_The_importance_of_specimen_height

What Information Do We Get or Can We Get From Powder X-ray Diffraction

- Lattice parameters
- Phase identity
- Phase purity
- Crystallinity
- Crystal structure
- Percent phase composition

What Information Do We NOT Get From Powder X-ray Diffraction

- Elemental Analysis
  - How much lithium is in this sample?
  - Is there iron in this sample
  - What elements are in this sample

- Tell me what this sample is ????
  - If a known compound in our database – then easy to identify. If not, then unless you know something about this sample, powder XRD won’t have answers !!! (maybe in the future)

Powder Preparation

- It needs to be a powder
  - (can also be a solid with a flat surface

- It is best if it is a pure powder

- Its nice to have about 200 mg of sample, but one can work with less

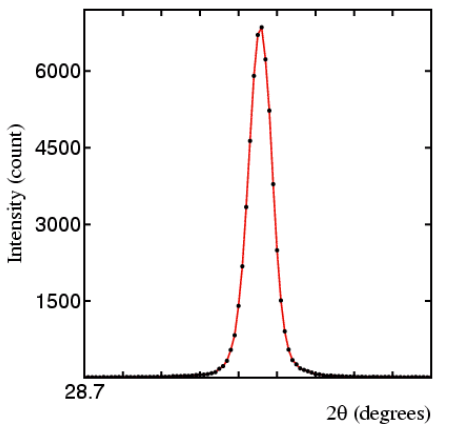
- The powder needs to be packed tightly in the sample holder. Lose powders will give poor intensities.

Data Collection

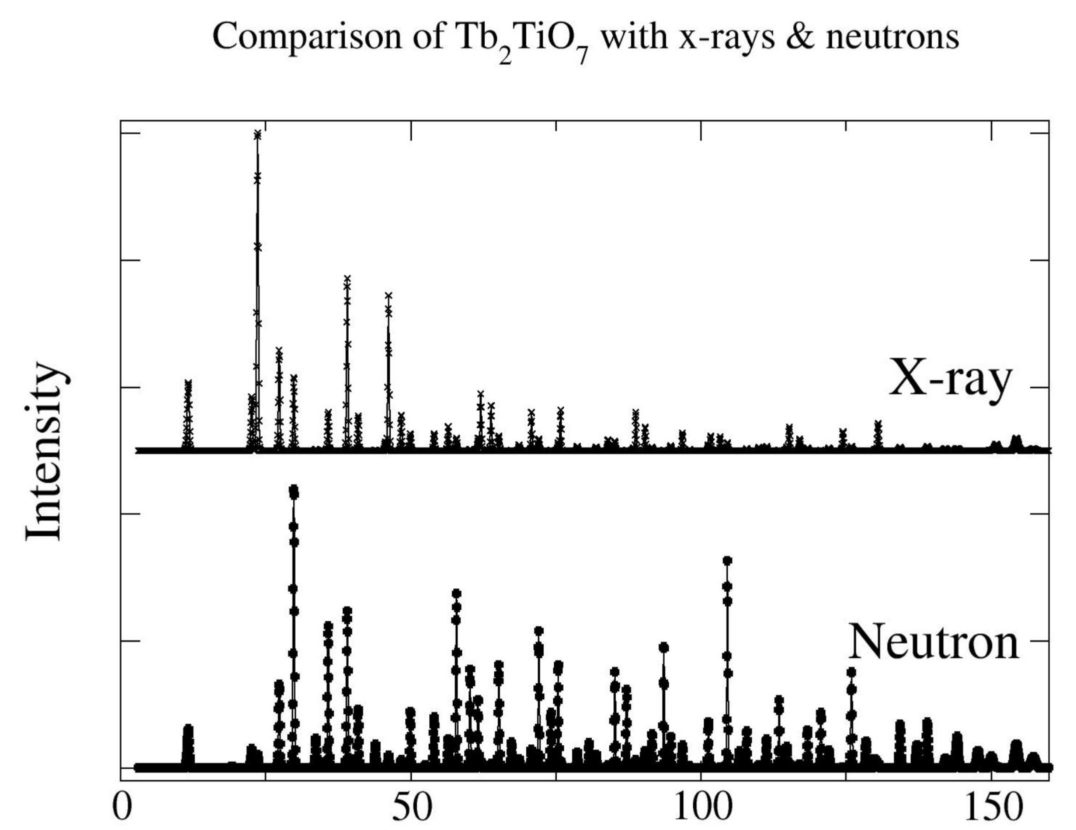
- The scattering intensity drops as $1/2(1+\cos^2 2\theta)$
  - This means that you don't get much intensity past 70° 2θ. A good range is 10-70° 2θ.
- How long should you collect (time per step)?
- Depends on what you want to do!
- Routine analysis may only take 15-60 min.
- Data for Rietveld analysis may take 12-18 hours to collect
- Newer detectors can cut that time by a factor of 4

X-ray and Neutron Diffraction Methods

- Step size should be consistent with the peak width.
- Need at least 5-7 points in the upper part of the peak, but not 20.
- Too many points, i.e. too small a step size, does not increase the resolution, accuracy or precision but just worsens the signal to noise.
- Step size correlates with data collection time – 0.02 to 0.05.



X-ray and Neutron Diffraction Methods



From: NXintro2powder-ppt_Toby ANL.pdf

Rietveld Method

- We can use X-ray (and neutron) diffraction for phase identification and phase purity. Extremely useful. We can refine crystal structures from powder.

- We can extract more information: Rietveld Refinement – developed by Hugo Rietveld

- We can obtain:
  - Unit cell dimensions
  - Phase quantities
  - Crystallite size and shapes
  - Atomic coordinates / bond lengths
  - Micro strain in the crystal lattice
  - Texture effects
  - Substitutions / vacancies

Important Considerations:

Need to know what phase you have

Unknown phase = NO Rietveld refinement

Requires EXCELLENT data quality

First refinement program by H. M. Rietveld, single reflections + overlapped, no other parameters than the atomic parameters. Rietveld, Acta Cryst. *22*, 151, **1967**.

Rietveld Software

- Fullprof
- GSAS
- TOPAS – educational version
- JANA

- TOPAS (Bruker)
- PDXL (Rigaku)
- Jade (MDI)
- WinX (Stoe)

Rietveld Method – It's a Refinement of a Model: Not a Structure Solving Method

To minimize the residual function:

$$WSS = \sum_i w_i \left(I_i^{\exp} - I_i^{calc} \right)^2, w_i = \frac{1}{I_i^{\exp}}$$

where:

$$I_i^{calc} = S_F \sum_k L_k \left| F_k \right|^2 S(2\theta_i - 2\theta_k) P_k A + bkg_i$$

$P_k = \text{preferred orientation function}$

$S(2\theta_i - 2\theta_k) = \text{profile shape function}$

$$(\text{PV}: \ \eta, \text{HWHM})$$

$$HWHM^2 = U \tan^2 \theta + V \tan \theta + W$$

$$P_k = \left(r^2 \cos^2 \alpha + \frac{\sin^2 \alpha}{r} \right)^{-3/2}$$

(WSS) = weighted sum of squared residuals

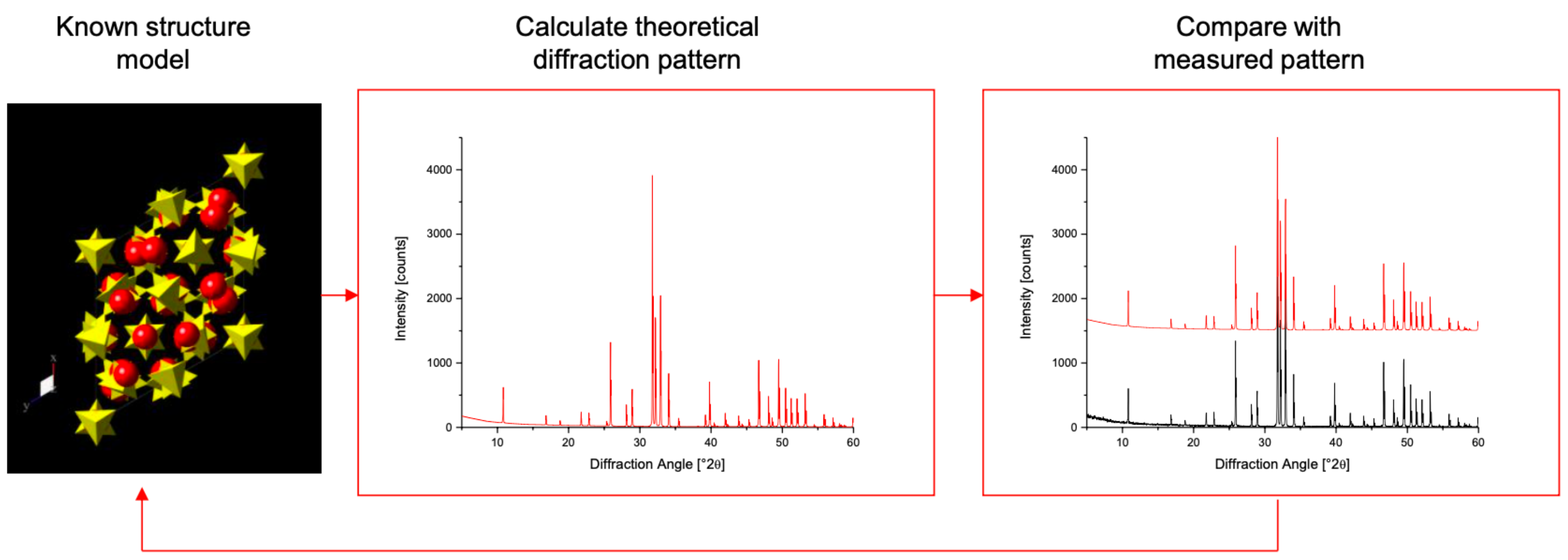
I^{calc} = calculated intensity

- The pattern depends on
  - Phases: crystal structure, microstructure, quantity, cell volume, texture, stress, elements…
  - Instrument: beam intensity, Lorentz-Polarization, background, resolution, radiation…
  - Sample: position, shape, dimensions

Each of these factors can be refined if applicable

From: http://mill2.chem.ucl.ac.uk/ccp/web-mirrors/lutterotti/~luttero/laboratoriomateriali/Rietveld.pdf

Rietveld Method



Known structure model

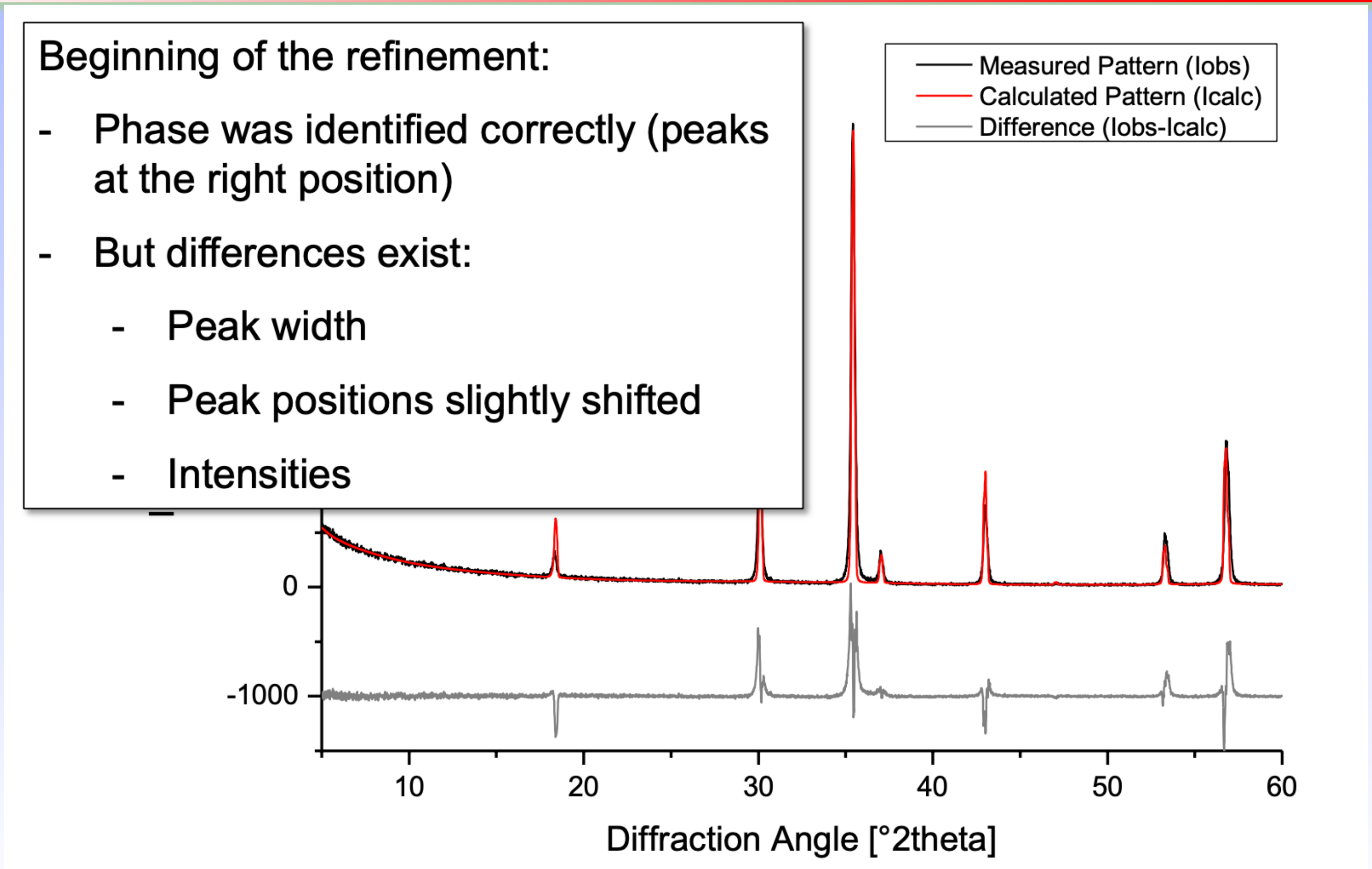
Calculate theoretical diffraction pattern

Compare with measured pattern

Optimize structure model, repeat calculation

From http://profex.doebelin.org/wp-content/uploads/2015/01/Lesson-5-Rietveld-Refinement.pdf

Rietveld Method

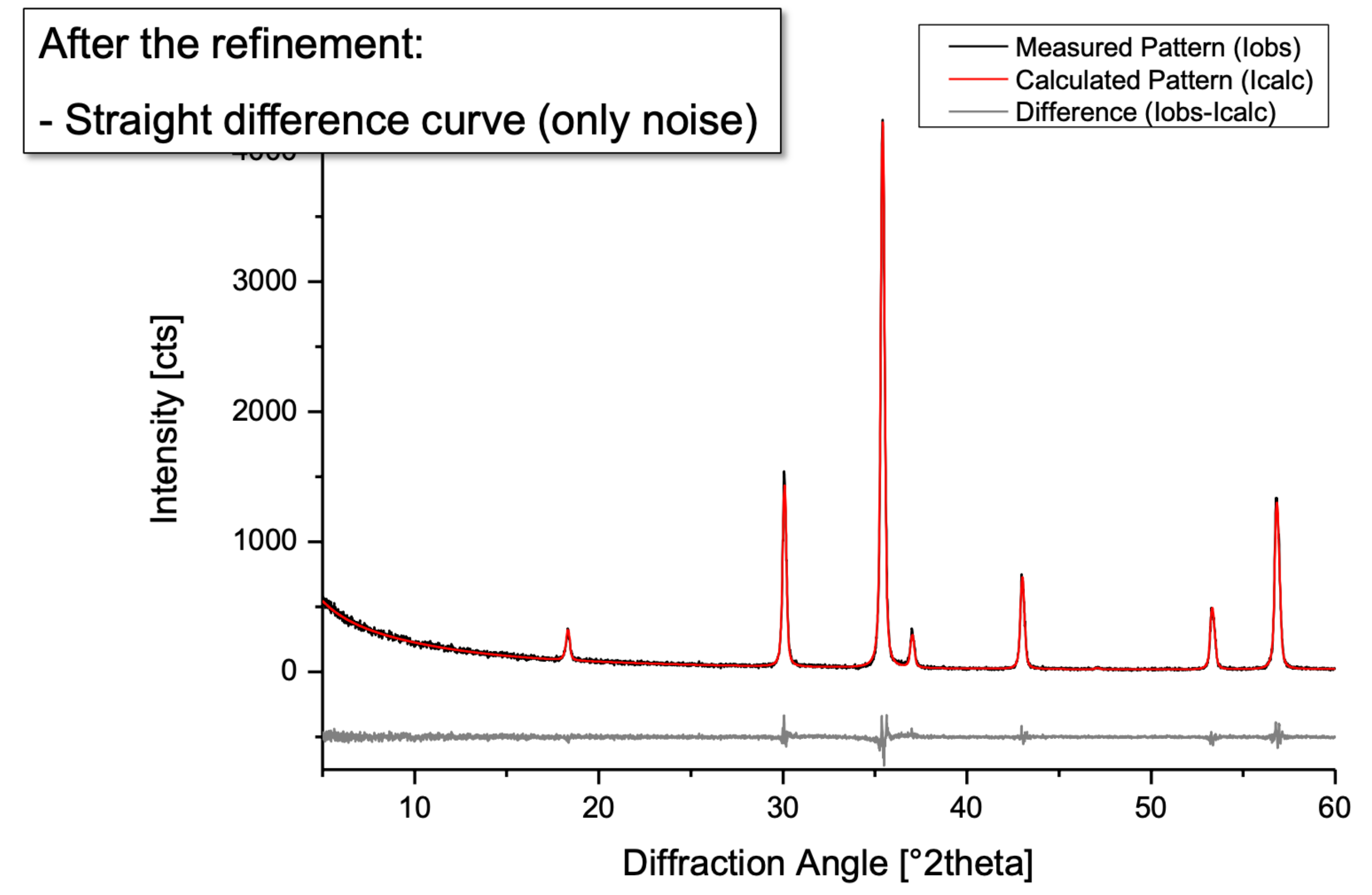


Beginning of the refinement:

- Phase was identified correctly (peaks at the right position)
- But differences exist:
  - Peak width
  - Peak positions slightly shifted
  - Intensities

From http://profex.doebelin.org/wp-content/uploads/2015/01/Lesson-5-Rietveld-Refinement.pdf

Rietveld Method



After the refinement:

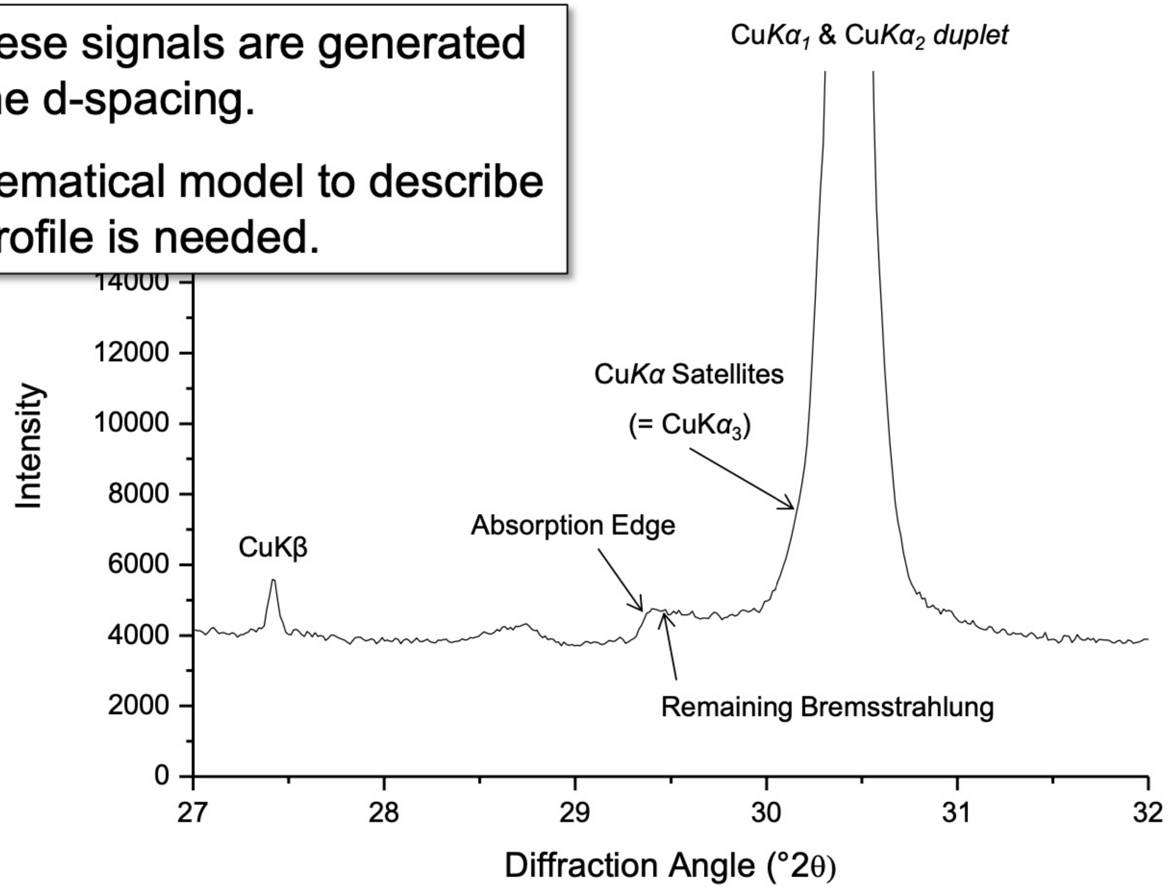
- Straight difference curve (only noise)

From http://profex.doebelin.org/wp-content/uploads/2015/01/Lesson-5-Rietveld-Refinement.pdf

Rietveld Method – Peak Profile

All these signals are generated by one d-spacing.

Mathematical model to describe the profile is needed.



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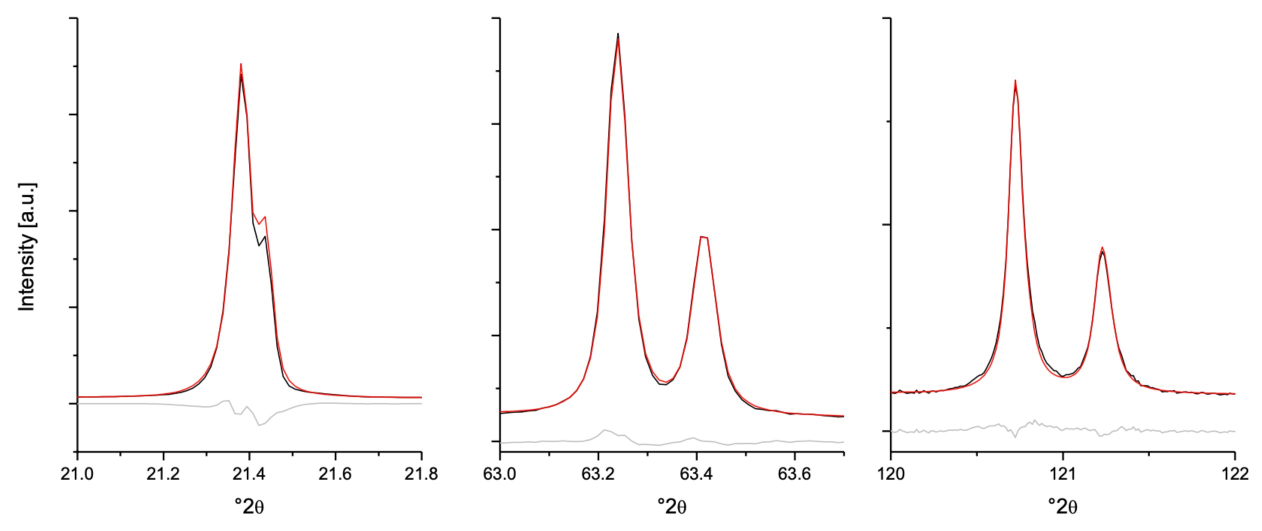
Rietveld Method – Peak Profile



Peak Shape Functions

Pseudo-Voigt
(gaussian and Lorentzian)
(Traditional Rietveld Function)

To model peak asymmetry

Pearson VII

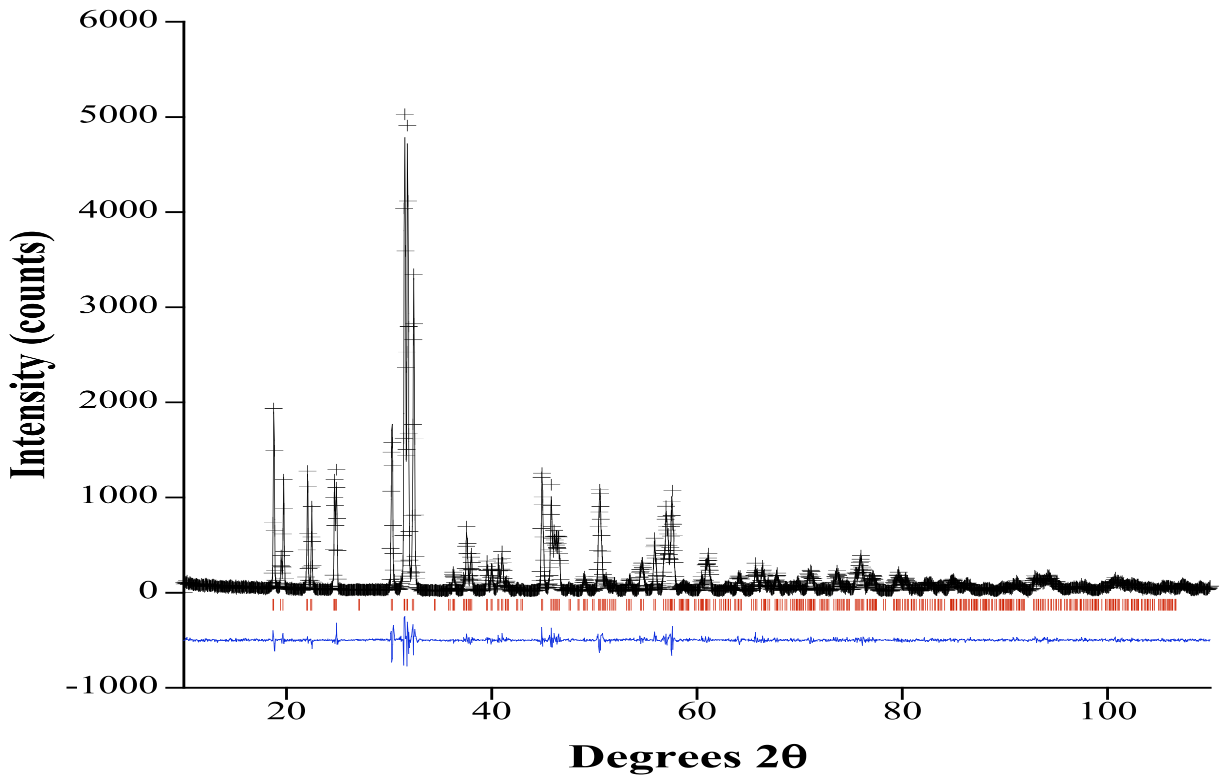
Thompson-Cox-Hasting
Pseudo Voigt

Split Pseudo Voigt

From http://profex.doebelin.org/wp-content/uploads/2015/01/Lesson-5-Rietveld-Refinement.pdf

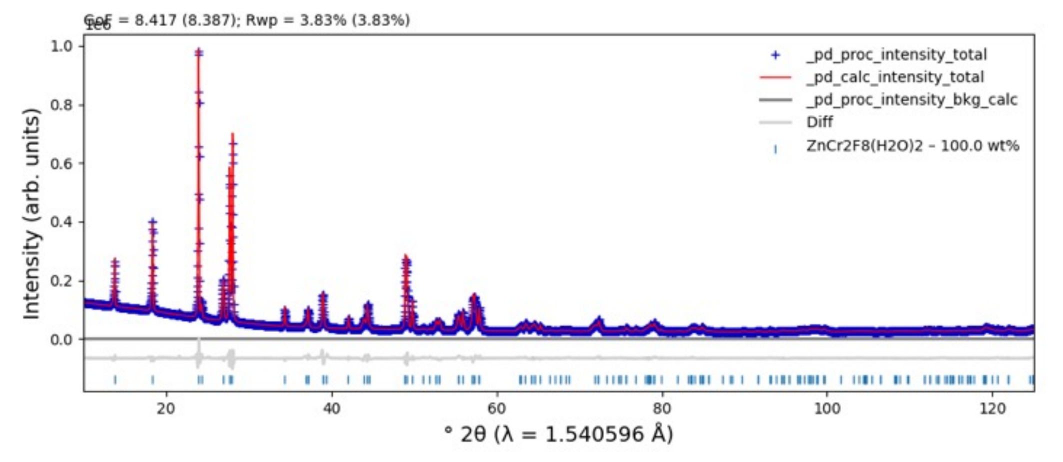
Rietveld Method

Rietveld Refinement of Pr_2NaRuO_6 using laboratory X-rays



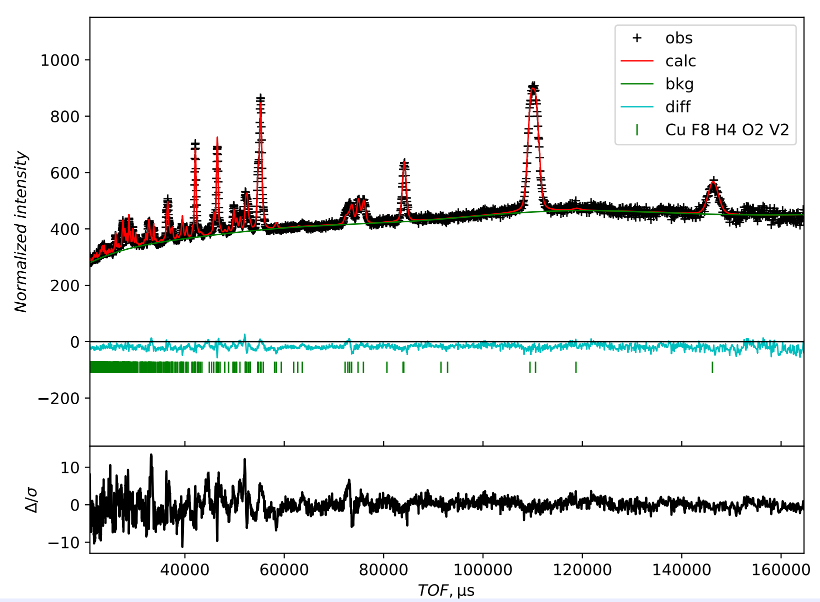
Rietveld Method

$ZnCr_2F_8(H_2O)_2$



XRD

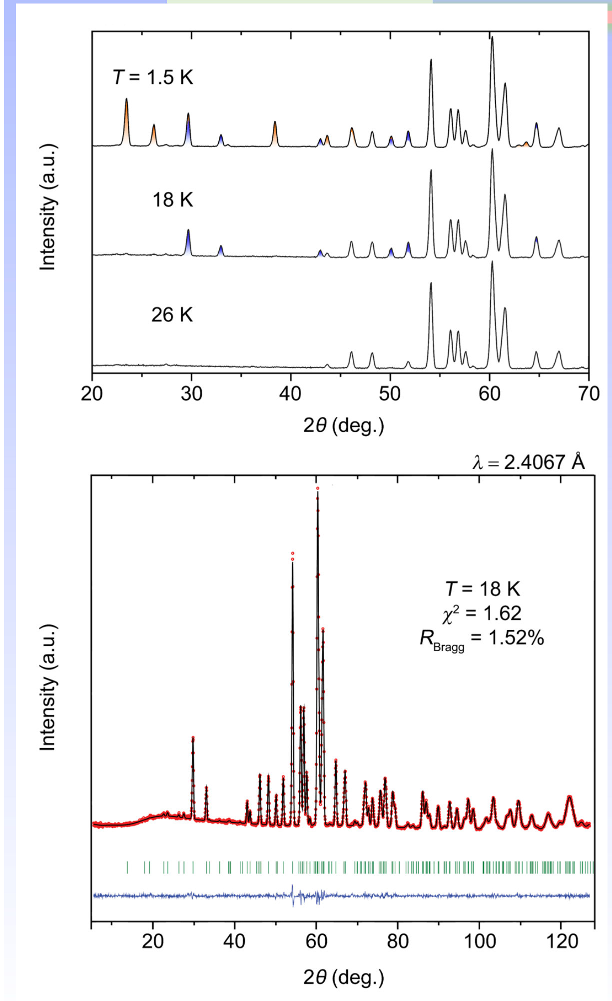
$ZnV_2F_8(H_2O)_2$

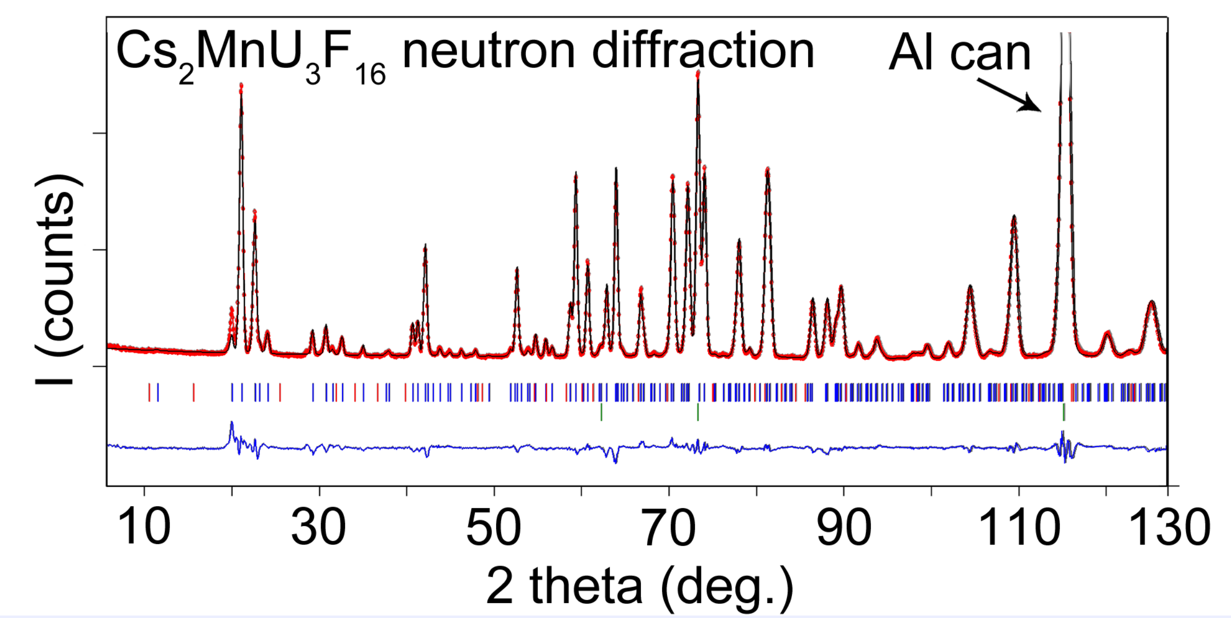


Neutron Time-of-Flight POWGEN

Rietveld Method

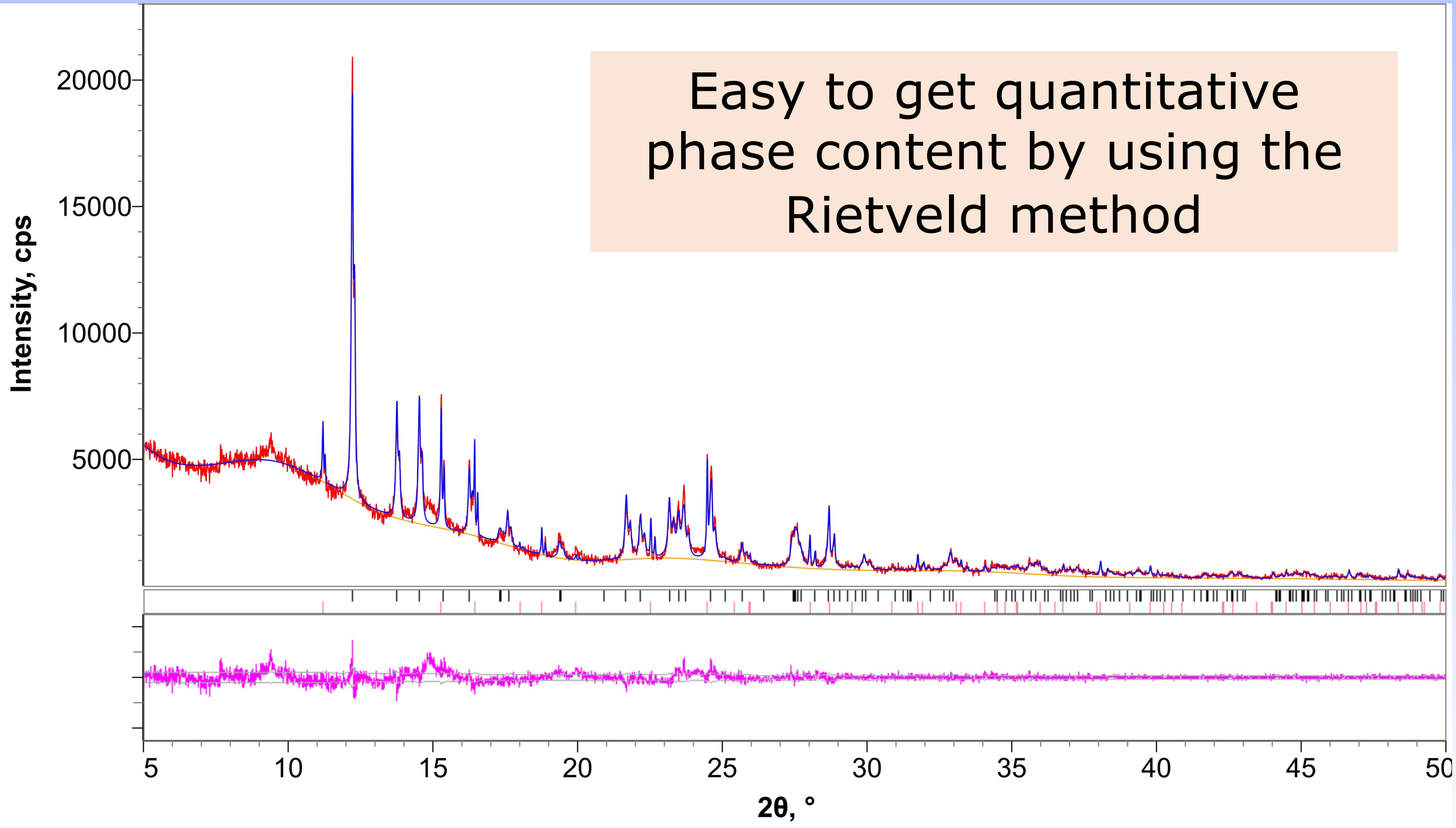
$CsMn2F_6$



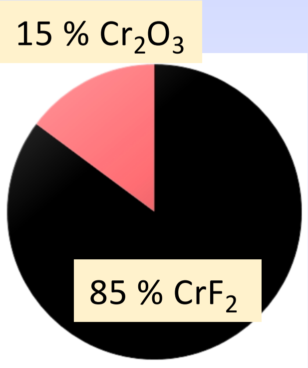


Neutron HFIR

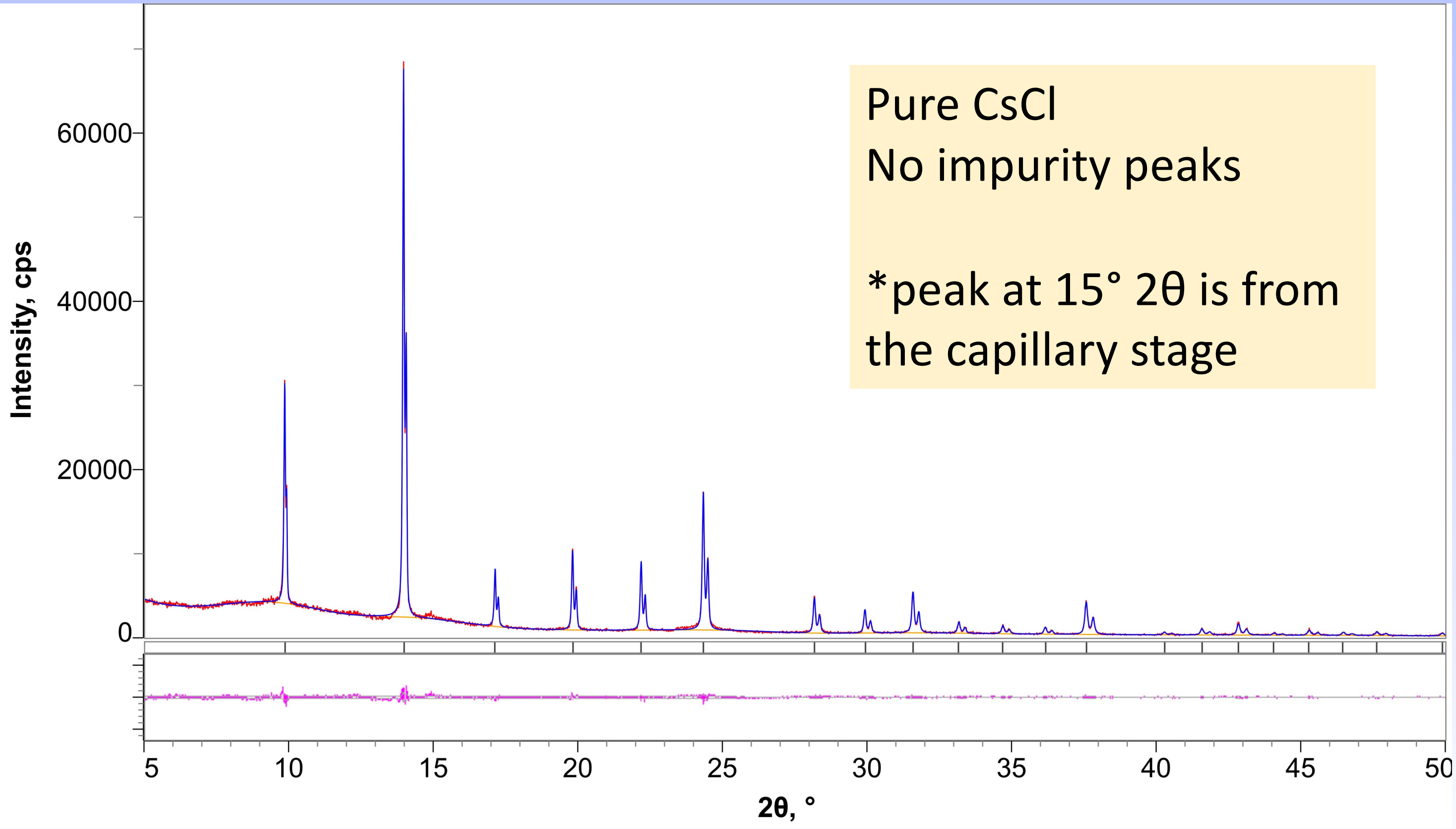
Rietveld Method – CrF_2 In Sealed Capillary



Easy to get quantitative phase content by using the Rietveld method



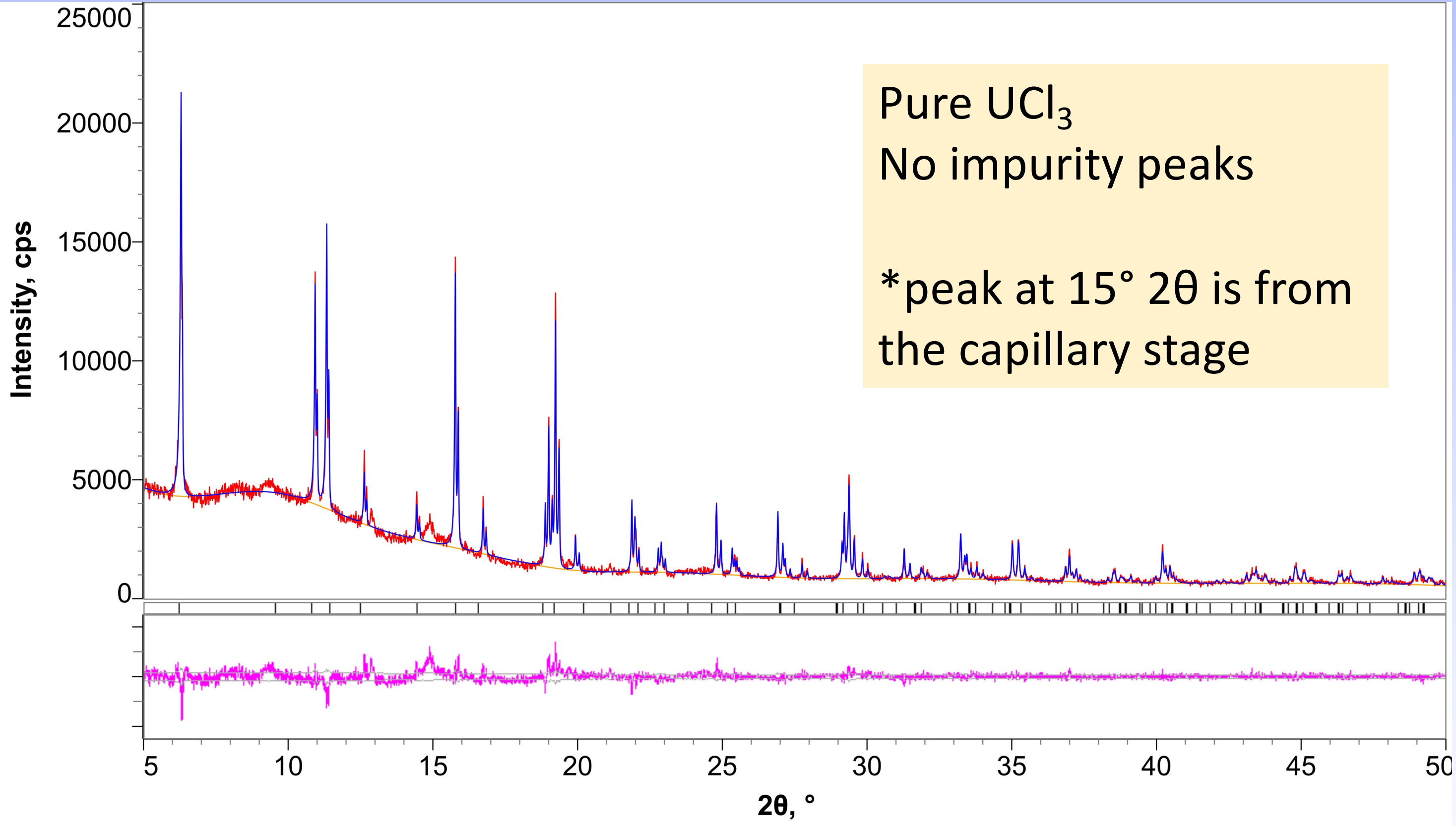
Rietveld Method – CsCl
In Sealed Capillary



Pure CsCl
No impurity peaks

*peak at 15° 2θ is from the capillary stage

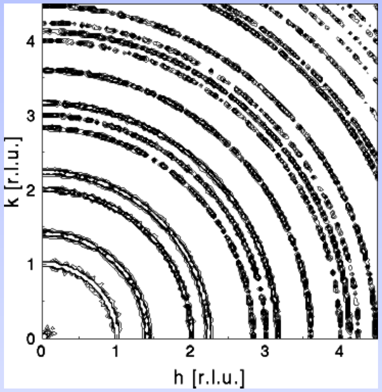
Rietveld Method – UCl_3 In Sealed Capillary

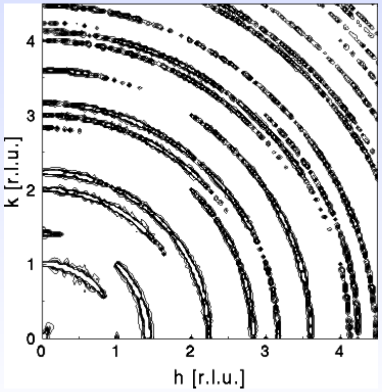


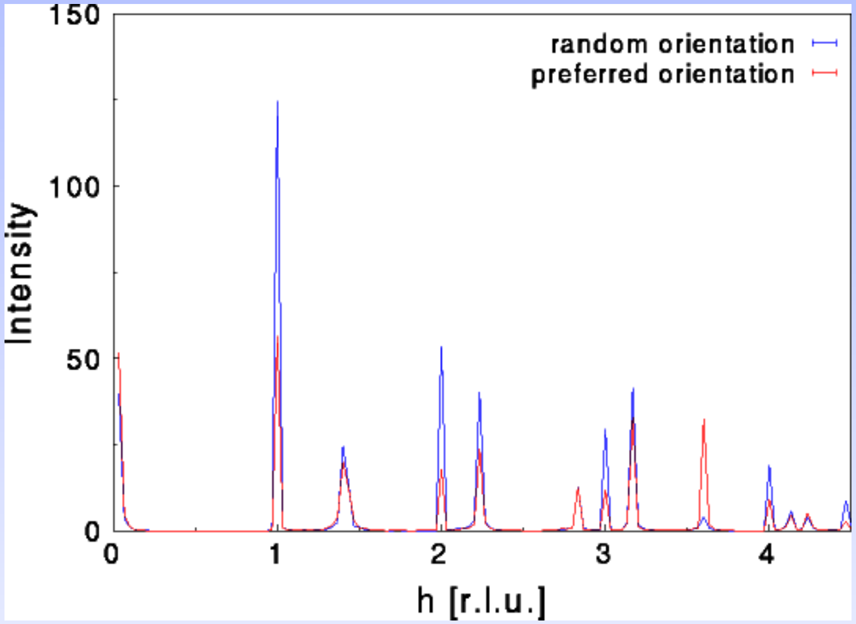
Pure UCl_3
No impurity peaks

*peak at 15° 2θ is from the capillary stage

Preferred Orientation







The top image shows 200 random crystallites. The bottom picture shows 200 oriented crystallites. Despite the identical number of reflections,several powder lines are completely missing and the intensity of other lines is very misleading. Preferred orientation can substantially alter the appearance of the powder pattern. It is a serious problem in experimental powder diffraction.