Basic powder diffraction and the Rietveld method

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Outline

- Basic introduction to diffraction
- Diffraction measurements
- Diffraction & periodicity
- X-rays or neutrons?
- Structure solution and refinement
  - Phase problem
  - Other factors contributing to observed intensity
  - The Rietveld method
  - Common problems
- Reading and literature

Basic introduction to diffraction

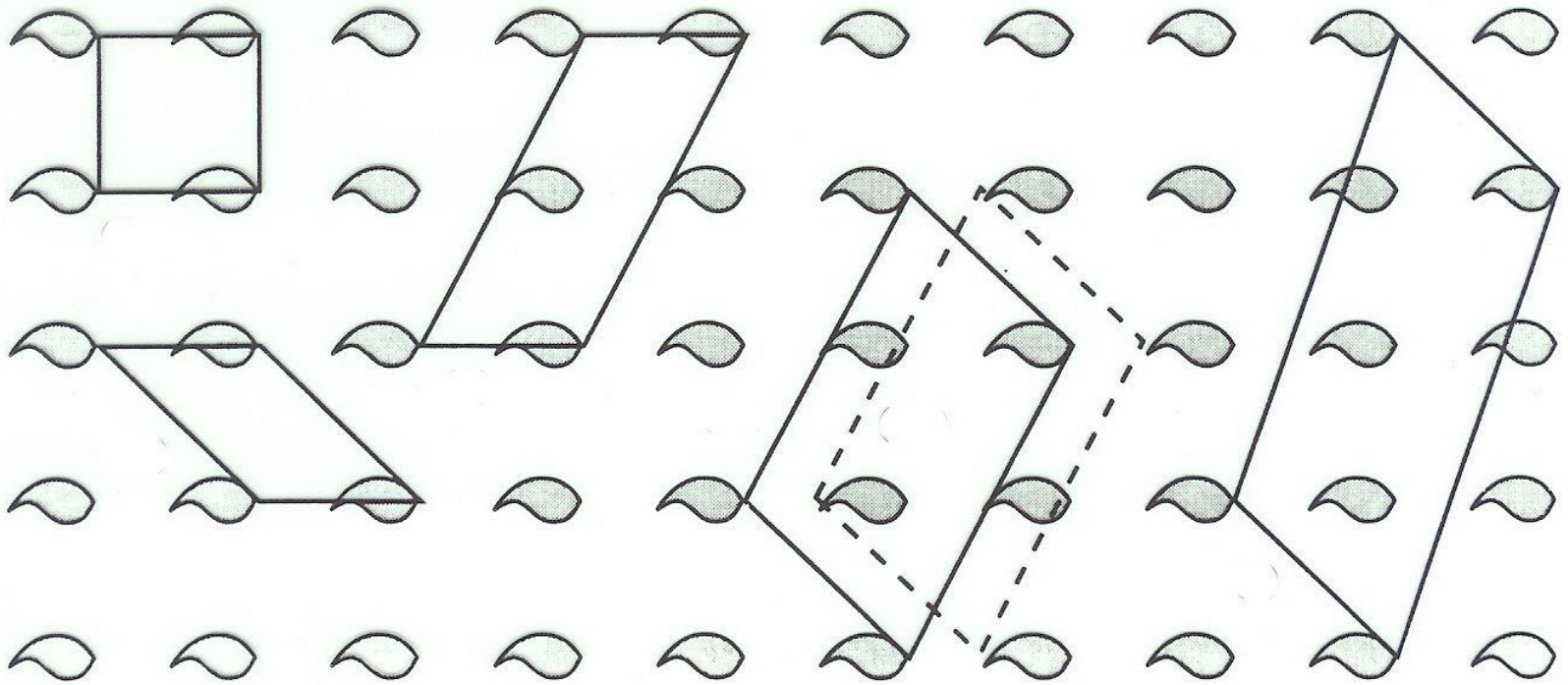
- The lattice
- Crystal systems
- Centering
- 3-D lattice types
- Miller indices/planes
- Bragg equation
- Ewald Sphere
- Reciprocal lattice
- Conditions for observing diffraction
- Laue diffraction

Lattice & unit cells: 1-D

Lattice + Motif = Structure

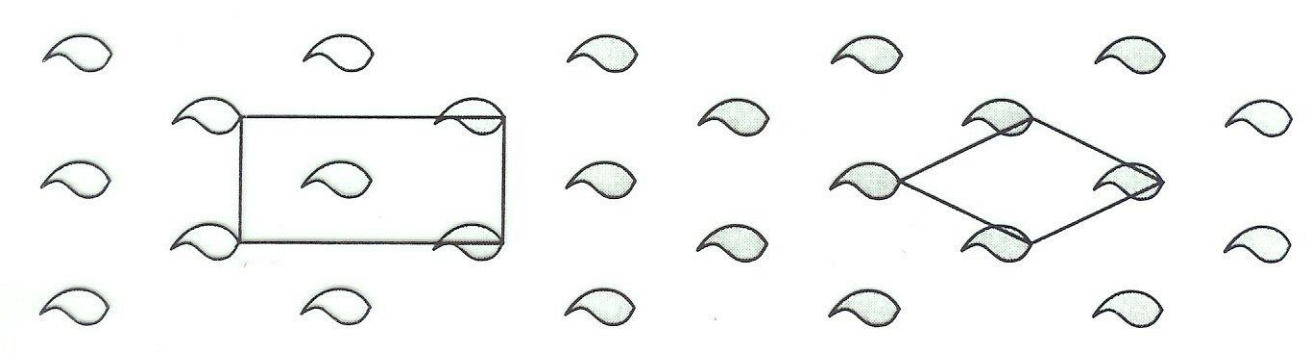
The motif can be an atom, molecule, part of a molecule or several molecules

Lattice & unit cell: 2-D



All the cells highlighted are equally valid. All will reproduce the 2-D lattice array. The convention is too choose the smallest cell that also represents the symmetry of the structure.

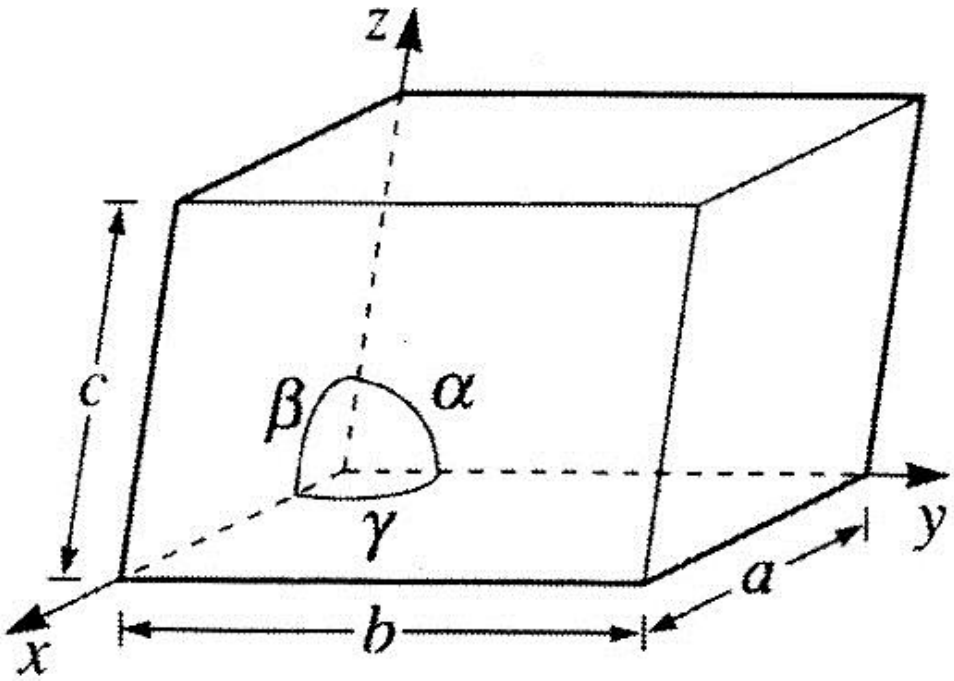
Lattice & unit cell: centering



Rules for unit cell selection:

- Unit cell should show the symmetry of the crystal
- Origin should be a geometrically unique point, priority given to an inversion centre
- Basic vectors should be as short as possible and the angle between them as close to 90° as possible.
- ALL angles diverting from 90° should be larger or smaller (convention is larger)

Lattice & unit cell: 3-D



The unit cell has lattice parameters defined by the cell length *a*, *b*, and *c*, and the cell angles α, β, and γ:
γ is angle between *a* and *b*
β is angle between *a* and *c*
α is angle between *b* and *c*

Atomic positions are given as xyz coordinates:
x is fraction of *a* axis
y is fraction of *b* axis
z is fraction of *c* axis

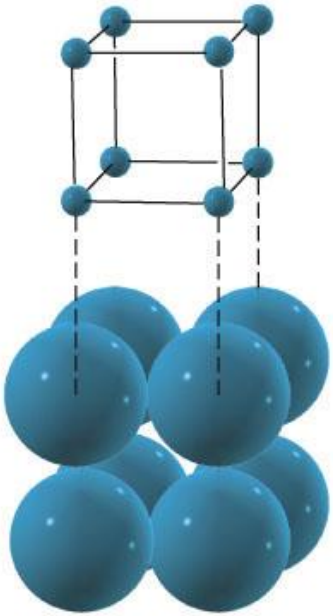
Conventions
- cell parameters are in Å or pm
- Angles are in °

Lattice & unit cell: 3-D crystal systems

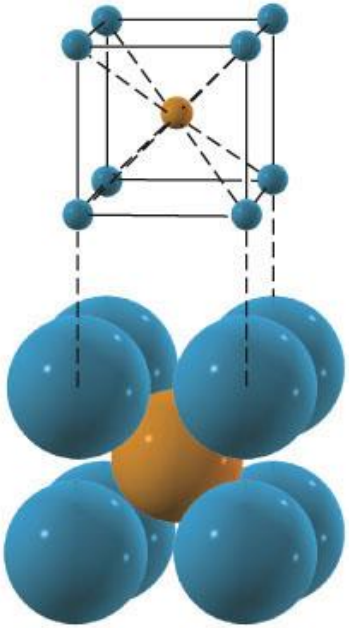
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$ $\beta \neq 90°$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$

Lattice & unit cell: 3-D cell setting

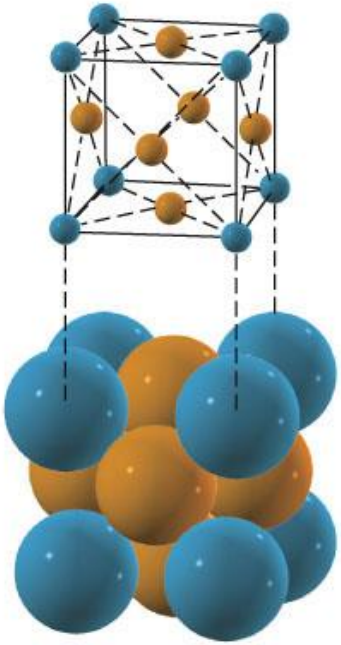
Primitive
P



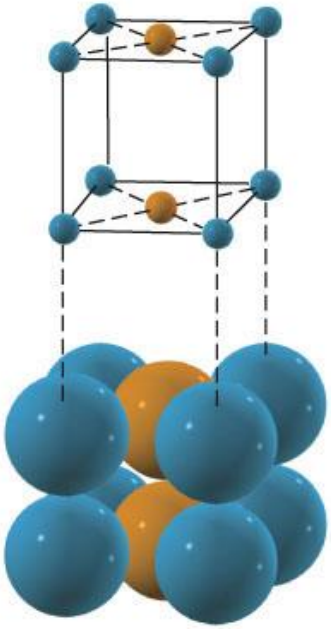
Body centred
I



Face centred
F

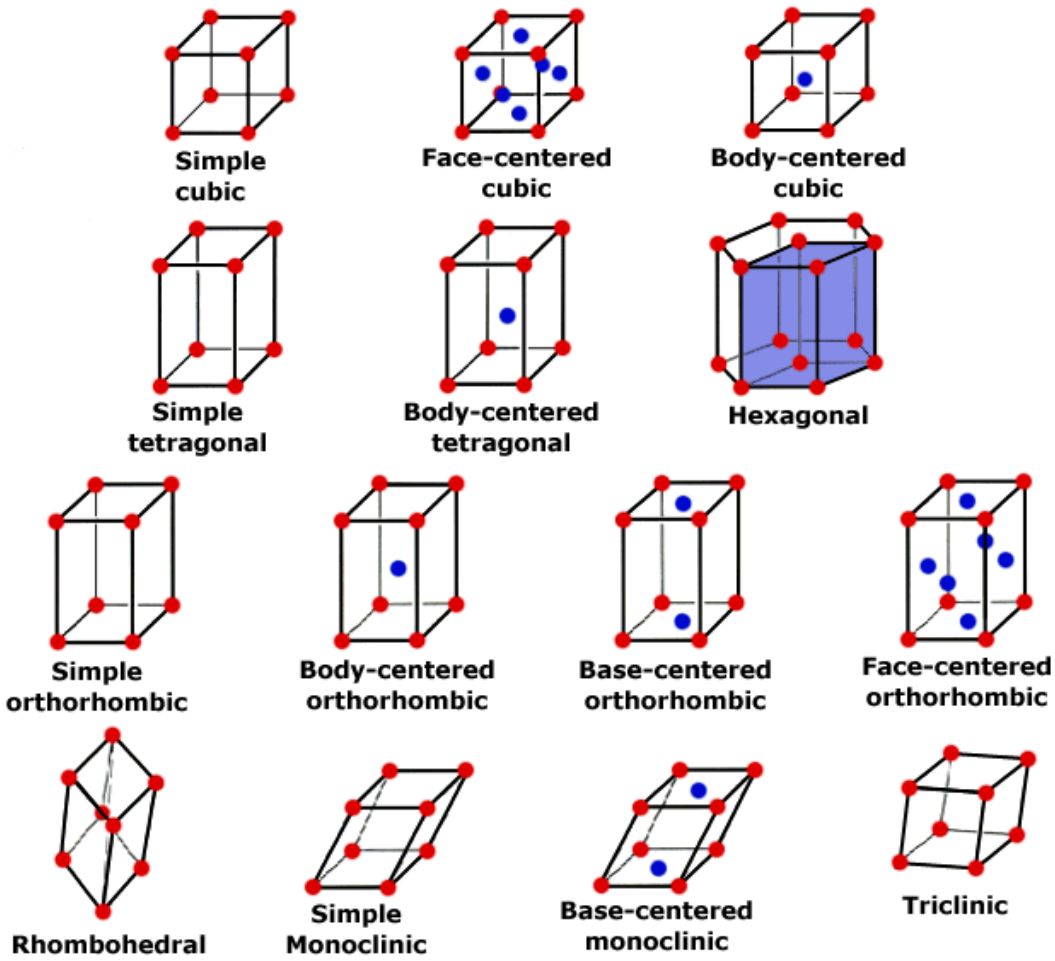


Side centred
C (A/B)



NB: Atom types are identical even though coloured differently

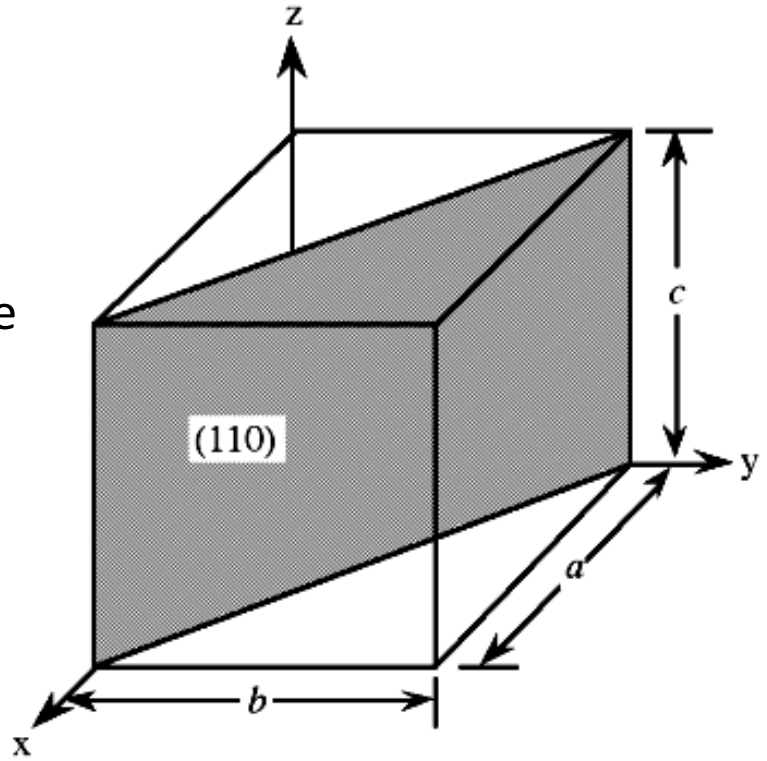
Lattice & unit cell: 3-D lattice types



7 crystal classes
14 Bravais Lattice types
230 space groups

Miller indices / planes

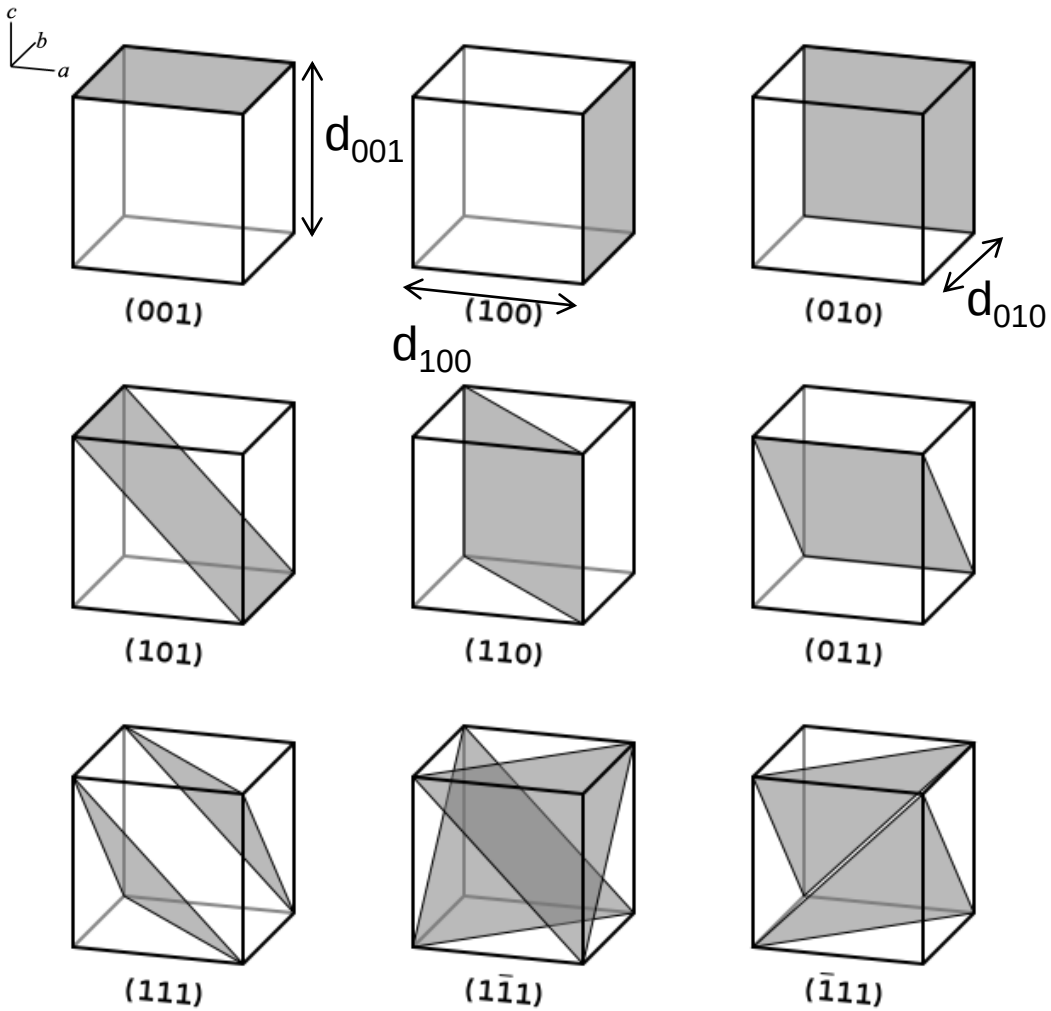
Unit cell planes can be defined by the notation called Miller indices. The Miller index is given as a hkl number where *h*, *k*, and *l* are reciprocals of the plane with the *x*, *y*, and *z* axes.



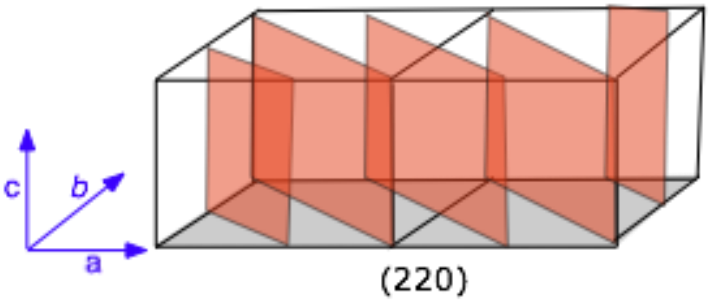
To obtain the Miller indices of a given plane requires the following steps:

Step 1. The plane in question is placed on a unit cell.
Step 2. Find its intercepts with each of the crystal axes.
Step 3. The reciprocal of the intercepts are taken.
Step 4. Multiply by a scalar to get a ratio of integers.

Miller indices

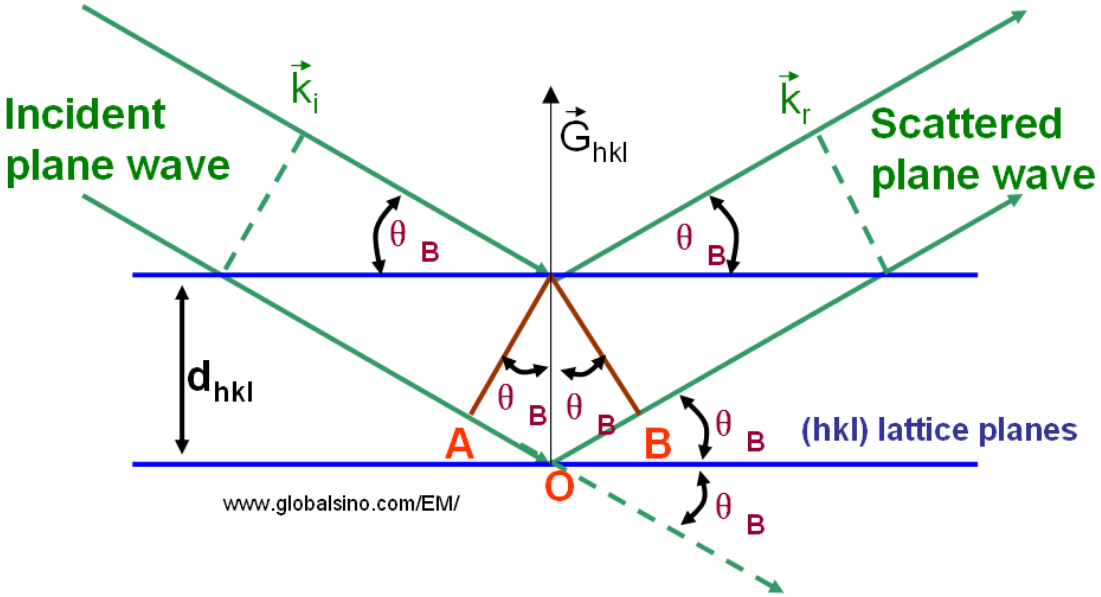


The higher the Miller index the less distance there is between equivalent planes, dividing the unit cell into ever smaller slices



For higher symmetry cells interplane distances are identical $d_{001} = d_{010} = d_{100}$ for cubic

The Bragg equation



- Constructive interference occurs when the waves reflected from adjacent scattering planes remain in phase – diffraction peak is observed
- The path difference travelled by waves between adjacent planes must be an integral multiple of the wavelength

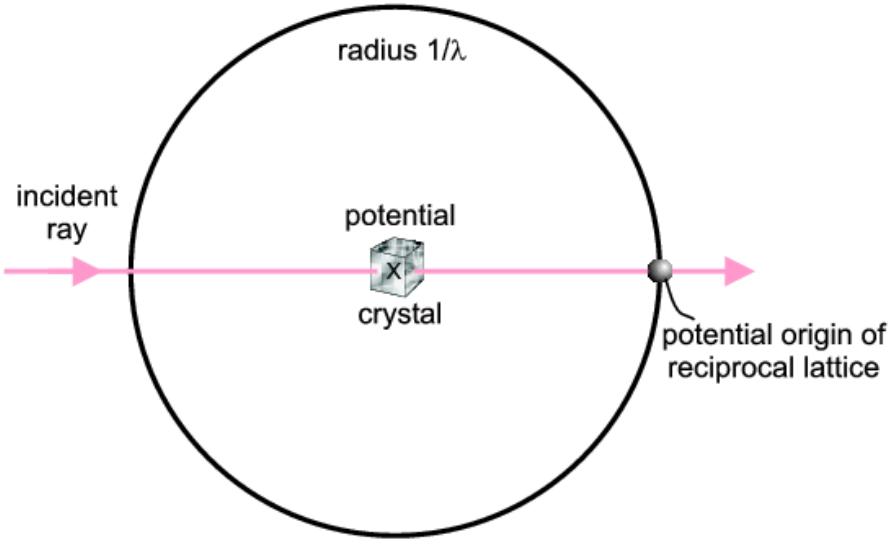
$$n\lambda = 2d\sin\theta$$

Distance between Miller planes

d-spacings in different crystal systems

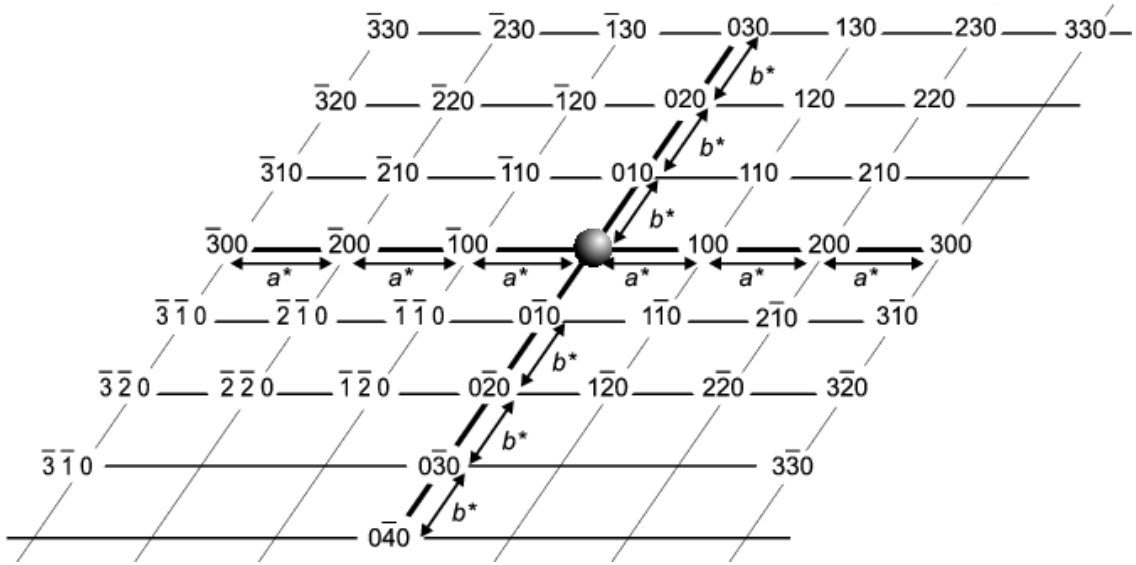
Crystal system	d_{hkl} as a function of Miller indices and lattice parameters
Cubic	$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$
Tetragonal	$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$
Orthorhombic	$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
Hexagonal	$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2}$
Monoclinic	$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$

Ewald sphere



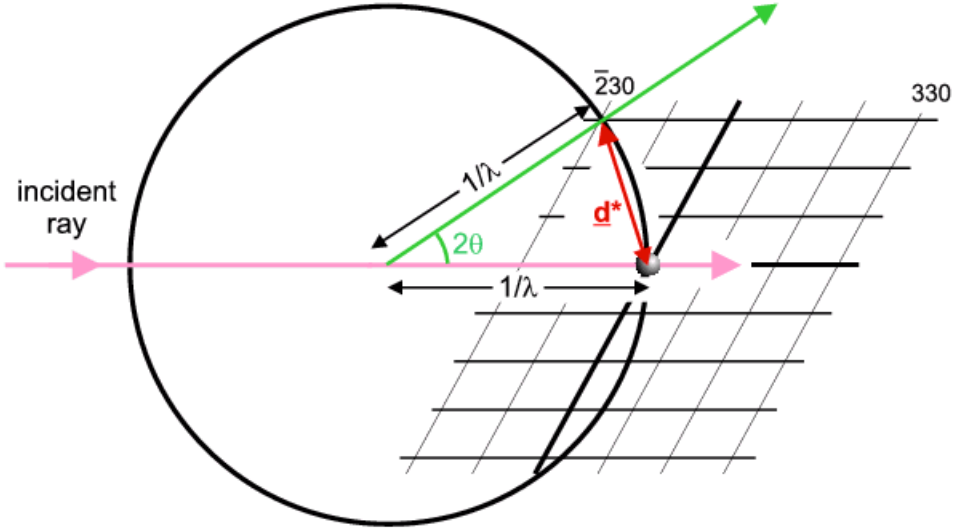
- A sphere of radius 1/λ (2-D projection shown above)
- Potential diffracted X-rays/neutrons can be along any radius from the centre of the sphere to the circumference (including out of plane in the projection above). This represents the experimental possibilities (λ, possible 2θs)

Reciprocal lattice



- Alternative view of the crystal structure (hk0 plane illustrated)
- The reciprocal lattice consists of points which represent diffraction possibilities
- Each point can be labeled with a Miller index
- The units of this lattice are a*, b* and c* and any point can be reached using the vector equation d* = ha* + kb* + lc*

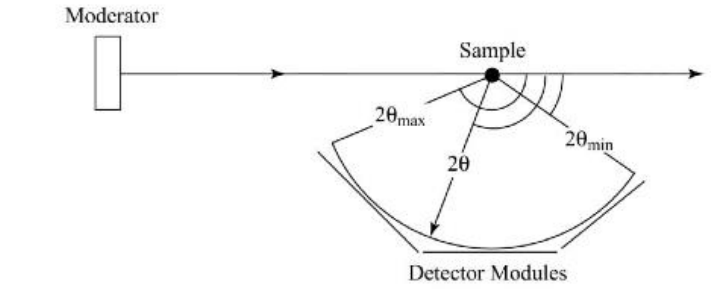
Condition for observing Bragg diffraction

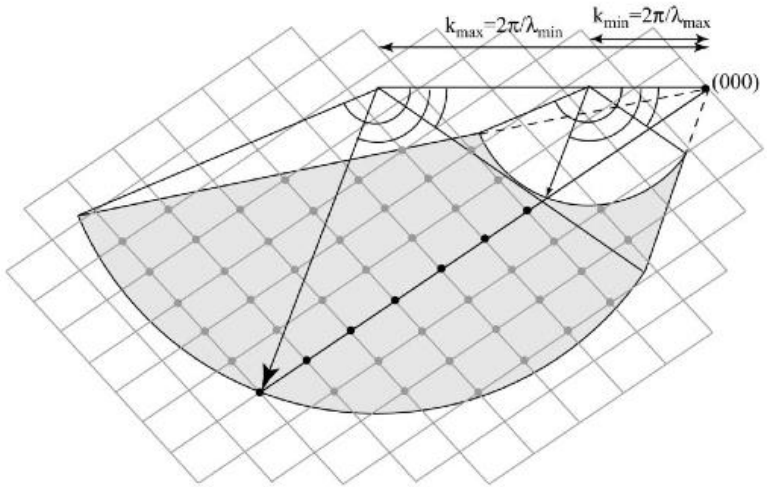


- Diffraction observed when a reciprocal lattice point intersects Ewald sphere
- Crystal rotation brings other lattice points into contact with Ewald sphere
- The vector from origin to lattice point is d* (reciprocal lattice spacing) is red – it is exactly equal to 1/d and its direction is perpendicular to the hkl plane
- The direction of the diffracted ray is indicated in green

Laue Diffraction

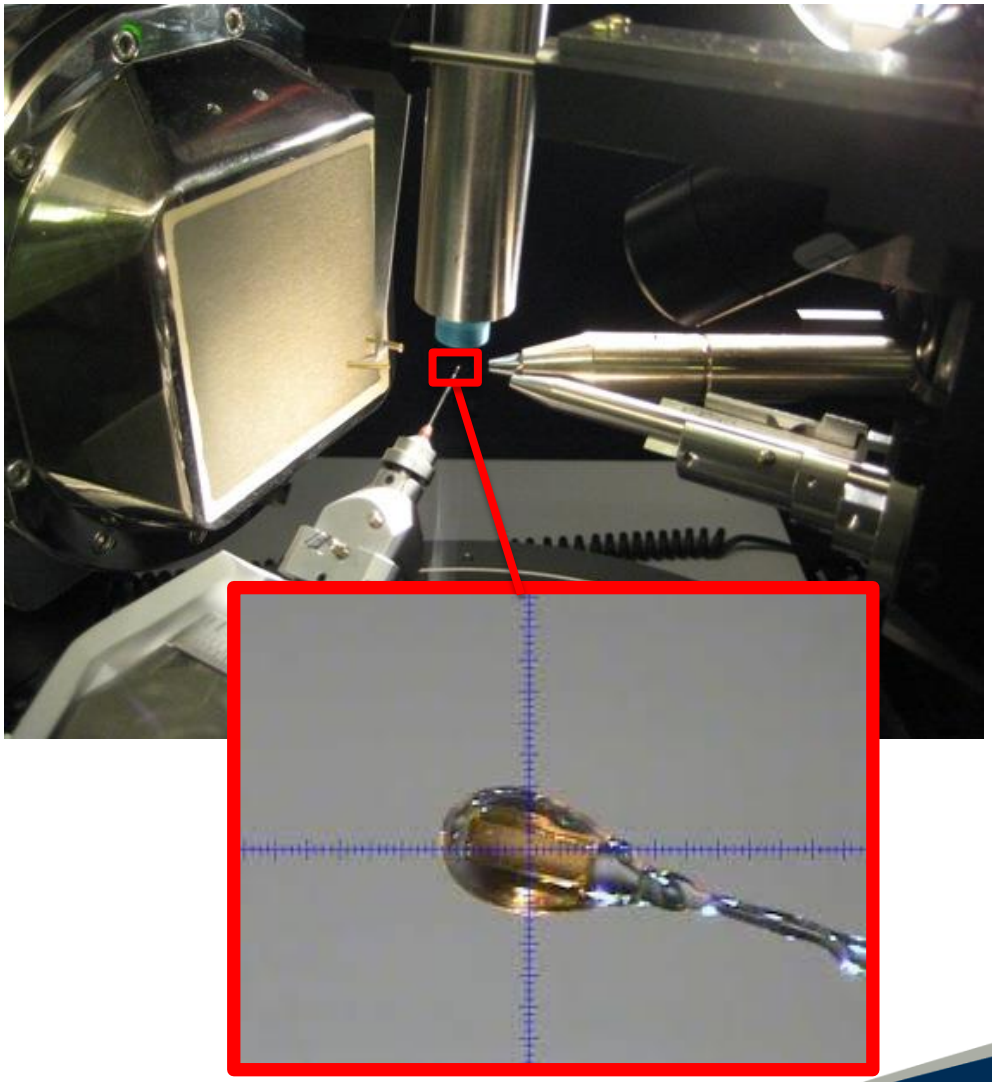
- Wavelength band to sample a larger volume of reciprocal space
- A wide wavelength band covers a large reciprocal space volume
- Limits are λ_{min}, λ_{max}, the accessible scattering angle of the instrument and the diffraction limit of the crystal
- All reciprocal lattice points that lie in the shaded region will be sampled simultaneously
- More chance of spatial overlap of reflections, particularly with large unit cells
- Detector technology becomes paramount – image plate v continuous output
- Wavelength band must be well characterised for data normalisation

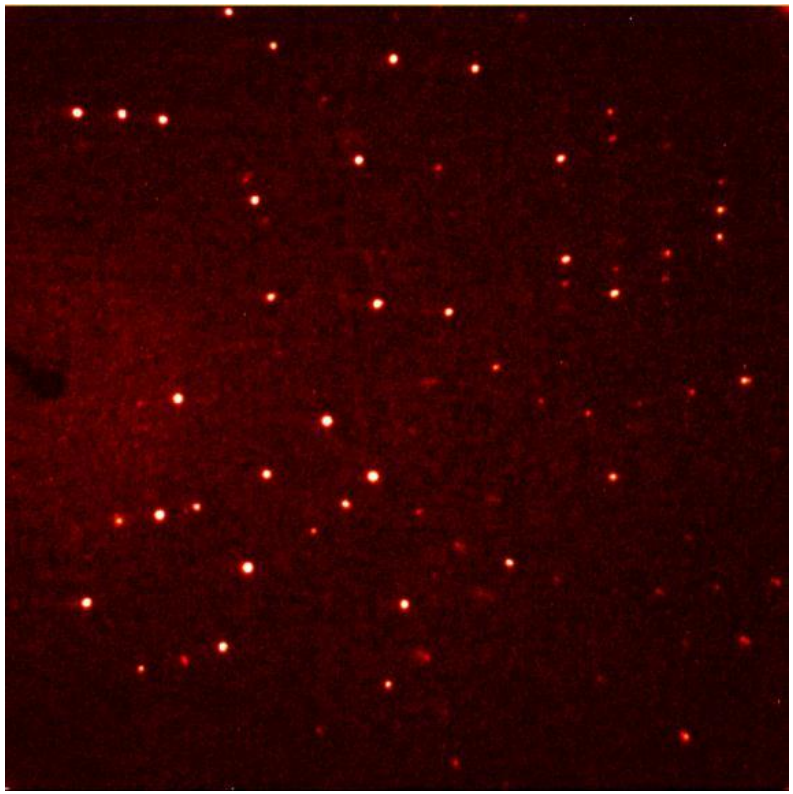




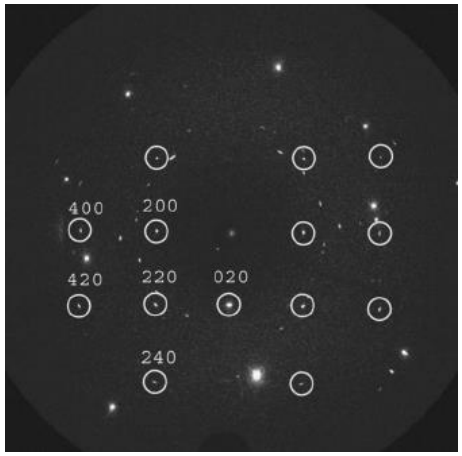
Diffraction measurements

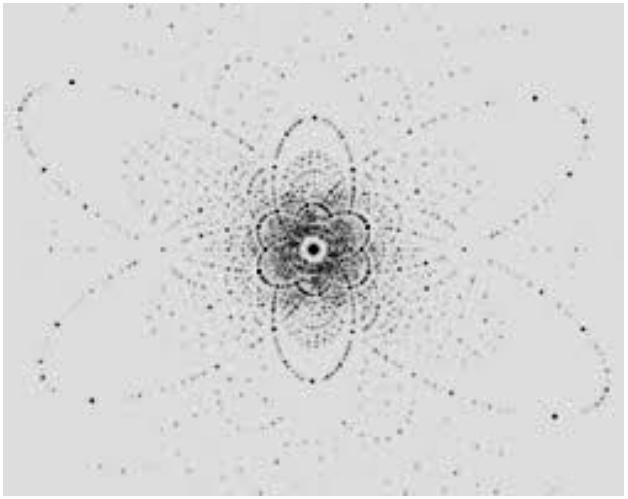
Single crystal diffraction

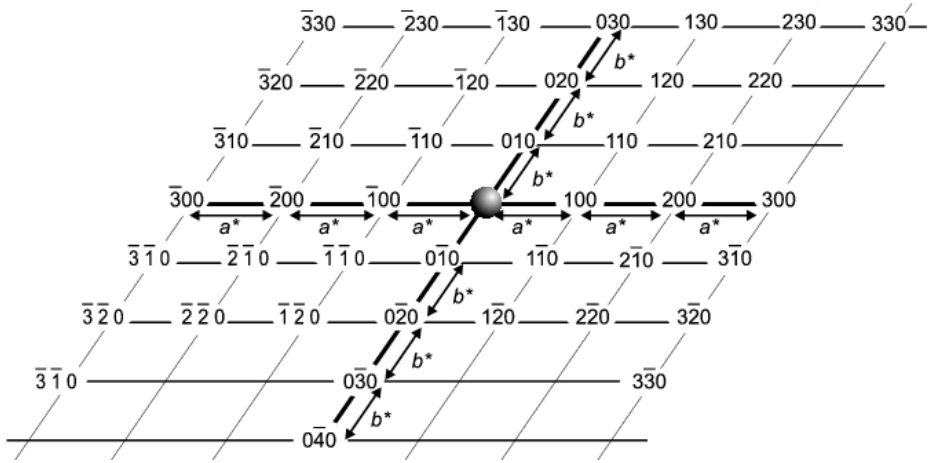




Single Crystal Diffraction

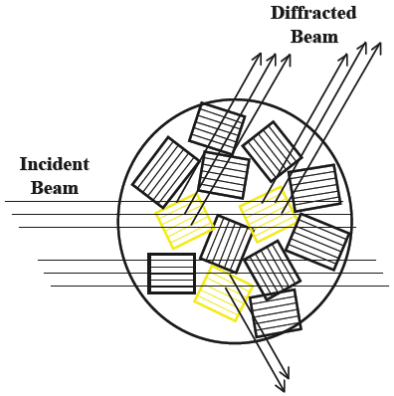


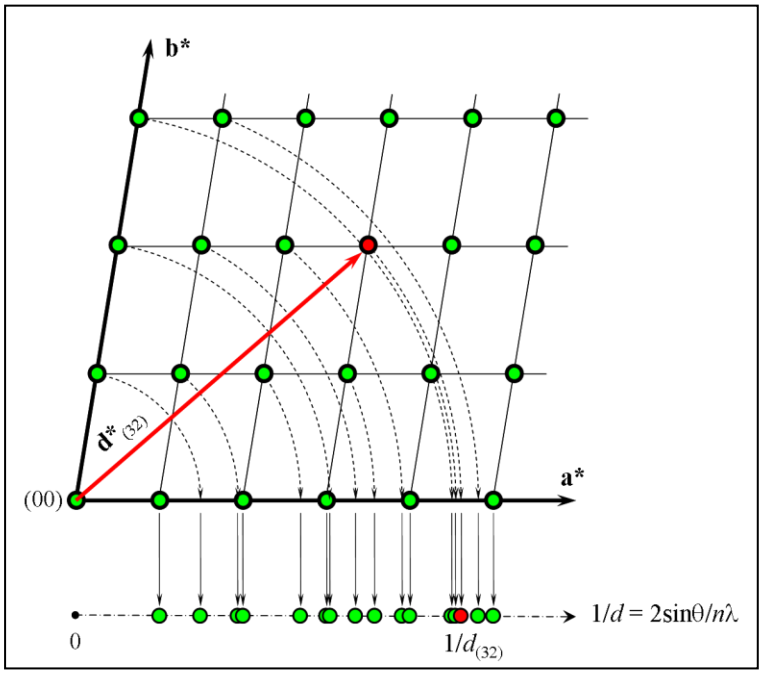




Direct observation of the reciprocal lattice

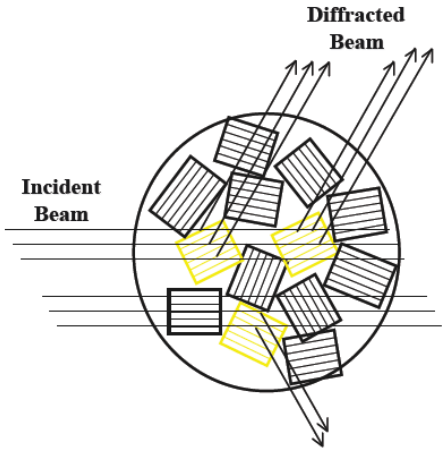
Powder diffraction in reciprocal space

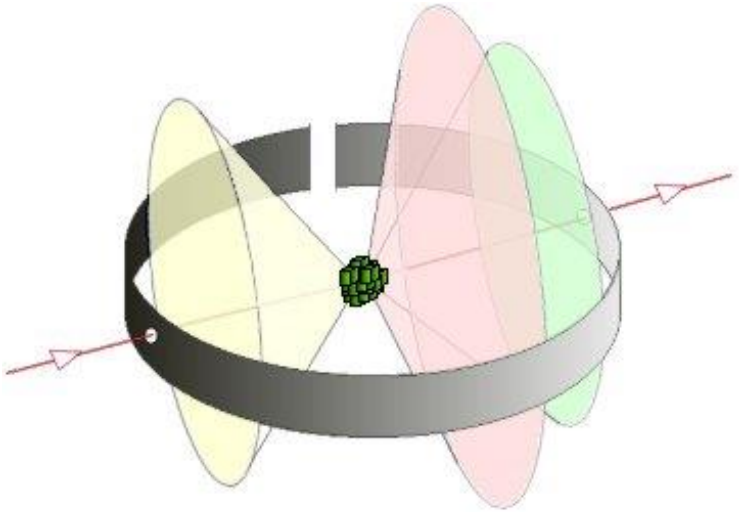


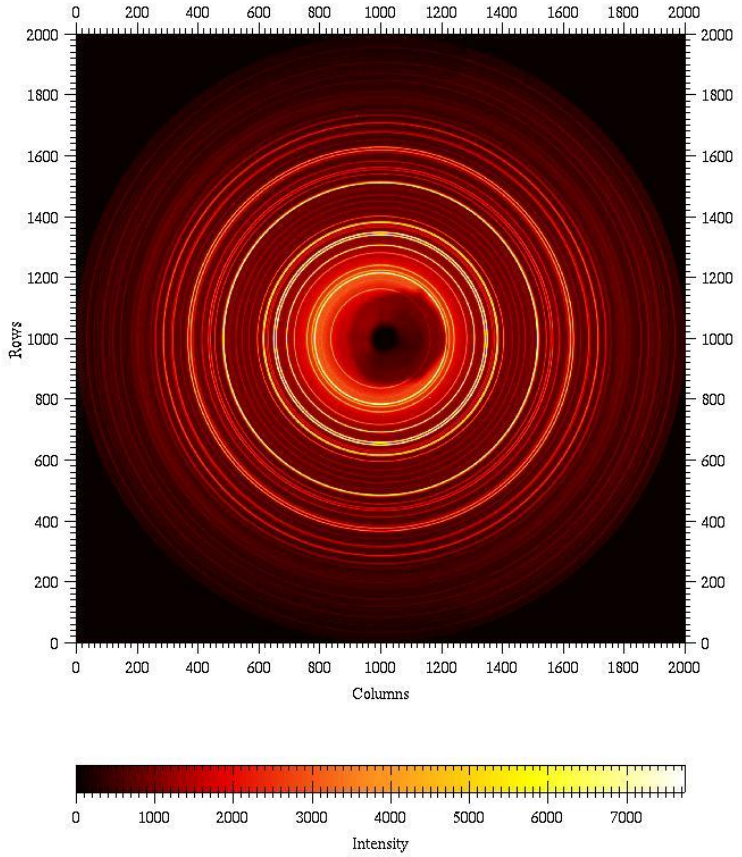


- Many crystallites with random orientation mean that each reciprocal lattice point will occur in every orientation possible, broadening into the surface of a sphere with radius d*
- The intersection of the Ewald sphere and the reciprocal lattice becomes a cone (intersection of 2 spheres)
- The directions of the vectors are lost and only the lengths of the reciprocal lattice vectors are measurable with powder diffractometers
- 3-D information collapsed into 1-D

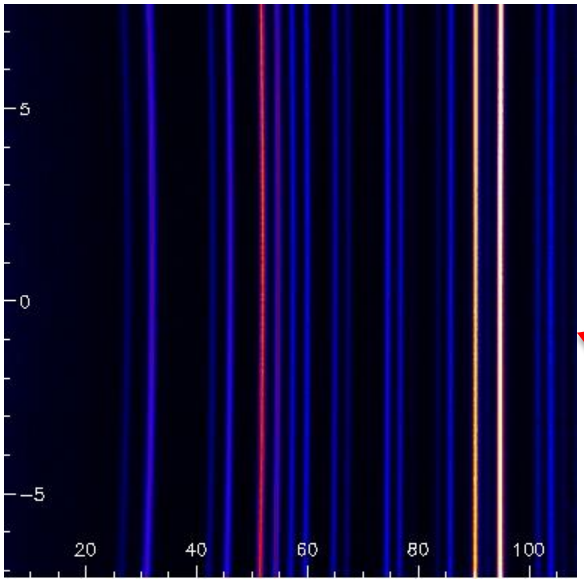
Powder diffraction

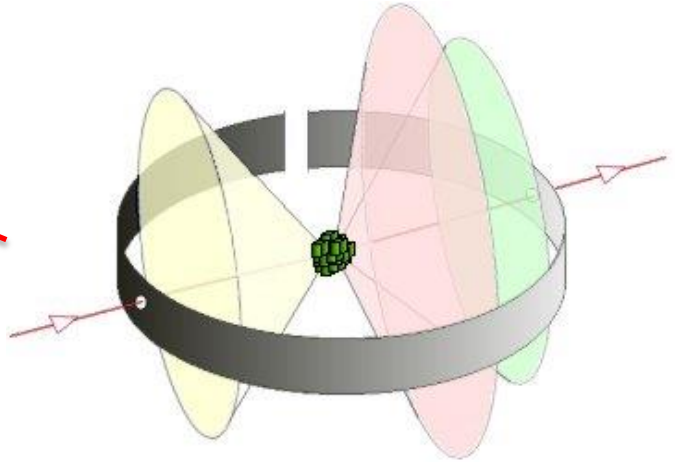


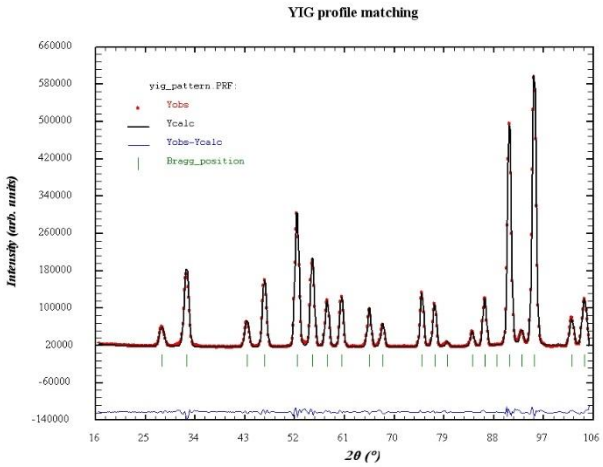




Powder diffraction







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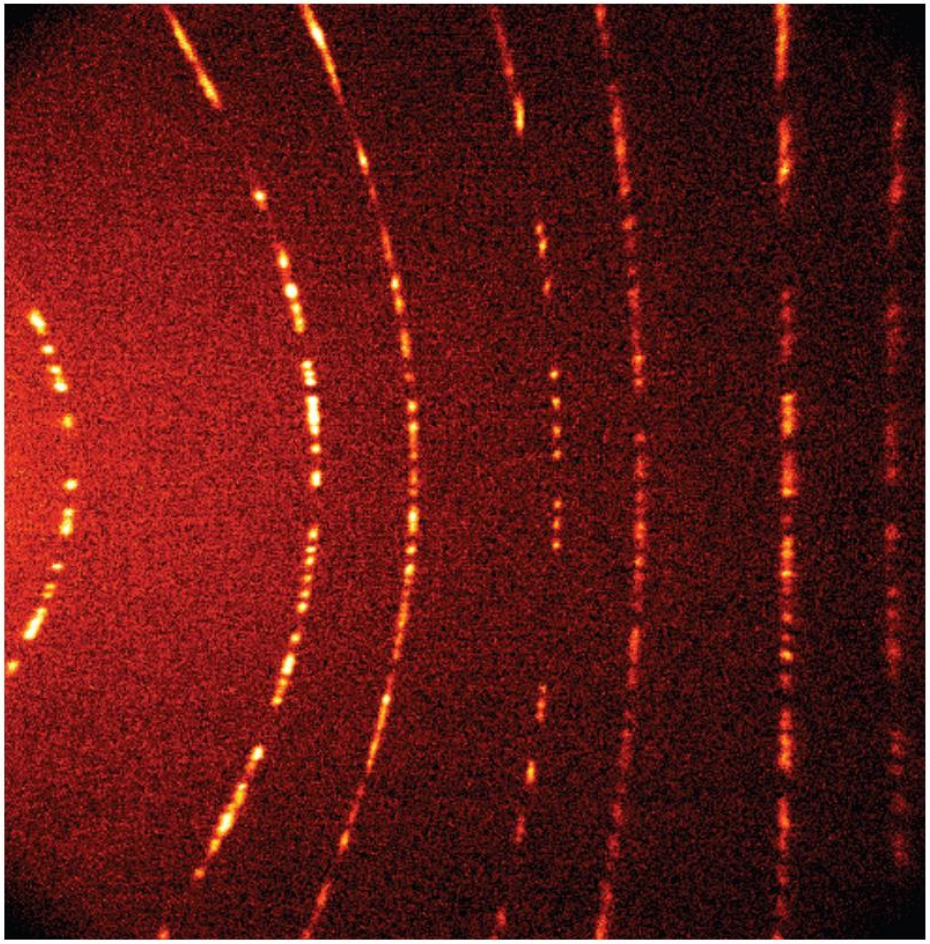
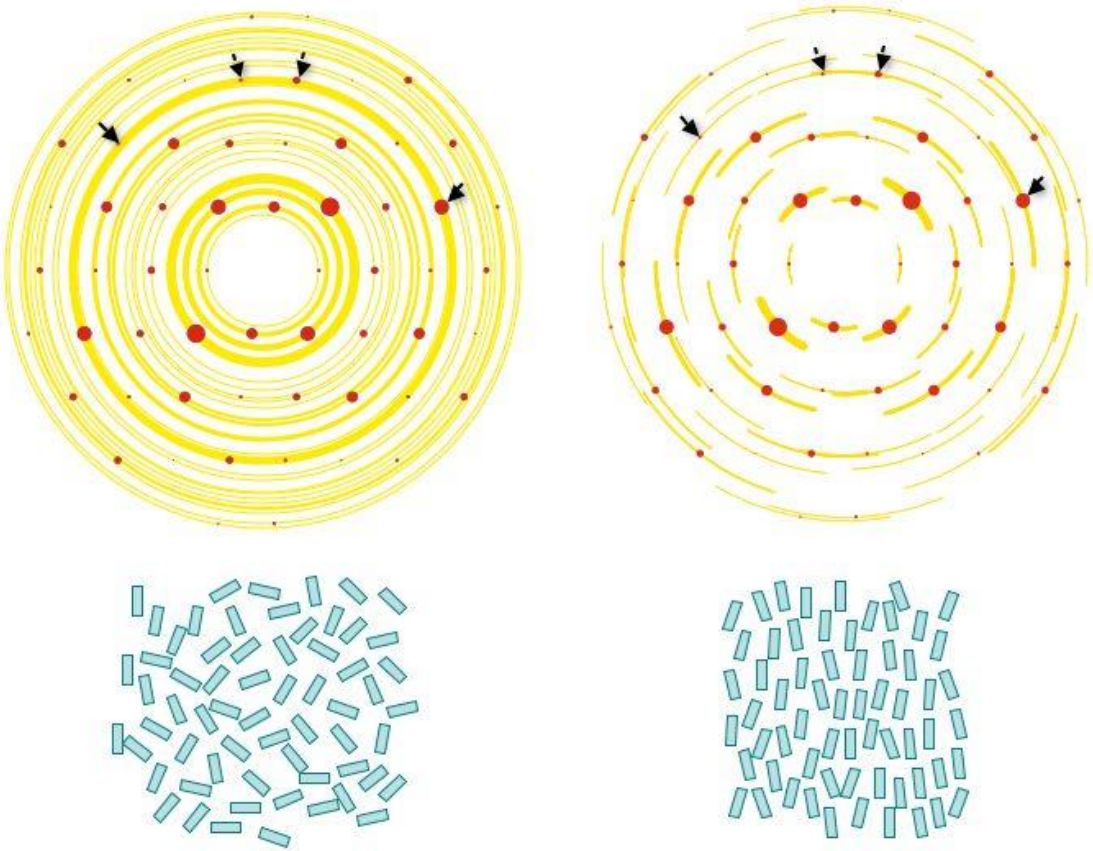
Not enough crystallites or a non-powder average



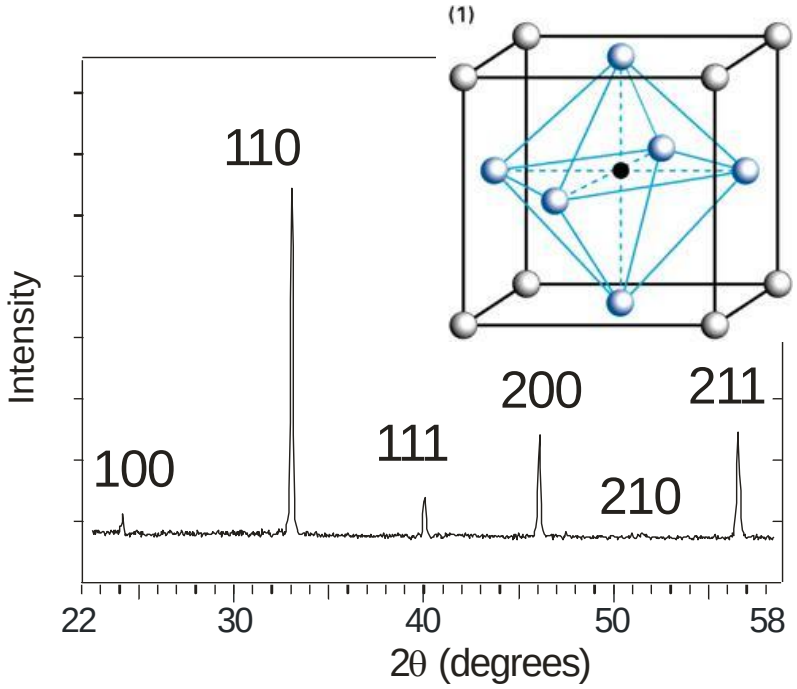
When number of crystals is too small, the pattern becomes “grainy” -- diffraction from individual crystals dominate.

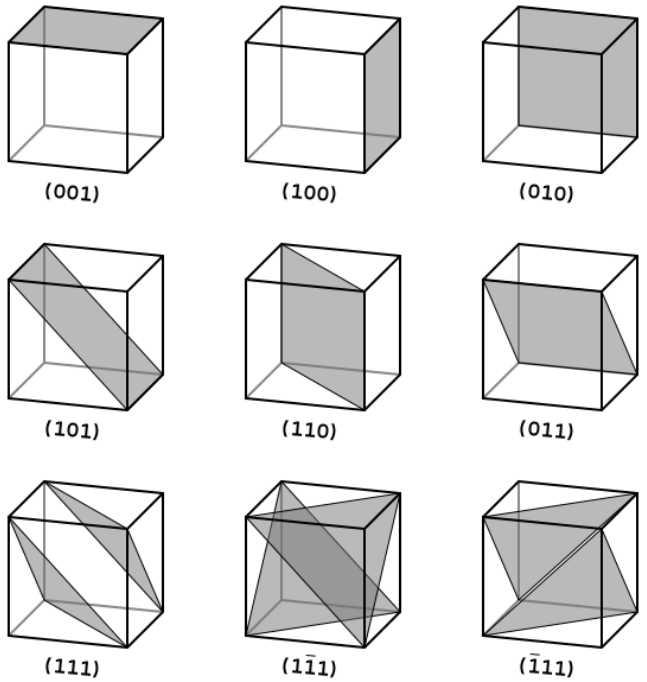
- Increase sample size
- Grind the sample to decrease domain size
- Oscillate or rotate the sample
- Use area detection & integrate the entire ring

Not enough crystallites or a non-powder average



Miller plane equivalence in powder diffraction





All equivalent planes occur at same scattering angle

All planes separated by the same distance occur at one scattering angle in powder diffraction

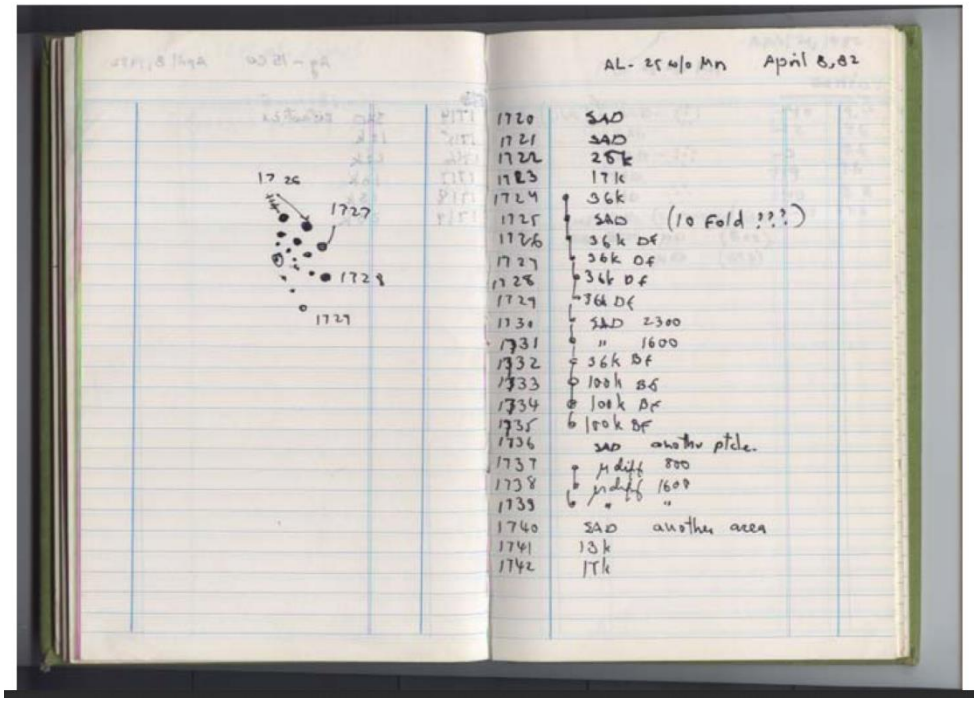
e.g. (511) and (333) occur at same 2θ for a cubic material

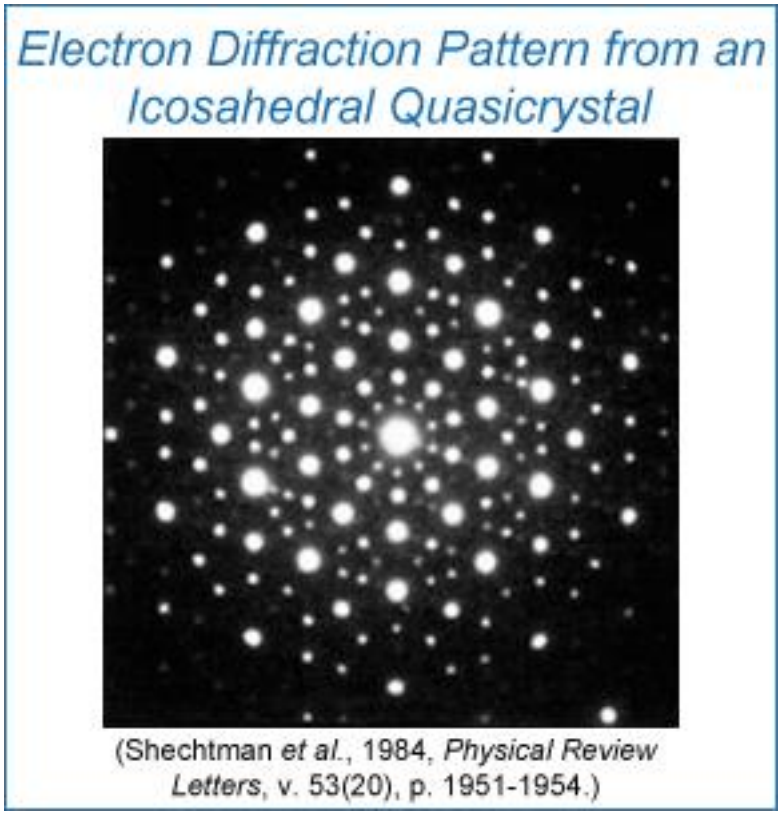
Diffraction and periodicity

Diffraction: Order and periodicity

- It was long thought that to give rise to diffraction a structure must be both **ordered** and **periodic** – in order to fill all available space and requires translational symmetry.
- This is represented by the **crystallographic restriction theorem** where only 2-, 3-, 4- and 6-fold rotational symmetries are allowed in periodic arrays.
- Aperiodic tiling patterns were discovered by mathematicians in the 1960s – popularised by Penrose tiling in the 1970s.
- Quasicrystals, displaying 5- or 10-fold rotational symmetry were discovered in the 1980s by Dan Shechtman and caused a paradigm shift in crystallography.
- Quasicrystals are **ordered**, **aperiodic** structures that lack translational symmetry but are formed from a large number of elements with regular spacing – hence they diffract.

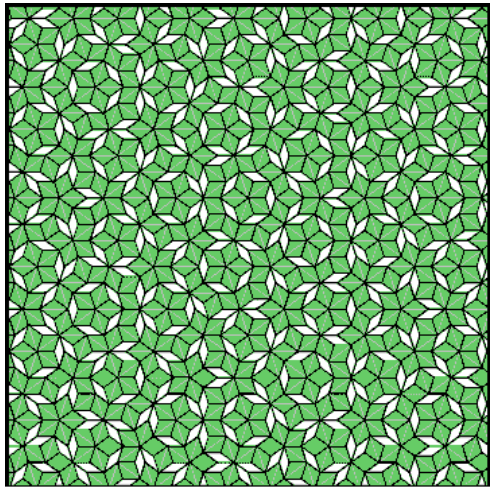
Dan Shechtman's lab book and first published electron diffraction pattern

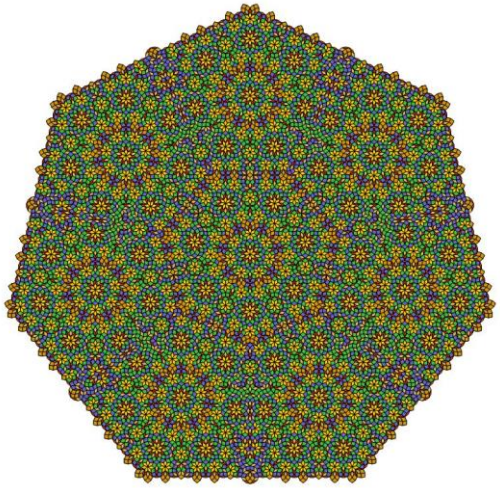


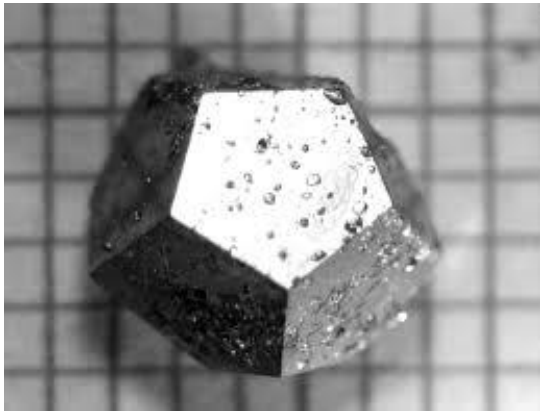


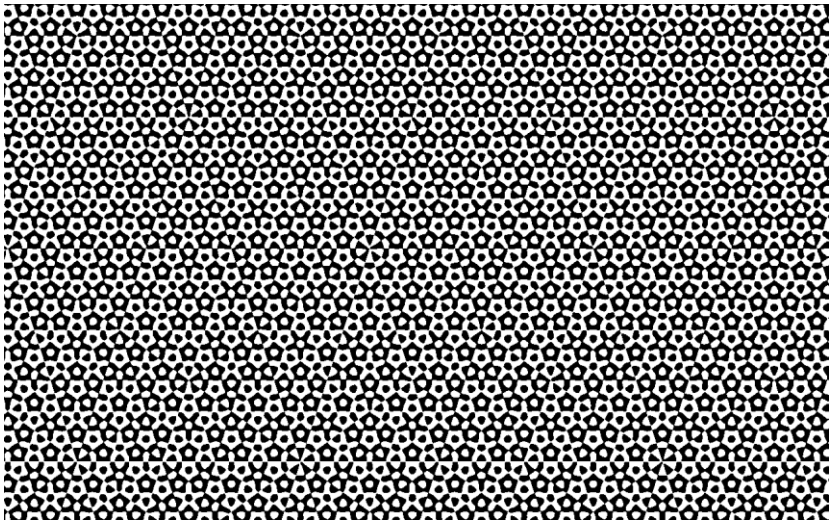
http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2011/shechtman-lecture_slides.pdf

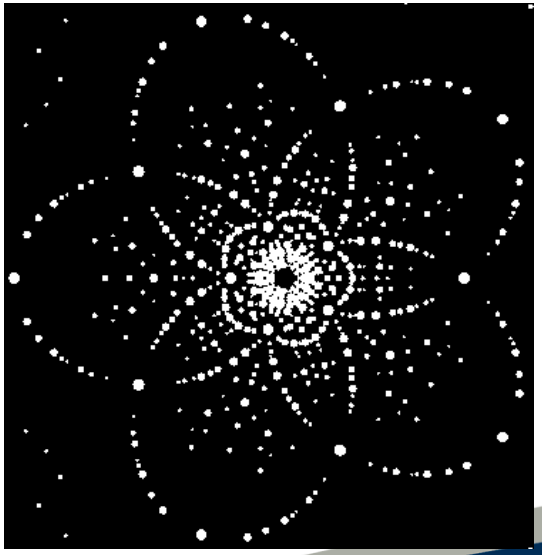
Quasicrystals and diffraction











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Using X-rays or neutrons for powder diffraction?

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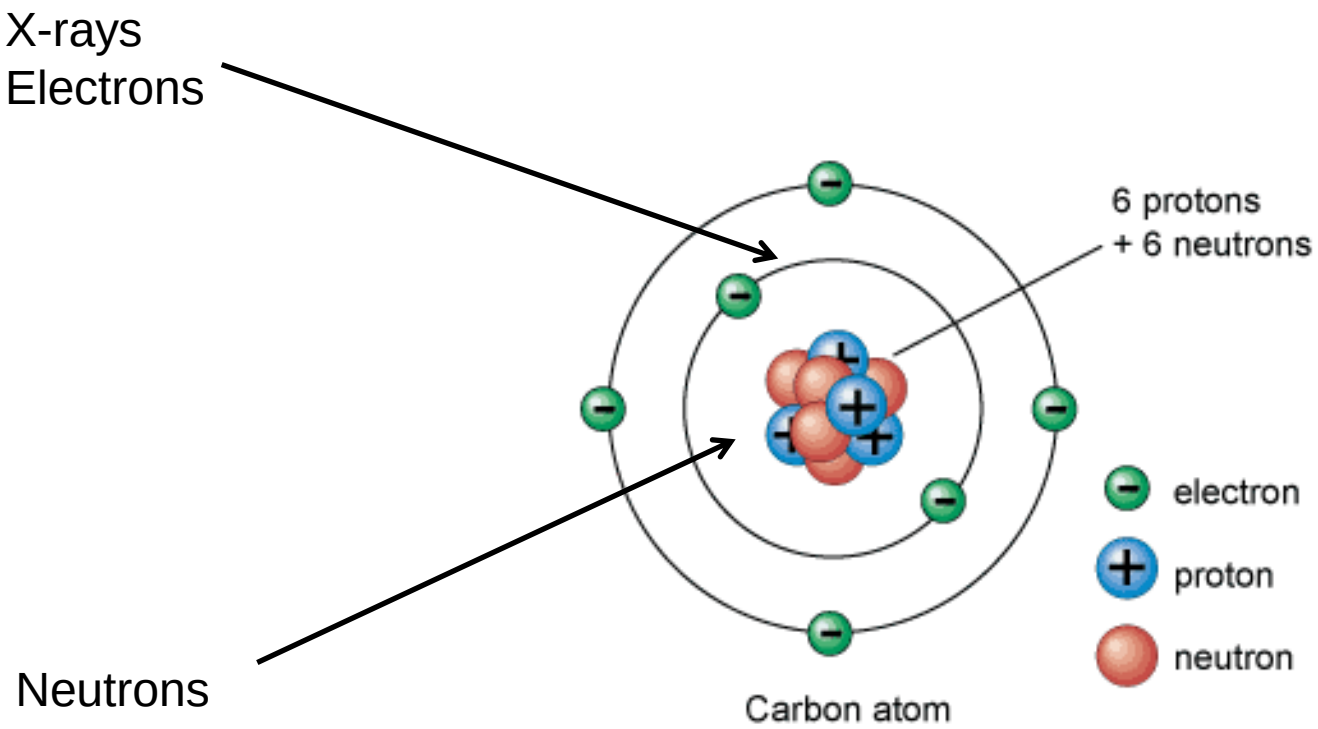
X-ray cf. neutron for diffraction

X-rays	Neutrons
Small samples	Large samples
Strong sample absorption	Low sample absorption
High energy (1 Å = 12.4 keV)	Low energy (1 Å = 81.81 meV)
Low penetration depth	High penetration depth
Light elements hard to detect	Light elements scatter well
Scattering power highly Q dependent	Scattering power almost Q independent
Neighbouring elements cannot be discriminated	Neighbouring elements can be discriminated
High availability (lab)	Low availability (large scale facility)
Cannot distinguish isotopes	Isotopes can be distinguished
Magnetic structures not easily probed	Magnetic structures easily probed

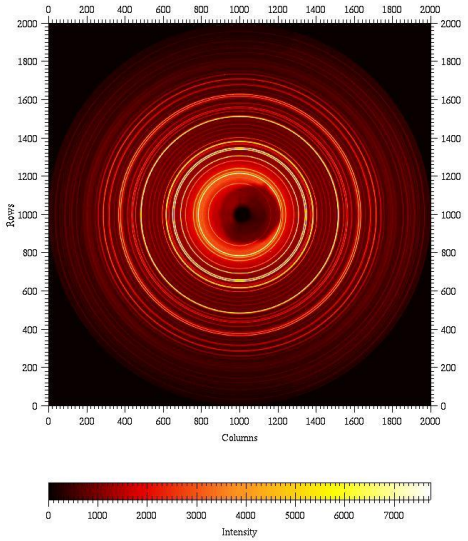
X-rays and neutrons are complementary probes for diffraction

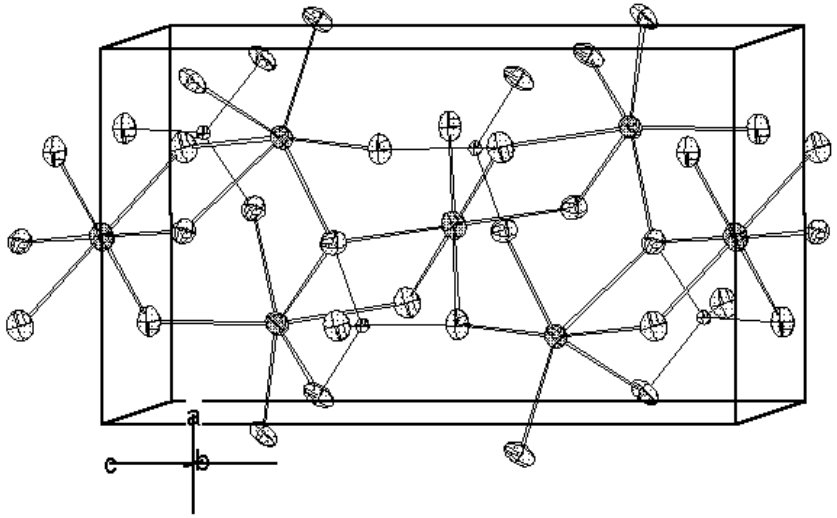


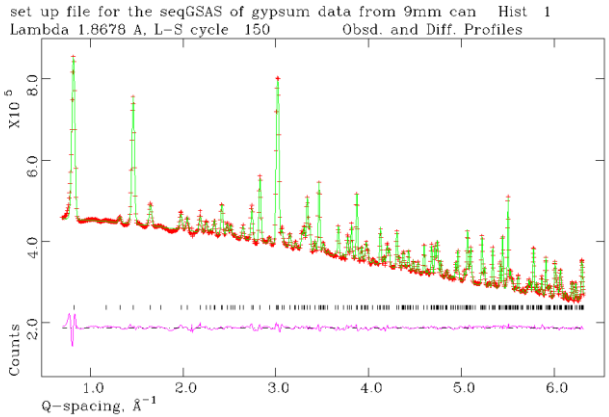
Neutron diffraction is used for problems that X-rays cannot address or inadequately address

Structure solution & refinement

Structure solution and refinement







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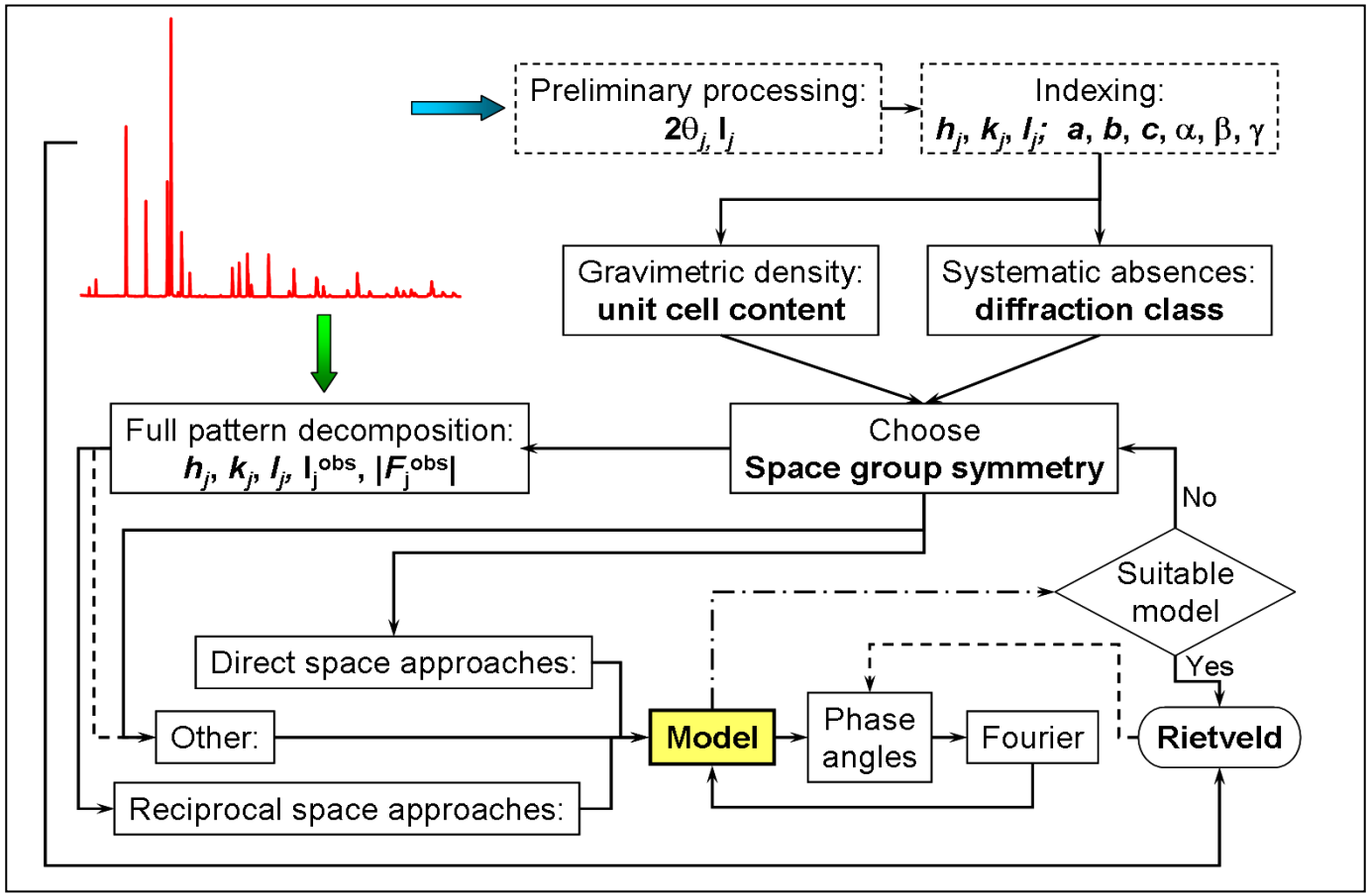
Process for structure solution



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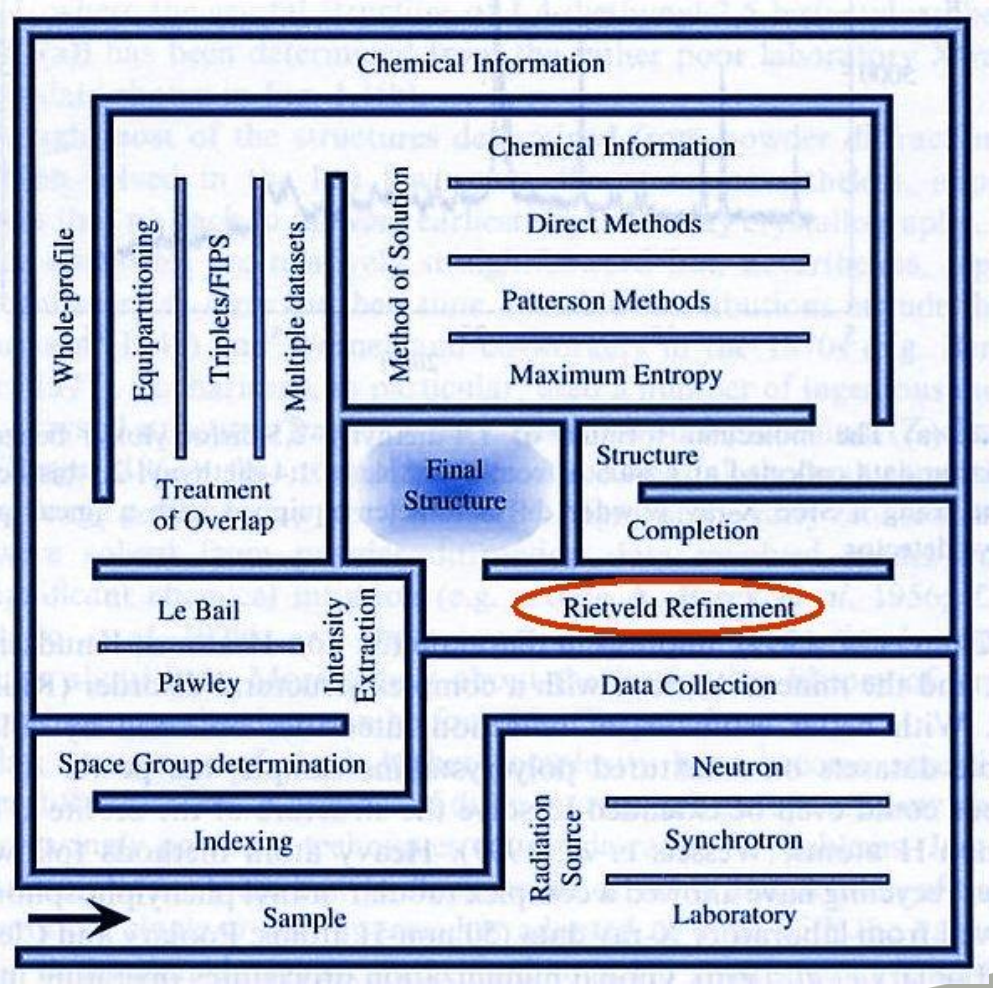
Another view of structure solution



Intensity and structure factor

$$I_{hkl} \propto |F_{hkl}|^2$$

Measured intensity proportional to F_{hkl}^2 and so we cannot tell whether F_{hkl} is positive or negative – the Phase problem

$$F_{hkl} \propto \Sigma f_i \exp[2\pi i(hx_i + ky_i + lz_i)] \exp(-U_i Q^2/2)$$

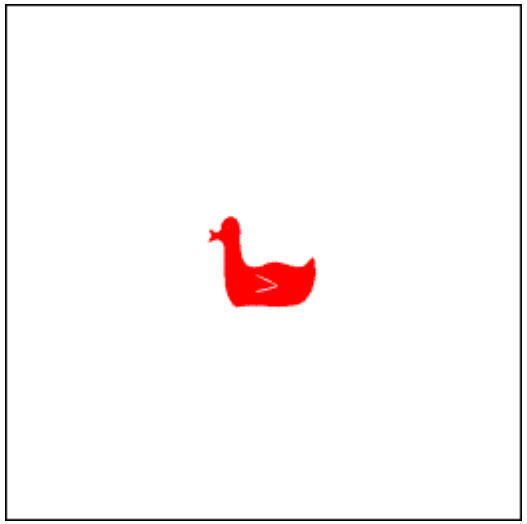
f_i is the scattering power (form factor of the ith site i.e. (x_i,y_i,z_i) and incudes fractional occupancy

Contribution of the ith site to the F_{hkl} in question

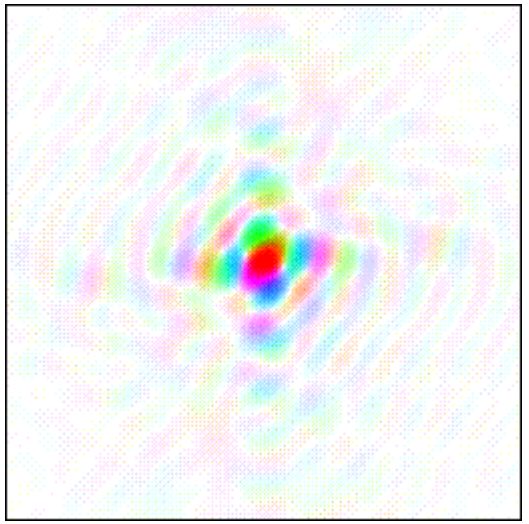
Atomic displacement of the ith atom site

The phase problem

Illustrated by the Fourier duck and cat



A duck

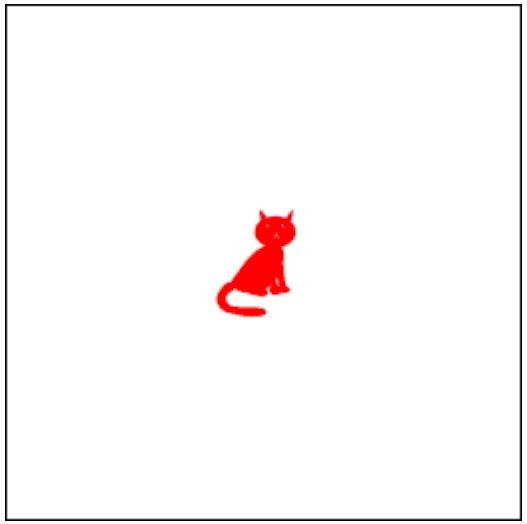


FT of a duck

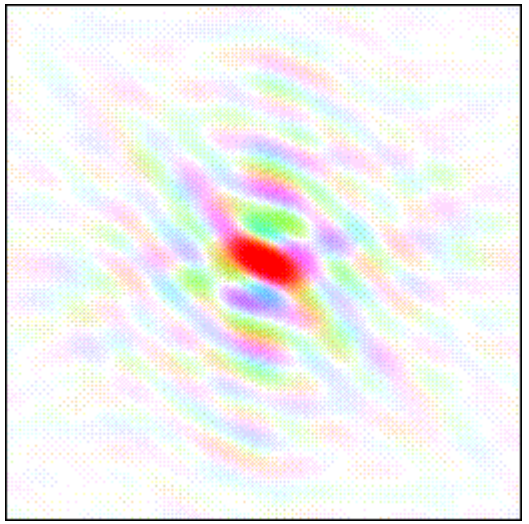
Credits to:
http://www.ysbl.york.ac.uk/~cowtan/fourier/magic.html

The phase problem

Illustrated by the Fourier duck and cat



A cat

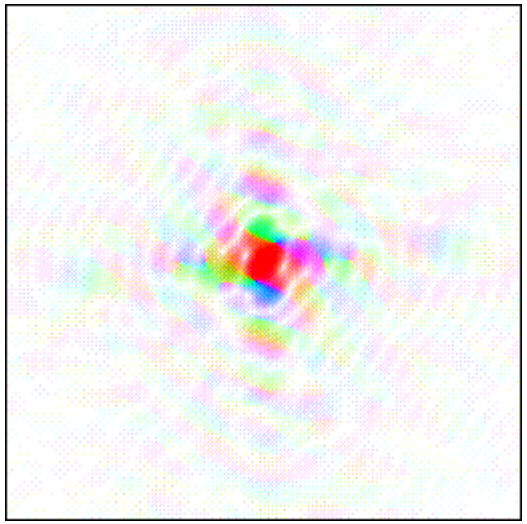


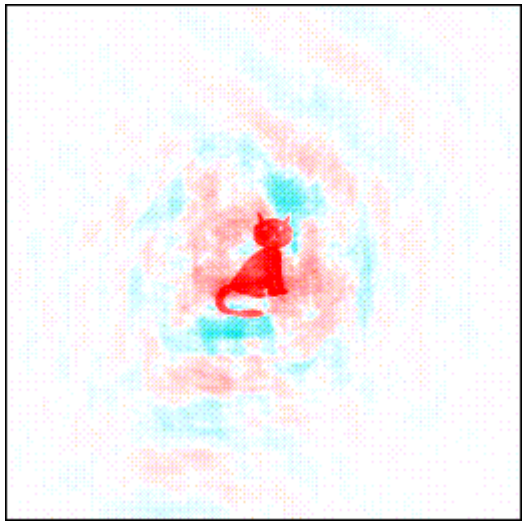
FT of a cat

Credits to:
http://www.ysbl.york.ac.uk/~cowtan/fourier/magic.html

The phase problem

Let's go a step further and mix them up. What happens if we take the magnitudes of the duck transform and the phases of the cat transform?



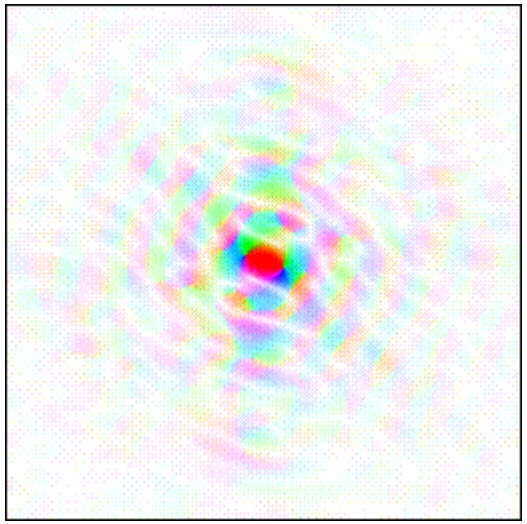


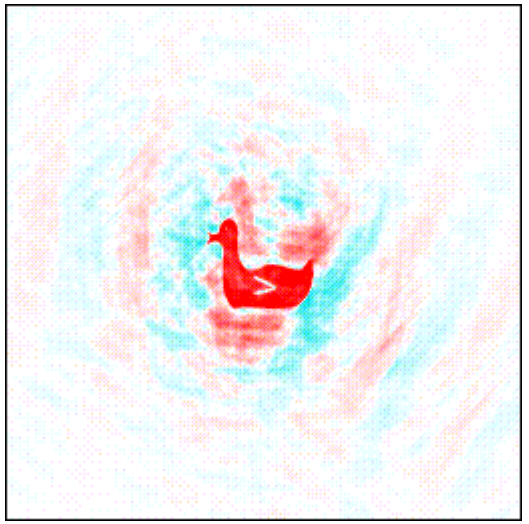
FT with the brightness (magnitudes) of the duck
FT and the colours (phases) from the cat FT

Credits to:
http://www.ysbl.york.ac.uk/~cowtan/fourier/magic.html

The phase problem

And the other way round? Cat FT magnitudes and duck FT phases…





In each case the image that contributed the phases is still visible, whereas the image that contributed the magnitudes is gone!

Credits to:
http://www.ysbl.york.ac.uk/~cowtan/fourier/magic.html

The phase problem

$$I_{hkl} \propto |F_{hkl}|^2$$

In diffraction we measure the magnitudes and not the phase. The phases contain the bulk of the information. This is why crystallography is hard….

…but not impossible. We can recover phase information from:

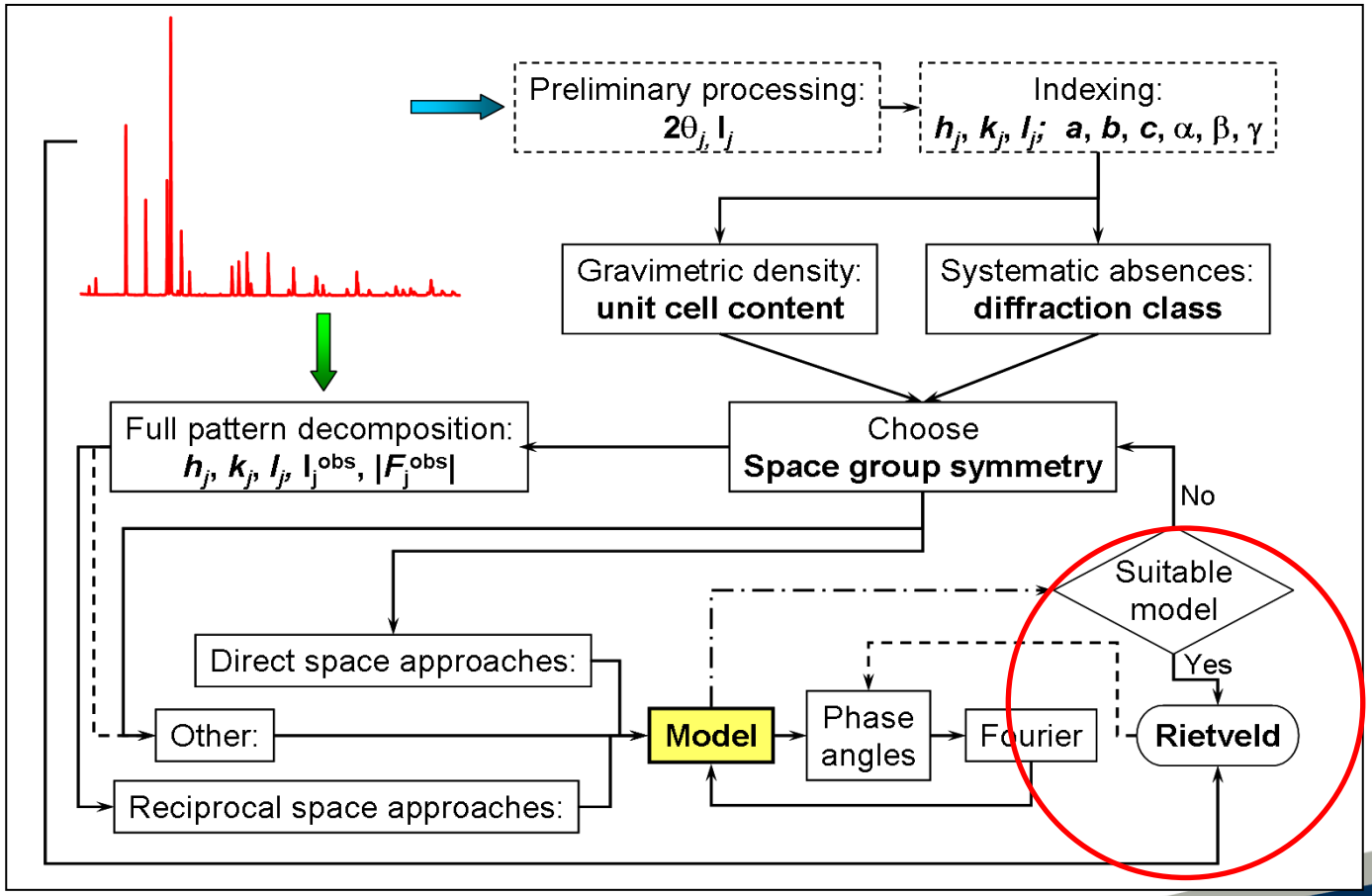
- Related or isostructural materials
- Knowledge of atom positions (heavy atoms from X-rays)
- Known motifs (molecules)
- Brute force

Other factors contributing to measured intensity

$$I_K = S M_K L_K |F_K|^2 P_K A_K E_K$$

- S is an arbitrary scale factor
  - used to adjust the relative contribution of individual phases to the overall diffraction pattern
- M is the multiplicity of the reflection
  - accounts for the fact that some observed diffraction peaks are actually the product of multiple equivalent planes diffracting at the same position 2θ (for example, (001) (100) (010) etc in cubic)
  - automatically calculated based on the crystal structure
- L is the Lorentz polarization factor
- P is the modification of intensity due to preferred orientation
- A is the absorption correction
- E is the extinction correction
- F is the structure factor, which is the amplitude of the scattering due to the crystal structure

Process of structure refinement



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The Rietveld method

J. Appl. Cryst. (1969). **2**, 65

A Profile Refinement Method for Nuclear and Magnetic Structures

BY H. M. RIETVELD

Reactor Centrum Nederland, Petten (N.H.), The Netherlands

(*Received* 29 *November* 1968)

A structure refinement method is described which does not use integrated neutron powder intensities, single or overlapping, but employs directly the profile intensities obtained from step-scanning measurements of the powder diagram. Nuclear as well as magnetic structures can be refined, the latter only when their magnetic unit cell is equal to, or a multiple of, the nuclear cell. The least-squares refinement procedure allows, with a simple code, the introduction of linear or quadratic constraints between the parameters.

Hugo M. Rietveld 1932-2016

- Originally written to analyse neutron powder diffraction data
- Both nuclear and magnetic structure refinement
- Adapted for X-ray methods in 1977 by Young
- Thousands of publications per year published using the method
- It is the reason powder crystallography is so successful!!

"NASA would never have sent an X-ray powder diffractometer to Mars without the Rietveld method" (David Blake, 2012)

Rietveld refinement software

Many programs out there. Well used examples include:

- GSAS
- GSAS-II
- Fullprof
- Topas
- Jana
- Maud
- Reitan
- BGMN
- Etc…

The Rietveld method

What it is not:

- For phase identification
- For structure solution

What it can tell us:

- Phase quantities
- Unit cell dimensions
- Atomic coordinates / bond lengths / substitutions and vacancies
- Strain and texture effects

What you need:

- Good quality data
- A good starting structural model
- An instrument description file

The Rietveld method

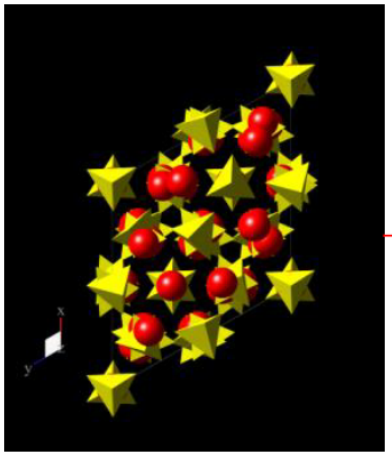
- The intensity, Y_{ic}, of each individual data point *i* is calculated using the equation:

$$Y_{ic} = Y_{ib} + \sum_{k=k1}^{k2} G_{ik} I_k$$

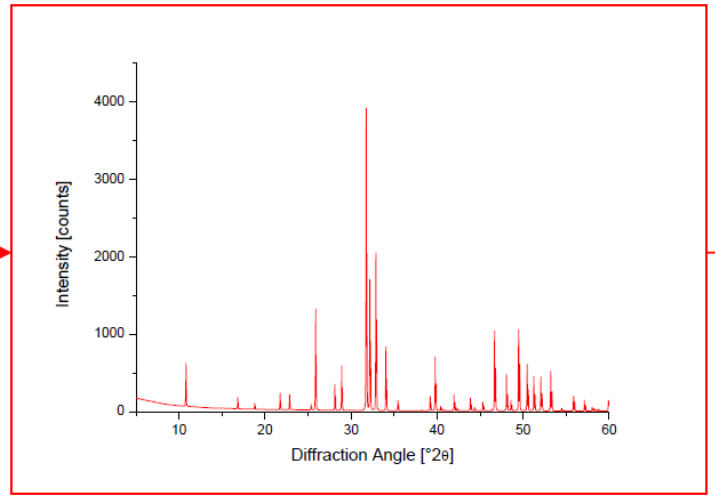
- We already know how to calculate I_K, the intensity of the Bragg diffraction peak k: $I_K = SM_K L_K |F_K|^2 P_K A_K E_K$
- Y_{ib} is the intensity of the background at point *i* in the pattern
- k1 - k2 are the reflections contributing to data point *i* in the pattern
  - sometimes multiple Bragg diffraction peaks overlap, resulting in multiple contributions to the observed intensity at a single data point
- G_{ik} is the peak profile function
  - this describes how the intensity of the diffraction peak is distributed over a range of 2theta rather than at a single point
  - this profile is due to instrument broadening, sample broadening, etc

The Rietveld method

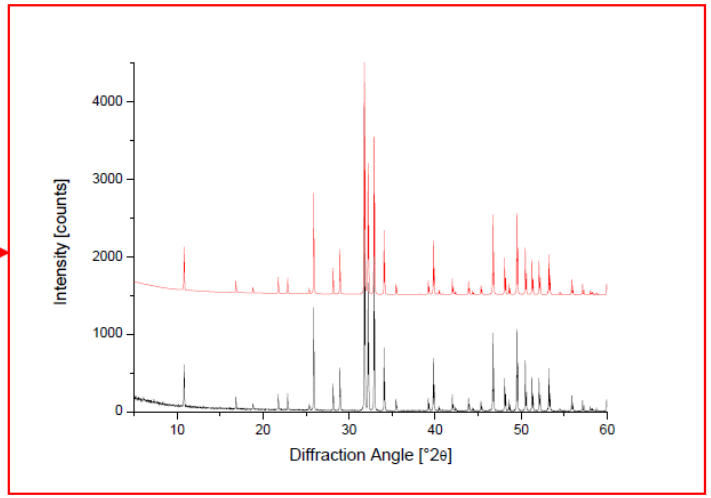
Known structure model



Calculate theoretical diffraction pattern



Compare with measured pattern



Optimize structure model, repeat calculation

Basic refinement procedure

Experimental diffraction pattern

Starting crystal structure (.cif, ICSD)

Instrument file (.inst, LaB_6 standard)

Refine:

- Background
- Lattice parameters
- Peak intensities
- Peak shapes
- Peak positions
- Phase fractions

Assess:

- Goodness of fit/R factors
- Impurity phases
- Peak/background shapes
- Difference pattern

bad peak position

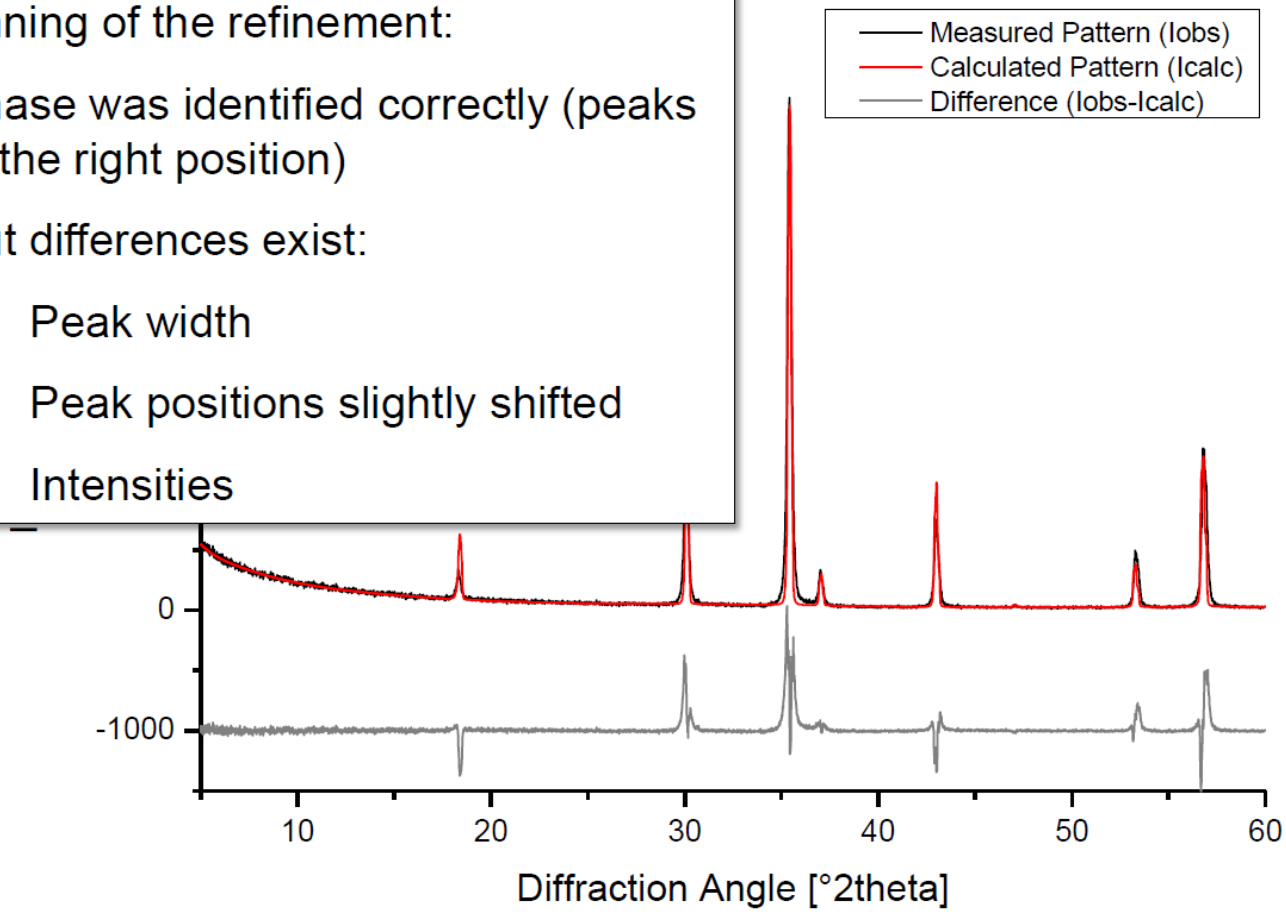
poor peak shape

peak intensities are off

Initial model

Beginning of the refinement:

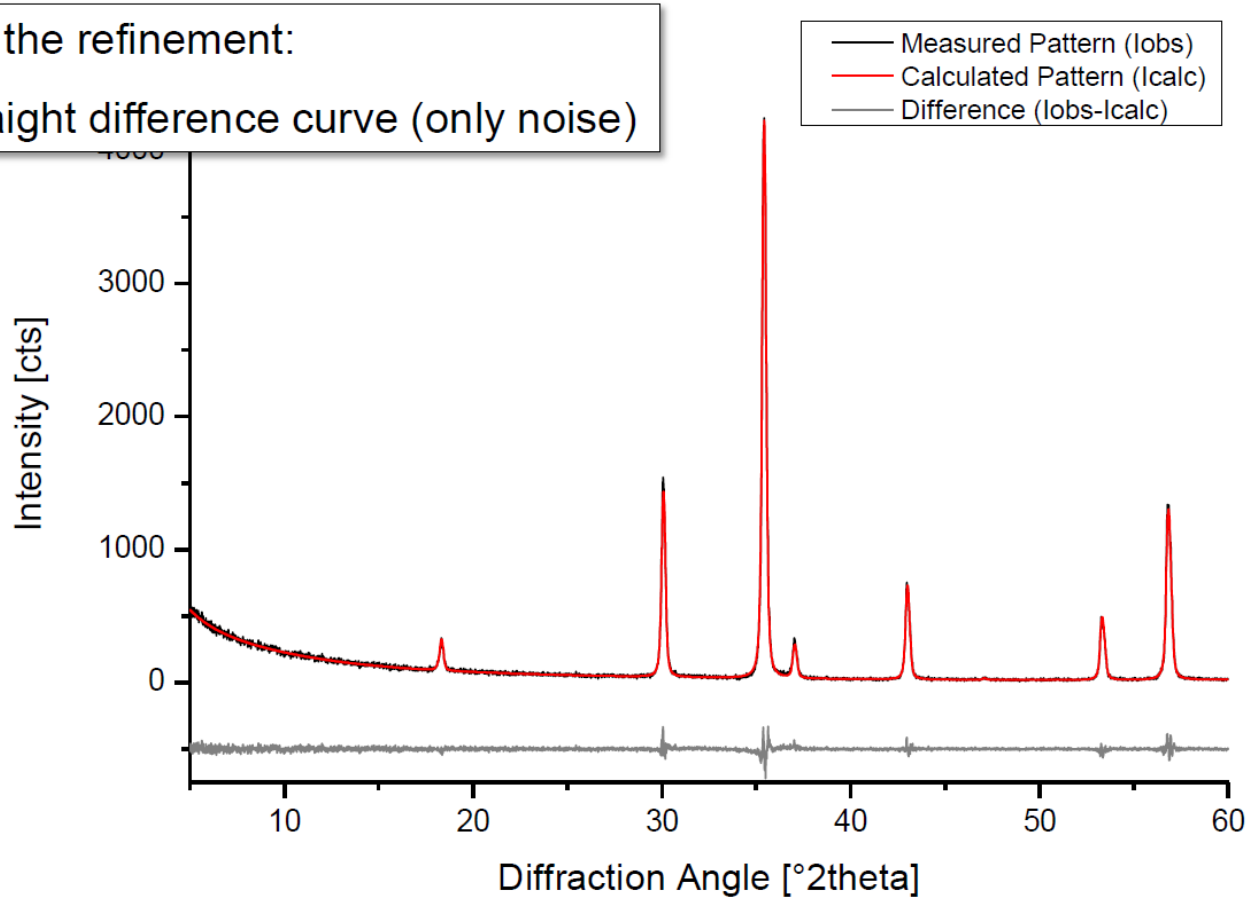
- Phase was identified correctly (peaks at the right position)
- But differences exist:
  - Peak width
  - Peak positions slightly shifted
  - Intensities



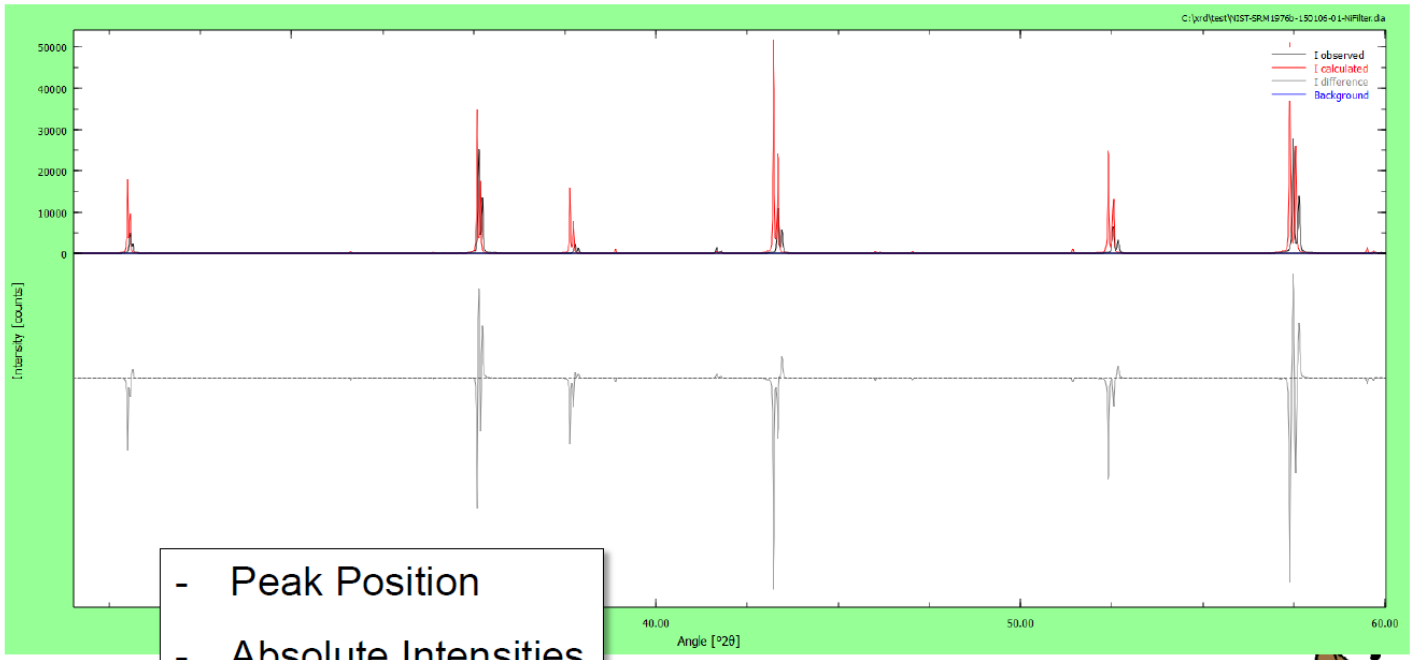
Final refined model

After the refinement:

- Straight difference curve (only noise)



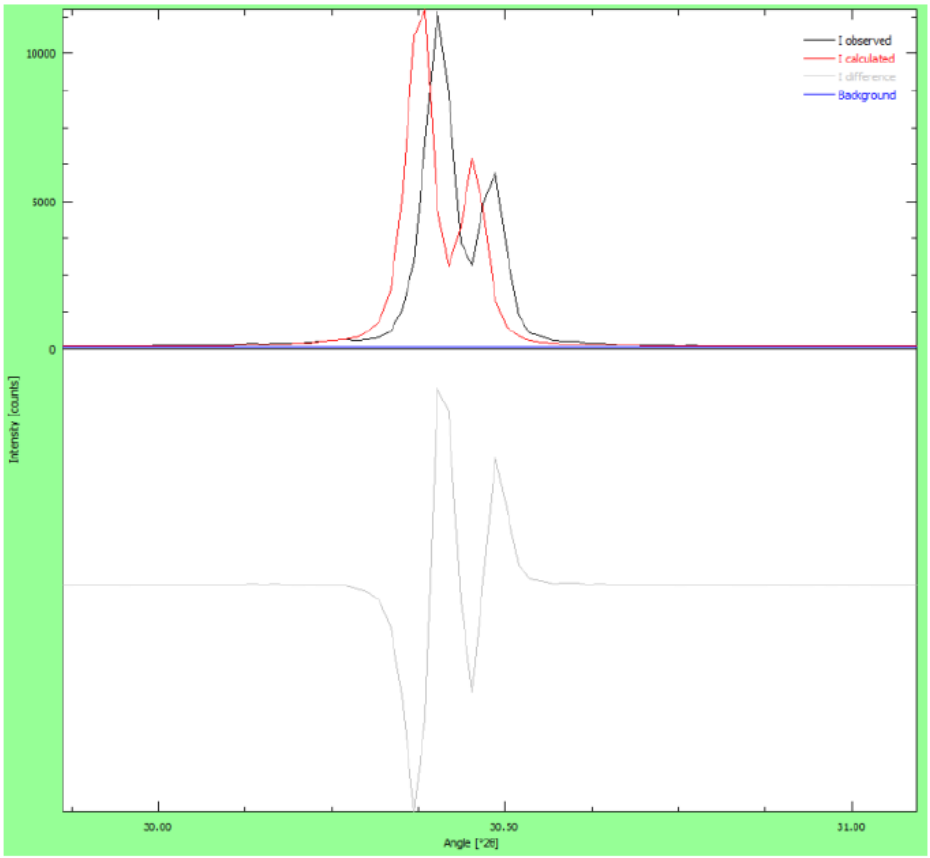
Common mismatches in data and model



- Peak Position
- Absolute Intensities
- Relative Intensities
- Peak Width

How to fix this?

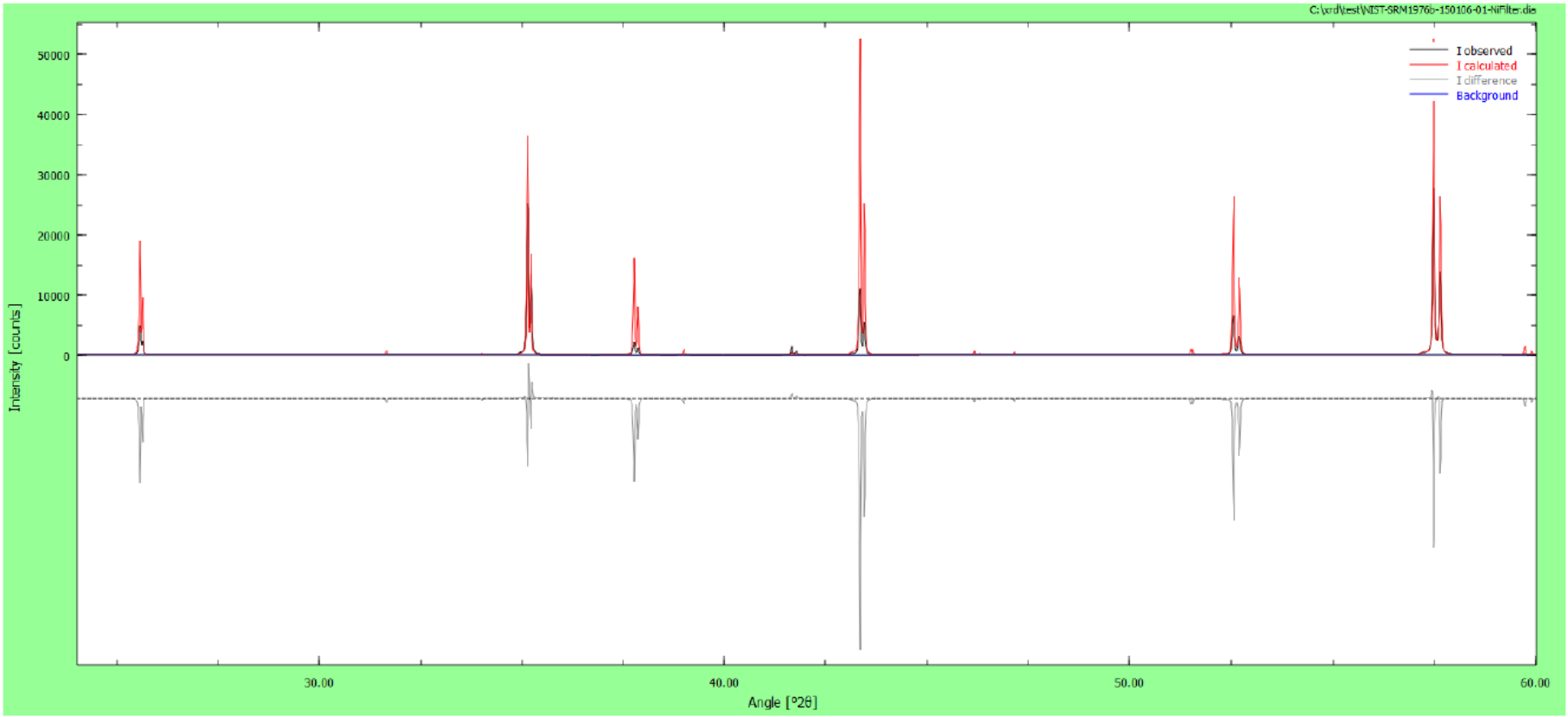
Peak position mismatch



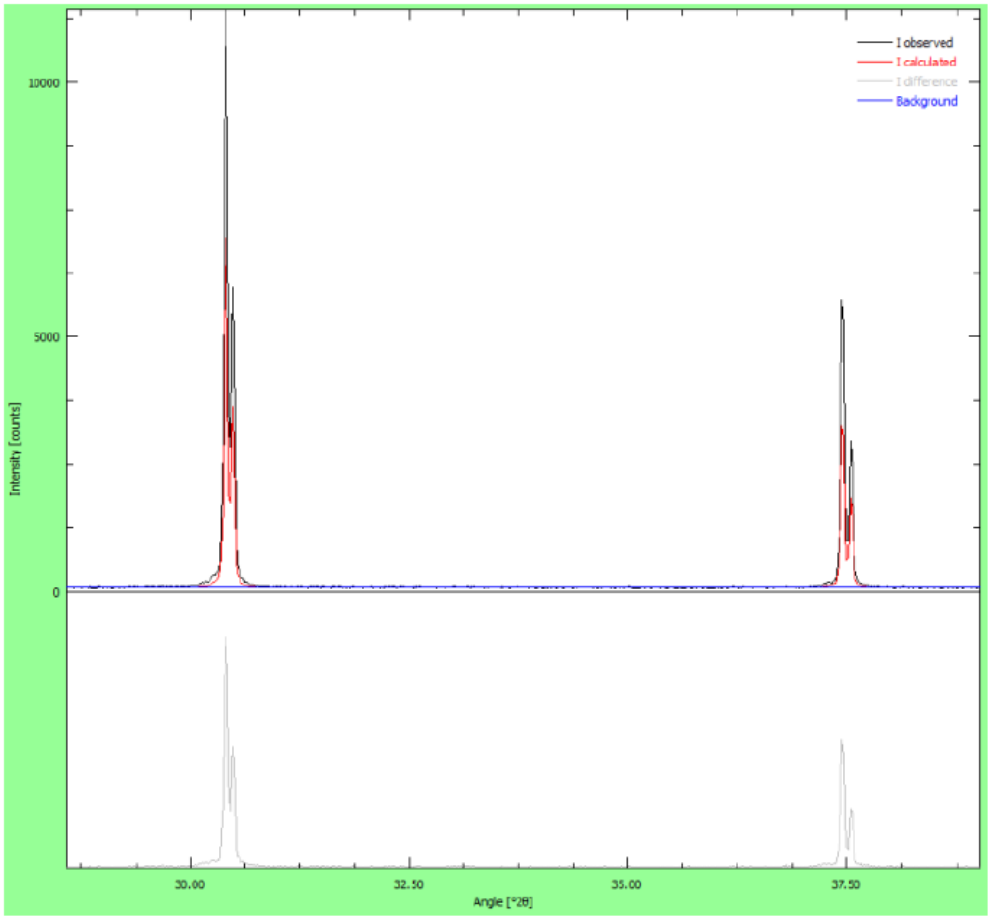
Wrong peak positions? Refine:

- Unit cell dimensions
- Zero point
- Sample height

Lattice parameters / zero point refined

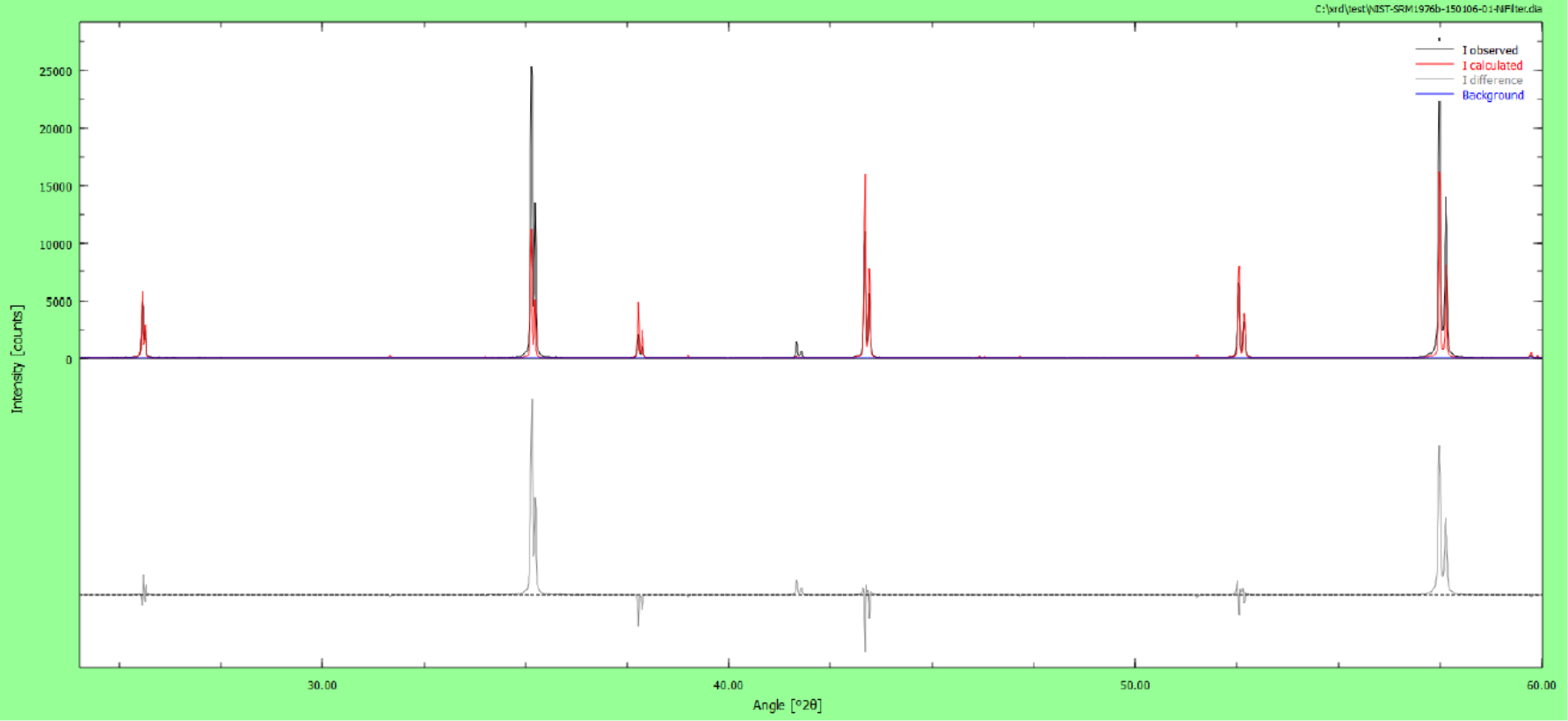


Wrong absolute intensities



Incorrect overall scaling factor

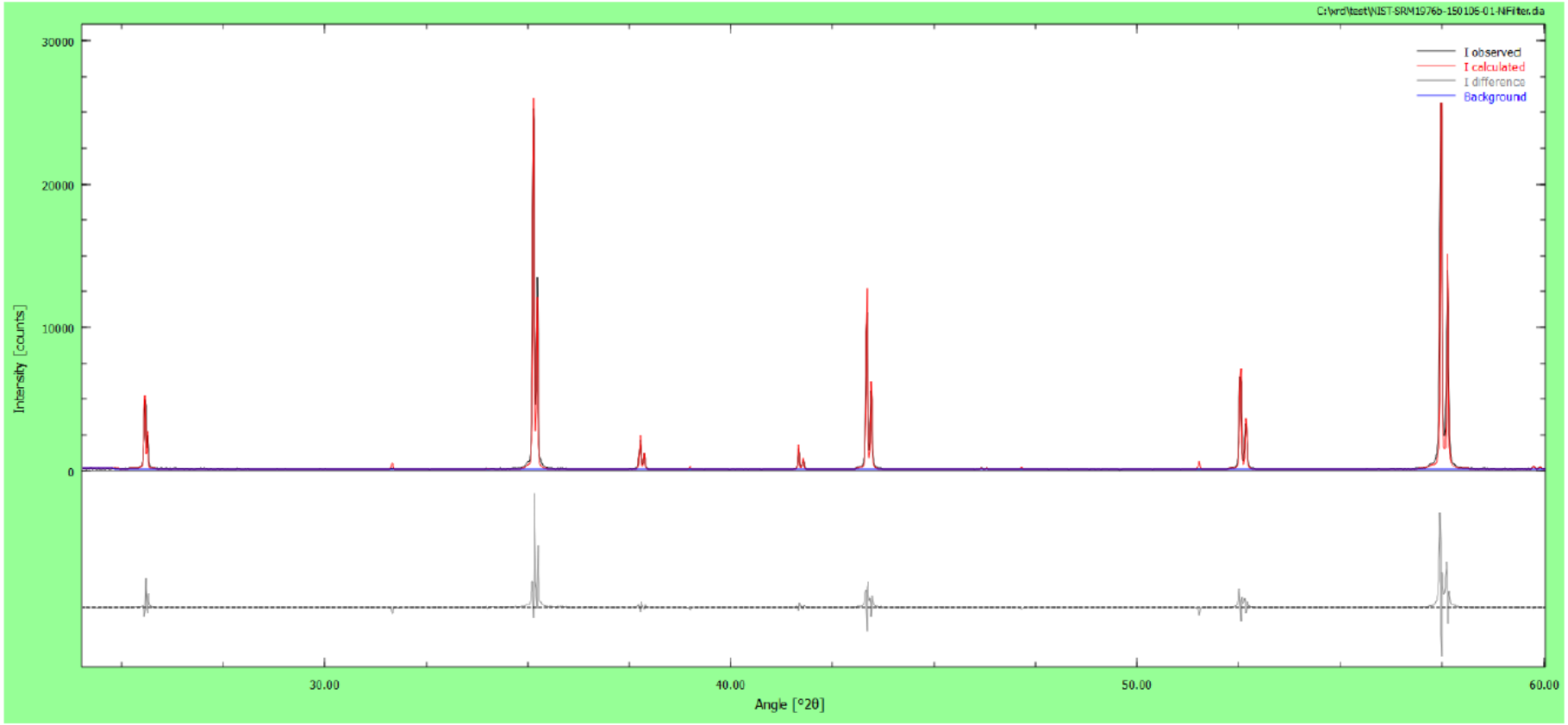
Refined scale factor



Better but still not fixed

Refine atomic model, site occupancy factors, displacement parameters, preferred orientation

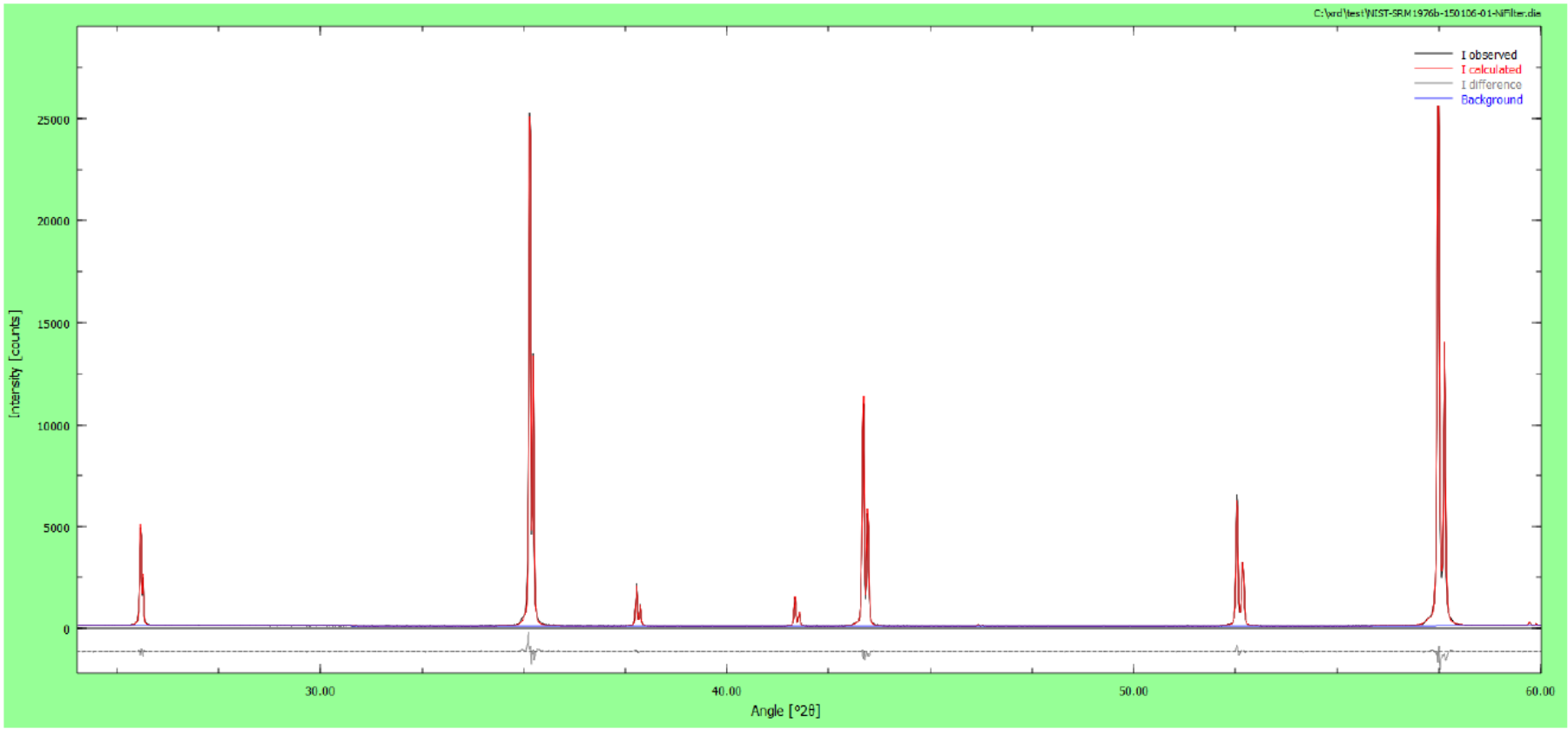
Refined atomic model



Better but still not complete

Refine peakshape, crystallite size and micro-strain

Final fit



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Complete guide for Rietveld refinement

J. Appl. Cryst. (1999). **32**, 36–50

Rietveld refinement guidelines

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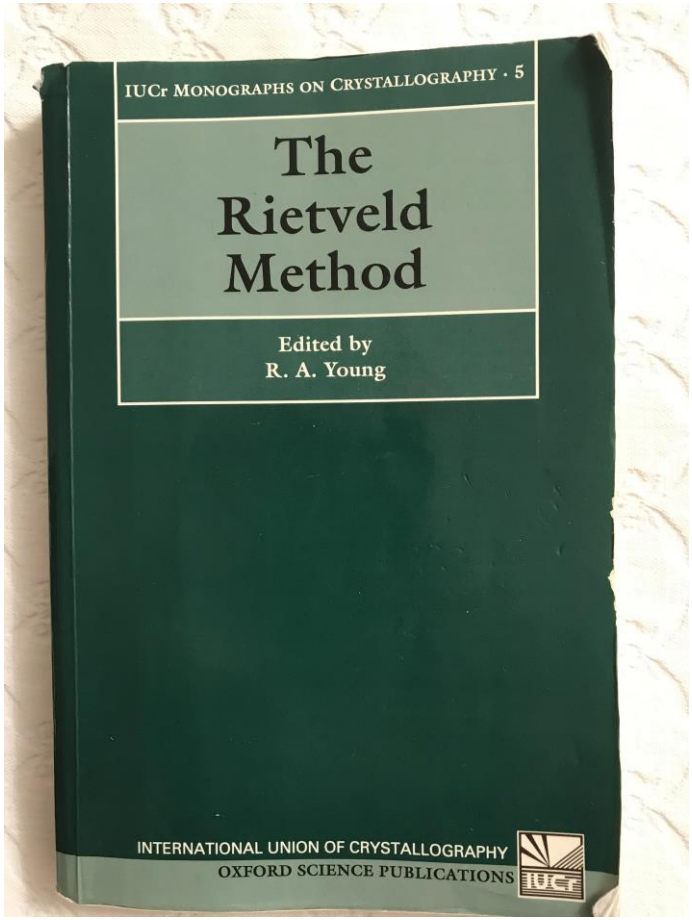
(*Received 23 February 1998; accepted 22 July 1998*)

Wise words…

13. Conclusions

Structure refinement using the whole-pattern or Rietveld method is a powerful technique for extracting structural details from powder diffraction data. With present methods, structures with up to 200 structural parameters can be refined successfully, if care is taken and the data are of sufficiently high quality. These guidelines are designed to provide a concise summary of some of the practical aspects of the technique. Small details play an important role in structure analysis using the Rietveld method and attention to these details, though often tedious, is usually rewarded with success.

Background and theory



Some common challenges/problems

- Incorrect starting crystal structure
- Poor quality data!
- False minimas
- Refinement diverges (“blows up”)
- Over interpretation
- Refine unnecessary variables
- Parameter correlation
- Which goodness of fit to choose? R vs. Chi sq?
- Preferred orientation
- High background
- Ignores non-Bragg diffraction peak information

Links to useful information

Rietveld videos…

- https://www.youtube.com/watch?v=rG14YjLK9xQ
- https://www.youtube.com/watch?v=mnxd5ACqR9E
- https://www.youtube.com/watch?v=mcuLF0Szd4w

Rietveld Tutorial links

- http://www.ccp14.ac.uk/solution/gsas/gsastutorials.html

Quasicrystal books and structure analysis

- https://www.jstor.org/stable/24936867?seq=1#page_scan_tab_contents
- https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5099788/