Lecture Notes for Rietveld Method

(Advanced Physical Tools and Techniques : PHYS5002)

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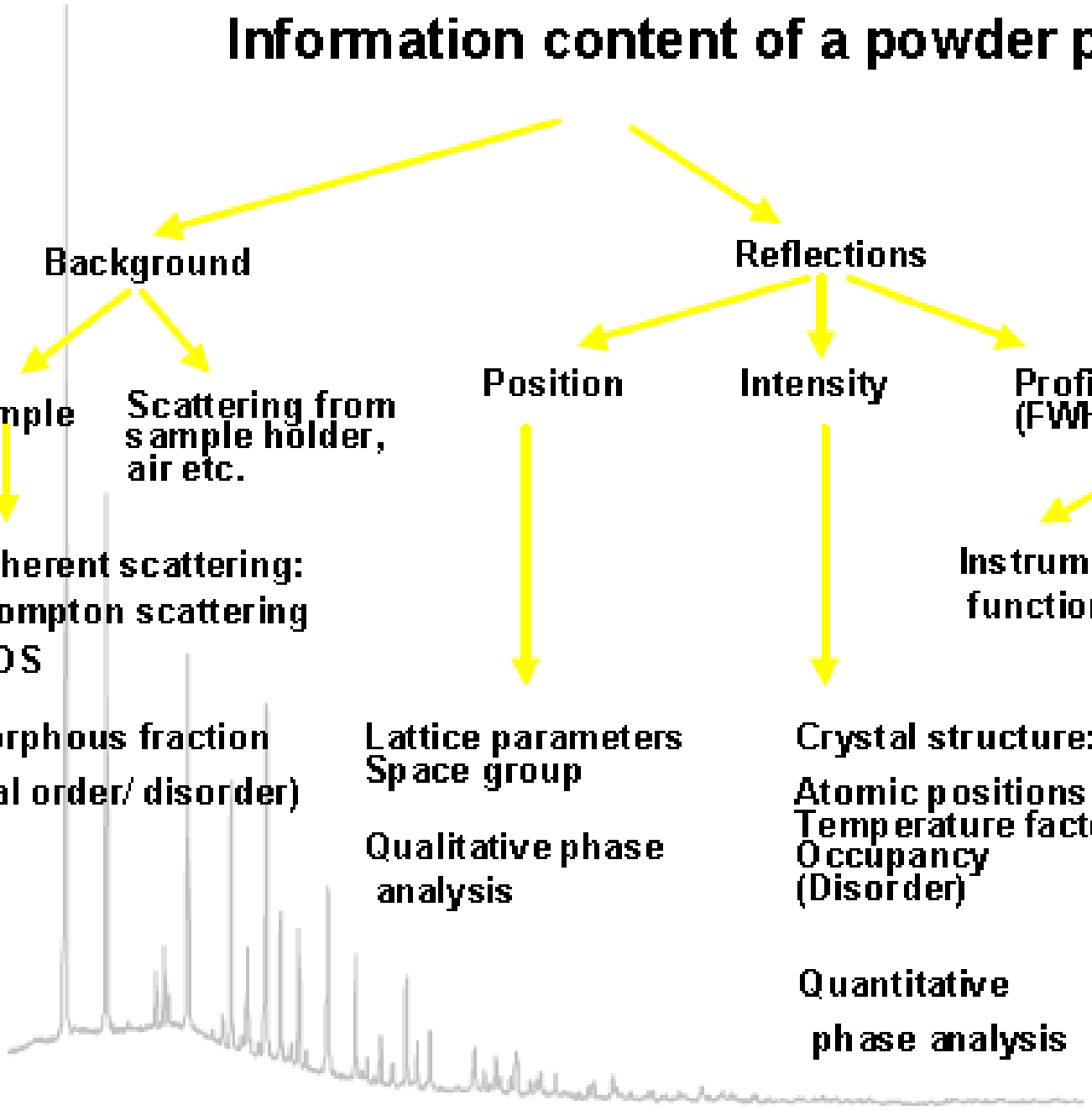
Structural Refinement based on the Rietveld Method

Information content of a powder pattern



Background

Reflections

Sample

Scattering from sample holder, air etc.

Position

Intensity

Profile (FWHM, peak shape)

Incoherent scattering:
a) Compton scattering
b) TDS

Amorphous fraction
(local order/ disorder)

Lattice parameters
Space group

Qualitative phase analysis

Crystal structure:

Atomic positions
Temperature factor
Occupancy
(Disorder)

Quantitative phase analysis

Instrument function

Sample broadening

Real structure:

Stress,
Strain
Crystallite size
Domain size,...

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

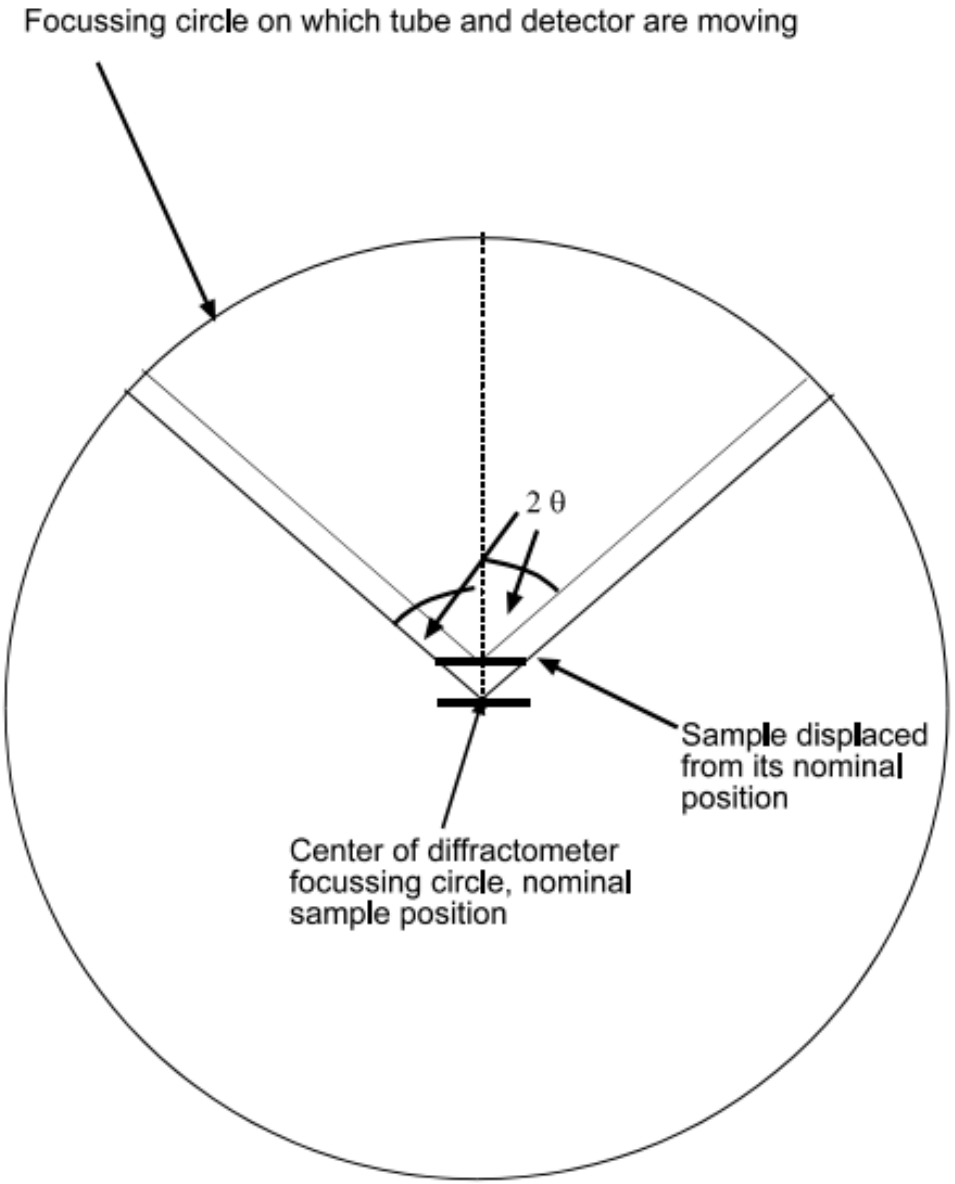
Experimental setup

- Make sure that the instrument is well aligned before collecting data!
  - Zero point
- Choose slits that will keep the full beam footprint on the the sample at all angles (otherwise your low angle intensities will be off)!
- The sample height needs to be correct, as incorrect sample height shifts the peaks
- Long counting times improve the signal to noise ratio and facilitate the extraction of integrated intensities
- Choose a low background sample holder (e.g., metal, not plastic)

Continuous Scan

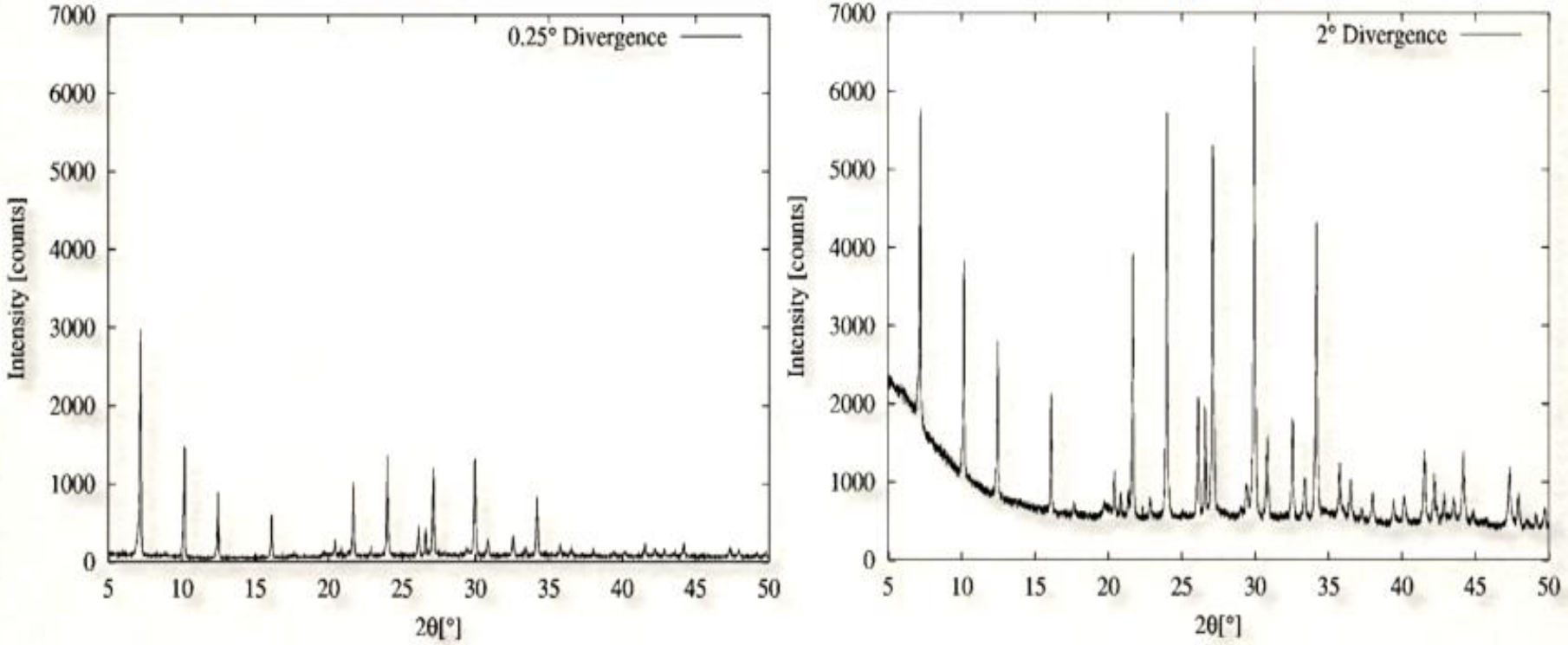
Step Scan

Effects of sample height displacement



- The sample should be sufficiently large that the beam will be always entirely inside its volume/surface (for Bragg-Brentano check at low angle and sample thickness/transparency).

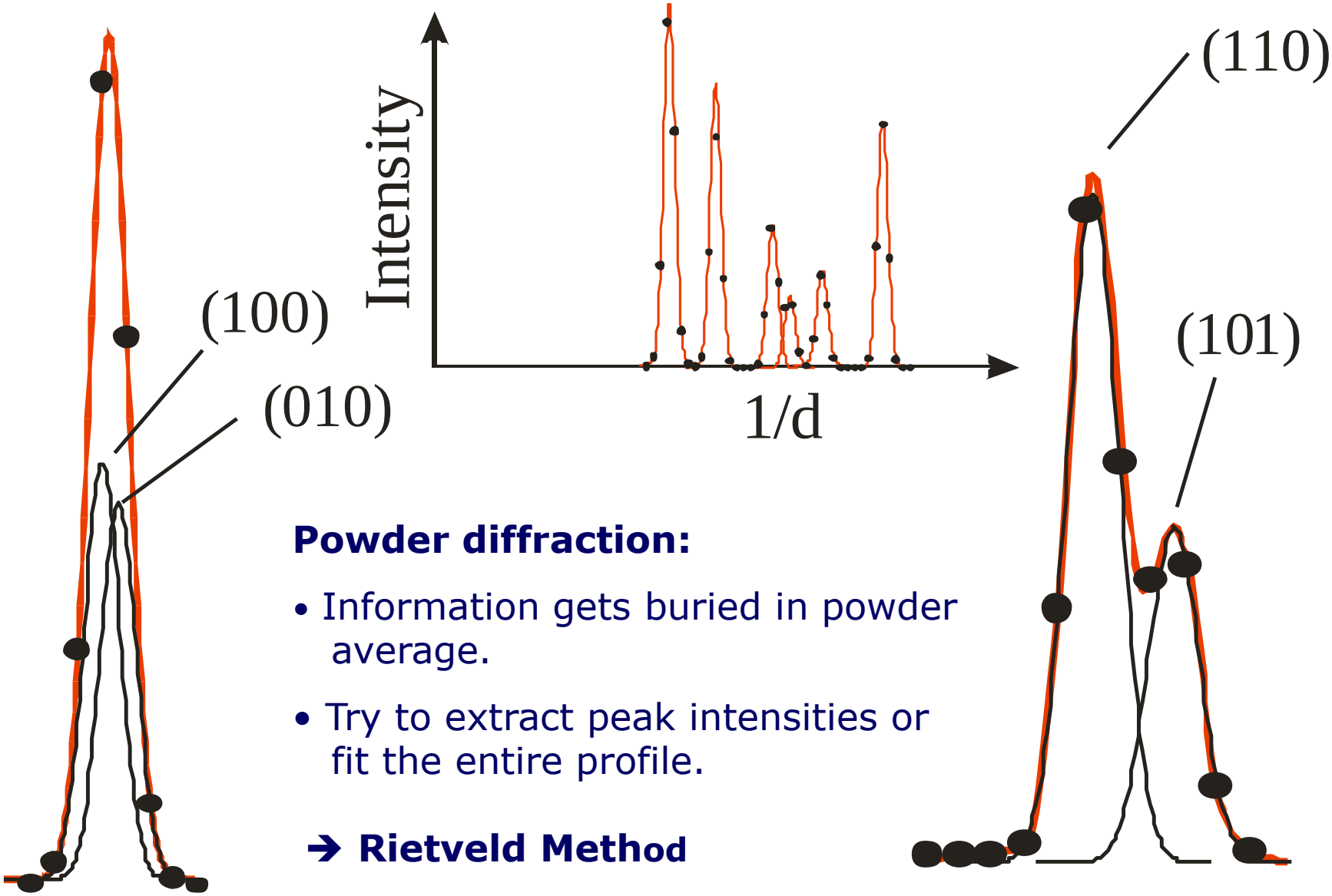
Zeolite sample, changing beam divergence, Krüger and Fischer, J. Appl. Cryst., 37, 472, 2004.



- On the right pattern, at low angle the beam goes out of the sample reducing relative peaks intensities and increasing air scattering/ background

The step size

- The step size should be compatible with the line broadening characteristics and type of analysis.
- In general 5-7 points in the half upper part of a peak are sufficient to define its shape.
- Slightly more points are preferred in case of severe overlapping.
- A little more for size-strain analysis.
- Too much points (too small step size) do not increase our resolution, accuracy or precision, but just increase the noise at equal total collection time.
- The best solution is to use the higher step size possible that do not compromise the information we need.
- Normally highly broadened peaks => big step size => less noise as we can increase the collection time per step (> 0.05)
- very sharp peaks => small step size (from 0.02 to 0.05 for Bragg-Brentano)



Powder diffraction:

- Information gets buried in powder average.
- Try to extract peak intensities or fit the entire profile.

➔ **Rietveld Method**

Diffraction Peak Intensities

Structure Factor:

X-ray case:

$$F_{(hkl)} = \sum_j f_j \exp\left[2\pi i\left(hx_j + ky_j + lz_j\right)\right]\exp\left[-B_j \sin^2\theta/\lambda^2\right]$$

Neutron case:

$$F_{(hkl)} = \sum_j b_j \exp\left[2\pi i\left(hx_j + ky_j + lz_j\right)\right]\exp\left[-B_j \sin^2\theta/\lambda^2\right]$$

Powder Peak Intensities:

$$I_{(hkl)} = s\, p_{(hkl)}\, L_\theta\, A_\theta\, P_{(hkl)} \left|F_{(hkl)}\right|^2$$

$$I_{(hkl)} \propto \left|F_{(hkl)}\right|^2$$

$F_{(hkl)}$ = structure factor
f_j = X-ray form factor
b = neutron scatt. length
h,k,l = Miller indices
x_j, y_j, z_j = atomic coordinates of atom j
B_j = thermal parameter
θ = diffraction angle
λ = wavelength
Σ over entire unit cell
$I(hkl)$ = intensity

Correction factors:

s = scale factor
L = Lorentz-polarization
p = multiplicity
A = absorption correction
P = preferred orientation

Why Neutrons?

Neutrons have No Charge!

- Highly penetrating
- Nondestructive

Neutrons have a Magnetic Moment!

- Magnetic structure
- Fluctuations
- Magnetic materials

Neutrons have Spin!

- Polarized beams
- Atomic orientation
- Coherent and incoherent scattering

The Energies of neutrons are similar to the energies of elementary excitations!

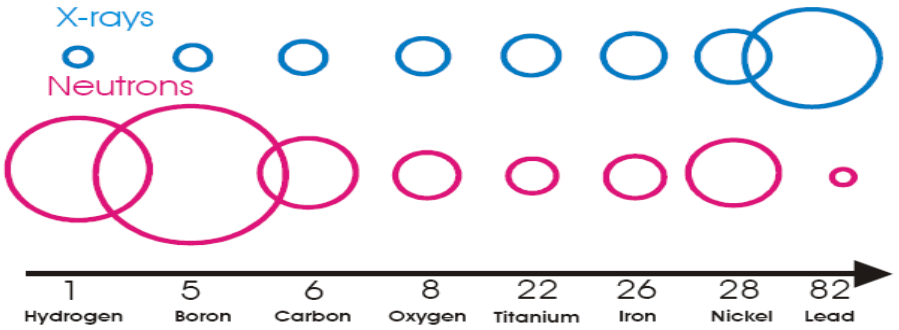
- Molecular Vibrations and Lattice modes
- Magnetic excitations

The Wavelengths of neutrons are similar to atomic spacing!

- Sensitive to structure
- Gathers information from 10^{-10} to 10^{-7} m
- Crystal structures and atomic spacings

Neutrons probe Nuclei!

- Light atom sensitive
- Sensitive to isotopic substitution



Powder Data Analysis

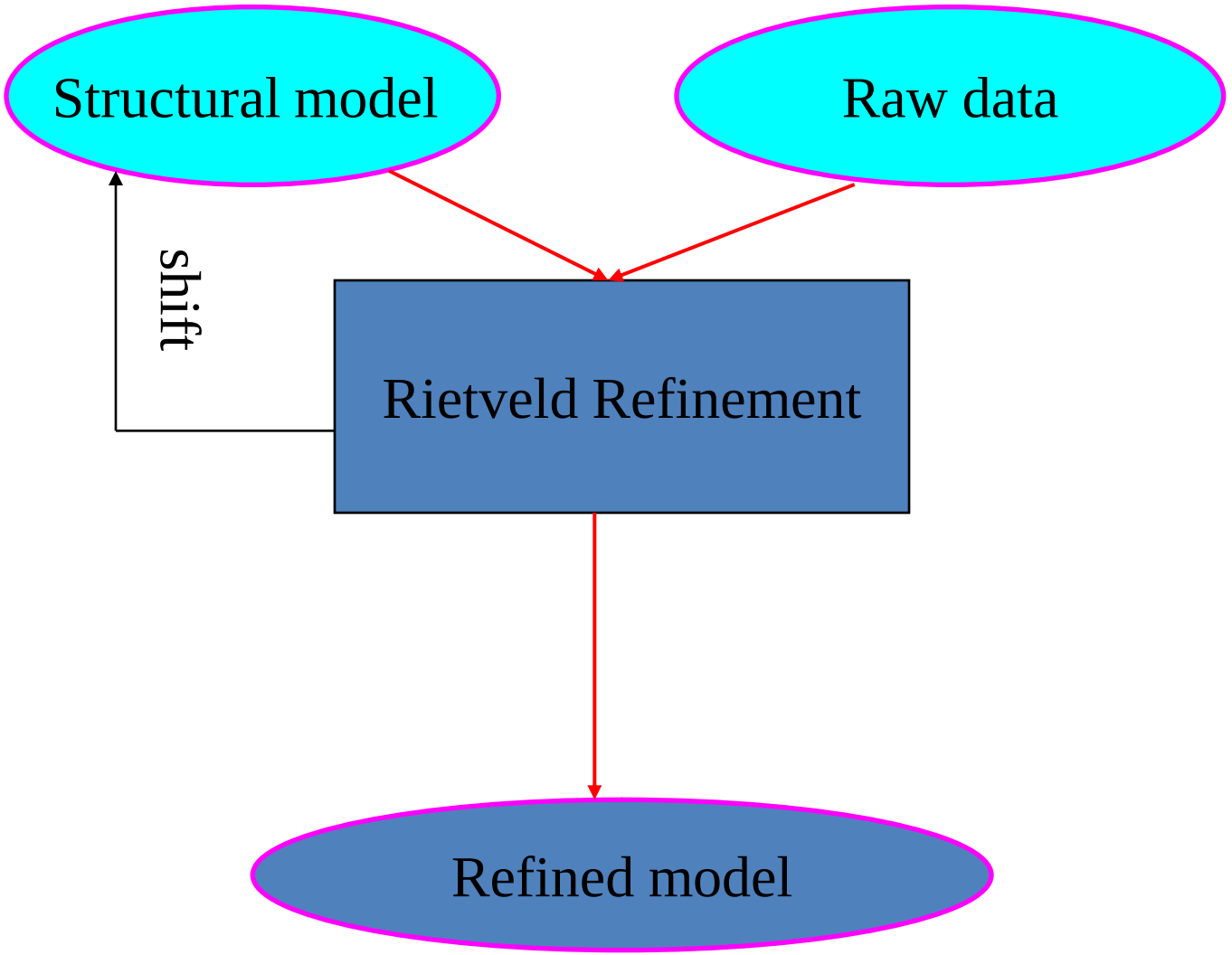
1) Record Powder Diffractogram (neutron and/or X-ray)
2) Identify the phase(s) (X-ray database)
3) Index phase (X-ray or neutron), i.e. find unit cell (i.e. crystal system)
4) Identify space group (X-ray or neutron)
5) If a structural model is available (isostructural compound known) proceed with Rietveld refinement
6) If no structural model is known proceed with ab-initio structure solution
7) Consider X-ray and neutron combined analysis
8) Consider different wavelengths
9) Consider different temperatures

Rietveld Method

- The Rietveld method refines user-selected parameters to minimize the difference between an experimental pattern (observed data) and a model based on the hypothesized crystal structure and instrumental parameters (calculated pattern)

- can refine information about a single crystal structure
  - confirm/disprove a hypothetical crystal structure
  - refine lattice parameters
  - refine atomic positions, fractional occupancy, and thermal parameter

- refine information about a multiphase sample
  - determine the relative amounts of each phase


Structural model
Raw data
shift
Rietveld Refinement
Refined model

Requirements of Rietveld Method

- **High quality experimental diffraction pattern**
- **A structure model that makes physical and chemical sense**
- **Suitable peak and background functions**

Describing the Crystal Structure

- **Space group**
- **Lattice parameters**
- **Atomic positions**
- **Atomic site occupancies**
- **Atomic thermal parameters**
  - **isotropic or anisotropic**

Where to get crystal structure information

- check if the structure is already solved
  - **websites**
    - Inorganic Crystal Structure Database (ICSD) available as free demo version
    - Crystallography Open Database http://www.crystallography.net/
    - Mincryst http://database.iem.ac.ru/mincryst/index.php
    - WebMineral http://www.webmineral.com/
  - **databases**
    - PDF4 from the ICDD
    - Linus Pauling File from ASM International
    - Cambridge Structure Database
  - **literature**
    - use the PDF to search ICSD listings and follow the references
- look for similar, hopefully isostructural, materials
- index the cell, and then try direct methods or ab-initio solutions

How many parameters can we refine?

- Each diffraction peak acts as an observation

theoretically, refine n-1 parameters for n diffraction peaks

- For refining a tetragonal crystal structure, there might be:
  - **scale factor**
  - **2nd order polynomial background: 3 parameters**
  - **2 lattice parameters**
  - **no atomic positions (all atoms are fixed)**
  - **3 or 4 thermal parameters**
  - **3 or 4 occupancy factors**
  - **zero shift and specimen displacement**
  - **5 profile shape parameters**

The Rietveld method is considered a milestone in crystal structure refinement.

The basic idea behind the Rietveld method is the calculation of the entire powder pattern using a variety of different refinable parameters.

Refinable Parameters:

Global parameters:

zero point
instrumental profile
profile asymmetry
background parameters
absorption

For each phase

atomic positions
thermal parameters
site occupancies
scale factor
lattice parameters
preferred orientation
crystallite size
strain
magnetic vectors

How do you know if a fit is good?

difference pattern

Residuals R

- **R** is the quantity that is minimized during least-squares or other fitting procedures
- $\mathbf{R_{wp}}$ is weighted to emphasize intense peaks over background
- $\mathbf{R_{exp}}$ estimates the best value R for a data set
  - an evaluation of how good the data are
- $\mathbf{R_{Bragg}}$ tries to modify the R for a specific phase

- *R-pattern,* $\boldsymbol{R_p}$*:* $$R_p = \frac{\sum |y_i - y_{ci}|}{\sum y_i}$$
- *R-weighted pattern,* $\boldsymbol{R_{wp}}$*:* $$R_{wp} = \left(\frac{\sum w_i (y_i - y_{ci})^2}{\sum w_i (y_i)^2} \right)^{1/2}$$
- *R-Bragg factor,* $\boldsymbol{R_B}$*:* $$R_B = \frac{\sum |I_{(hkl)}('obs') - I_{(hkl)}(calc)}{\sum I_i('obs')}$$
- *R-expected,* $\boldsymbol{R_e}$*:* $$R_e = \left[\frac{(N-P)}{\sum w_i y_i^2} \right]^{1/2}$$

Goodness of fit, $\boldsymbol{S}$*:* $$S = \frac{R_{wp}}{R_e}$$

GOF (Chi^2)

- The easiest way to get low Chi^2 values is to collect noisy data
- R_B gives information about the agreement between the structural model and the pattern
- The most important judgment is in all cases the visual judgment!

R. Young's Refinement Strategy

1. scale factor
2. zero shift
3. linear background
4. lattice parameters
5. more background
6. peak width, w
7. atom positions
8. preferred orientation
9. isotropic temperature factor B
10. u, v, and other profile parameters
11. anisotropic temperature factors

Rietveld Programs

- Free
  - GSAS + ExpGUI
  - **Fullprof**
  - Rietica
  - PSSP (polymers)
  - Maud
  - PowderCell (mostly for calculating patterns and transforming crystal structures, limited refinement)
- Commercial
  - PANalytical HighScore Plus
  - Bruker TOPAS (also an academic)
  - MDI Jade or Ruby

Features Available in Fullprof

- Choice of peak shape for each phase
- Background: fixed, refinable points, polynomial function, Fourier series …
- Multi phase (up to 16 phases)
- Preferential orientation
- Absorption correction for cylinder and flat plate sample shape
- *hkl* dependence FWHM for strain and size effects
- Quantitative analysis
- Atomic distances and angles calculations

How works *FullProf*

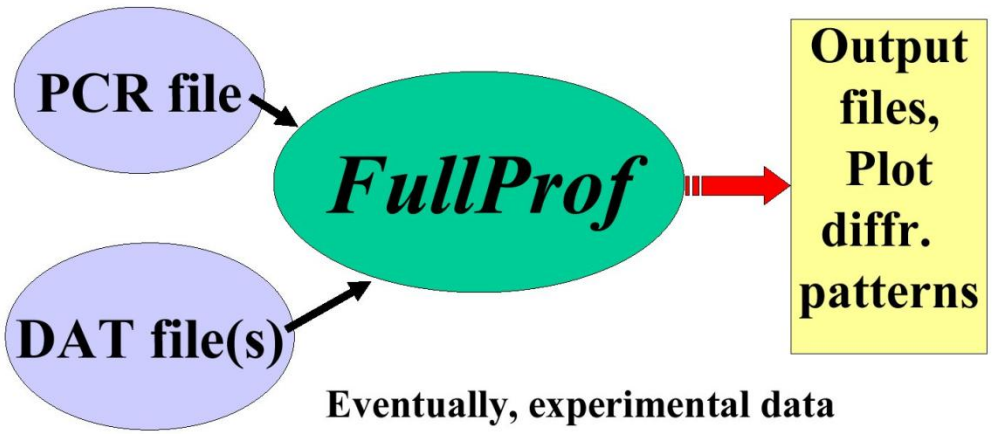
Minimal input:

Input control file (extension ' *.pcr* '): PCR-file
Model, crystallographic/magnetic information

DAT file(s) → **Format depending on the instrument, usually simple**

PCR file →

- ➔ **Many variables and options**
- ➔ **Complex to handle**
- ➔ **Hint: copy an existing (working) PCR-file and modify it for the user case, or...**
- ➔ **USE the new GUI: EdPCR**



Output Files

- **.OUT** — output file of the calculation: details of refinement, correlation matrix, intensities, FWHM, $2\theta_H$, ...
- **.SUM** — summary of the .OUT file
- **.BAC** — background file
- **.PRF** — Y_{obs}, Y_{calc}, Y_{obs}-Y_{calc}, $2\theta_H$
- **.RPA** — summary of refined parameters
- **.SYM** — list of symmetry operators
- **.FOU** — *hkl* and F^2 list for Fourier maps
- **.HKL** — complete list of reflections for each phase
- **.MIC** — microstructural information

Quantitative Phase Analysis

$$W_j = \frac{S_j Z_j M_j V_j / t_j}{\sum_i^N S_i Z_i M_i V_i / t_i}$$

where, W_j is the weight fraction for the jth phase;
S_j is scale factor for the jth the phase;
Z_j is the number formula units per cell for the jth phase;
M_j is the mass of the formula unit;
V_j is the unit cell volume;
t_j Brindley coefficient that comes into effect when the linear absorption coefficients of phases in powder differ a lot to each other.

- **Do not start by refining all parameters as the same time !**

  1- scale factor

  2- + zero shift of detector, 1st background parameter and lattice parameters

  3- + atomic positions, overall Debye-Waller factor

  4- + asymmetry parameters

  5- + atom occupancies (if required)

  6- + individual isotropic thermal parameters

  7- + additional background parameters

  8- + instrumental or physical aberrations

- **In all cases, it is essential to plot frequently the calculated and experimental patterns: examination of the difference plot is a quick and efficient method to detect blunders in the model or in the input file which control the refinement process**

References

1. The Rietveld Method by R.A. Young.

2. Fundamentalsof powder diffraction and structural characterization of materials by Pecharsky,Vitalij K., Zevalij and Peter Y., 2009.

3. Manual of Fullprof Software

4. Powder Diffraction: Theory and practice, R E Dinnerbier and Simon Billinge