FACULTÉ DES SCIENCES ET TECHNOLOGIES
Département Physique

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Advanced Characterization Methods II
Diffraction

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Outline

1- Introduction

2- Diffraction peaks

3- Experimental methods

4- Diffraction peak intensity

5- The Rietveld method

6- Shape of a diffraction peak

7- Parameters in a Rietveld refinement

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1- Diffraction

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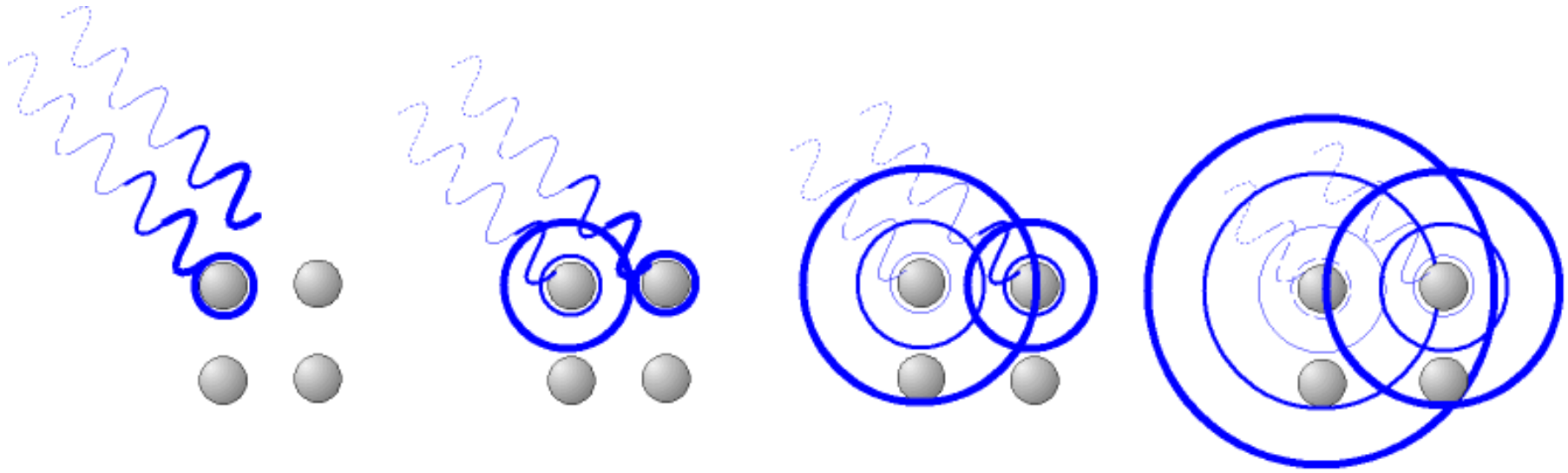
X-ray diffraction



- Incoming radiation → excitation of an atom
- Rayleigh scattering
  - Same energy than incoming radiation, in all directions
- Path differences between scattering from each atom → wave displacement between scattered waves
- Periodic arrangement of atoms + wavelength ~ distance between atoms
  - Formation of constructive interference → diffraction

Image wikipedia

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Diffraction with X-rays, electrons, neutrons

X-rays

- Relatively cheap and simple (laboratory diffractometer)
- interaction with the electronic cloud
- Rayleigh scattering
- “Normal” penetration depth → millimeter size objects

Electrons

- Beam generated by a cathode, relatively simple
- Charged particles, Coulomb forces
- Scattering against protons and electrons
- Shallow penetration depth
  → ~100 nm

Neutrons

- source = nuclear reactor
- Strong interaction with nucleai
- Effect of the magnetic moment
- No scattering by electrons
- Deep penetration depth
  → centimeter size objects

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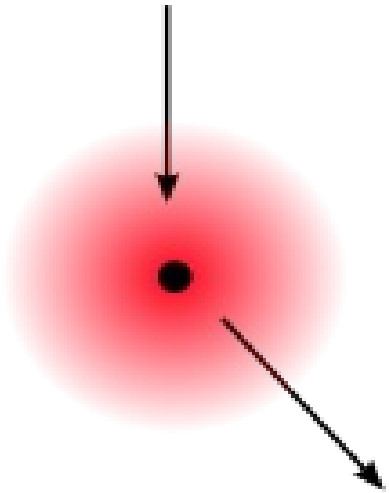
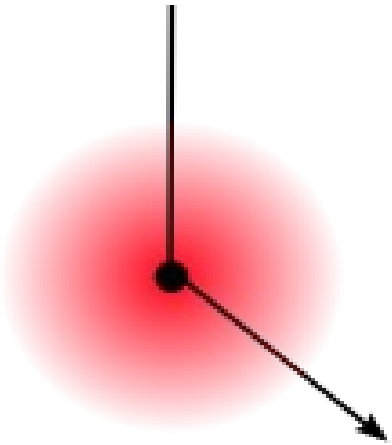
Diffraction with X-rays, electrons, neutrons



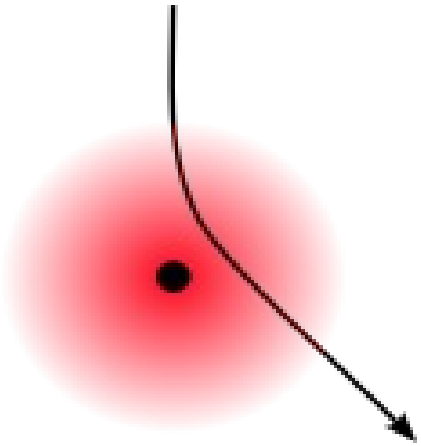
X-rays

Rayleigh scattering
Interaction with
electronic cloud



Neutrons

Strong interaction
Interaction with the
nucleus



Electrons

Coulomb interaction
Interaction with both
electrons and protons

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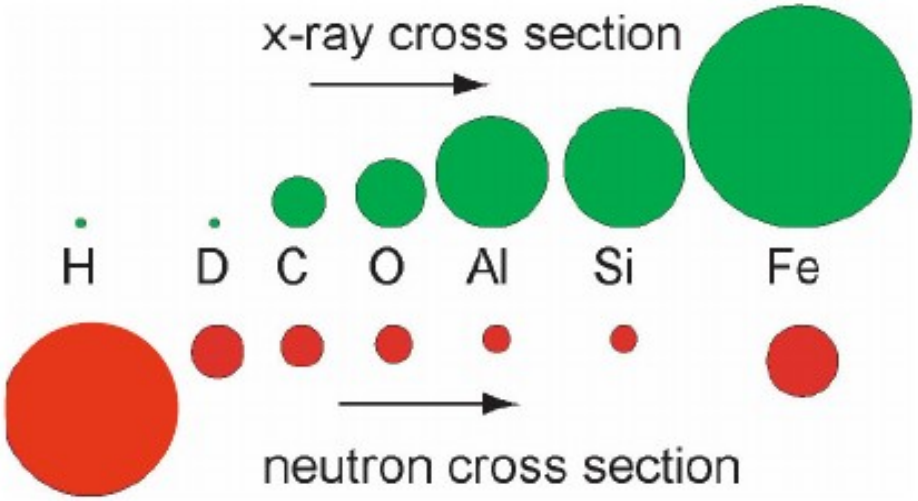
X-ray / neutrons scattering power

X-rays

- Probe the electronic cloud
- Scattering power increases as Z^2

Neutrons

- Strong interaction
- Not systematic vs. atomic number



Scattering power

Scale for X-rays reduced by a factor of ~1.5

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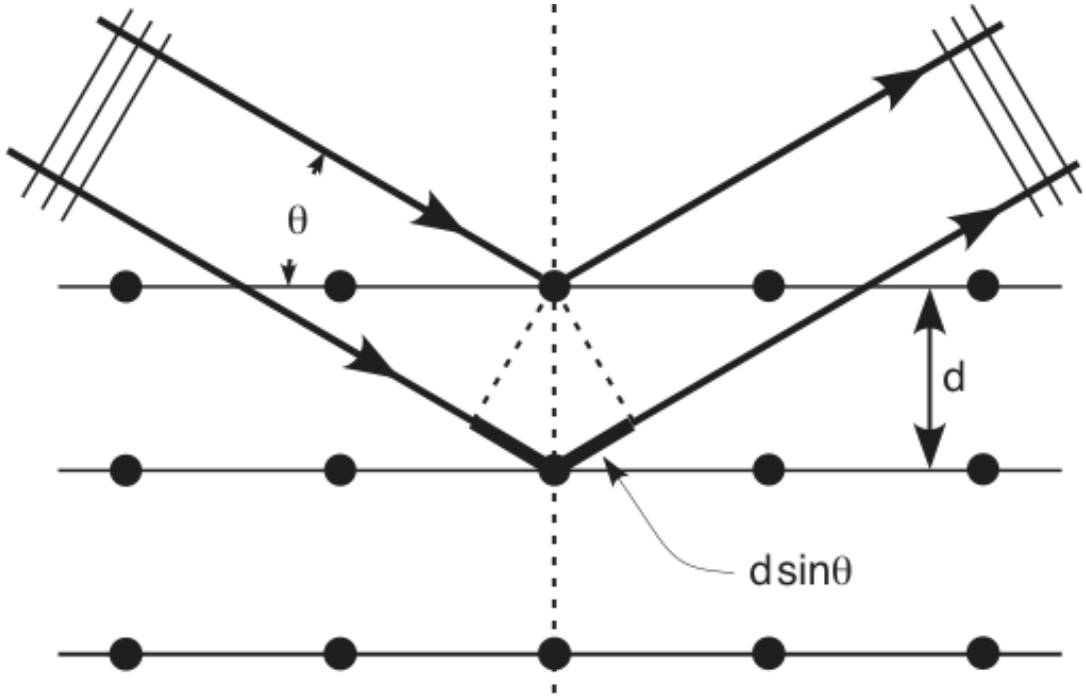
Geometrical interpretation: Bragg's law

$$n\,\lambda = 2\,d_{hkl}\,\sin\theta$$



λ : incident wavelength

d_{hkl} : distance between 2 crystal plane families

θ : Bragg angle

n : order of diffraction (integer)

2 d sin θ = path difference between 2 scattered waves

Attention: crystallographic planes do not exist
Wave are scattered by the atoms, not planes

Image wikipedia

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2- Diffraction peak

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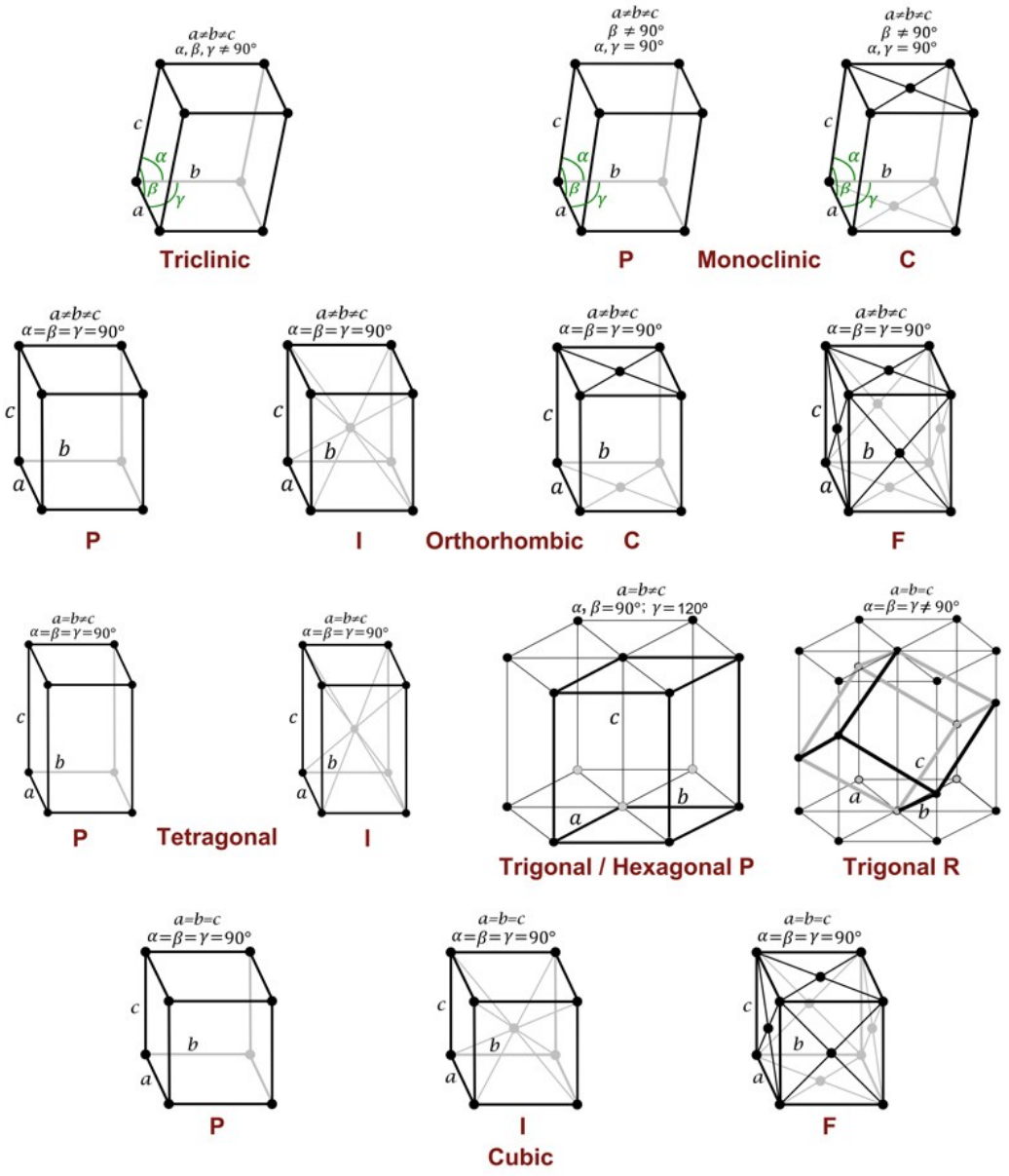
7 lattice systems –14 Bravais lattices



Lattice systems: cubic, hexagonal, tetragonal, orthorombic, monoclinic, triclinic

Additional configurations

- P = primitive, all lattice points at corners of the cell
- C = additional lattice point at the center of one face
- F = additional lattice points at every face centers
- I = additional lattice point at the center of the cell
- R = specific to trigonal system

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230 crystallographic space groups

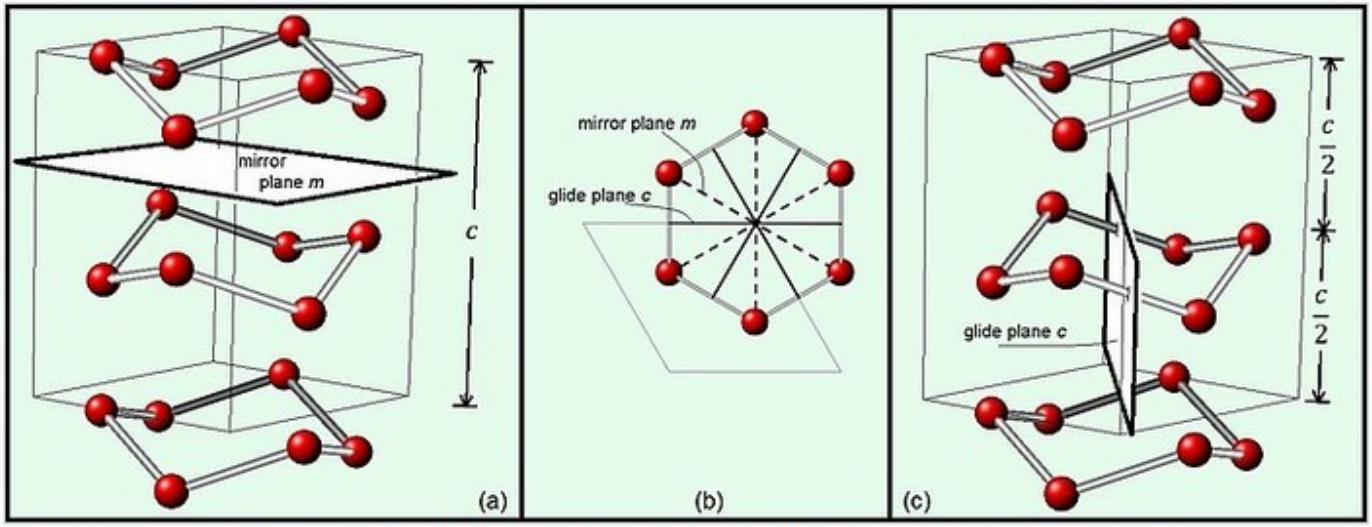
Represent all symmetry configuration in a crystal

230 possibilities

Notation is a list of symmetry elements

Each crystal structure can be defined with

- Space group
- Cell parameters
- Atomic positions



The space group of hexagonal H_2O ice is $P6_3/mmc$. The first *m* indicates the mirror plane perpendicular to the c-axis (a), the second *m* indicates the mirror planes parallel to the c-axis (b), and the *c* indicates the glide planes (b) and (c). The black boxes outline the unit cell.

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Planes and Miller indices

Crystallographic planes labeled with their Miller indices: *h*, *k*, *l*

- (h,k,l) : plane with Miller indices h, k, and l
- {h,k,l} : set of all planes that are equivalent to (h,k,l) by the symmetry of the lattice
- Laue-Bragg indices: hkl (without any bracketing) for a reflection in powder X-ray diffraction

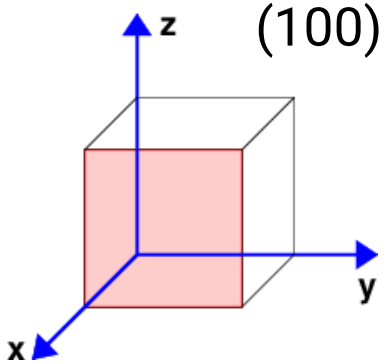
Simple formula between Miller indices and distance between planes in a family

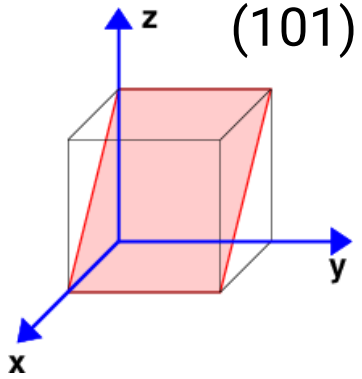
- cubic : $1/d^2_{hkl} = (h^2 + k^2 + l^2)/a^2$

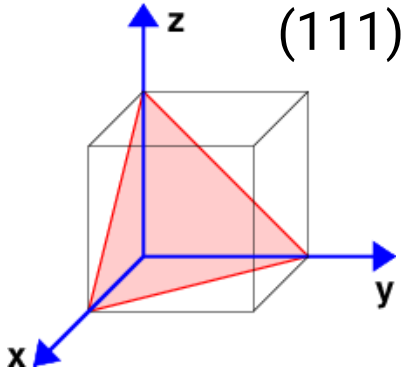
Usually: relatively prime integers (except for centered cells C)

Not true for Laue indices (diffraction)

- Ex : 002 can be n=2 in Bragg's law for 001
- Ex : 003 can be n=3 in Bragg's law for 001
- But, some crystals do not have a 001 diffraction line but have 002 → watch out.







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Extinction conditions

Extinctions :

- Destructive interference for some plane families
- No diffraction

Structure factor

$$F_{hkl} = \sum_{j=1}^{s} f_j \exp\left[2i\pi\left(hx_j + ky_j + lz_i\right)\right]$$

- s : number of atoms in the unit cell
- f_j : scattering factor for atom j
- x_j, y_j, z_j : position of atom j in the unit cell

Diffraction intensity proportional to F^2

Extinction conditions: structure factor is 0, $F_{hkl} = 0$

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Example: body centered cubic

Crystal body centered cubic

- 2 identical atoms (f_i is the same)
- Atomic positions
  - 0,0,0
  - ½,½,½

Structure factor

$$F_{hkl} = f\left[1 + e^{i\pi(h+k+l)}\right]$$

Extinction if $F = 0 \rightarrow h+k+l = 2n+1 \rightarrow h+k+l$ is odd

- 100 : extinction
- 110 : diffraction
- 111 : extinction
- etc

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Illustrations : cubic, I lattice (centered)

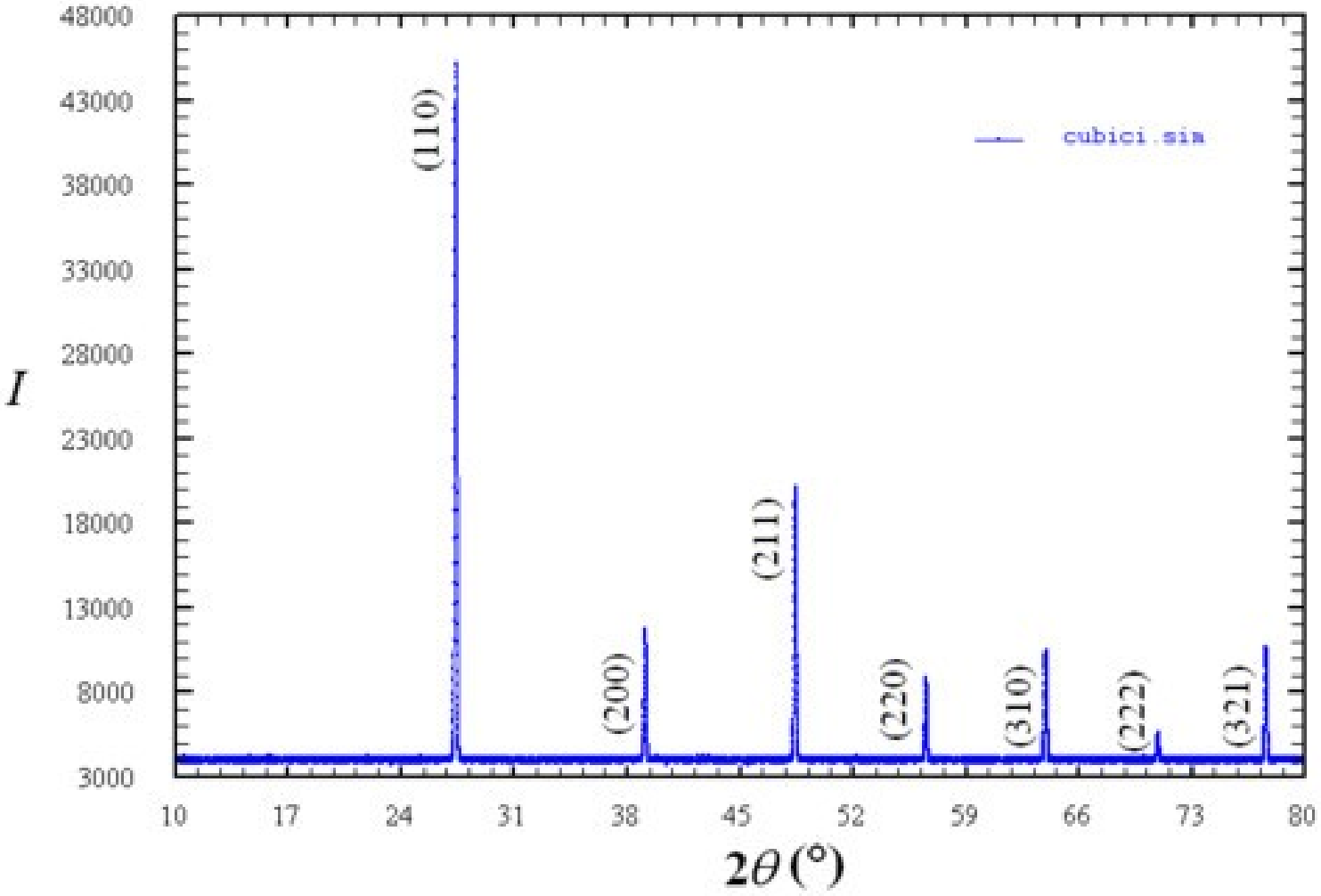

Image wikipedia

Powder diffraction diffractogram, bcc crystal.

Peak position: Bragg's law

Peak list : those with
$|F| \neq 0$

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3- Experimental techniques

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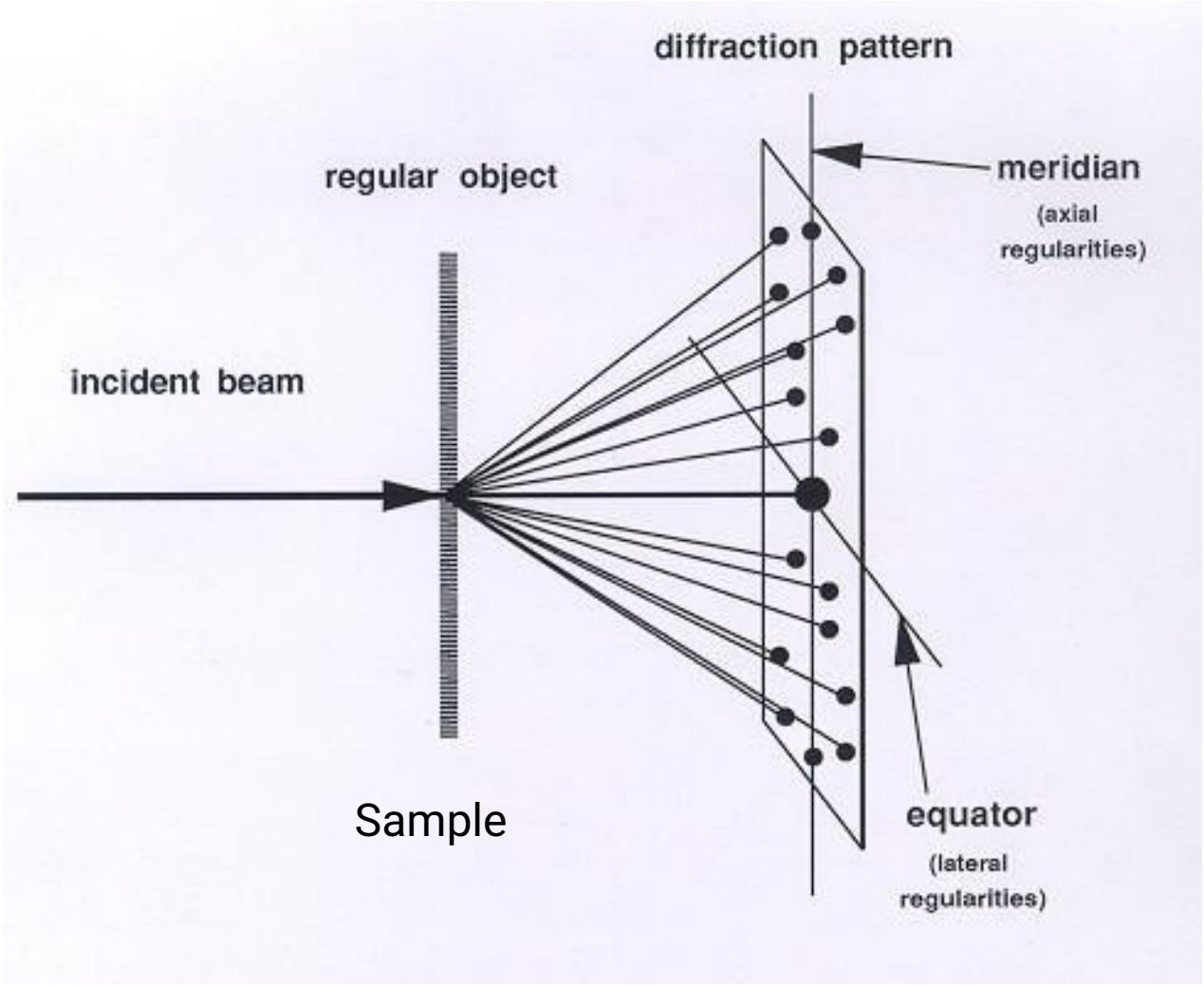
Basic X-ray diffraction layout

X-ray source



Detector

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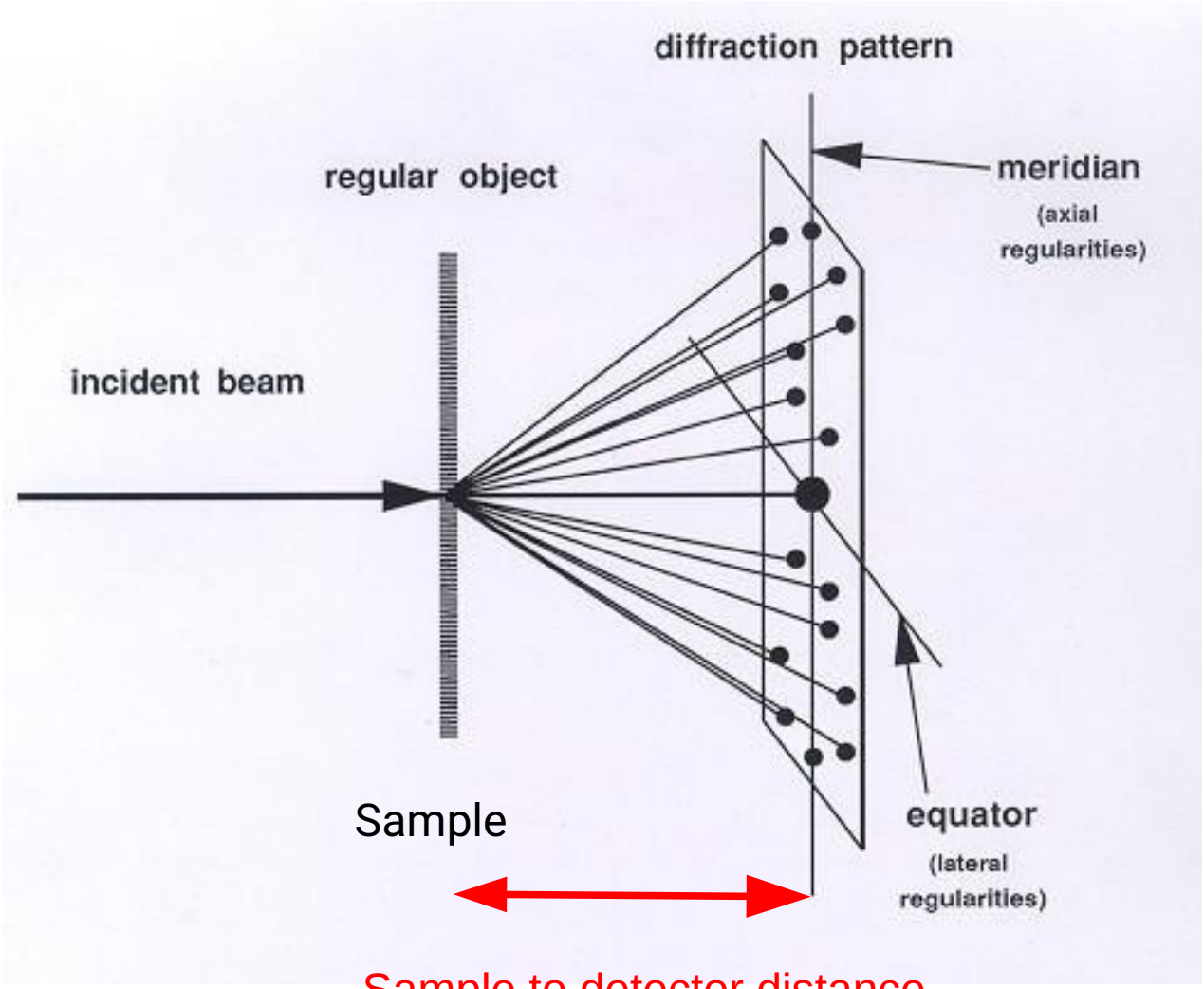
Key parameters



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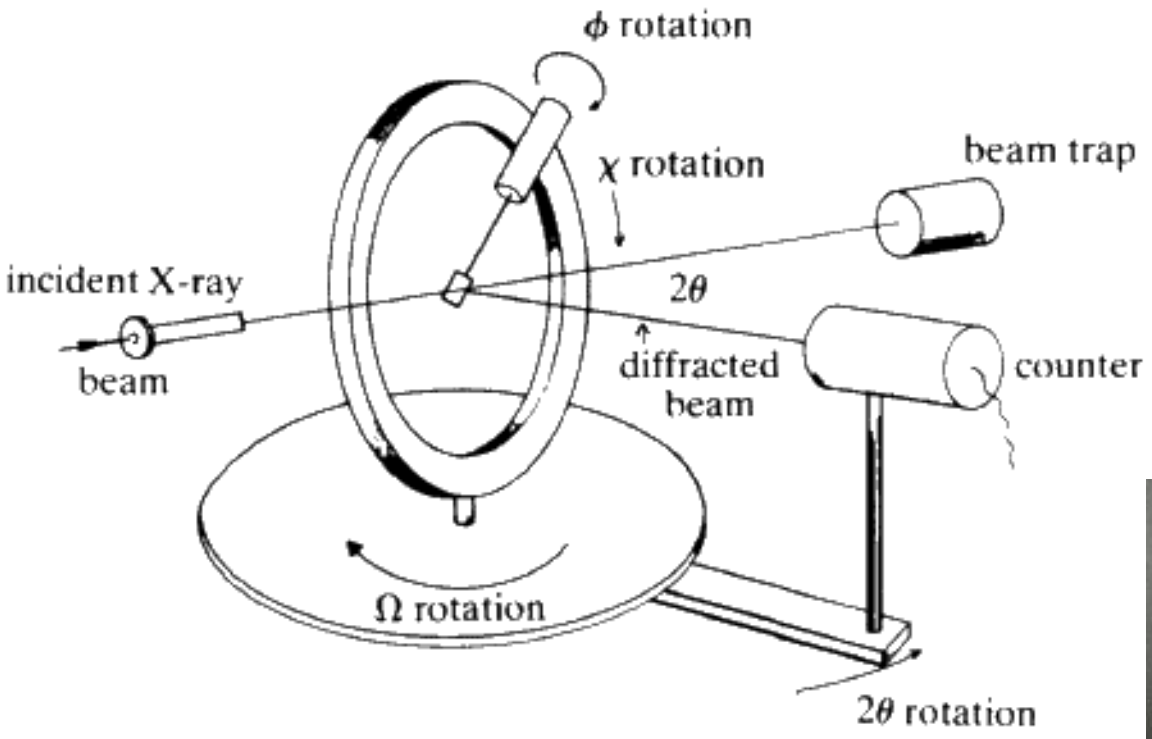
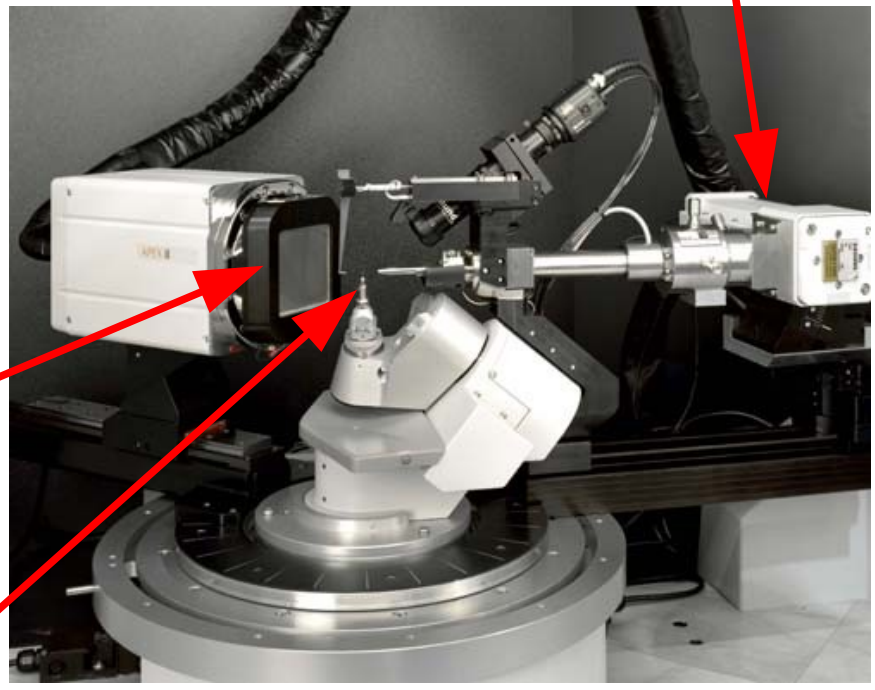
More advanced layout



Objectives: rotate the crystal to cover reciprocal space



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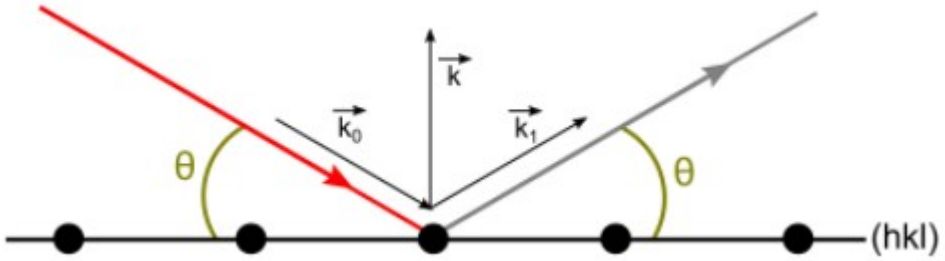
Laue diffraction condition

There are 2 conditions for diffraction to occur

- Distance between planes must match Bragg's law
- The diffracting planes must perpendicular to the incoming and diffracted beam



Conveniently expressed by the Laue conditions

- Scattering vector must be a node of the reciprocal lattice

$$\vec{K} = \vec{k'} - \vec{k}.$$

k_0 : incoming wave vector (norm 1 / λ)
k_1 : scattered wave vector (norm 1 / λ)
K : scattering vector (norm 2 sin θ / λ)

$$\vec{K} = h\vec{e_1^*} + k\vec{e_2^*} + l\vec{e_3^*}$$

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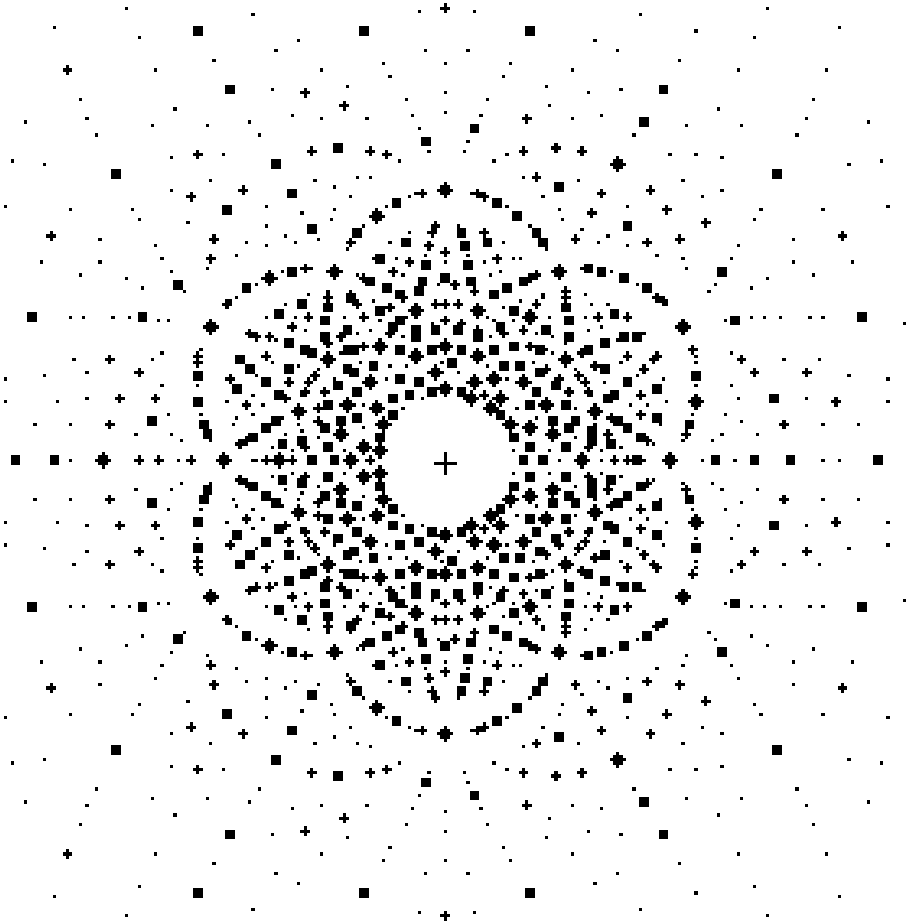
Laue diffraction technique

Single crystal

Polychromatic incoming X-ray beam

Diffraction signal: many points

Diffraction for all planes / directions that satisfy the Laue conditions



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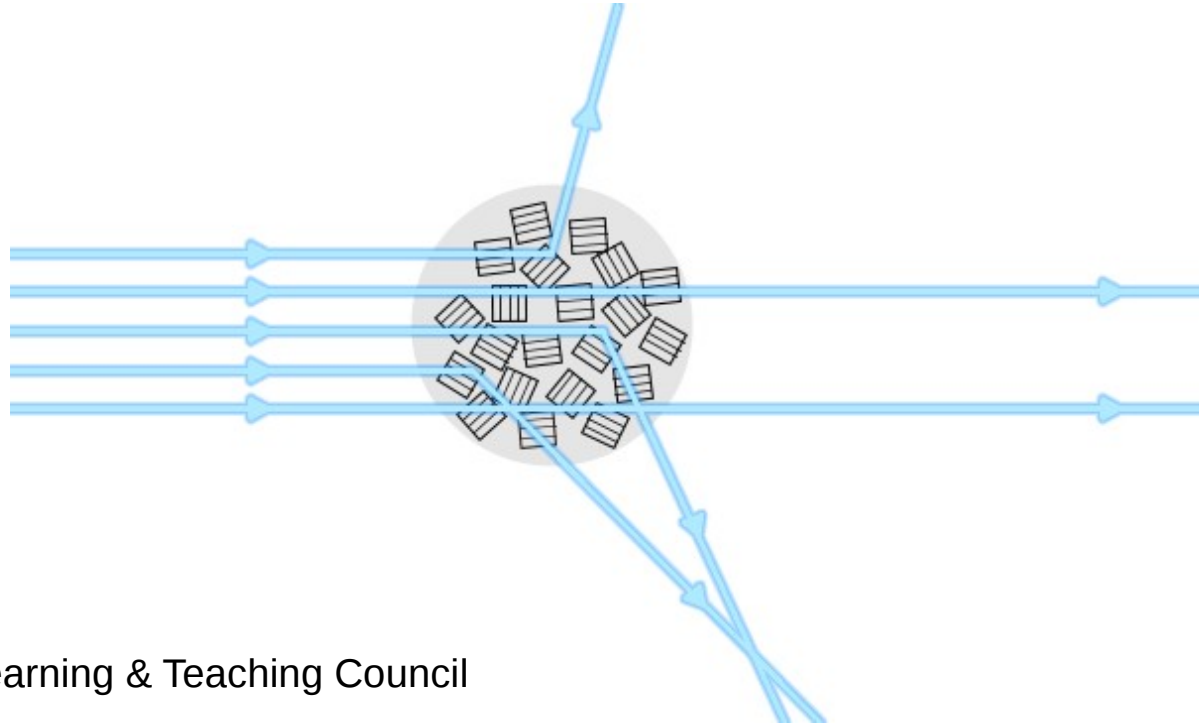
Powder X-ray diffraction

Powder = ensemble of many crystals, with a somewhat random orientation

The orientation of the diffracting plane does not matter anymore (there is always one that will work), only 2θ matters, the angle between the incoming and the scattered beams

Diffraction figures: circles, one for each 2θ value with no extinction



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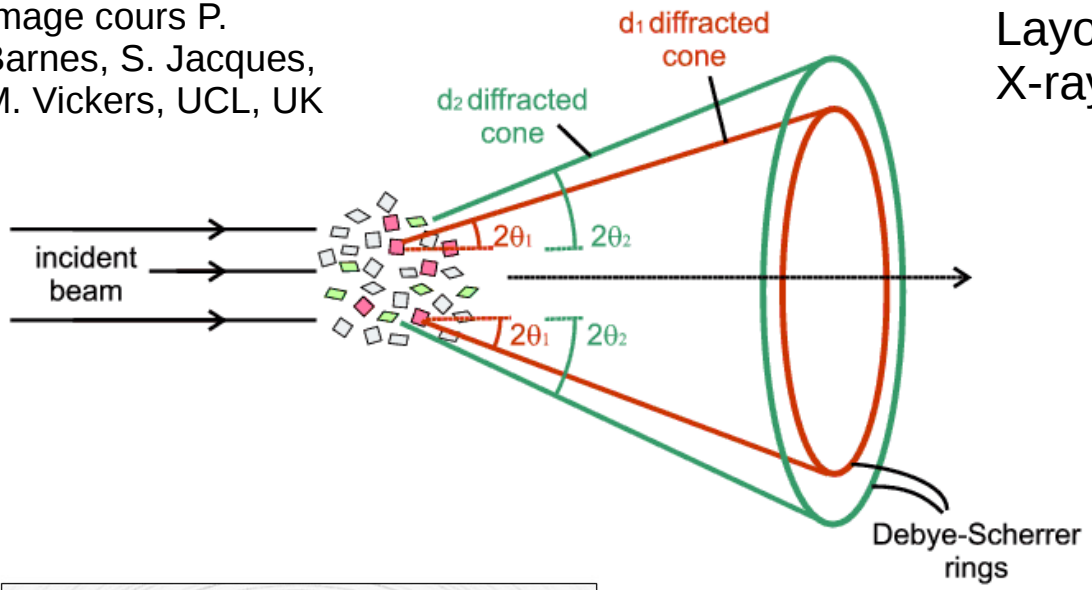
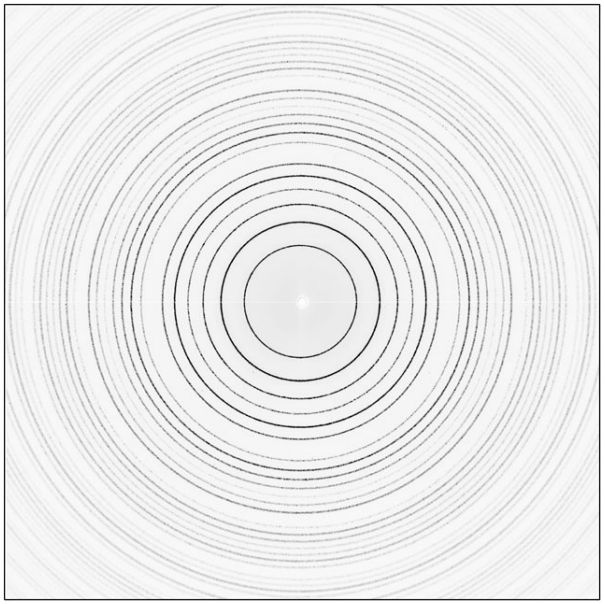
Powder X-ray diffraction

Image cours P. Barnes, S. Jacques, M. Vickers, UCL, UK

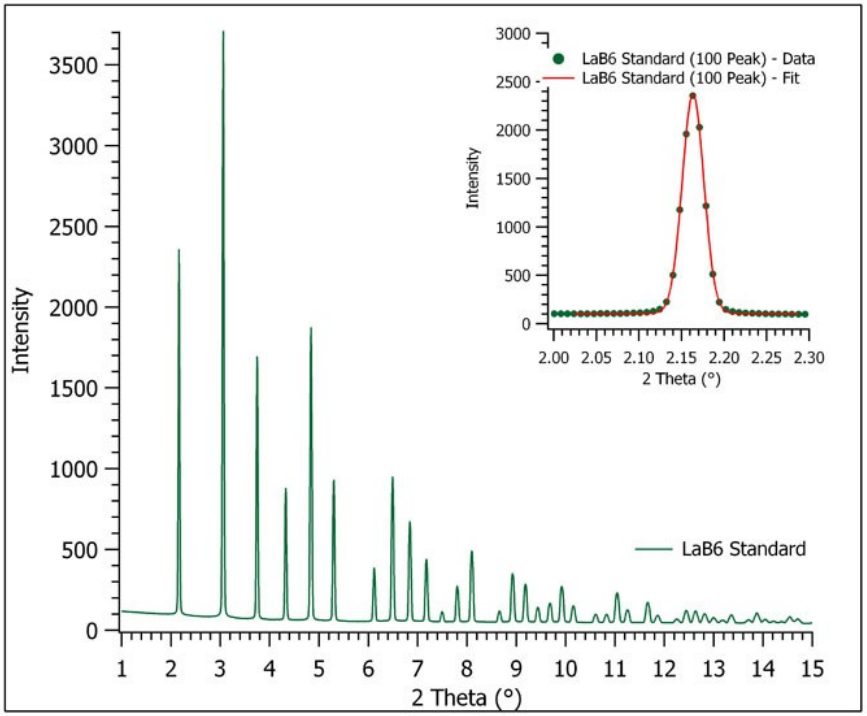


Layout for powder X-ray diffraction



Diffraction image for LaB_6

Integrated diffraction spectrum for LaB_6



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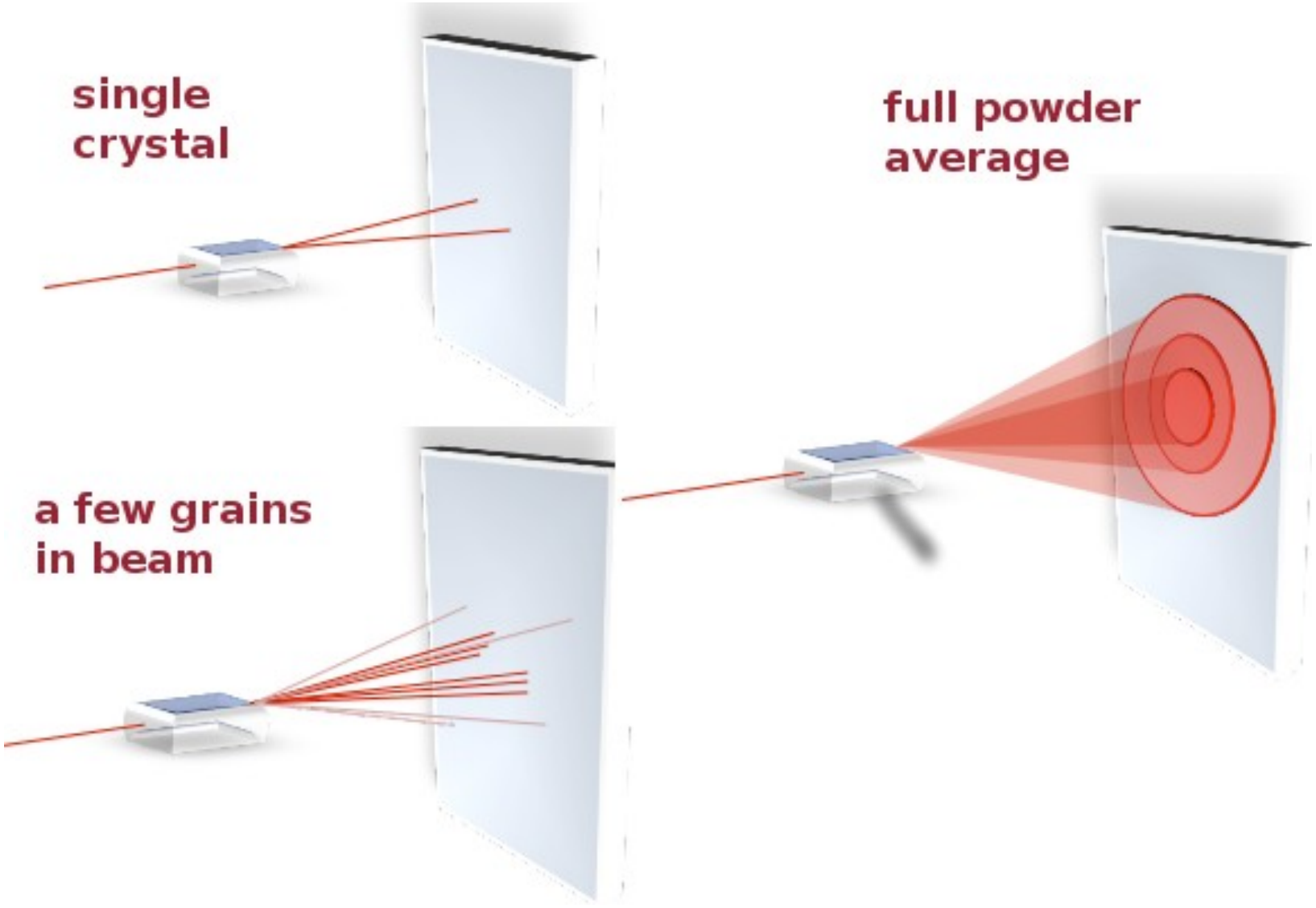
Single crystal vs. multiple grains vs. powder



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4- Diffraction peak intensity

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Intensity of a diffraction peak

In a single crystal, there are 3 effects controlling diffraction intensities

$$I(hkl) = |F(hkl)|^2 * LP(\lambda,\theta) * TF(\lambda,\theta)$$

- *F* : Structure factor, atom types and arrangement
- *LP* : Lorentz and polarization
- *TF* : Temperature

In a polycrystal, there is 4th effect

$$I(hkl) = m_{hkl} * |F(hkl)|^2 * LP(\lambda,\theta) * TF(\lambda,\theta)$$

- m_{hkl} : multiplicity
- Others : same as single-crystal

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Structure factor – $|F(hkl)|^2$

Diffraction intensity proportional to the square of the norm of *F*

$$I_{hkl} = A \mid F_{hkl} \mid^2$$

Ex : body centered crystal

- I(100) = 0 ;
- I(110) = 4 A f^2 ;
- I(111) = 0 ;
- I(200) = 4 A f^2 ;
- I(210) = 0 ;
- I(211) = 4 A f^2 ;
- Etc

f is the atomic scattering factor

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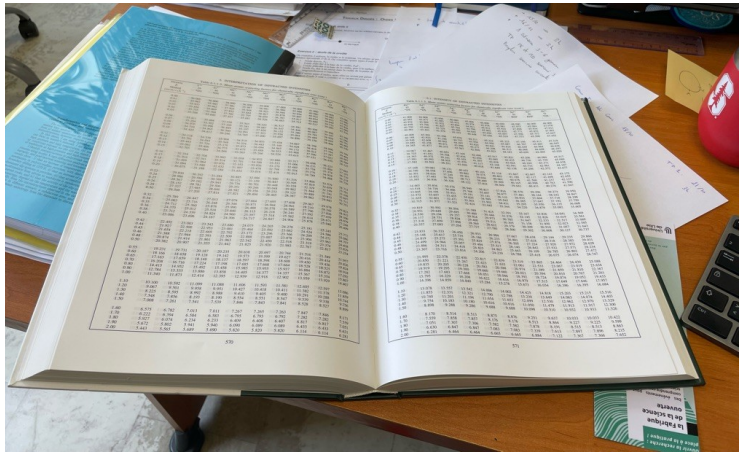
Atomic scattering factor *f* (X-rays)

Effect of

- Number of electrons
- Wavelength : *f* increases with λ
- θ angle : *f* decreases with θ

There are tables available. They are built-in in most processing software.

→ International Tables for Crystallography, Section C 6.1.1.4



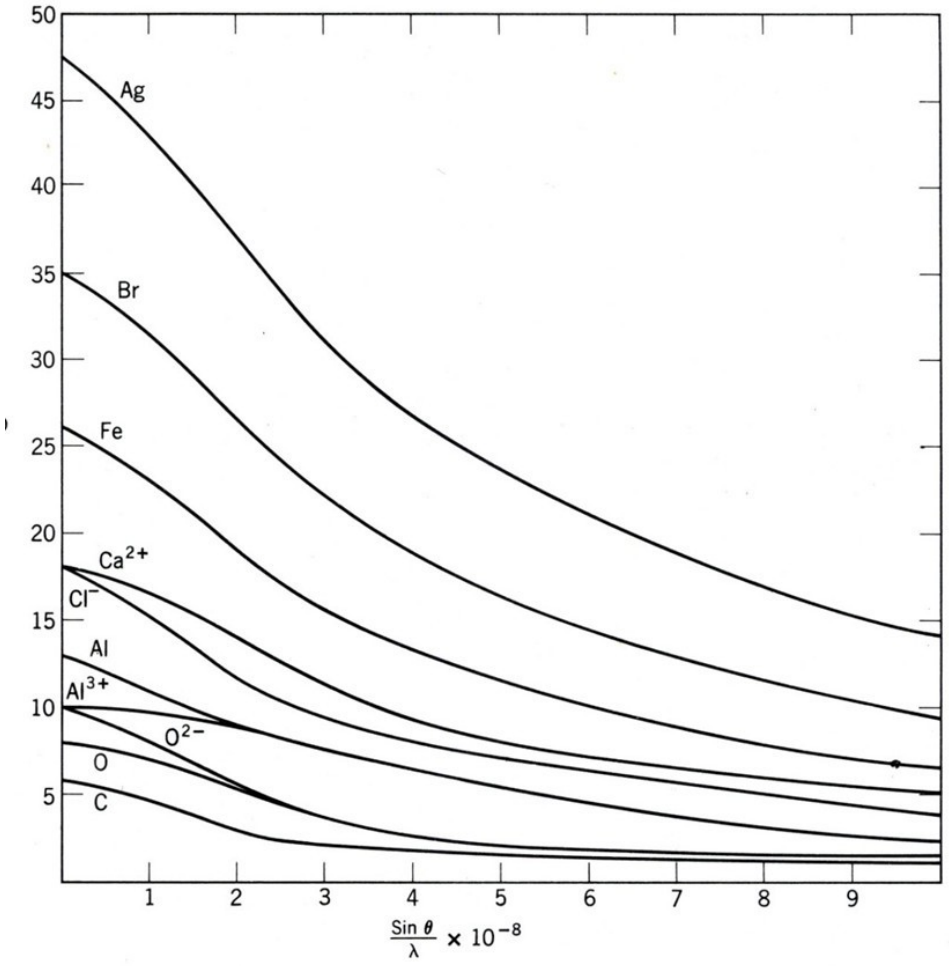


Fig. 3-15. Diffracting power of a few common atoms and ions (after C. W. Bunn, *Chemical Crystallography*, Oxford University Press, 1945).

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Effect of temperature – ***TF(λ,θ)***

Thermal motion of atoms

- Network of atoms is not truly periodic
- Decreases peak intensities
- Expresses itself differently from one atom to another in the structure

Debye-Waller factor = B-factor = temperature correction

One formula is as follow

$$f = f_0 \exp\left[-B\frac{sin^2\theta}{\lambda^2}\right]$$

One B-value for each atom in the structure

B-values are taken from experimental data

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Effect of temperature – ***TF(λ,θ)***

$$f = f_0 \exp\left[-B\frac{sin^2\theta}{\lambda^2}\right]$$

B-values are taken from experimental data.

There are no true physical models to guess what they should be.

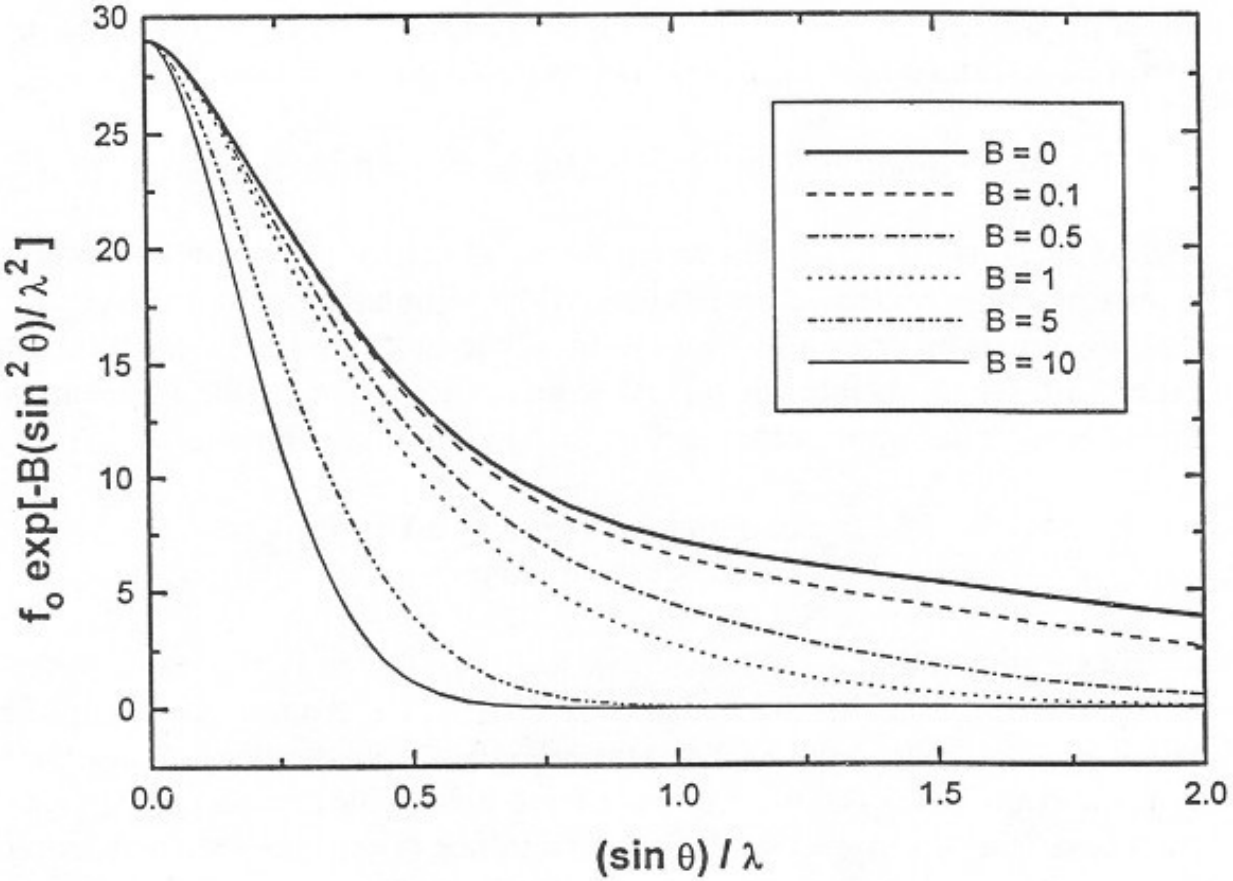

Figure 3.14. The effect of atomic thermal motion on the copper scattering factor.

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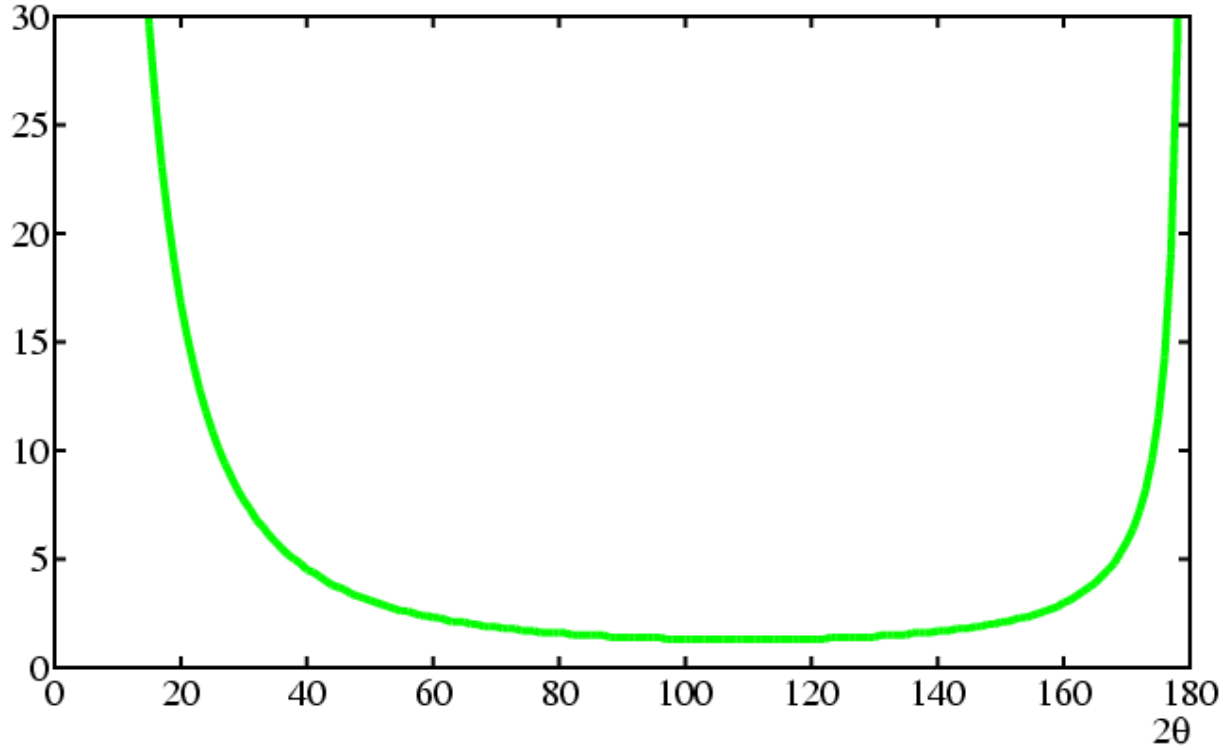
Lorentz correction – ***L(θ)***

For geometrical reasons, diffraction is more efficient at small 2θ values.

This is called the Lorentz correction.

$$L = \frac{1}{\sin\theta \sin 2\theta}$$



Figures:
Advanced Certificate in Powder Diffraction on the Web
School of Crystallography, Birkbeck College, University of London
http://pd.chem.ucl.ac.uk/pdnn/chapter.htm

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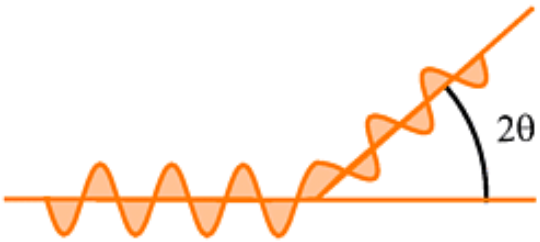
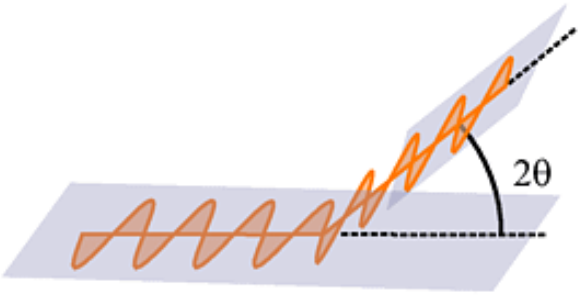
Polarization correction – ***P(θ)***

X-ray beams are often polarized (depends on the source). This adds an additional correction...



Polarization in the plane of diffraction
Weaker diffraction intensity



Polarization orth. to diffraction plane
No effect

The exact formula depends on the X-ray source and the experiment.

Some examples:

- Case (1): Polarization in the diffraction plane, $P = \cos^2 2\theta$
- Case (2): Polarization normal to the diffraction plane, $P = 1$
- Case (3): No polarized X-rays, $P = (1 + \cos^2 2\theta)/2$
- ...

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Multiplicity (powder) – m_{hkl}

In powder diffraction, diffraction from symmetry-equivalent planes are on top of each other

- Cubic crystal, 100 peak:
  diffraction from planes such as (100), (010), (001), (-100), (0-10), (00-1)
- Cubic crystal, 110 peak :
  planes (110), (101), (011), (-110), (1-10), (-1-10), (-101), (10-1), (-10-1), (0-11), (01-1), (0,-1-1)

Effect on intensities :

- The peak intensity for 100 is multiplied by 6 relative to the single-crystal
- The peak intensity for 110 is multiplied by 12 relative to the single-crystal
- This is the multiplicity factor

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Multiplicity for a cubic crystal

All can be calculated from the crystal structure.

In general, for cubic crystal:

- $n_1 00$ (ex 100) : 6
- $n_1 n_1 0$ (ex 110) : 12
- $n_1 n_1 n_1$ (ex 111) : 8
- $n_1 n_2 0$ (ex 210) : 24
- $n_1 n_1 n_2$ (ex 221) : 24
- $n_1 n_2 n_3$ (ex 321) : 48

For other structures : there are tables.

Most are built-in to the data processing sofware packages.

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Intensity of a diffraction peak

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$$I(hkl) = |F(hkl)|^2 * LP(\lambda,\theta) * TF(\lambda,\theta)$$

- *F* : Structure factor, atom types and arrangement
- *LP* : Lorentz and polarization
- *TF* : Temperature

In a polycrystal, there is 4th effect

$$I(hkl) = m_{hkl} * |F(hkl)|^2 * LP(\lambda,\theta) * TF(\lambda,\theta)$$

- m_{hkl} : multiplicity
- Others : same as single-crystal

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Illustrations

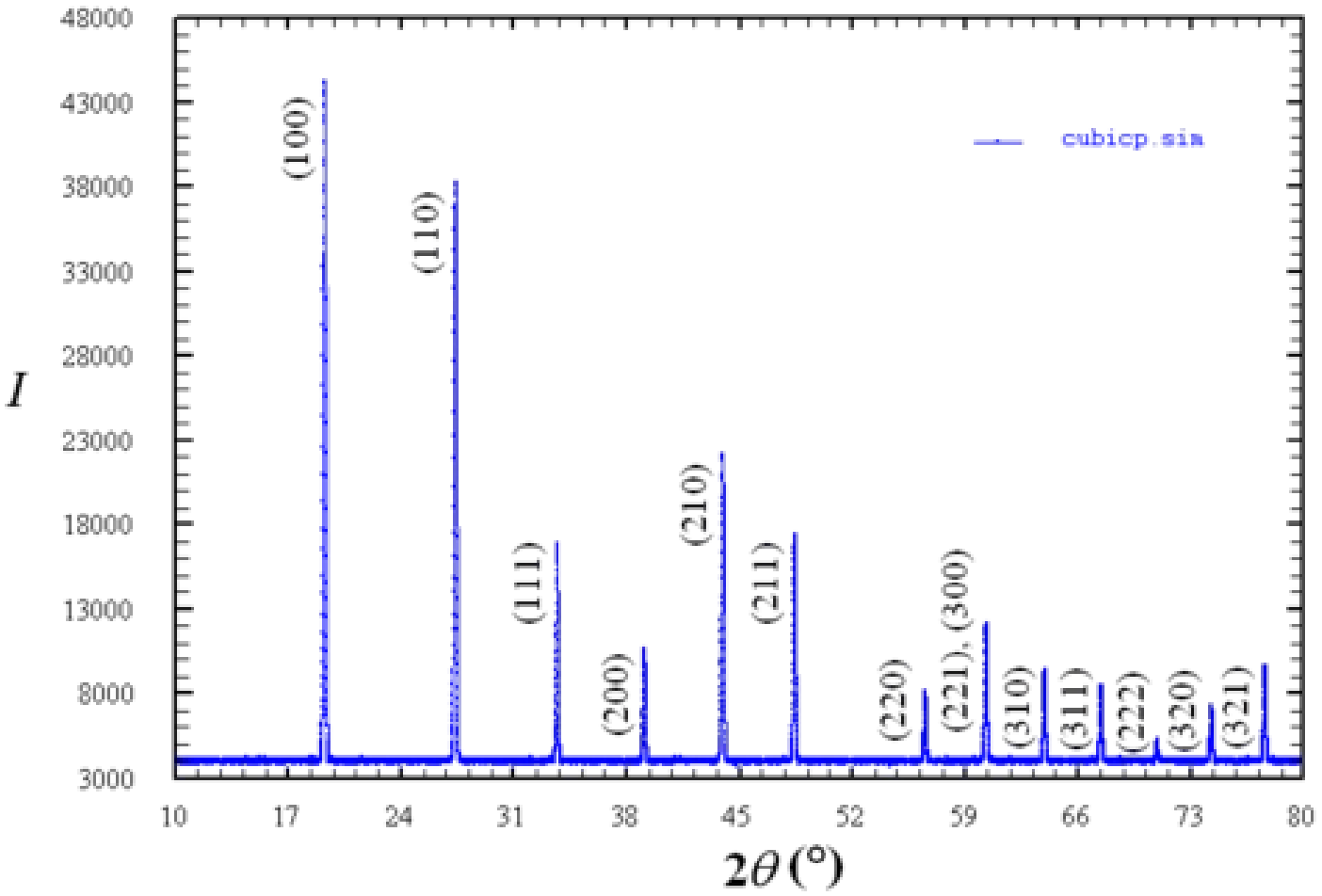

Image wikipedia

Powder diffraction for a simple cubic system.

Peak positions: Bragg's law

List of peaks : extinction conditions

Intensity for peaks: formula on previous slide.

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Illustrations : cubic, P-lattice (primitive)

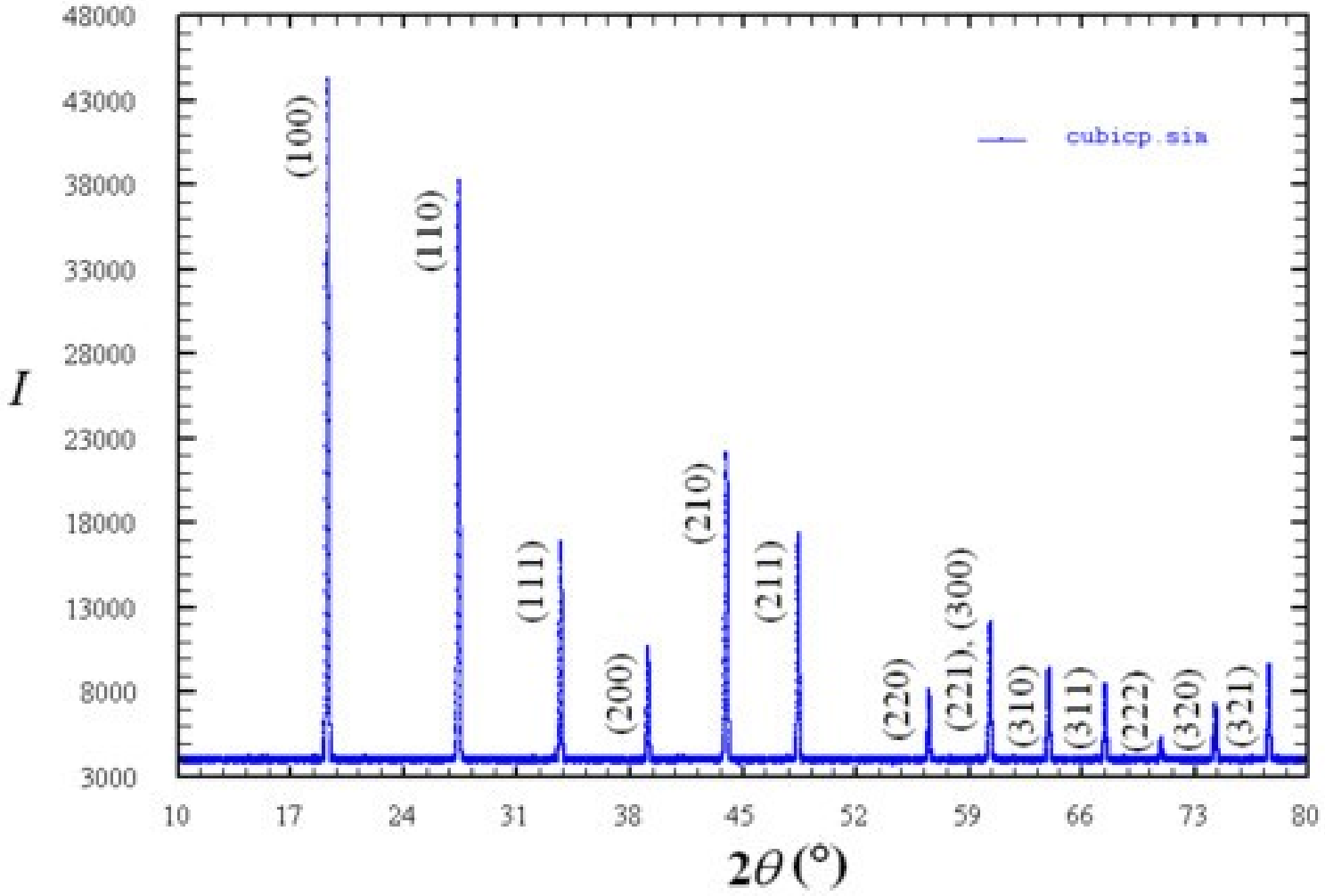

Image wikipedia

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Illustrations : cubic, I-lattice (centered)

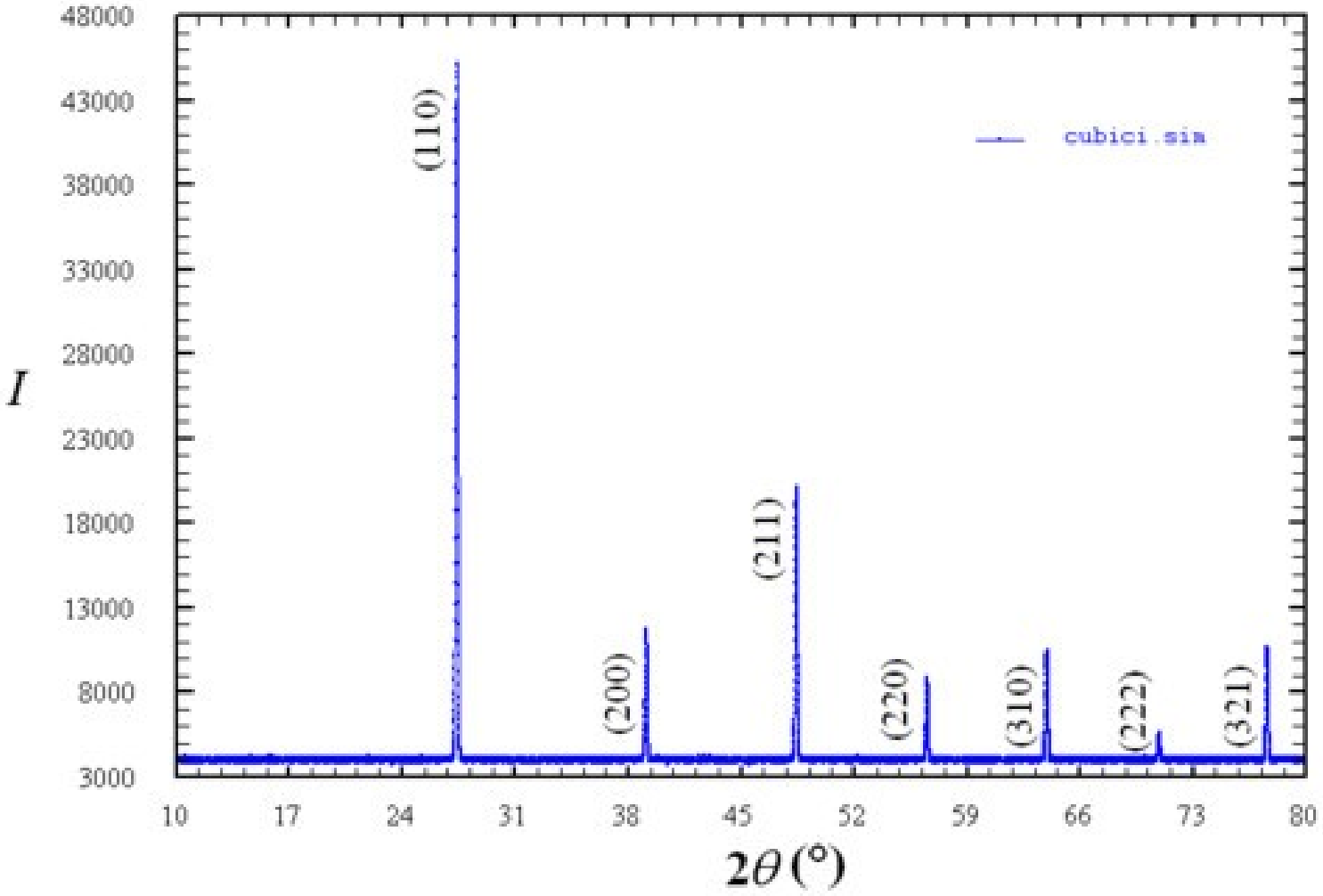

Image wikipedia

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Illustrations : cubic, F-lattice (face centered)

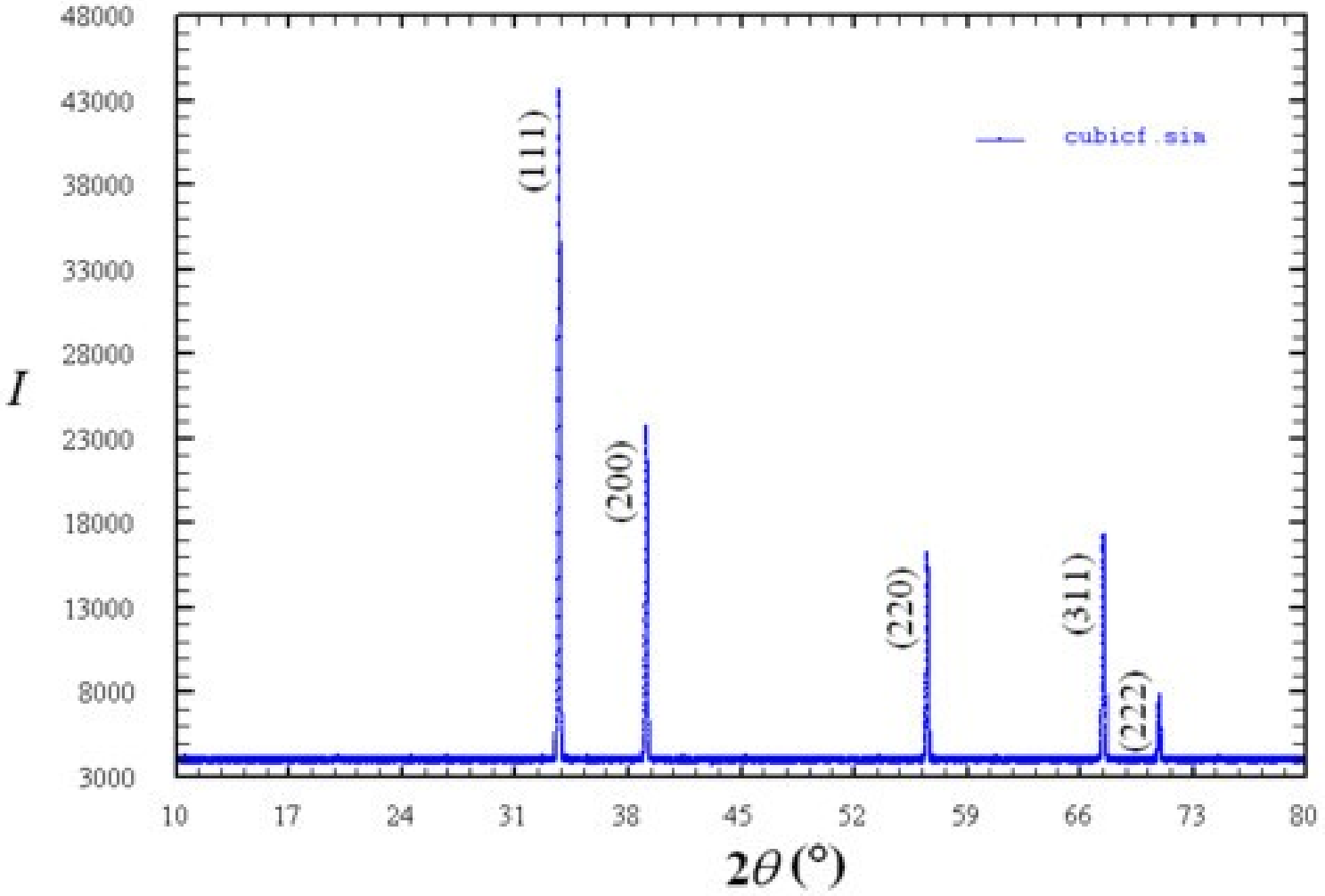

Image wikipedia

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5- The Rietveld method

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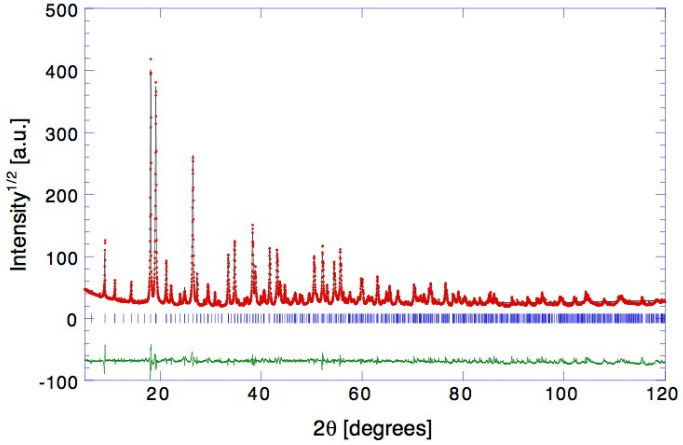
The Rietveld method

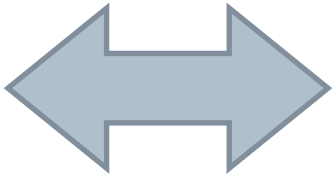
Objectives:

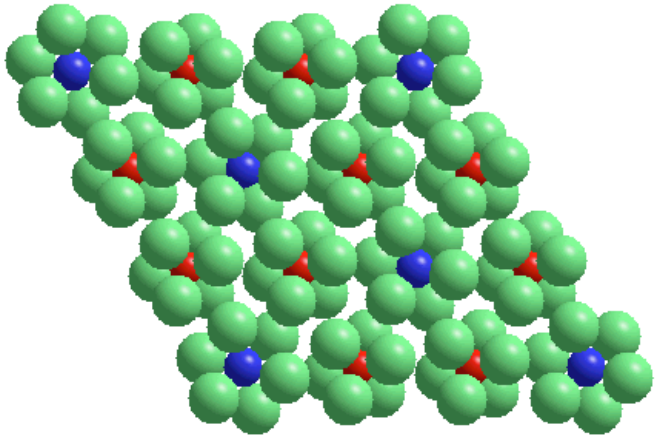
- Entirely reconstruct a powder diffraction signal

Method:

- Physical model based on hypotheses (structure, phase distribution, etc)
- Least-square minimization to refine parameters (phase proportions, cell parameter, grain sizes, etc)







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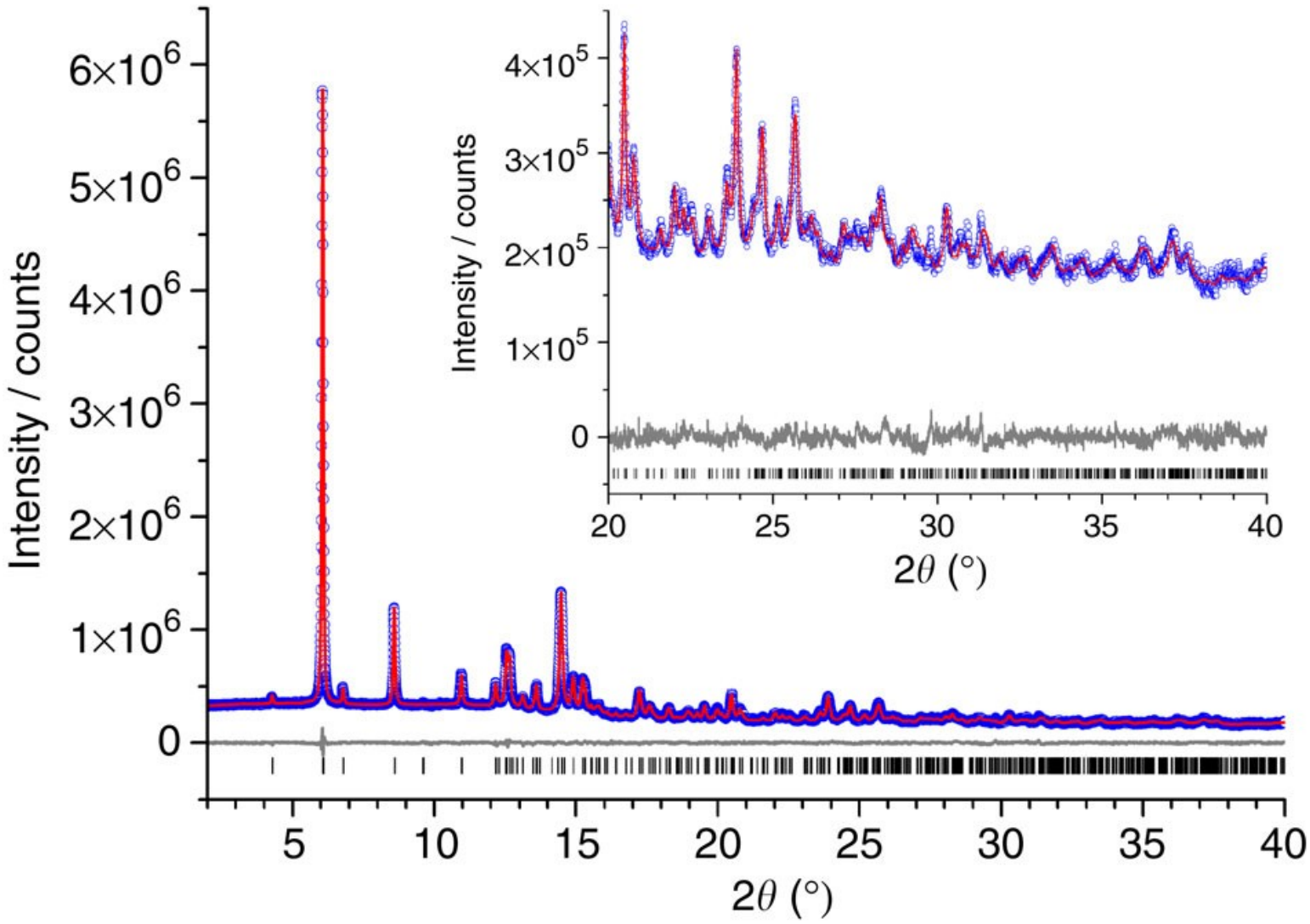
Objectif



Blue: experimental data

Red: calculated data

Gray : difference $[(I_{obs} - I_{calc})]$

Black ticks: pic positions for the structure

Coronado, *Nature Communications*, 2012

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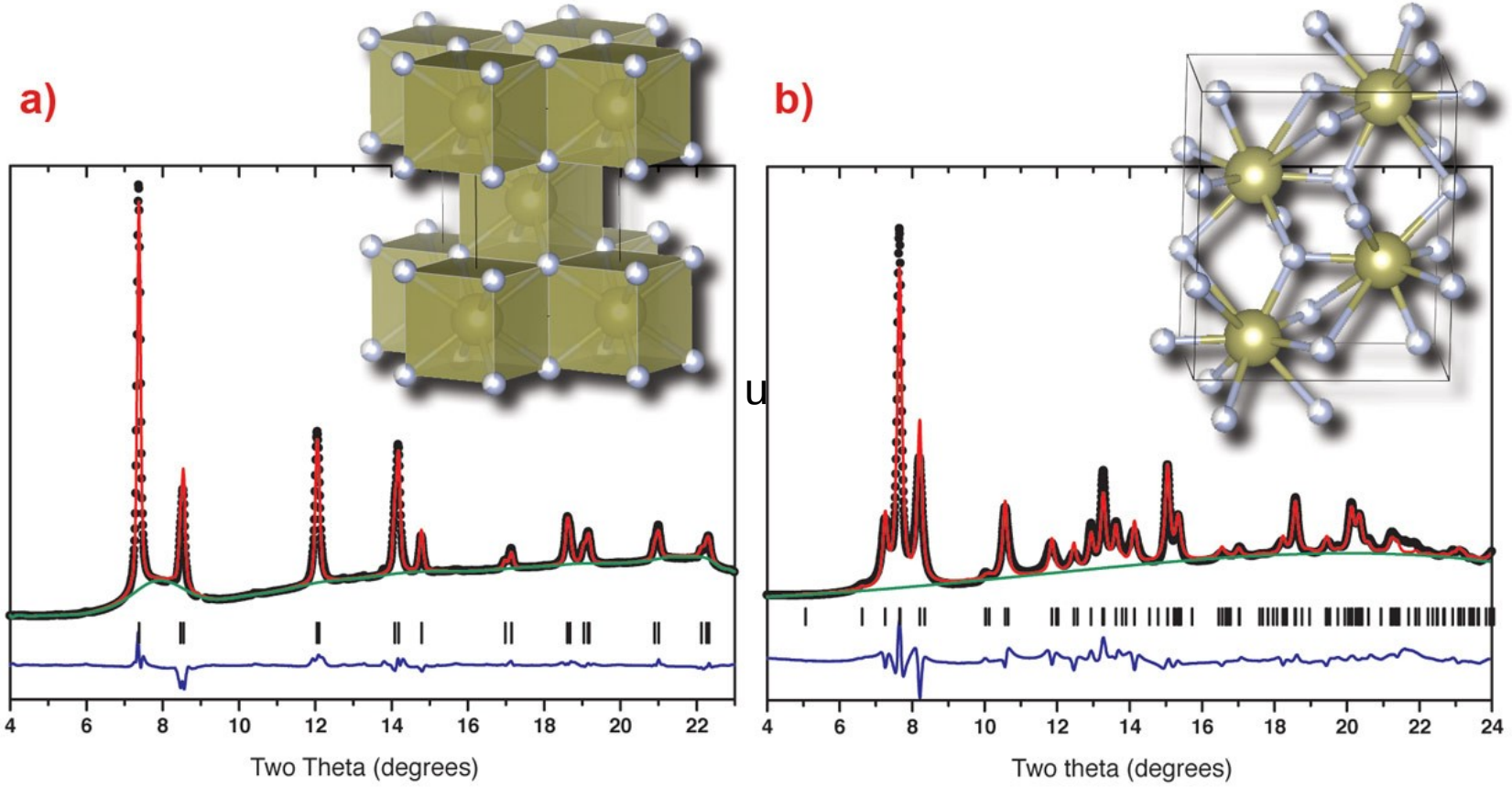
Sample applications



Same composition (Hf_3N_4) but different structures at different conditions. (a) 12 GPa and 1500 K (b) 19 GPa.

Source : ESRF Spotlight 16/07/2013

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Minimization of

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

Theoretical spectrum formula

$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k \left|F_{k,j}\right|^2 S_j\left(2\theta_i - 2\theta_{k,j}\right) P_{k,j} A_j + bkg_i$$

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Modeled spectrum

$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k \left|F_{k,j}\right|^2 S_j\left(2\theta_i - 2\theta_{k,j}\right) P_{k,j} A_j + bkg_i$$

Modeled spectrum depends on

- Phase: crystal structure, microstructure, amount, cell parameters, texture, stress, etc
- Experimental parameters: beam intensity, radiation, Lorentz correction, polarization, background signal, resolution, aberrations, etc
- Sample: position, shape, dimension, orientation

Each quantity should be expressed as parameters that can be

- Set by hand
- Optimized

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Modeled spectrum

$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k \left|F_{k,j}\right|^2 S_j\left(2\theta_i - 2\theta_{k,j}\right) P_{k,j} A_j + bkg_i$$

At each point in $2\theta_i$, the spectrum is calculated accounting for

- backgrounds

- diffraction intensity (peak area)

- broadening (peak shape)

- number and positions of the peaks

- number and proportions in phases or materials

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In real life

(nearly) no-one tries to solve all equations by hand, but you need to know the meaning of the different terms.

There are many dedicated software packages, including:

- *GSAS* (Larson and B. Von Dreele, Los Alamos):
  the most well-known. Very efficient for structure refinements Not easy to use but very large user community. Graphical user interface with Expgui.

- *MAUD* (Luterroti, Univ. Trento) :
  written for materials science. Good at quantitative analysis of compositions, microstructures, textures, etc. Graphical user interface.

- *FullProf* (Rodriguez-Carvajal, ILL, Grenoble) :
  most efficient for magnetic effects. Good at structure refinements. No graphical user interface when I wrote the slide.

In the practicals, we will use MAUD.

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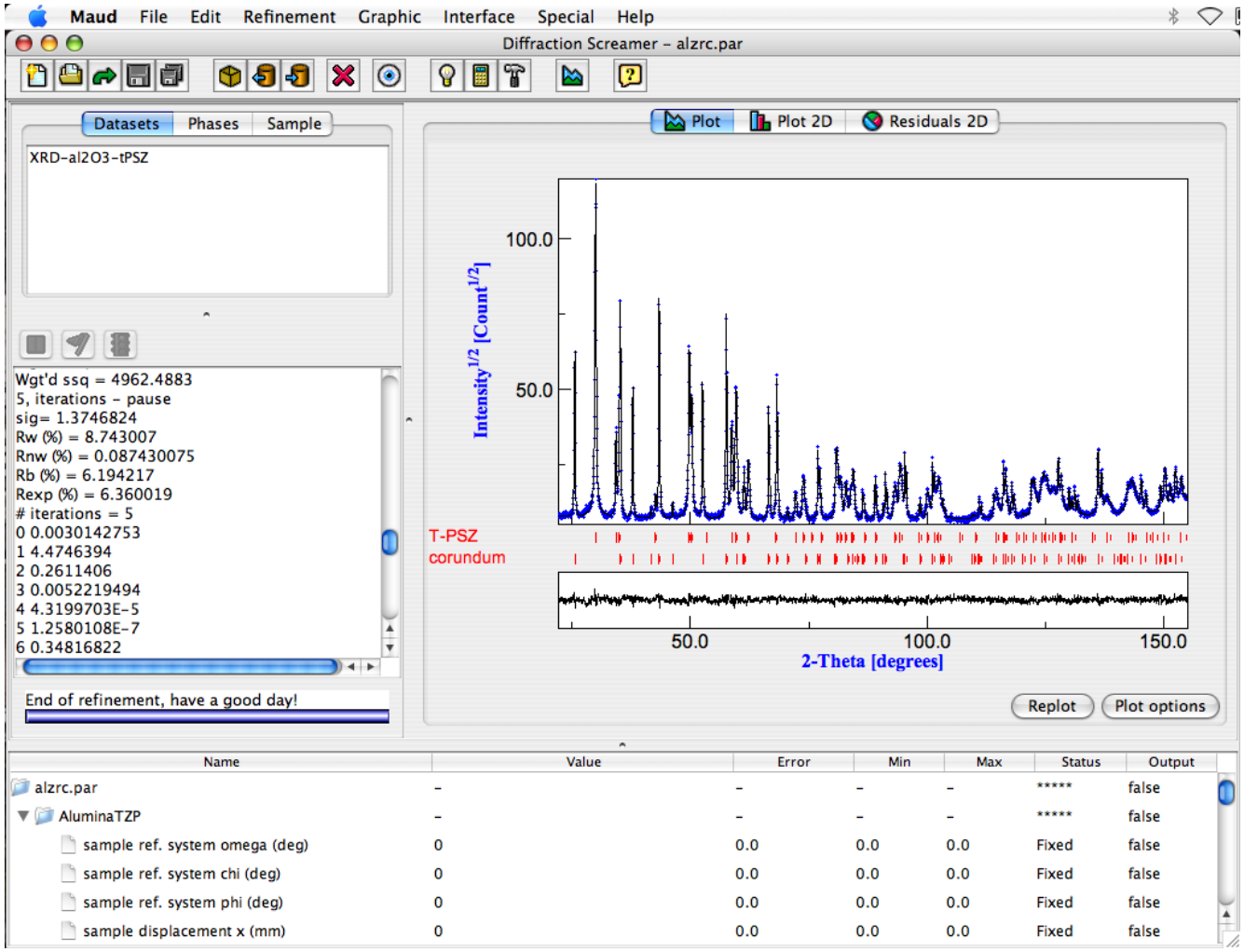
MAUD GUI



http://maud.radiographema.com/

Lucas Lutterotti, Univ. Trento, Italie

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6- Peak shape

Many figures from:
Advanced Certificate in Powder Diffraction on the Web
School of Crystallography, Birkbeck College, University of London
http://pd.chem.ucl.ac.uk/pdnn/chapter.htm

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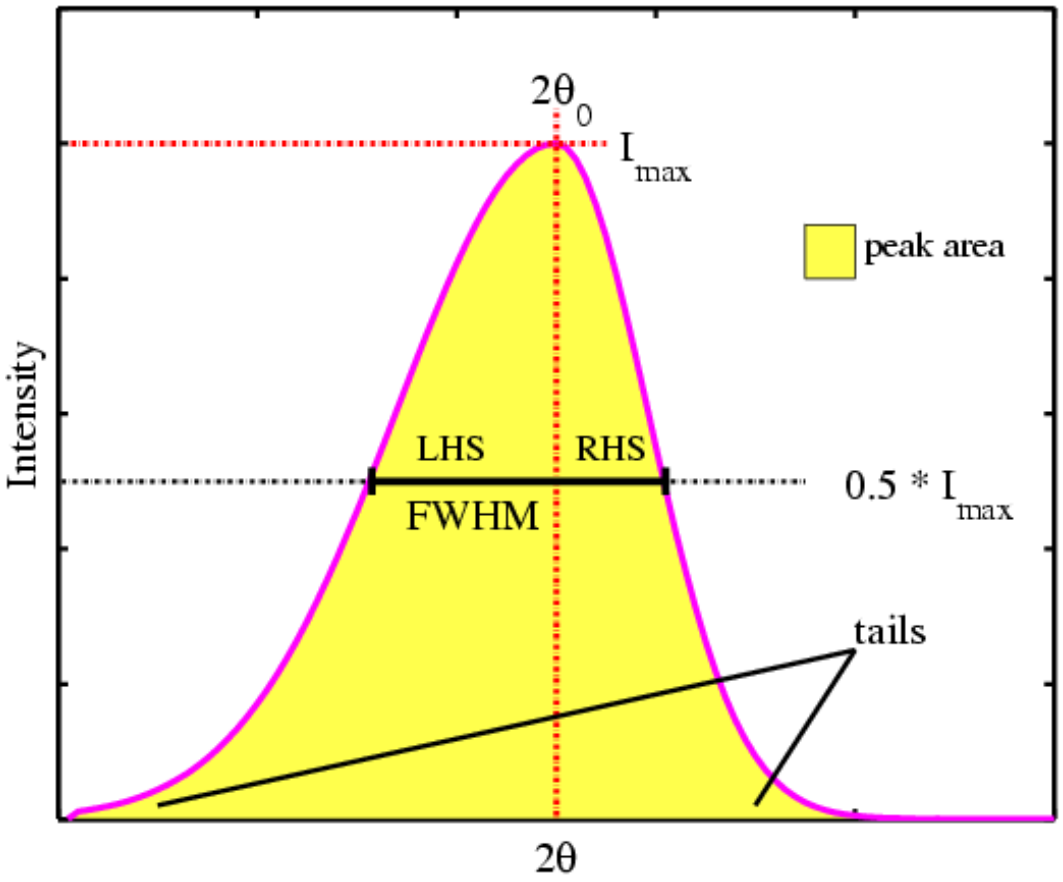
Diffraction peak shape



Key parameters

- Peak height (I_{max})
- Peak area (= peak intensity)
- Peak width (FWHM : Full Width at Halt Maximum)
- Asymmetry

Diffraction intensity

- Intensity = all contributions to the diffraction peak
- Peak area
- *NOT* peak height

Typical FWHM: 0.05° – 0.2°

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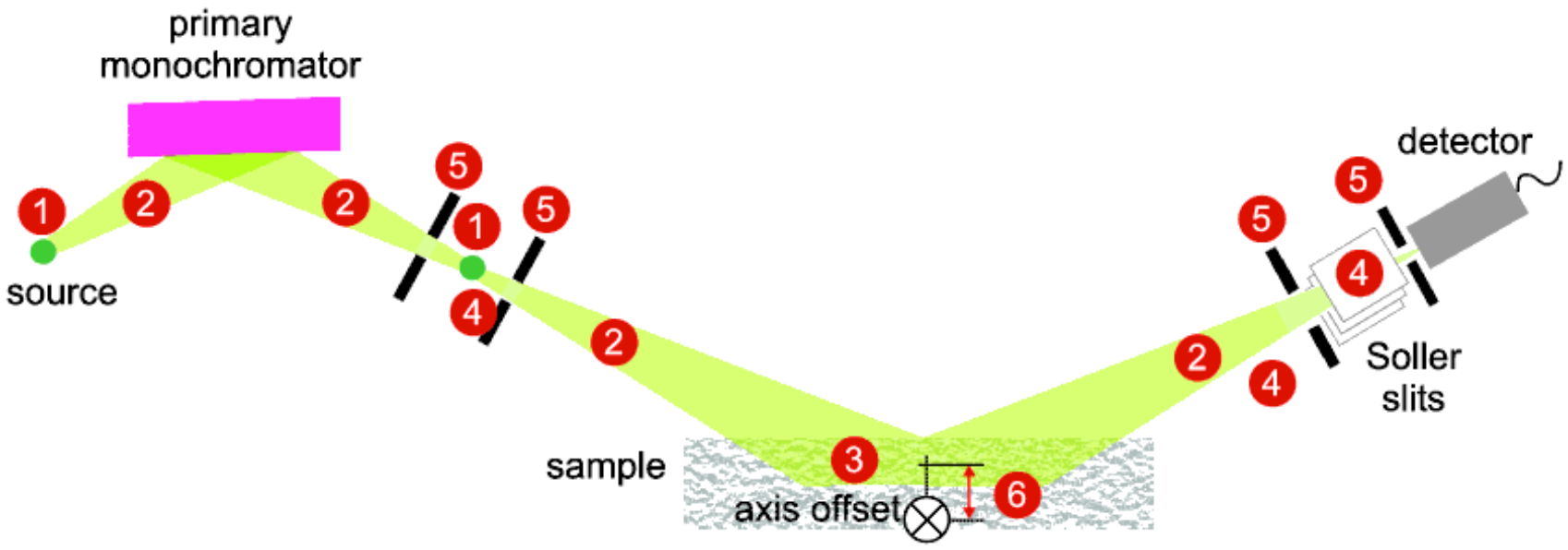
Peak broadening sources

Effects of the **instrument**

- Geometrical parameters
- Non-monochromatic beam
- Beam divergence
- Pixel size on the detector
- Etc

Those contributions are calibrated on a ***standard*** (a model sample)



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Peak broadening sources

Effects of the **instrument**

- Geometrical parameters
- Non-monochromatic beam
- Beam divergence
- Pixel size on the detector
- Etc

Effect of the **sample**

- Diffraction domain sizes
- Distortions of the crystals (micro-strain): dislocations, concentration, etc
- Structural defects: stacking faults, etc

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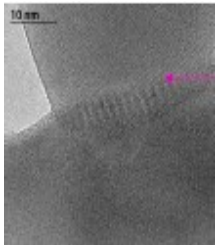
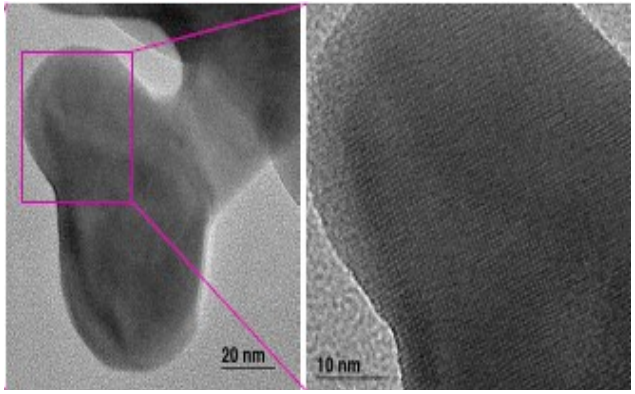
Domain sizes

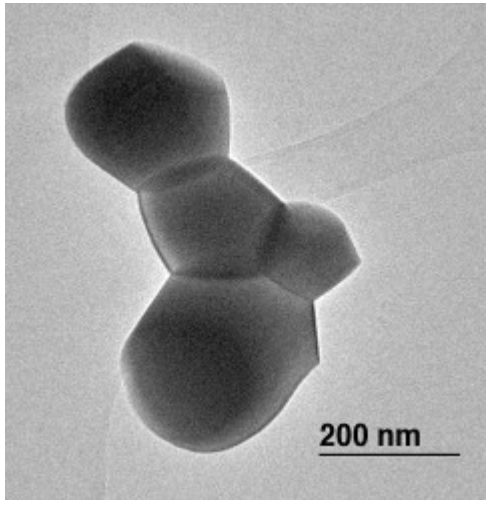
Peak width is sensitive to grain size (the coherent domain size, in fact)

Domain size is not always equal to grain size

Measurable for domains < 0.2 µm







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Fundamental equation (Sherrer equation)

$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

Peak width (*B*) is inversely proportional to the average domain size (*L*).

Effect is more visible at large 2θ angles.

Other parameters

- Wavelength
- K : constant (~ 0,9)

Physical origin: interference between scattered photons are less sharp if the crystal is small (not enough sources).

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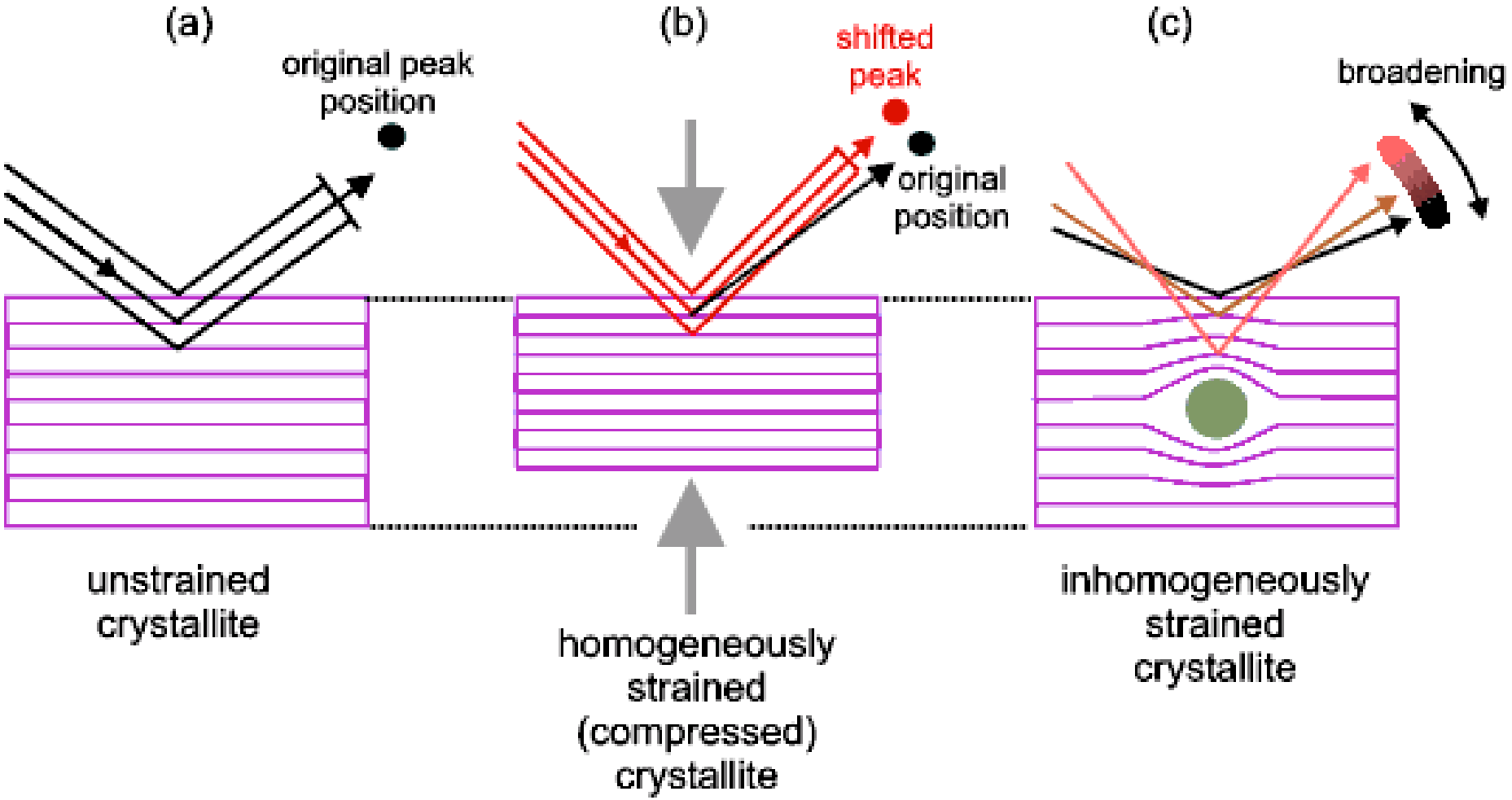
Micro-strains



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7- Parameters for Rietveld refinements

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Modeled spectrum

$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k \left|F_{k,j}\right|^2 S_j\left(2\theta_i - 2\theta_{k,j}\right) P_{k,j} A_j + bkg_i$$

At each point in $2\theta_i$, the spectrum is calculated accounting for

- backgrounds

- diffraction intensity (peak area)

- broadening (peak shape)

- number and positions of the peaks

- number and proportions in phases or materials

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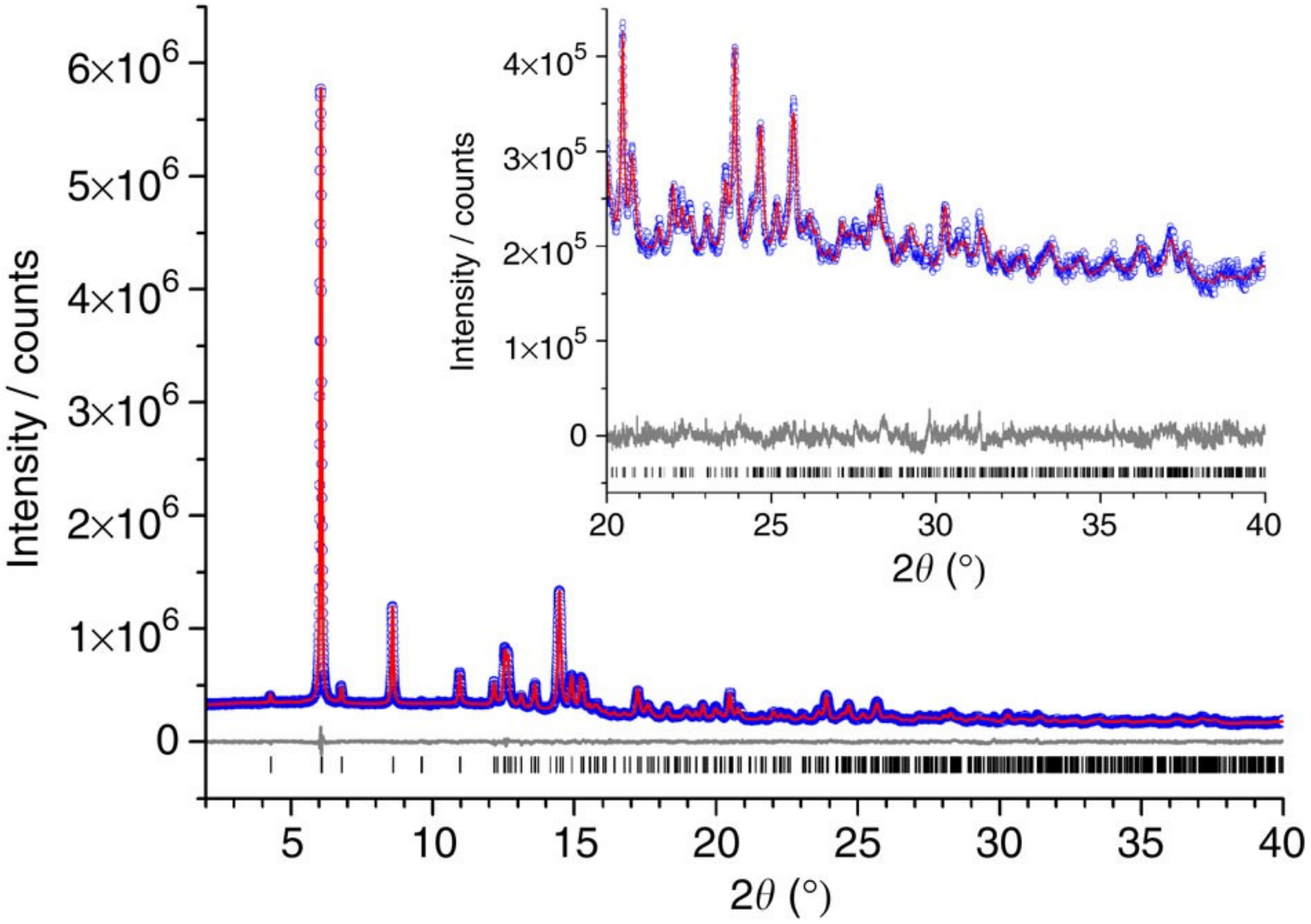
Example of analysis



Calculated parameters

- Background
- Number and positions of diffraction peaks
- Diffraction intensities
- Peak shape

Coronado, *Nature Communications*, 2012

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$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k \left|F_{k,j}\right|^2 S_j\left(2\theta_i - 2\theta_{k,j}\right) P_{k,j} A_j + \boxed{bkg_i}$$

Model for background

- Often, polynomial function in 2θ :

$$bkg(2\theta_i) = \sum_{n=0}^{N_b} a_n (2\theta_i)^n$$

- More complex functions are possible as well.

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Sample composition

$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k \left|F_{k,j}\right|^2 S_j\left(2\theta_i - 2\theta_{k,j}\right) P_{k,j} A_j + bkg_i$$

Scaling factor

- S_F : global scaling factor, linked to diffraction acquisition time and detector efficiency
- f_j : volume fraction for phase *j*
- V_j: unit cell volume for phase *j*

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Position and number of peaks

$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k \left|F_{k,j}\right|^2 S_j\left(2\theta_i - 2\theta_{k,j}\right) P_{k,j} A_j + bkg_i$$

Position and number of peaks

- Crystalline structure for each phase
- Unit cell parameters for each phase

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Peak intensities

$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k \left|F_{k,j}\right|^2 S_j\left(2\theta_i - 2\theta_{k,j}\right) P_{k,j} A_j + bkg_i$$

Diffraction peak intensities

- L : Lorentz correction (geometrical effect, depends on angle θ) and beam polarization correction
- F : generalized structure factor: structure factor, atomic scattering coefficients, multiplicity, temperature factors
- P : effect of texture and grain orientations (cf “Imperfection” class)
- A : absorption due to the sample itself

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Peak shape

$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k \left|F_{k,j}\right|^2 S_j\left(2\theta_i - 2\theta_{k,j}\right) P_{k,j} A_j + bkg_i$$

Diffraction peak shape

- Instrument : ad-hoc functions, mixing gaussians, lorentzians, pearson, etc
- Effect of grain sizes
- Effect of microstrains

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Analysis procedure

Start with a standard (LaB_6, CeO_2, etc)

- Known crystallographic parameters
- Known grain size
- No or very little microstrains

A diffraction experiment ***always starts*** by collecting diffraction of a ***standard***.

If data from the standard is bad or missing, the experiment is completely lost.

Use the standard and what you know on the experiment to calibrate the software

- Incident beam
- Position and detector properties
- Instrumental effect on diffraction intensities
- Instrumental effect on peak shapes

Once they are known, those parameters are fixed, and ***never touched again***.

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Analysis procedure

Experiment

- Pick the right instrument
- Pick the proper experimental conditions
- Pick a proper sample preparation technique
  - In particular, Rietveld refinement is based on statistics: one need to see many grains (~1000) in the beam

Rietveld refinement

- Load the data
- Enter the expected crystallographic parameters
- Adjust some parameters by hand (cell parameters, average intensity, background)
- Refine background and mean intensity
- Refine peak positions
- Refine peak shapes
- Refine fine crystallographic parameters (temperature-corrections, etc)
- Analyze results

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Why so much effort ?

Pros of Rietveld analysis

- Directly uses measured diffraction intensities
- Uses the full spectrum (as broad as possible)
- Less sensitive to model errors
- Less sensitive to experimental errors
- Less sensitive to biases from the person processing the data

Cons of Rietveld analysis

- Needs a model
- Needs a broad spectrum (in 2θ)
- Rietveld analysis takes a while to learn (1 to 2 years)
- Can lead to false positives
- Single-crystal X-ray diffraction is always better resolved

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Practicals coming up

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