Joint French-Swedish school on X-rays and Neutrons techniques for the study of functional materials for energy

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Diffraction

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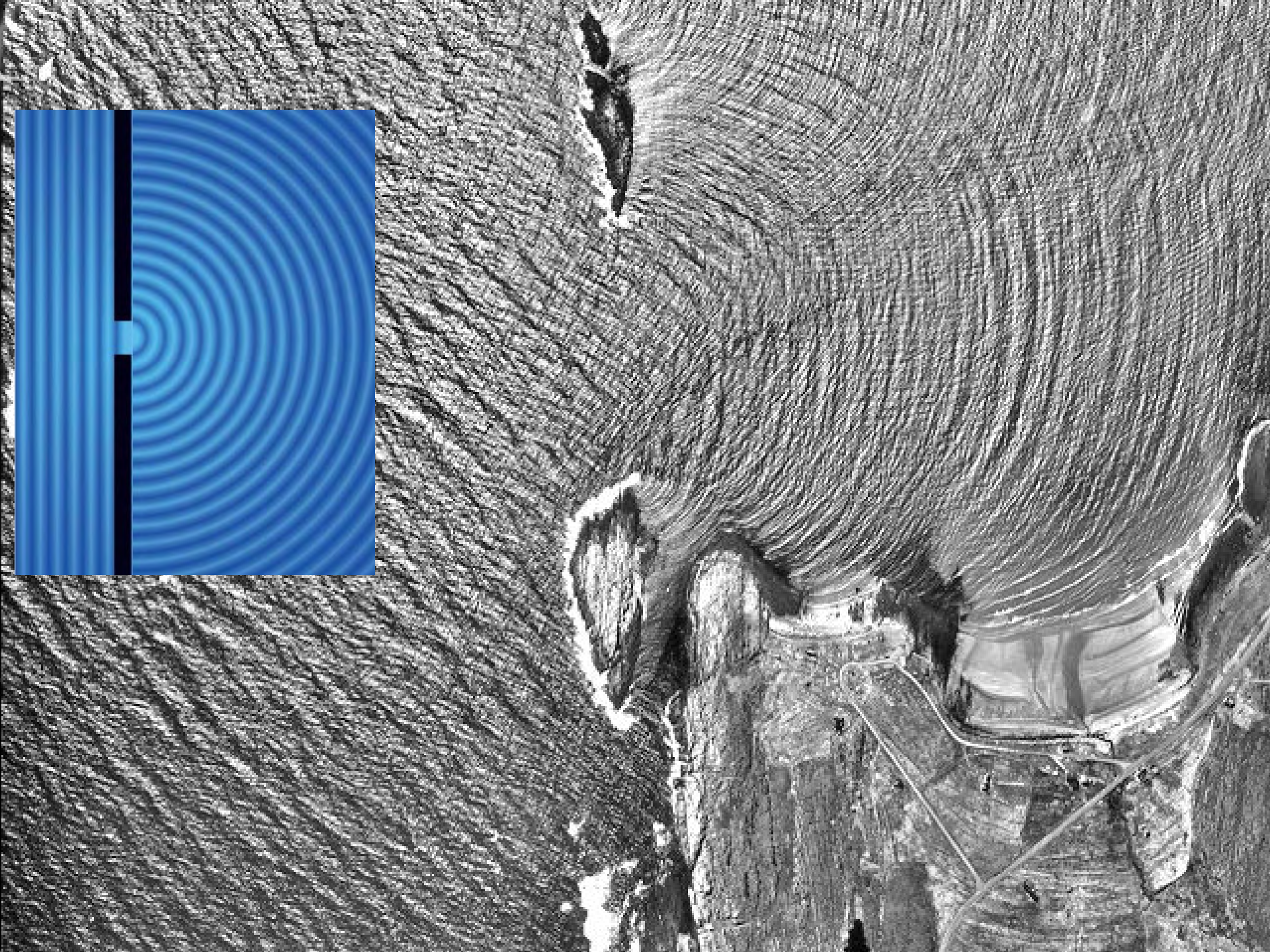
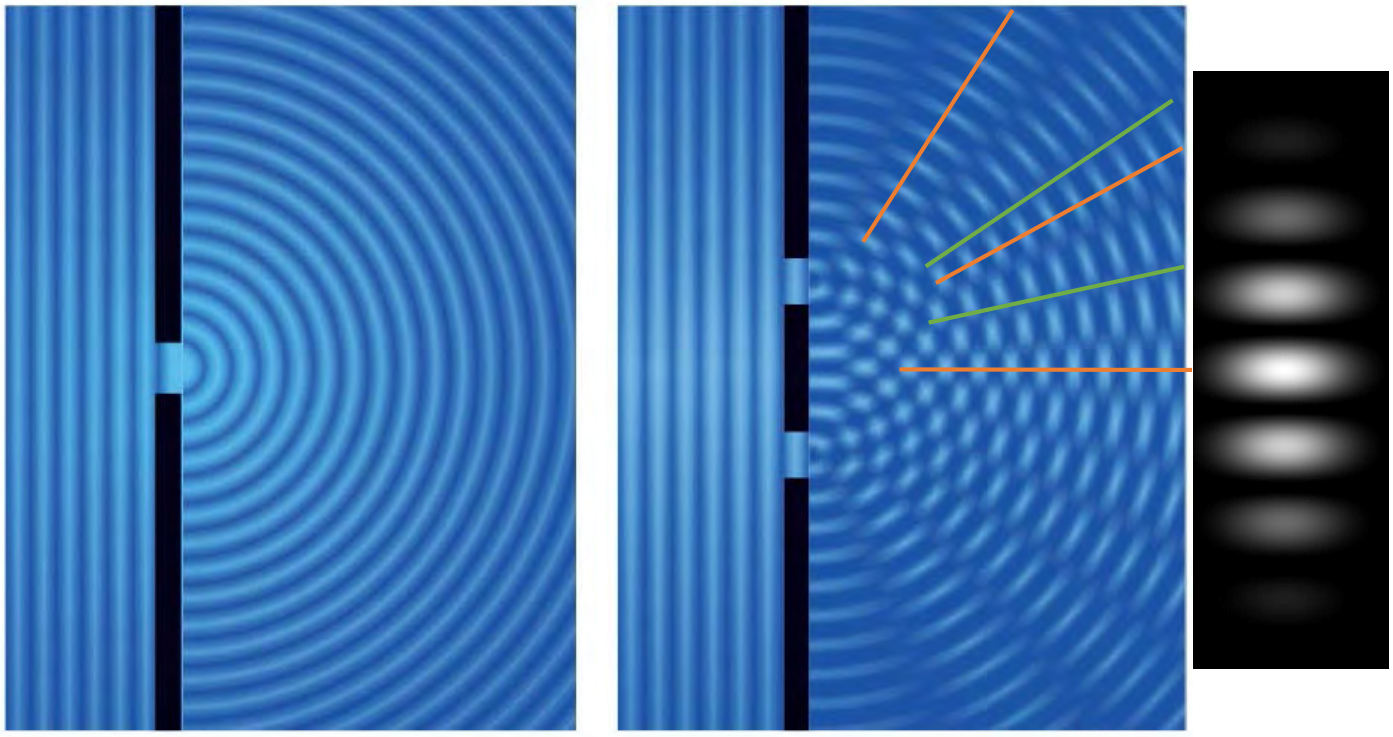


What happens to a plane wave that hits a slit?



Single slit

Double slit

- Diffraction refers to the apparent bending of waves around small objects and the spreading out of waves past small apertures.

→ *Condition:* Slit width comparable to the wave length of the incident wave

- Double-slit: interference pattern

Diffraction by Crystalline Solids

In our context, diffraction is the elastic scattering of a coherent wave by the atoms in a crystal.

A diffraction pattern results from interference of the scattered waves.

Crystalline materials = long-range 3D periodic atomic arrays

Interatomic distances ~ 0.5 – 2.5 Å

Waves of comparable wavelengths will be diffracted:

- X-rays = EM radiation, λ ~ 0.1 – 100 Å
- Neutrons
- Electrons

} $\lambda = h/mv$

→ *X-rays, neutrons and electrons are diffracted by crystals*

→ *X-ray, neutron and electron diffraction patterns contain information about 3D arrangement of atoms in crystals*

What is a crystal?

A: Crystals are powerful tools that have the ability to energize, soothe, cleanse, heal, transform, and inform the energy fields they come into contact with.

B: A crystal is a solid where the atoms form a periodic arrangement

C: A crystal has essentially a sharp diffraction pattern

IUCr Online Dictionary of CRYSTALLOGRAPHY

Acta Cryst. (1992), A**48**, 928

→ Reciprocity

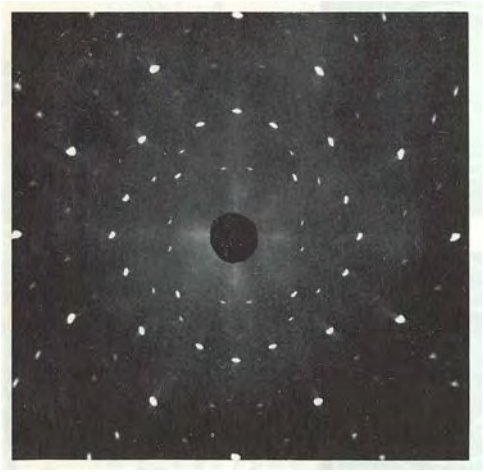
Reciprocity

Cristal space = Direct space

Diffraction space = Reciprocal space

Crystal

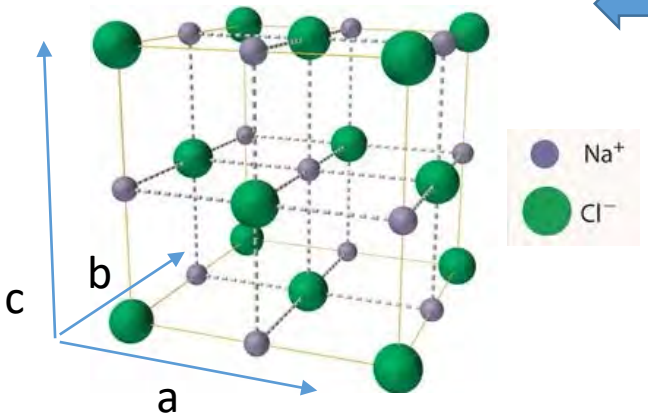
FT

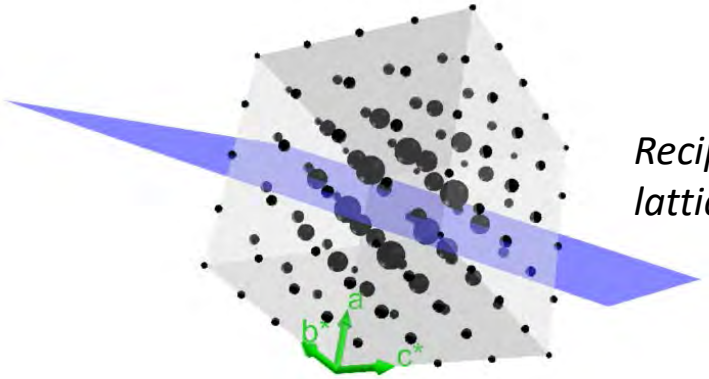


Diffraction pattern

FT^{-1}

Crystal structure





Reciprocal lattice

Diffraction condition:

Real space description (Bragg):

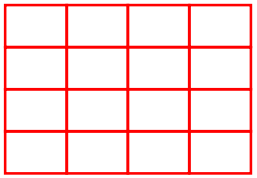
$\lambda=2d_{hkl}\sin\vartheta$

Momentum (k) space description (von Laue):

$\vec{k}-\overrightarrow{k_0}=\overrightarrow{d^*_{hkl}}$

Reciprocity

Lattice



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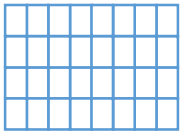


Reciprocal lattice

$*$
convolution

X
product

Motif, atoms in Unit cell

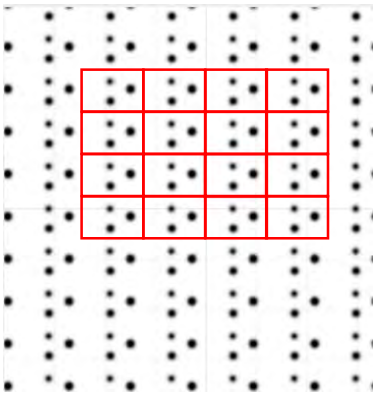
FT

Structure factor

=

=

Crystal Structure



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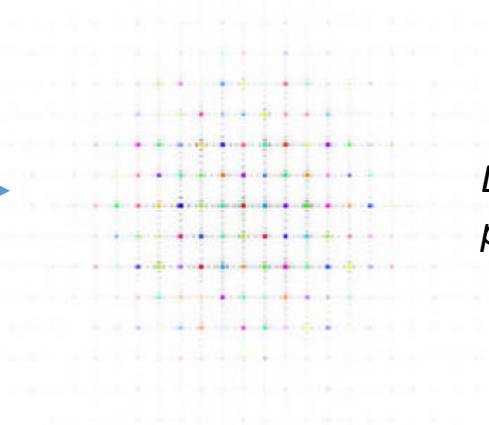


Diffraction pattern

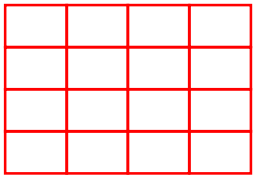
$$C(\vec{r}) = L(\vec{r}) * M(\vec{r})$$

$$C(\vec{h}) = FT\{C(\vec{r})\} = FT\{L(\vec{r}) * M(\vec{r})\} = L(\vec{h}) \times F(\vec{h})$$

Fft.jar http://escher.epfl.ch/

Reciprocity

Lattice



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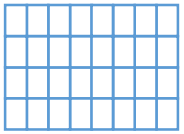


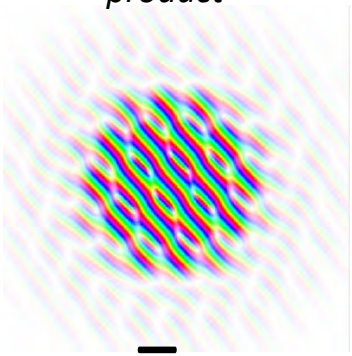
Reciprocal lattice

*
convolution

X
product

Motif, atoms in Unit cell

FT

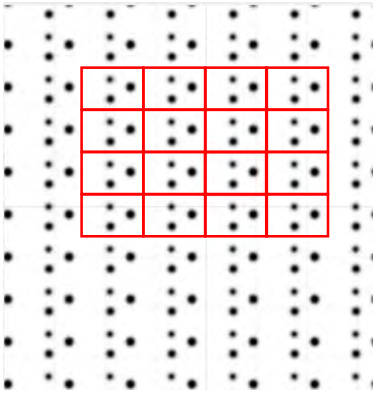


Structure factor

=

=

Crystal Structure



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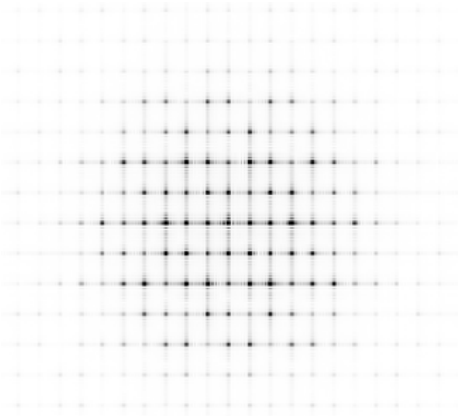


Diffraction pattern

→ In which direction does scattering occurs?

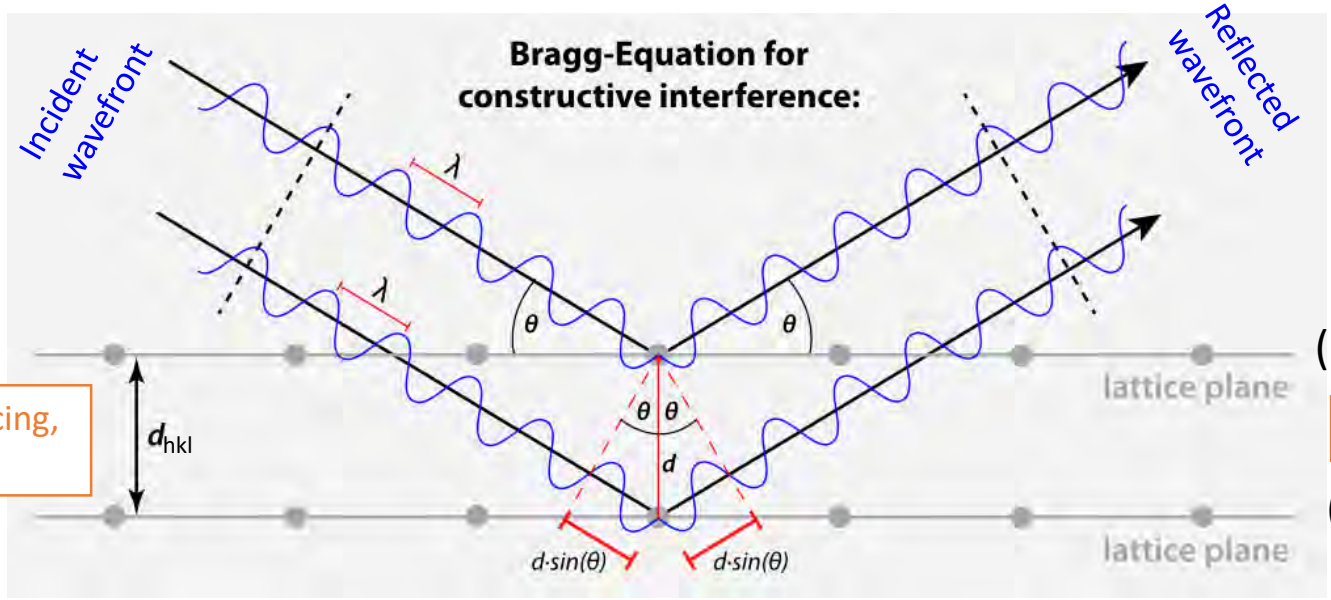
→ How strong is the scattering in a given direction?

Fft.jar http://escher.epfl.ch/

In which direction does scattering occurs?

Bragg'law: Simplistic, but usefull view of diffraction

- Atoms arranged in parallel planes in a crystal
- Incident X-rays reflected off the planes (specular)
- Peaks in diffraction patterns referred as « reflections »



Interplanar spacing, d-spacing

Miller indices

$$n.\lambda = 2.d_{hkl}.\sin(\theta)$$

n=1, because n^{th} order diffraction from (hkl) planes with d-spacing d can be treated as 1st order diffraction from (nh,nk,nl) plane with spacing d/n

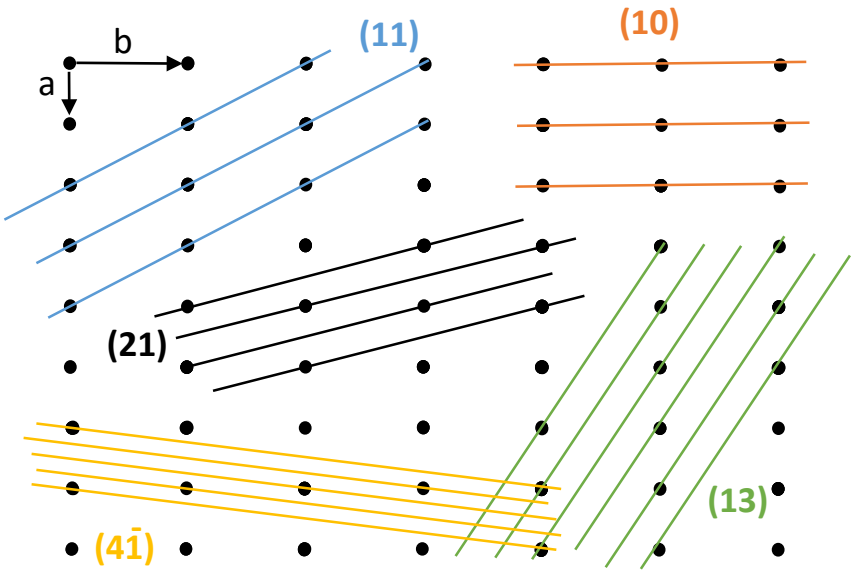
Miller indices

Notation used for imaginary atomic planes in crystal, (hkl)

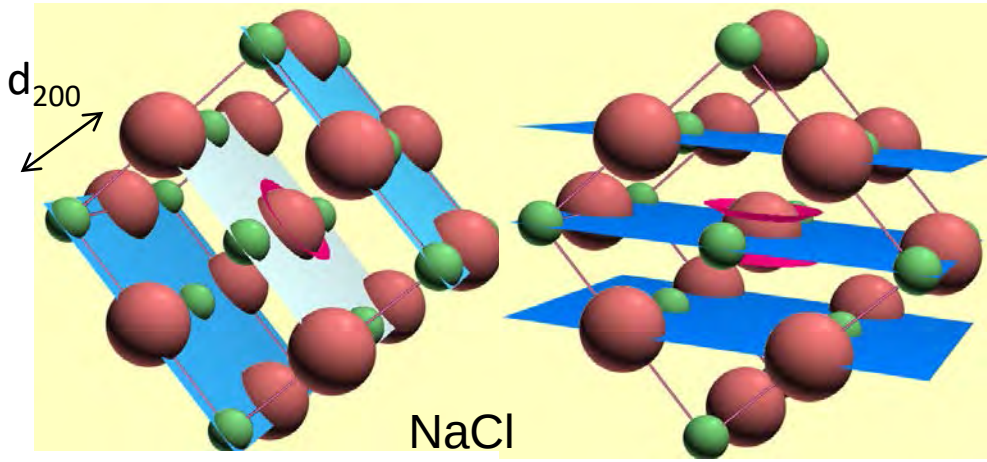
For each set of parallel planes:

- Take the plane closest to the one that passes through the origin
- Write down the intercepts with the crystallographic axes (as fraction of the unit cell edges): 1/h, 1/k, 1/l
- Take reciprocals of the factions to assign Miller indices, (hkl)

2D exemples



3D exemples



(200) planes (220) planes

D-spacings and cell-parameters

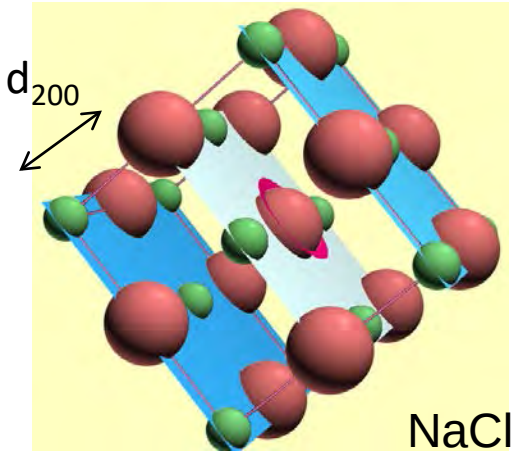
D-spacing in crystals are related to the unit cell parameters *a*, *b*, *c*, *α*, *β*, *γ*
For orthogonal crystal systems:

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

Application:

-From know unit cell parameters, we can predict peak position

-From experimentatlly observed peak positions, we can determine unit cell parameters



(200) planes

$$\frac{1}{{d_{200}}^2} = \frac{2^2}{a^2} + \frac{0^2}{b^2} + \frac{0^2}{c^2}$$

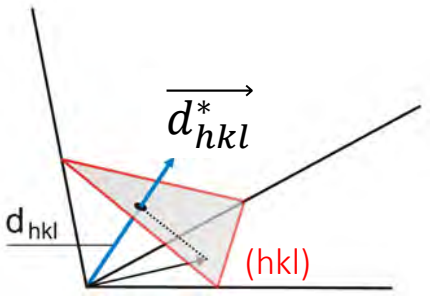
$$d_{200} = \sqrt{\frac{a^2}{2^2}} = \frac{a}{2}$$

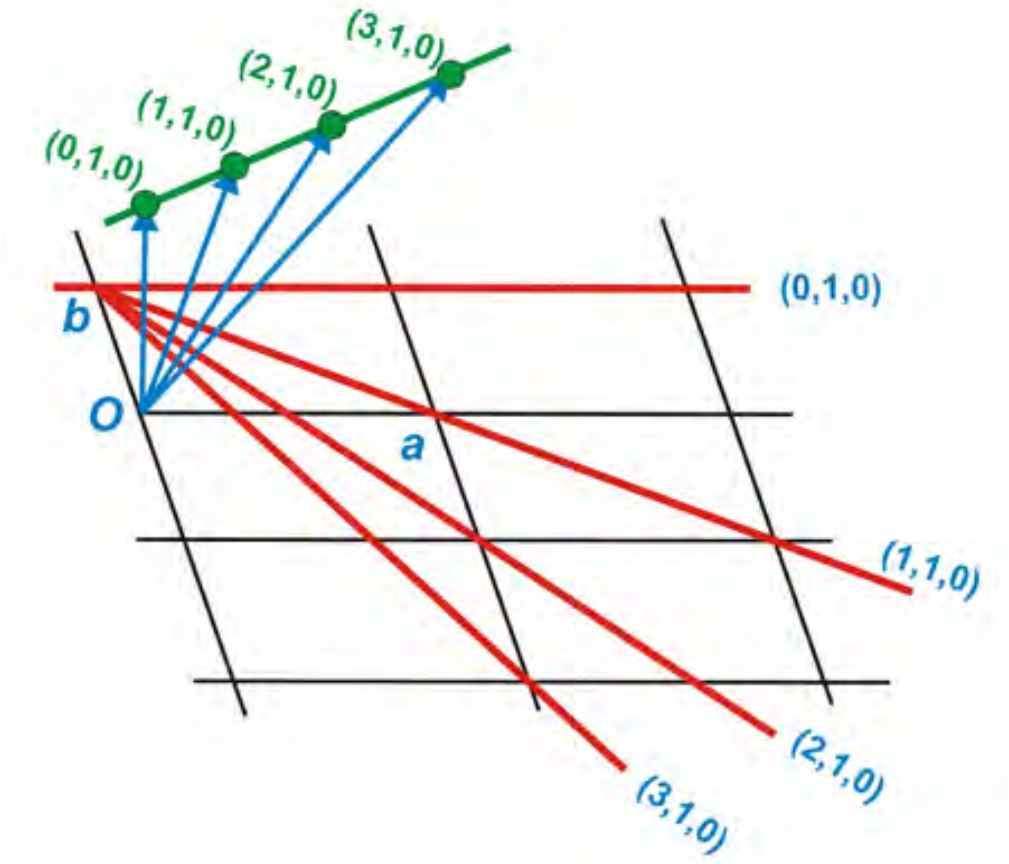
$$\lambda = 2.d_{200}.\sin(\theta)$$

For λ=1,54Å, $2\vartheta_{200}$= 31,7° → a=5,64Å

Reciprocal Lattice

RL vector: $\overrightarrow{d^*_{hkl}}$ normal to (hkl) planes, with $d^*_{hkl} = \frac{1}{d_{hkl}}$





Reciprocal Lattice

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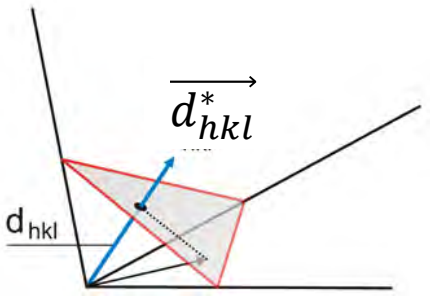
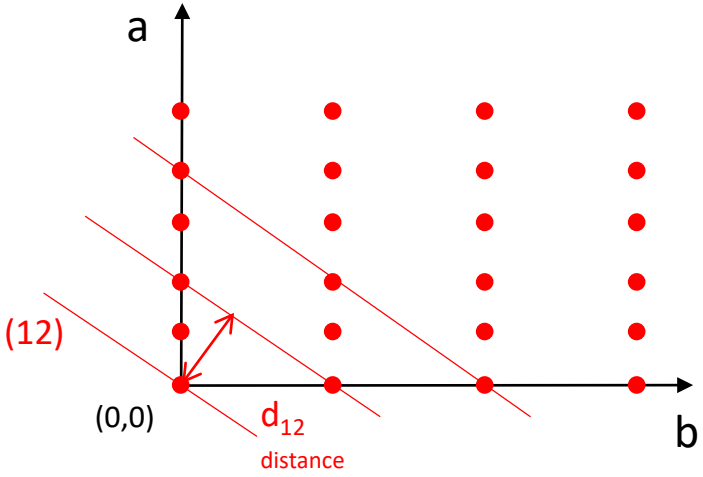


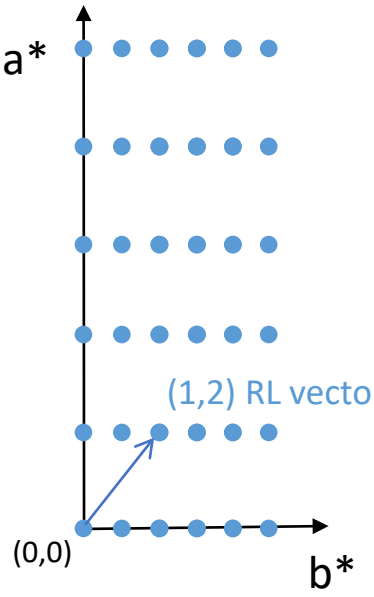
For a set of direct lattice vectors a_i, reciprocal lattice vectors a_i^* are defined by the conditions:

$$a_i . a_j^* = \delta_{ij}$$

$$\vec{a}^* = \frac{\vec{b} \wedge \vec{c}}{V}, \vec{b}^* = \frac{\vec{c} \wedge \vec{a}}{V}, c^* = \frac{\vec{a} \wedge \vec{b}}{V}$$



Direct space



$\mathbf{d}^*_{hk} = h\mathbf{a}^* + k\mathbf{b}^*$

Reciprocal space

Laue condition: Ewald construction

Bragg's Law

$$\lambda = 2.d_{hkl}.\sin(\theta)$$

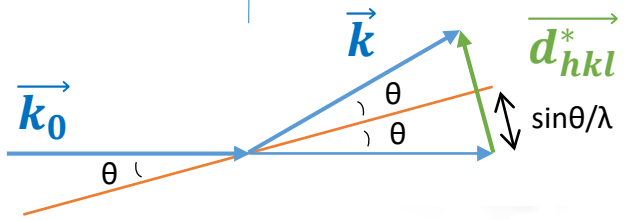
$$\frac{1}{d_{hkl}} = \frac{2}{\lambda}\sin(\theta)$$

$$\overrightarrow{d^*_{hkl}} = \vec{k} - \overrightarrow{k_0}$$

Laue condition

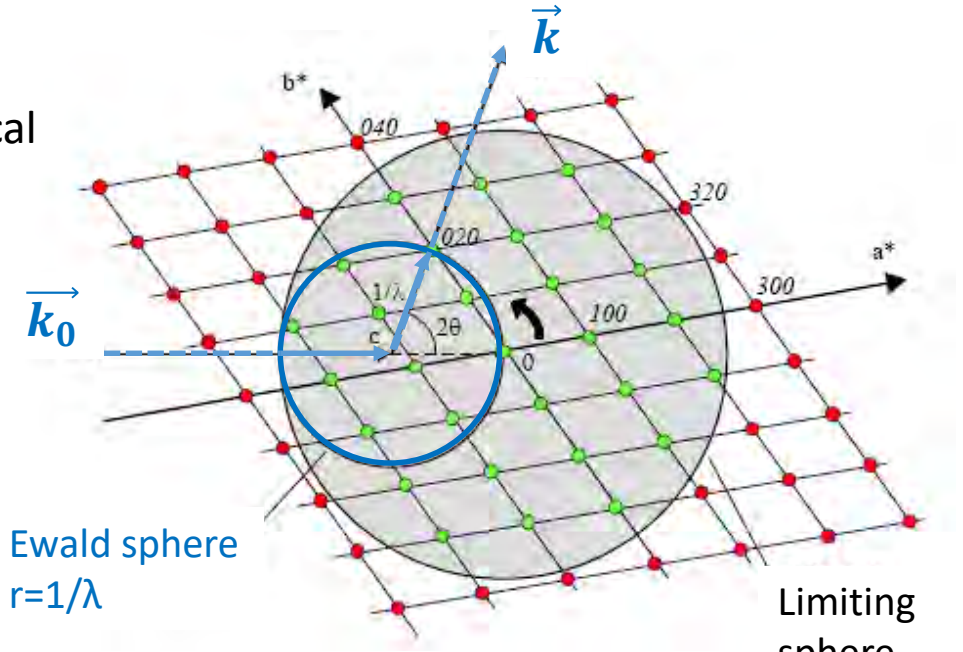
$$d^*_{hkl} = \frac{2}{\lambda}\sin(\theta)$$

(Wave-vector: k=1/λ)



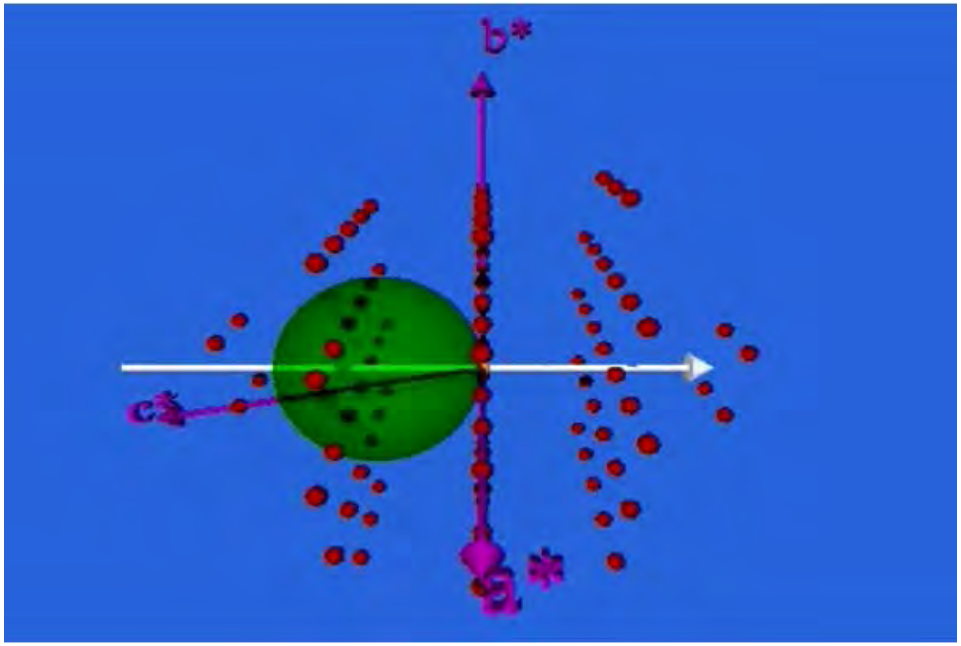
The construction of EWALD sphere is a graphical representation of the LAUE conditions:

Diffraction condition is satisfied when a reciprocal lattice node intersects the Ewald sphere

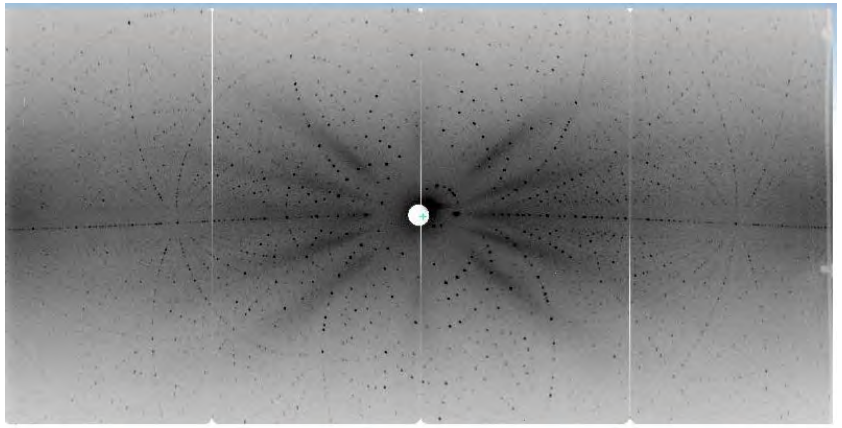


Ewald sphere (shell)

http://escher.epfl.ch/



Laue image



→ every accessible *hkl* plane is in reflection position for a particular wavelength

Shows the direction of each diffracted beam:

- crystal in a random orientation may not give any diffraction
- use of polychromatic radiation: Laue

Shows which reflections are observable for a given wavelength: limiting sphere

Only reciprocal lattice points which lie within the limiting sphere will be observed

Single crystal vs powder

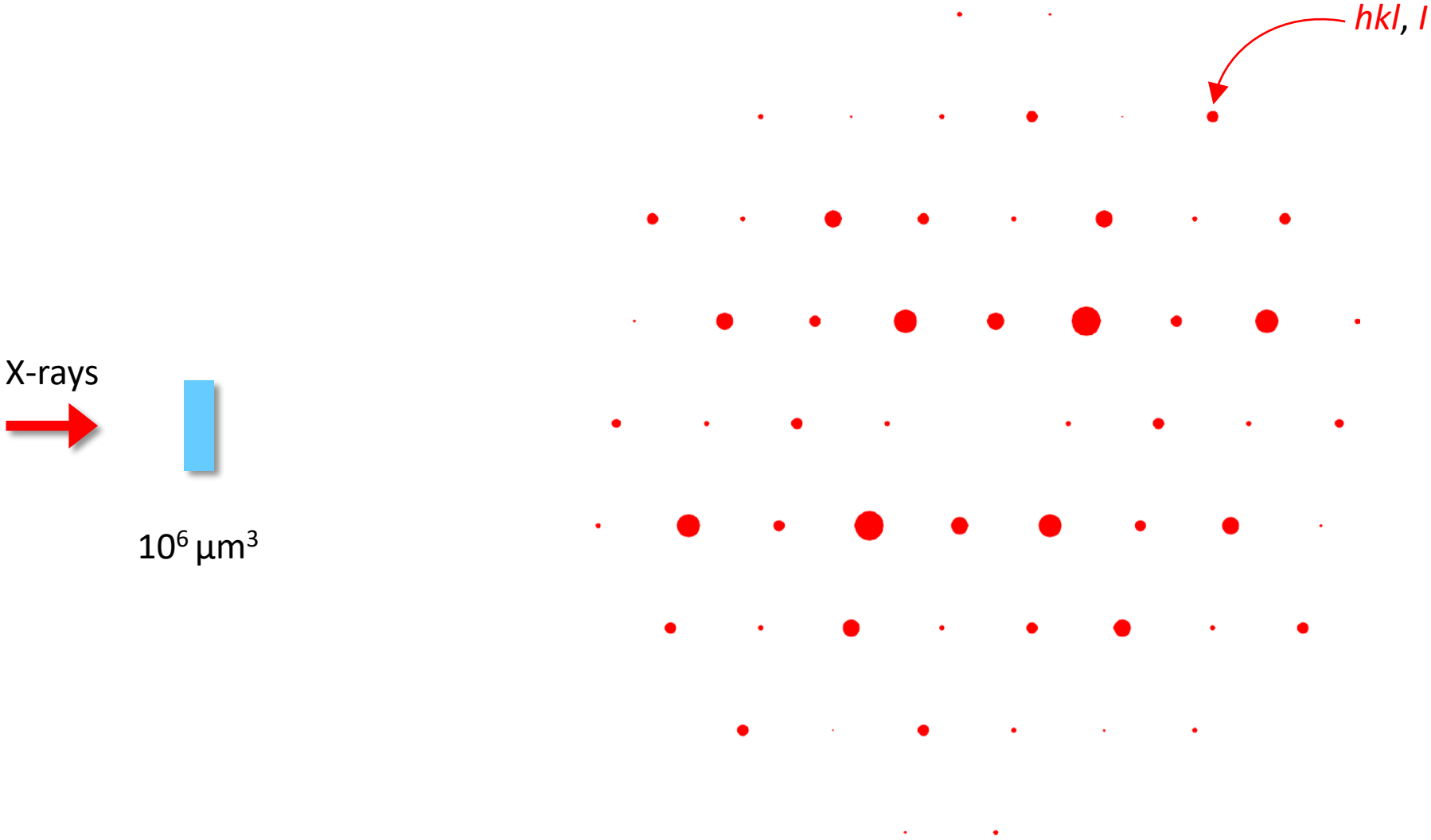
azurite

pigment

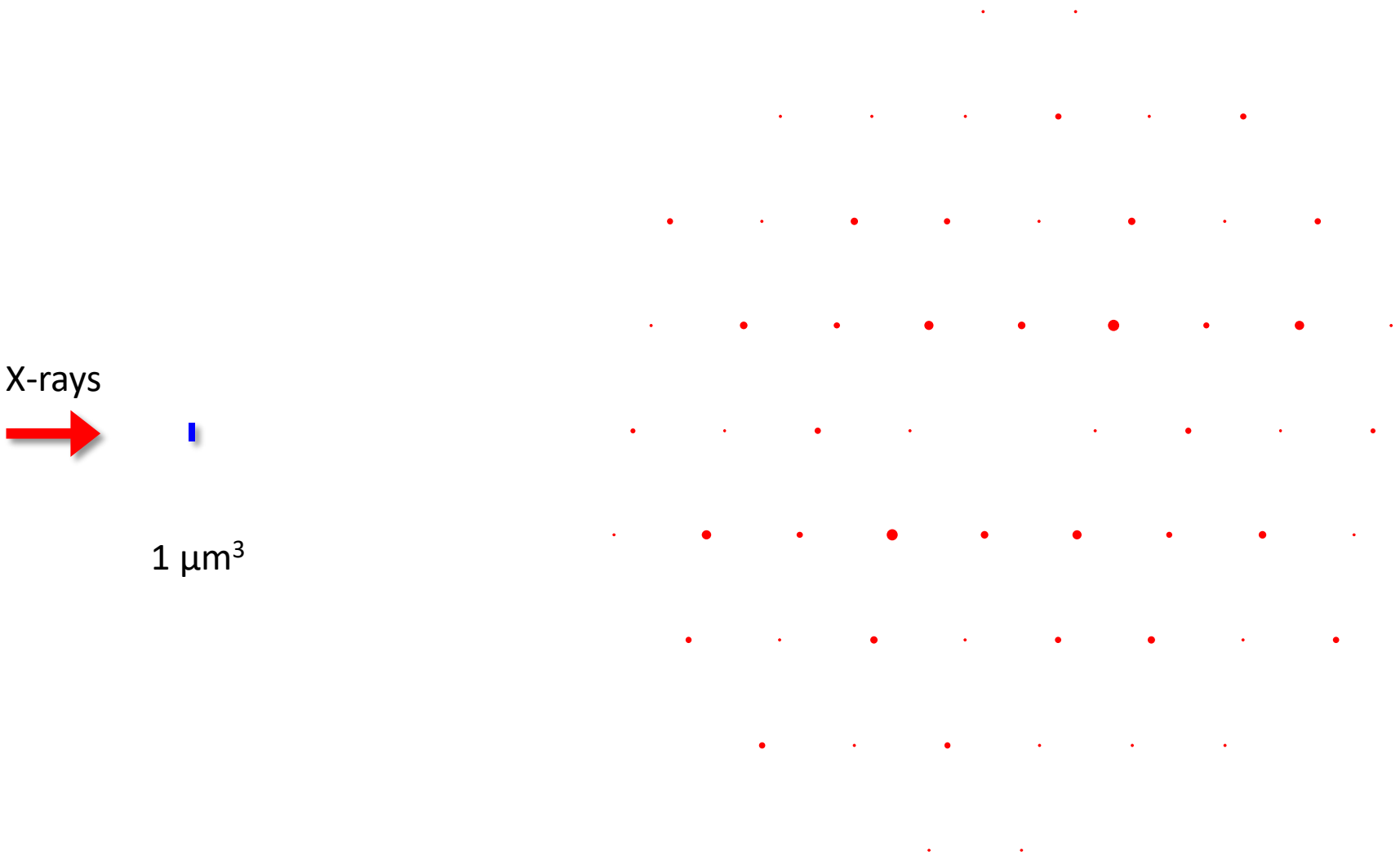
Cristal : V ~ $10^6 mm^3$

Cristallite : V < $1mm^3$

Single crystal diffraction

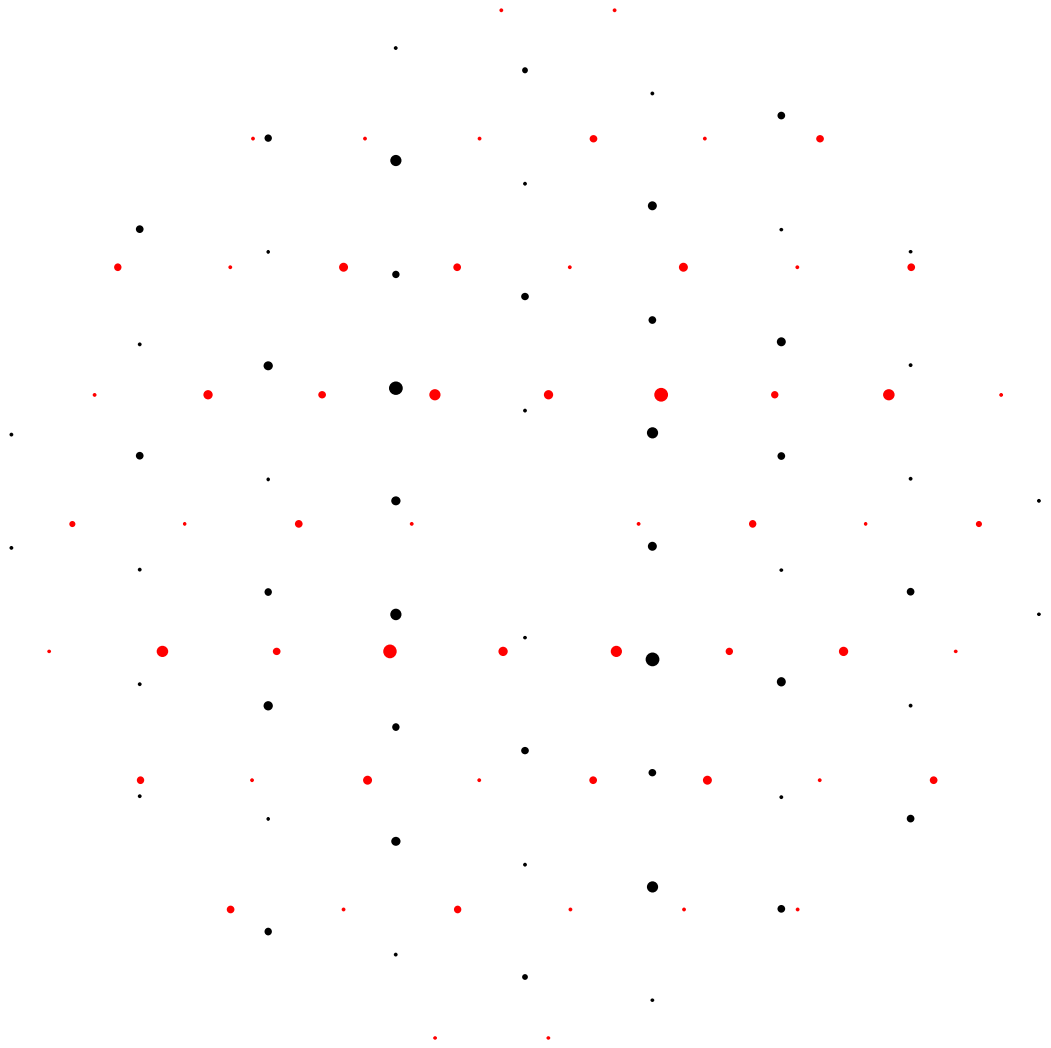


Powder diffraction



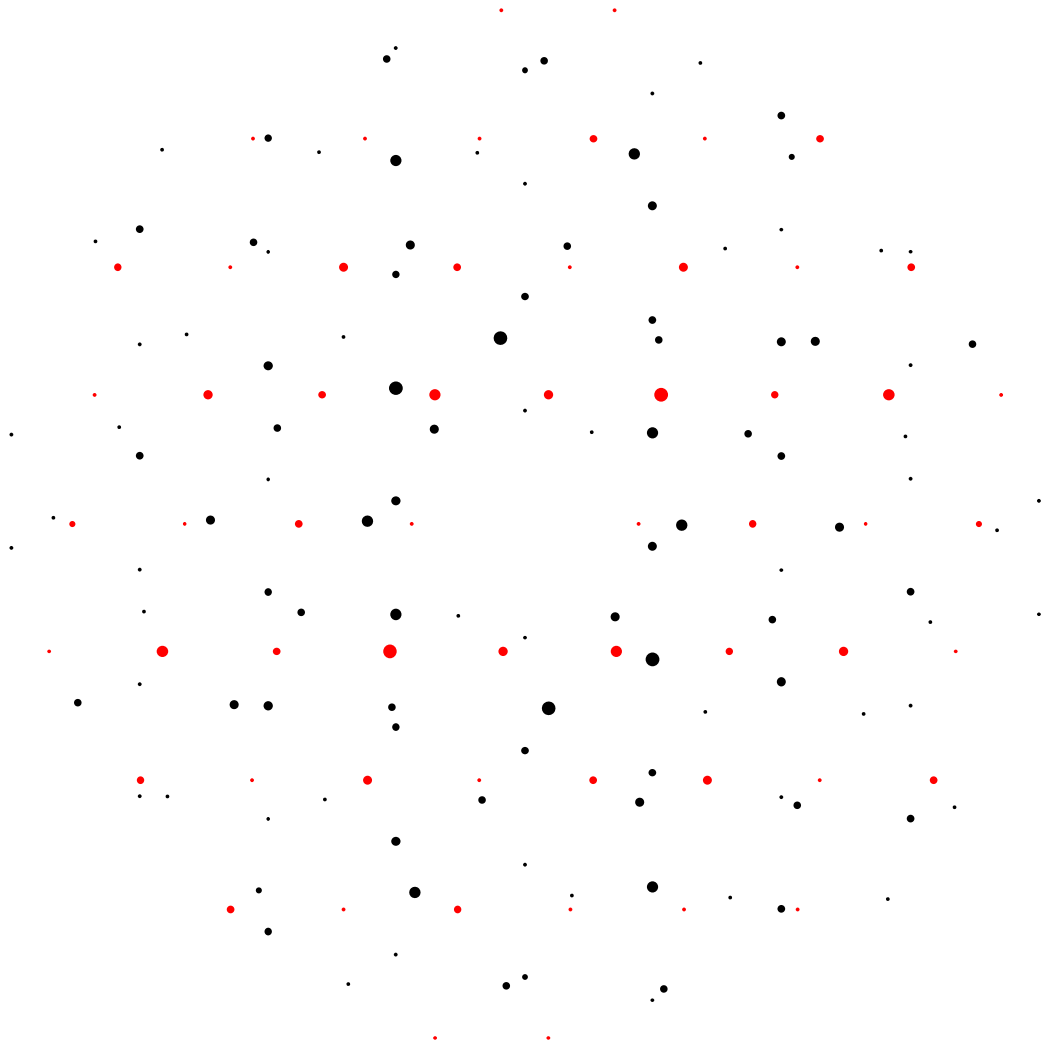
Powder diffraction

X-rays



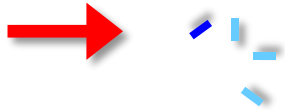
Powder diffraction

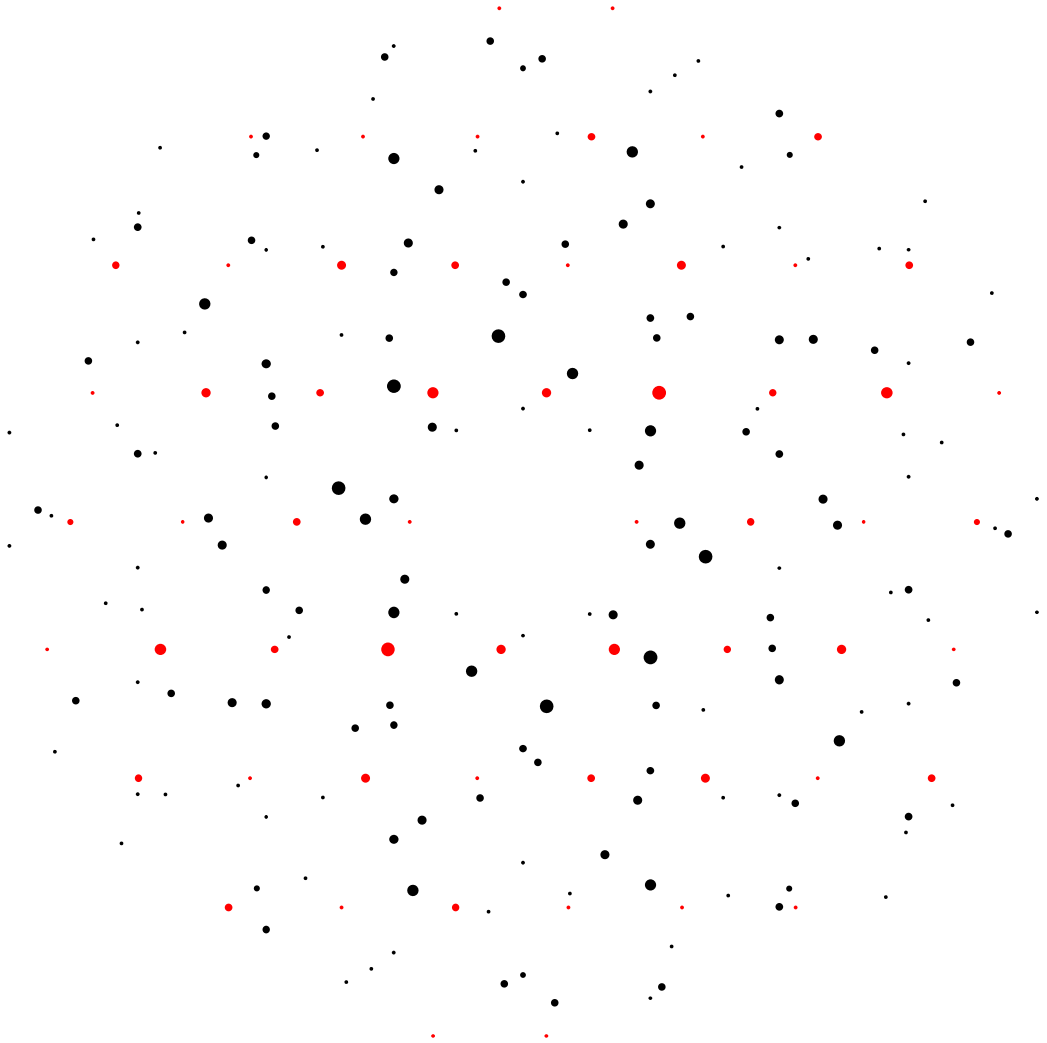
X-rays



Powder diffraction

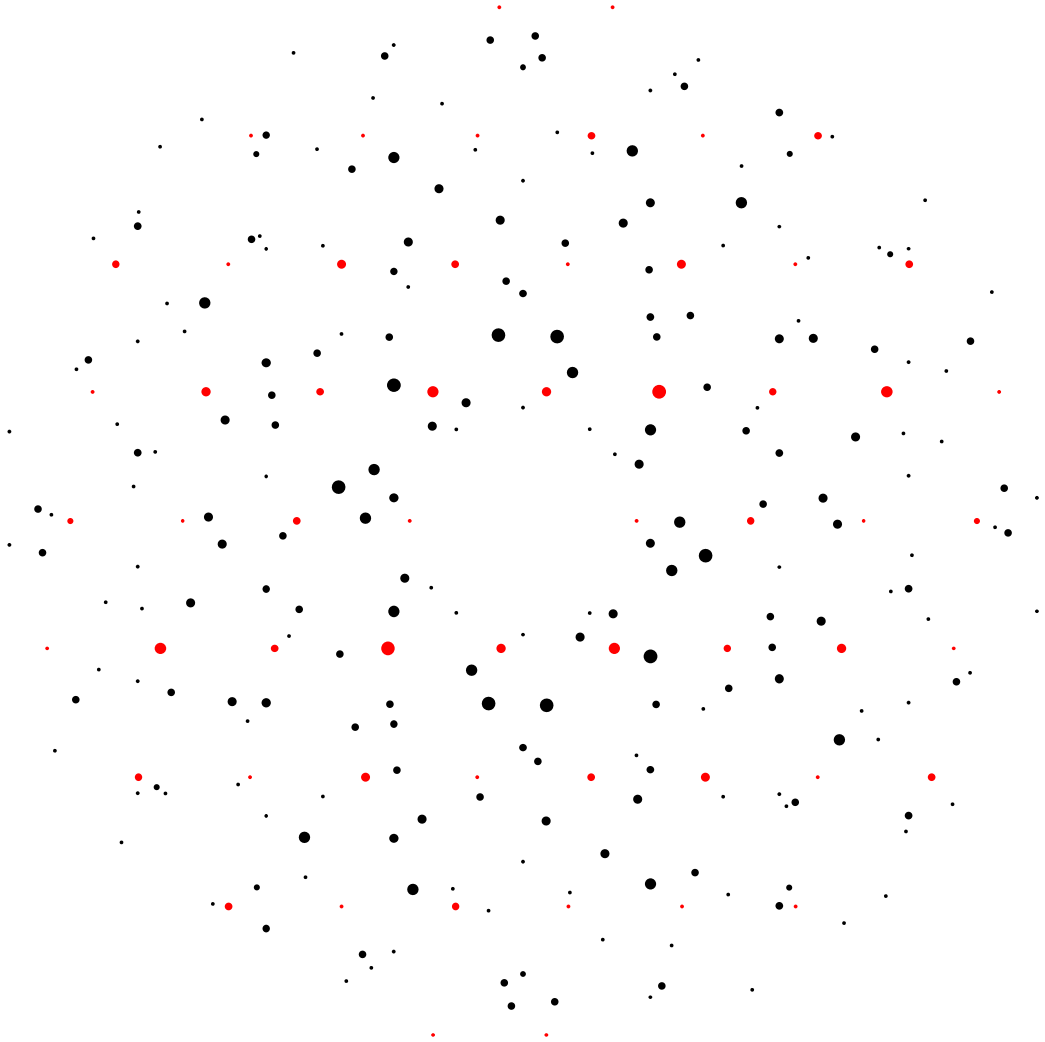
X-rays





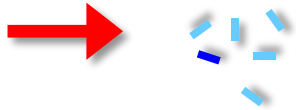
Powder diffraction

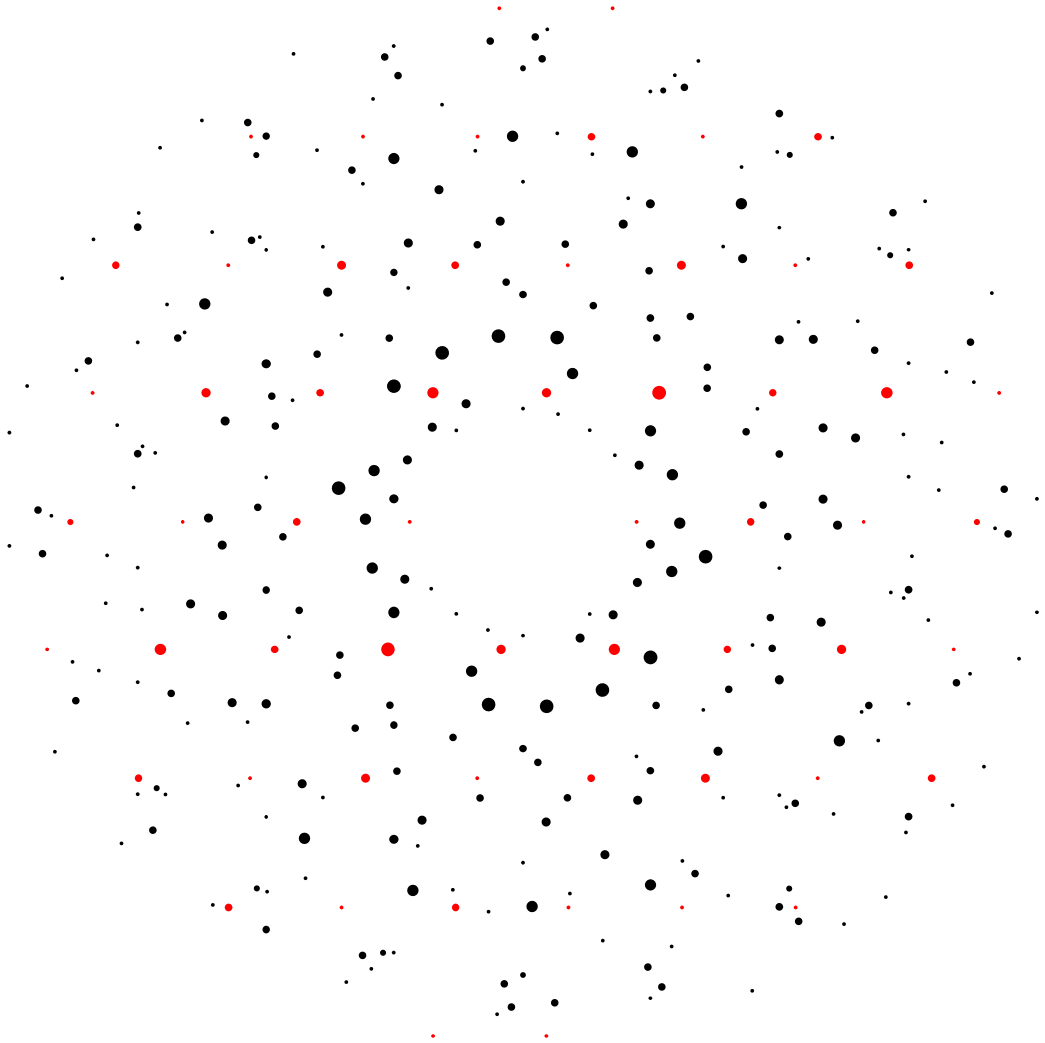
X-rays



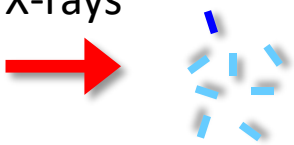
Powder diffraction

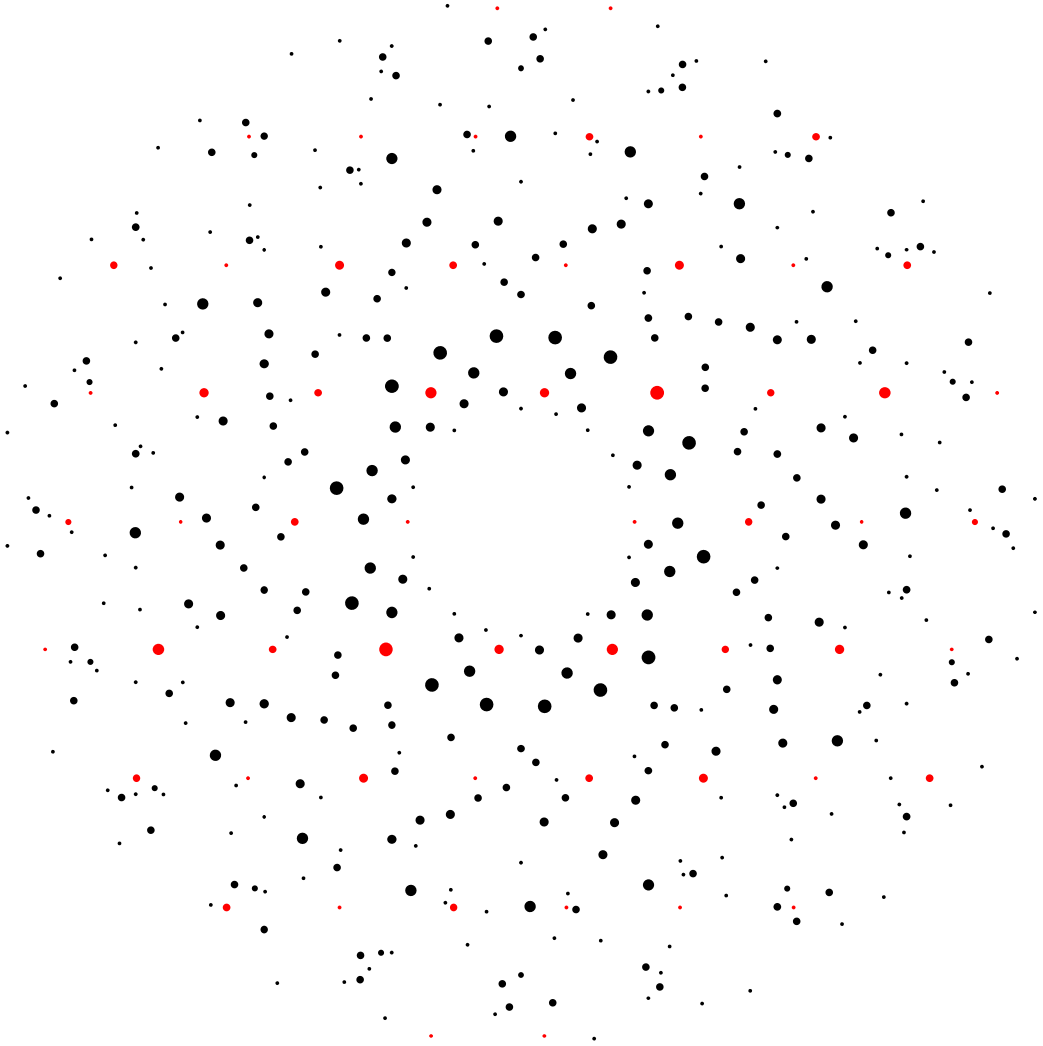
X-rays



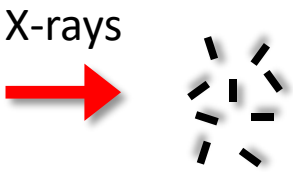


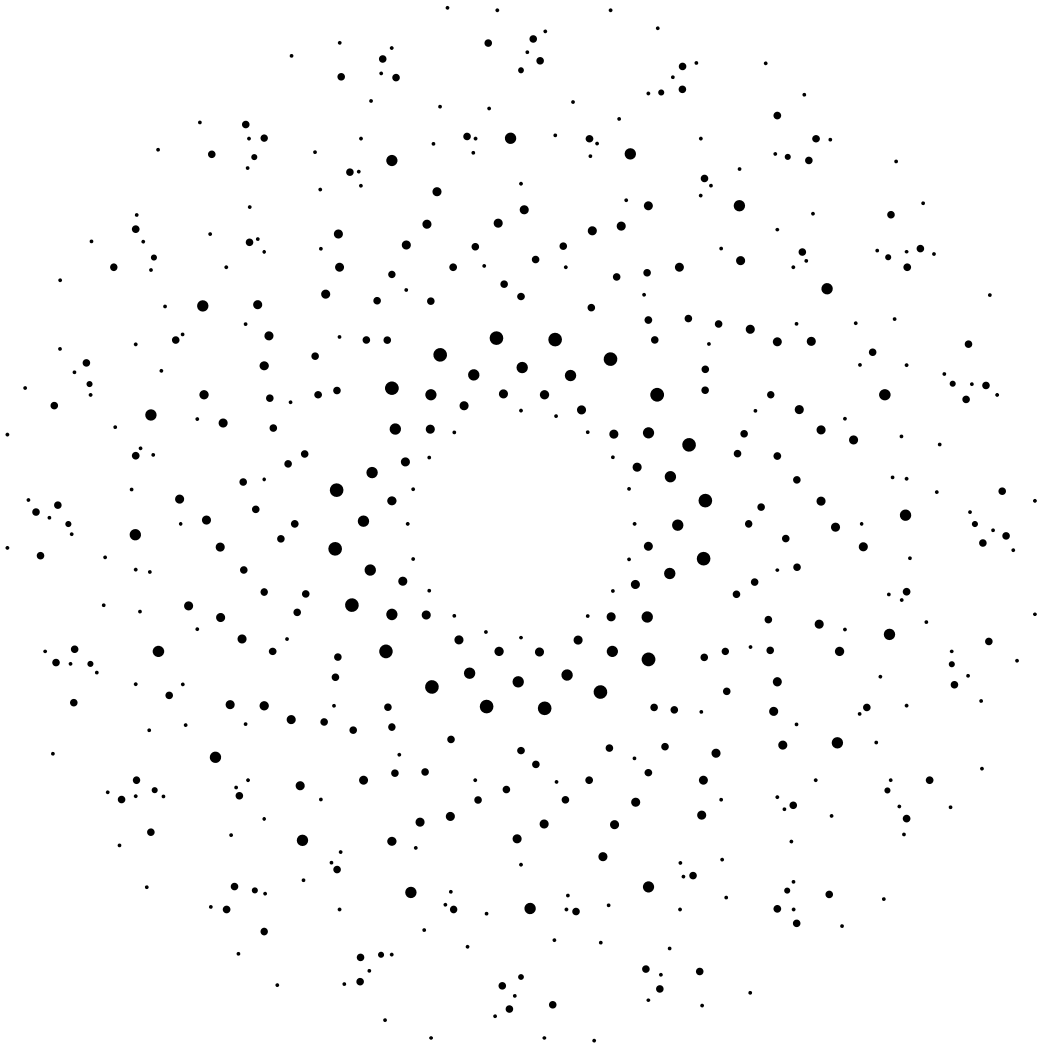
Powder diffraction



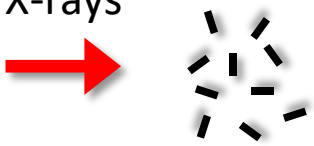


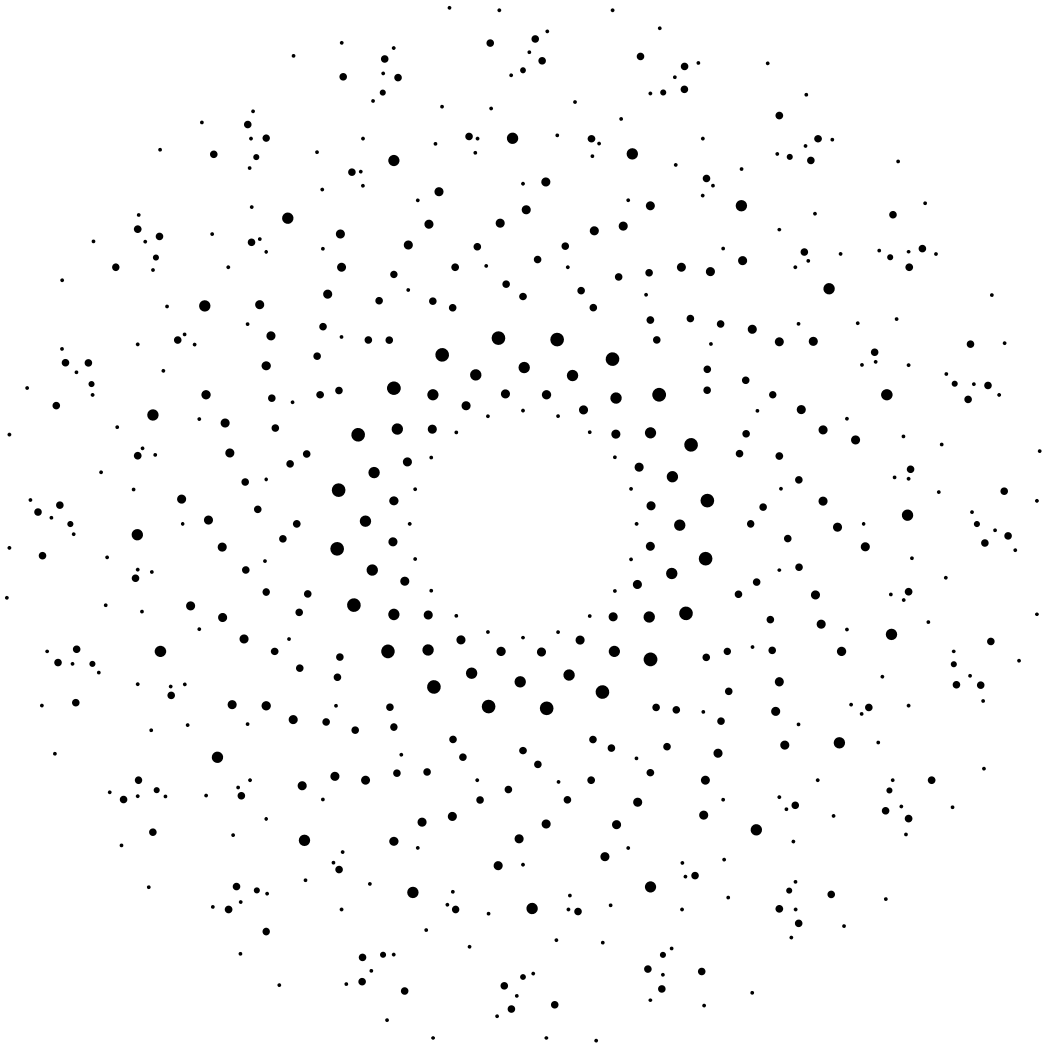
Powder diffraction



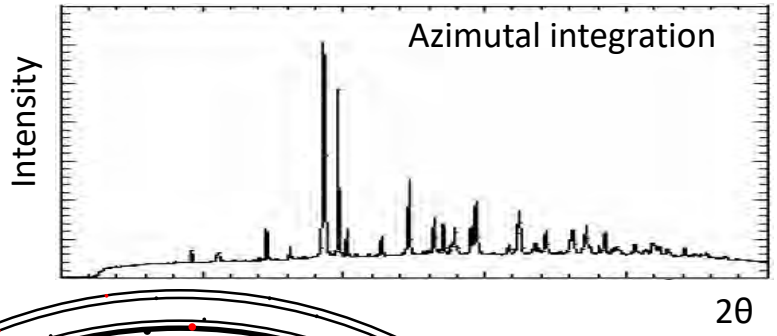


Powder diffraction

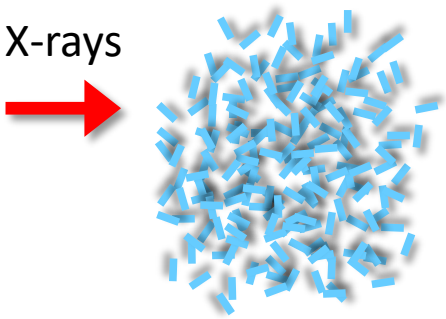


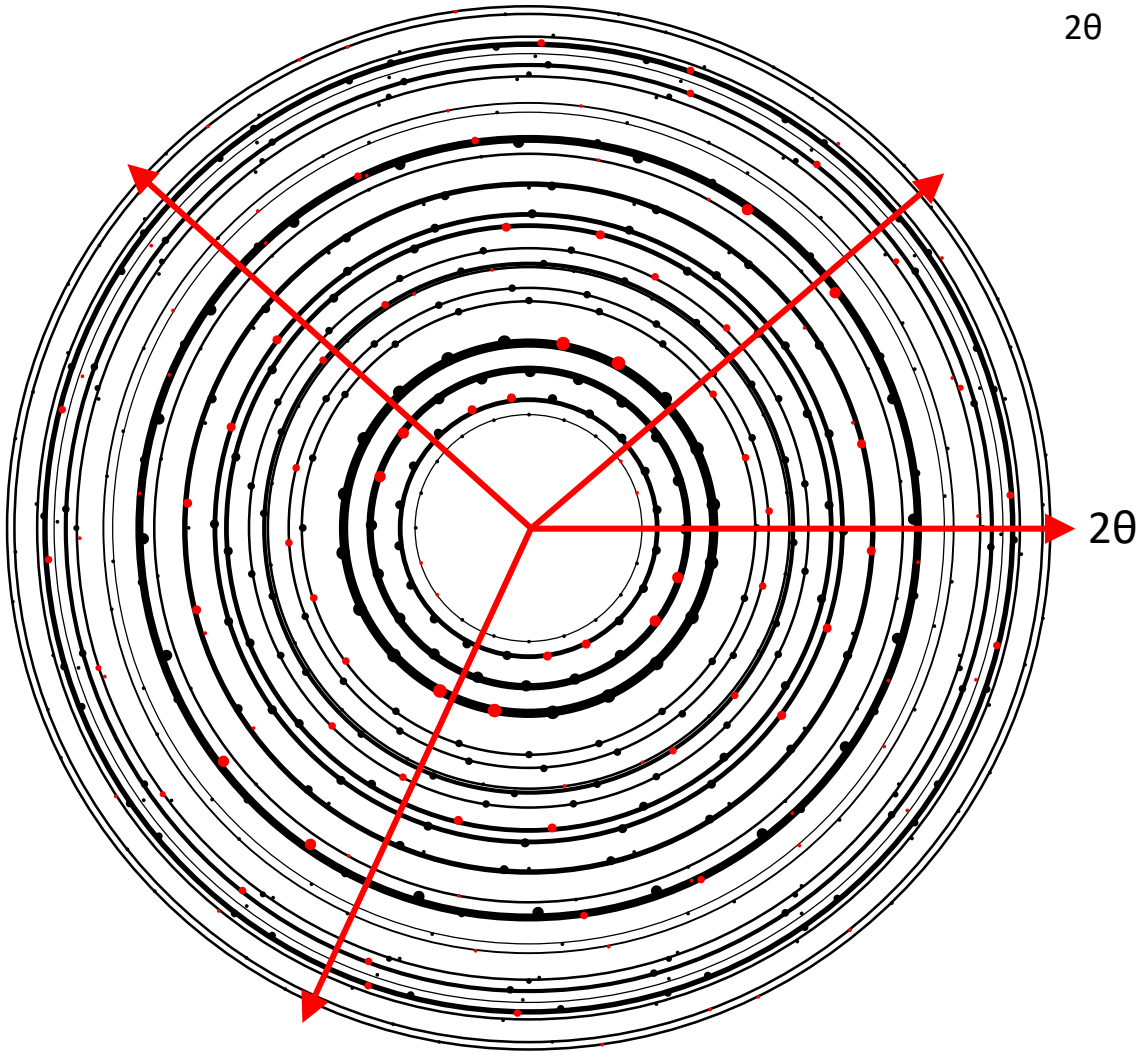


Powder diffraction



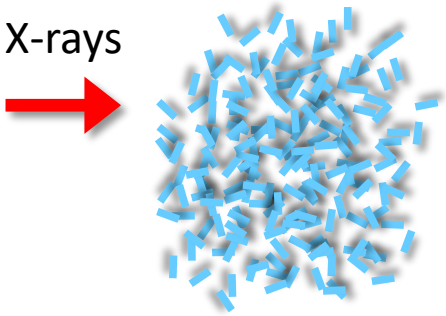
Orientation is lost:
3D→1D

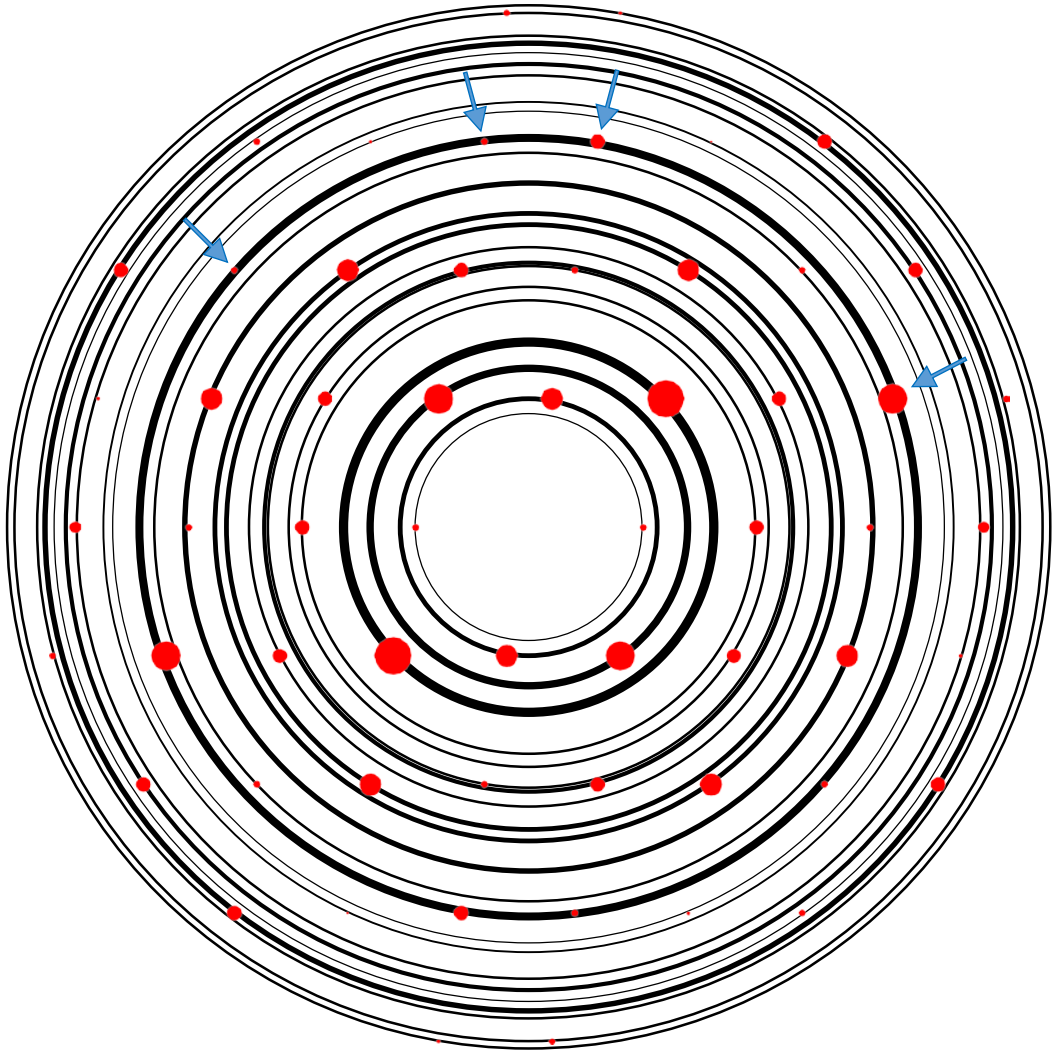




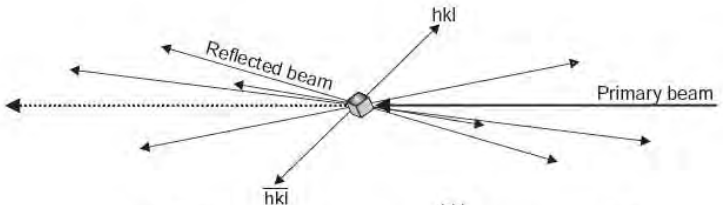
Powder diffraction

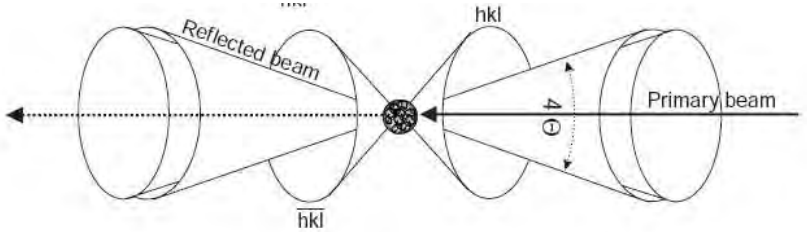
Reflection Overlap Problem





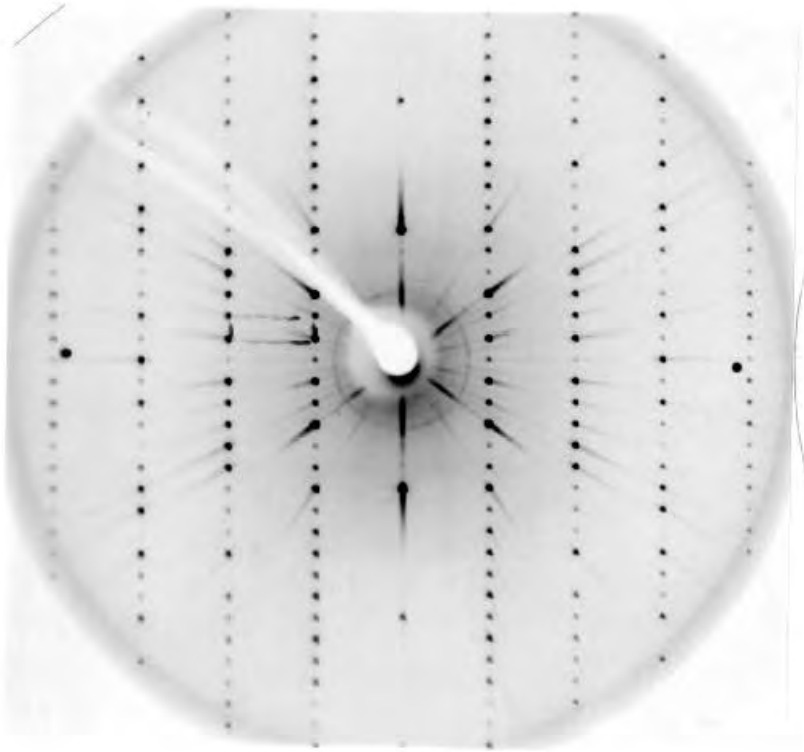
Single crystal vs Powder



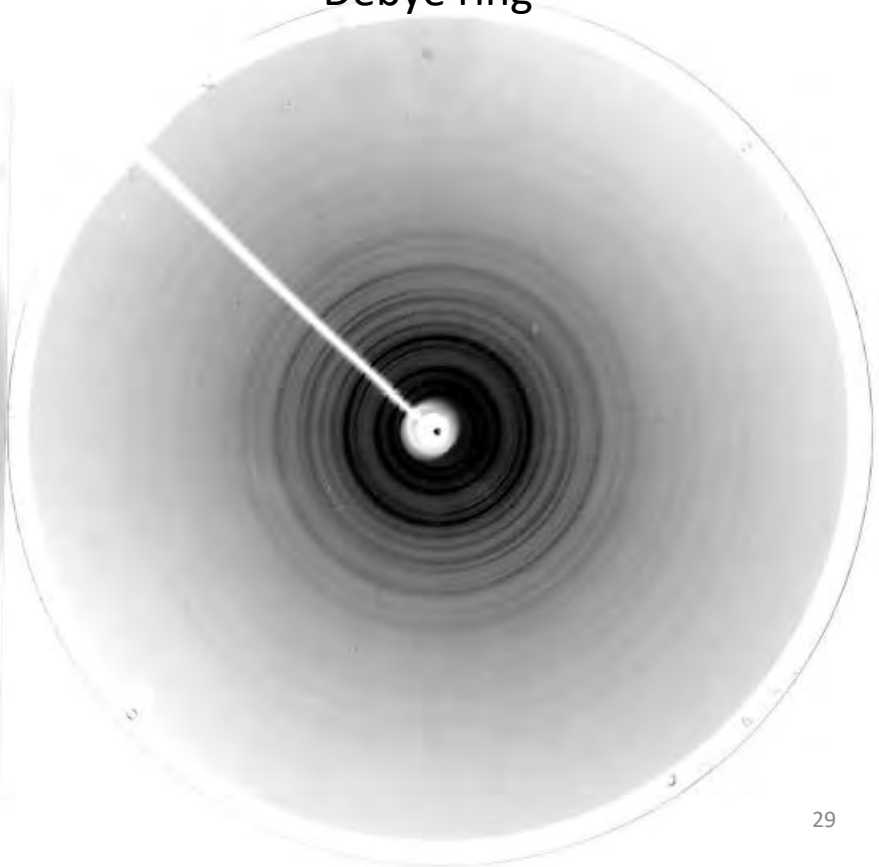


Bragg spots

Debye ring



© R. Cerny



How strong is the scattering in a given direction?

Motif,
atoms in Unit cell

FT

Structure factor

F(hkl)

$M(\vec{r})$

Unit cell * individual atoms * thermal motion

$$F_{hkl} = FT\{M(\vec{r})\}$$

$$F_{hkl} = \sum_{j \subset cell} f_j T_j \, e^{-2\pi i(hx_j + ky_j + lz_j)}$$

Property of the atom
→ *Information about atom types*

Structure property of the unit cell
→ *Information about atomic positions*

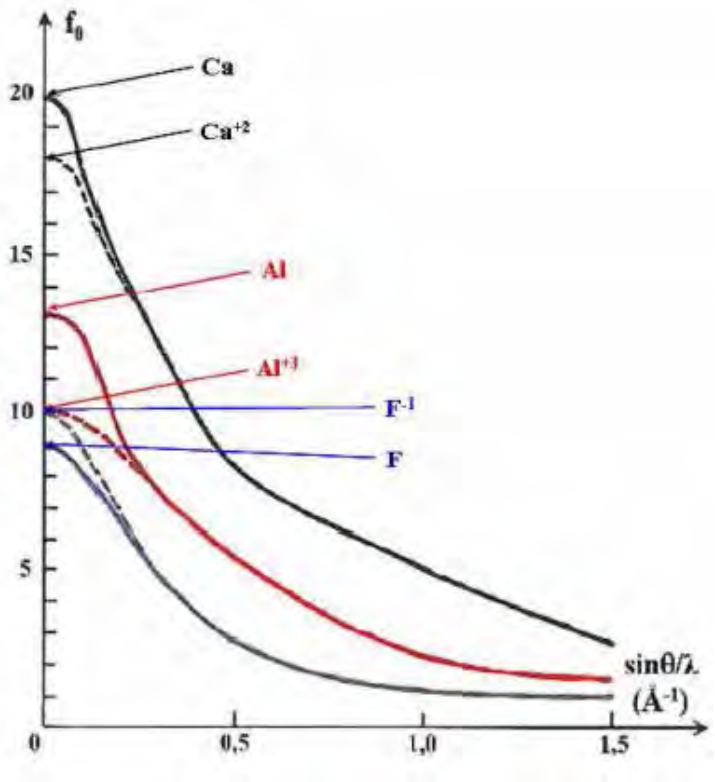
F_{hkl} ~ Collective scattering power of the atoms in the unit cell

The structure factor

$$F_{hkl} = \sum_{j \subset cell} f_j T_j \, e^{-2\pi i(hx_j + ky_j + lz_j)}$$

Atomic scattering factor of atom j with atomic fractional coordinate (x_j, y_j, z_j).
FT of its scattering density:

-for X-rays: $f_j = f_j(Q)$ atomic form factor



The structure factor

$$F_{hkl} = \sum_{j \subset cell} f_j T_j \, e^{-2\pi i(hx_j + ky_j + lz_j)}$$

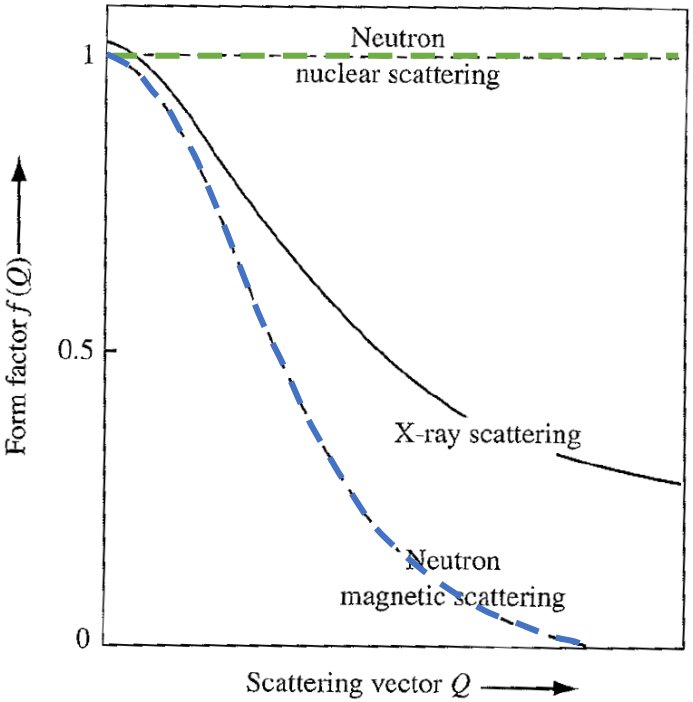
Atomic scattering factor of atom j with atomic fractional coordinate (x_j, y_j, z_j).
FT of its scattering density:

-for X-rays: $f_j = f_j(Q)$ atomic form factor

-for Neutrons:

Nuclear $f_j = b_i$, fermi length

Magnetic $f_j = ½ \gamma r_e f_m(Q)(\vec{M}_\perp \cdot \vec{S})$



$Q = 4\pi \sin(\theta)/\lambda$

the broader the distribution of the scatterer in real space, the narrower the distribution in Q; i.e., the faster the decay of the form factor

The structure factor

$$F_{hkl} = \sum_{j \subset cell} f_j T_j \, e^{-2\pi i(hx_j + ky_j + lz_j)}$$

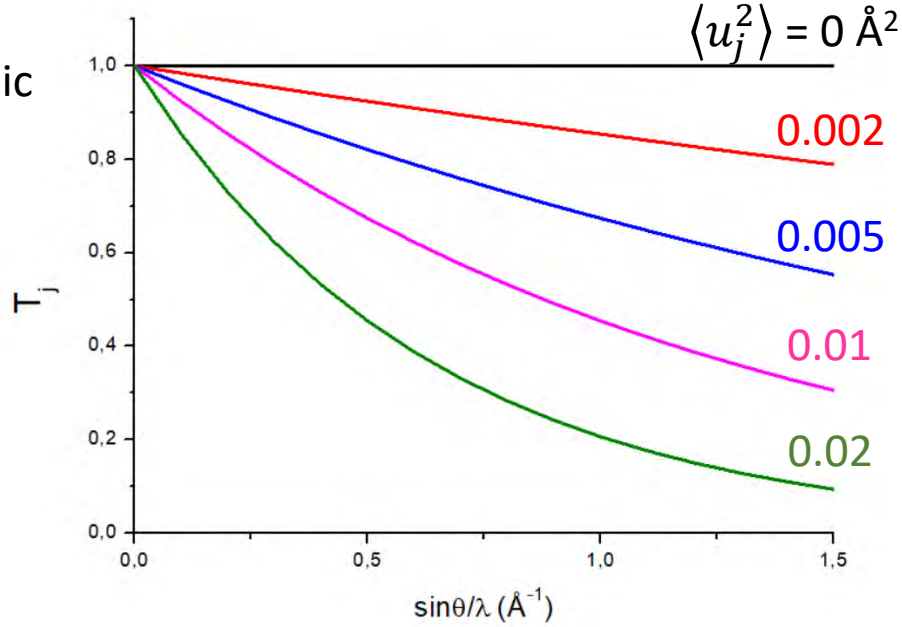
Atomic Displacement Parameter

Historically called **Temperature factor** or **Debye–Waller factor** describe the attenuation of scattering caused by atomic displacements (thermal, static).

In the approximation of an isotropic harmonic oscillator: $T_j = e^{-B_j\left(\frac{\sin\theta}{\lambda}\right)^2}$

With $B_j = 8\pi^2\langle u_j^2\rangle$ with units of Å²

$\langle u_j^2\rangle$ is the mean squared displacement of atom j



How strong is the scattering in a given direction?

The diffracted intensity I_{hkl} is the quantity accessible to measurement in a diffraction experiment (proportional to the number of diffracted particles arriving in the detector)

In the kinematic approximation (we neglect the double diffraction), we have:

$$I_{hkl} = S.C_{hkl}.\left|F_{hkl}\right|^2$$

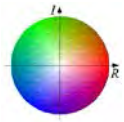
S : scale factor

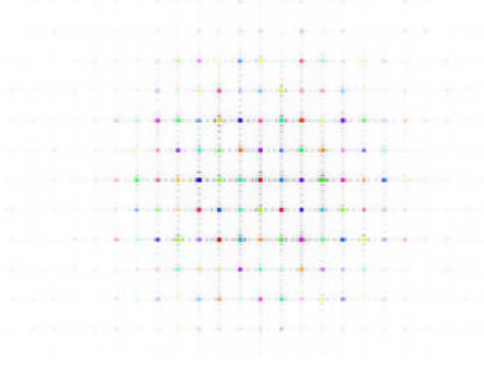
C_{hkl}: experimental corrective term

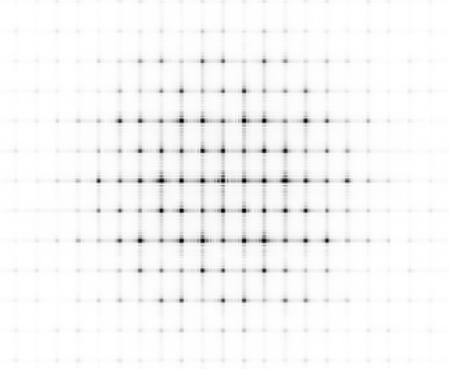
instrument (Lorentz, polarization, slit effects...)

sample (multiplicity, absorption, preferential orientation, extinction...)

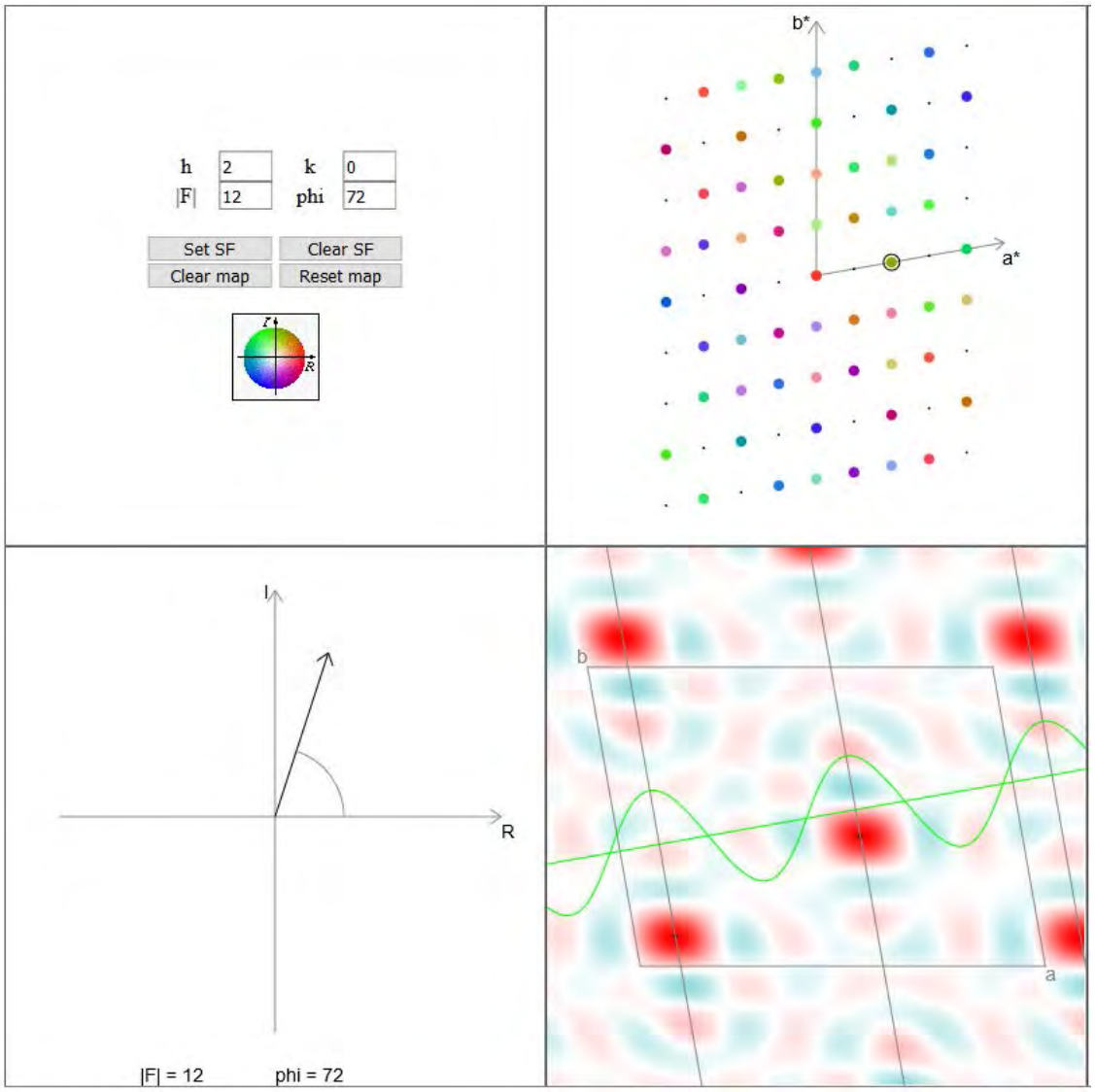
F_{hkl}: structure factor, complexe number → the phase of F is not measured



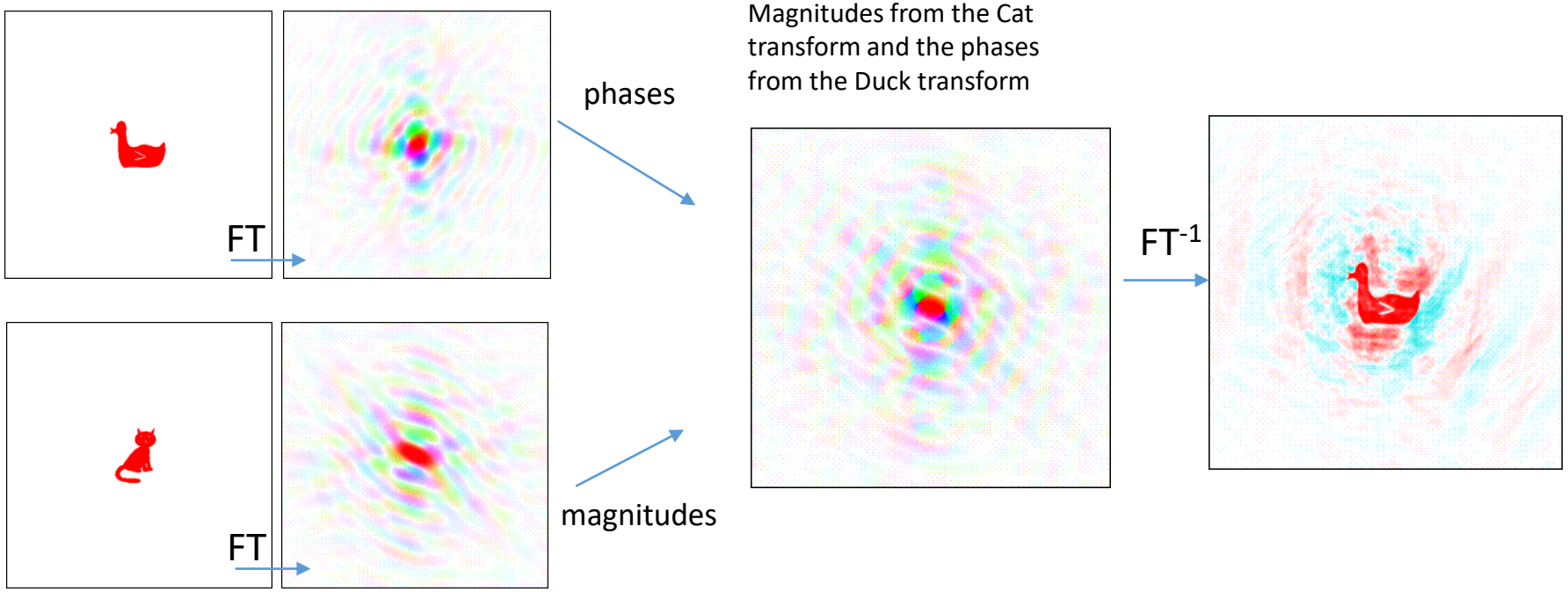




http://www.ysbl.york.ac.uk/~cowtan/sfapplet/sftut2.html



The phase problem



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

In diffraction experiments, we collect only the diffraction magnitudes, and not the phases. Unfortunately the phases contain the bulk of the structural information!

→ Use symmetry to reduce the problem

Effects of symmetry on diffraction

Point symmetry:

Point group symmetry operations of the crystal are reflected in the diffraction pattern

Friedel's law:

$F(\overline{hkl}) = F^*(hkl)$ where $F^*(hkl)$ is the complex conjugate of $F(hkl)$.

→ The squared amplitude is centrosymmetric : $|F(hkl)|^2 = |F(\overline{hkl})|^2$

Symmetry of the diffraction pattern: Laue-group
point symmetry of the crystal + a center of symmetry

It is not possible to tell from the symetry of the diffraction pattern whether or not the crystal has a center of symmetry. The information is buried in the intensity distribution of the diffraction pattern.

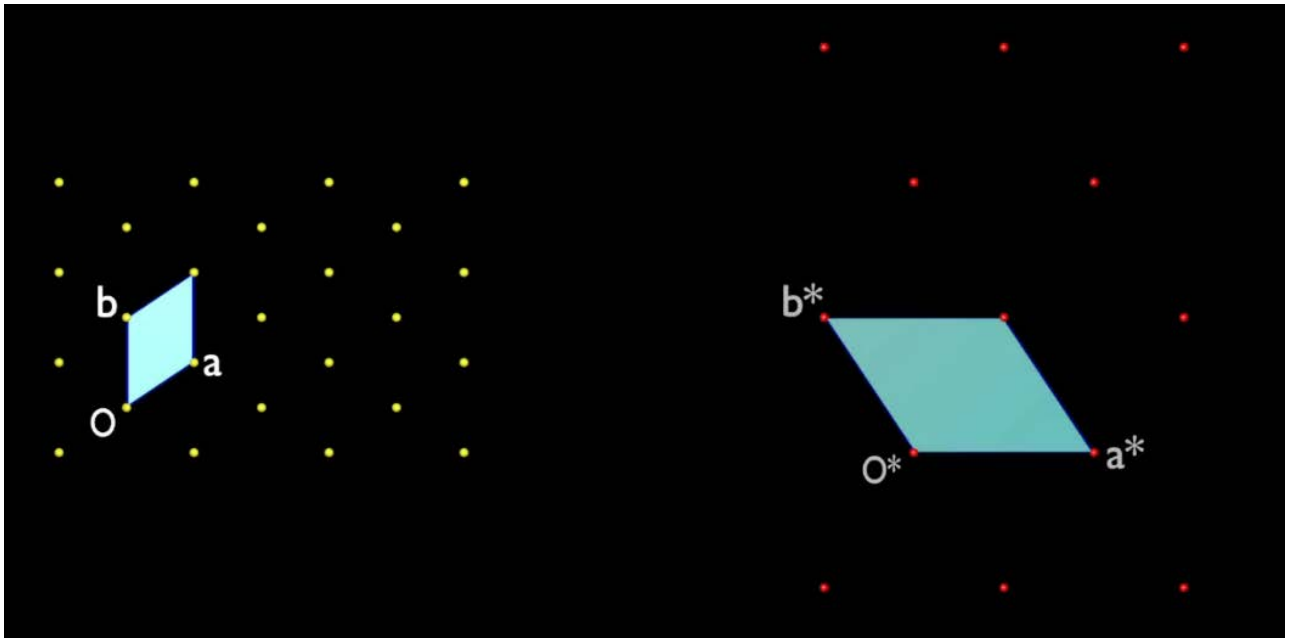
Crystal system	Crystal class	Laue-group	Symmetry equivalent reflections
triclinic	1, -1	1	2: hkl, -h-k-l
monoclinic	2, m, 2/m	2/m	4: hkl, -h-k-l, h-kl, h-kl
orthorhombic	222, mm2, mmm	mmm	8: hkl, -h-k-l, h-kl, h-kl, -hkl, hk-l, -h-kl, h-k-l
tetragonal	4, -4, 4/m	4/m	8: hkl, -h-k-k, khl, -k-h-l hk-l, -h-kl, kh-l, -k-hl
	422, -42m, 4mm, 4/mmm	4/mmm	16
trigonal	3, -3	3	6
	321, 3m1, -3m1	-3m1	12
	312, 31m, -31m	-31m	12
hexagonal	6, -6, 6/m	6/m	12
	622, -62m, 6mm, 6/mmm	6/mmm	24
cubic	23, m-3	m-3	24
	432, -43m, m-3m	m-3m	48

Systematic absences

Translational symmetry operations that have the effect of making some structure factors have zero value in a systematic way

- Non-primitive lattice
- Screw axes and glide planes

Exemple:



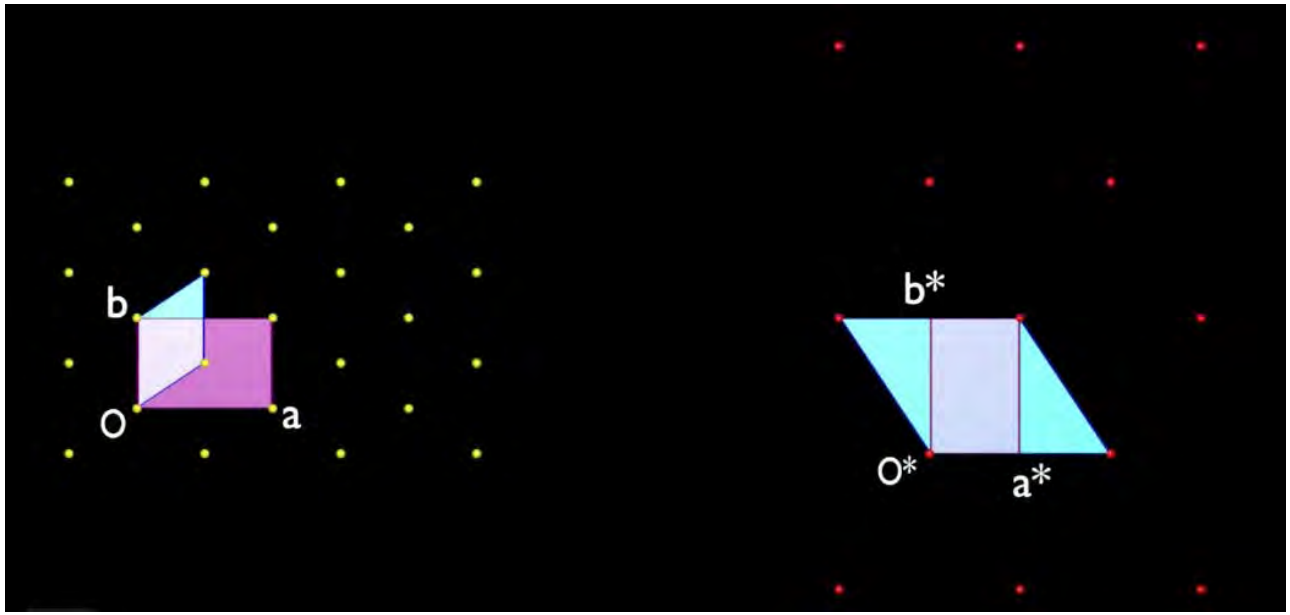
Systematic absences

Translational symmetry operations that have the effect of making some structure factors have zero value in a systematic way

- Non-primitive lattice
- Screw axes and glide planes

Exemple:

Centered cell



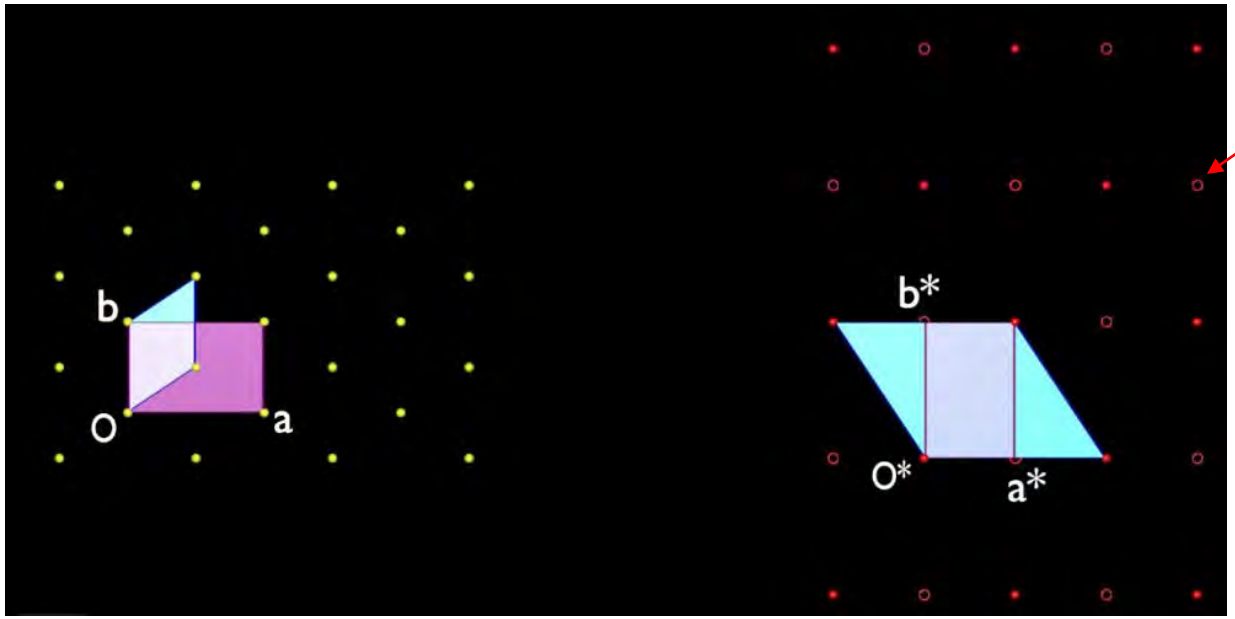
Systematic absences

Translational symmetry operations that have the effect of making some structure factors have zero value in a systematic way

- Non-primitive lattice
- Screw axes and glide planes

Exemple:

C centered cell



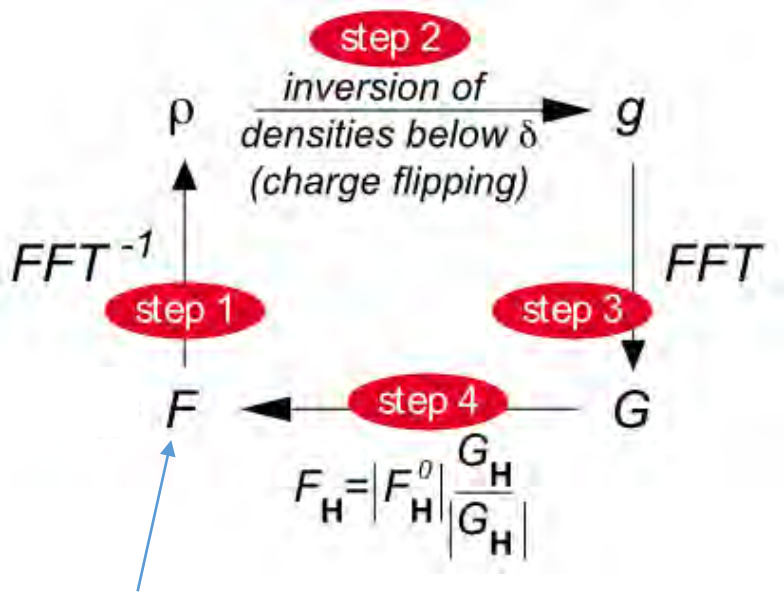
Systematic absence for h+k=2n+1

→ Used to identify the symmetry elements with translation and select the space group

Determination of crystal structure

Several method exist to overcome the phase problem

Exemple:



Random (or zero) phases on experimental data

The charge flipping algorithm

Oszlanyi & Süto, Acta Cryst. 2004, 2005

This algorithm is based on a simple property: the electron density is always positive.

1.Calculate the inverse Fourier transform of the structure factors. The resulting electron density ρ(**x**) has positive and negative peaks due to the wrong phases.

2.The negative peaks (up to a small limit δ) are set positive (charge flipping) and a new electron density function is established.

3.The Fourier transform of this new density is calculated.

4.The phases of the new structure factors are kept but the amplitudes of the structure factors are replaced by the experimental ones.

This procedure continues in a loop with step 1 to 4 until a converging solution is found.

Charge flipping App : Nicolas Schoeni and Gervais Chapuis
École Polytechnique Fédérale de Lausanne, Switzerland

Refinement of the crystal structure

- The crystal structure deduced using direct methods can be refined by adjusting the atomic fractional coordinates and atomic displacement parameters to give best agreement between measured and calculated structure factors.

- Least-square refinement

The most common approach is to minimize the function:

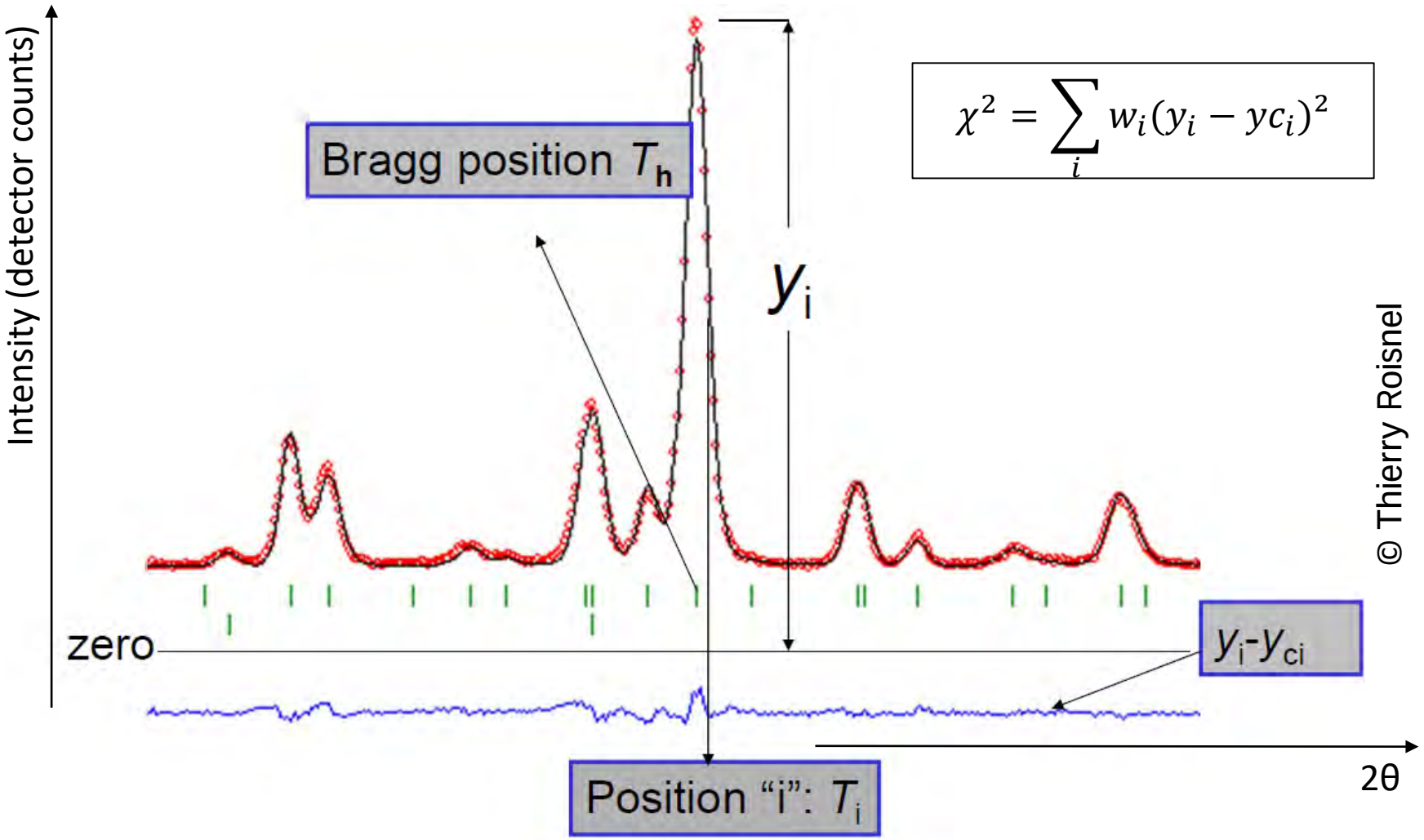
$$\chi^2 = \sum_i w_i (y_i - yc_i)^2$$

y is the intensity of an observed reflections, yc is the value calculated from the structural model for the same reflection, and w is an assigned weight usually representing the estimate of the precision of the measured quantity ($w_i=1/y_i$)

-For single crystal: $y_i = I_{hkl} = |F_{hkl}|^2$

-For powder: 1D projection of the 3D reciprocal space, Bragg peaks with similar d's overlap

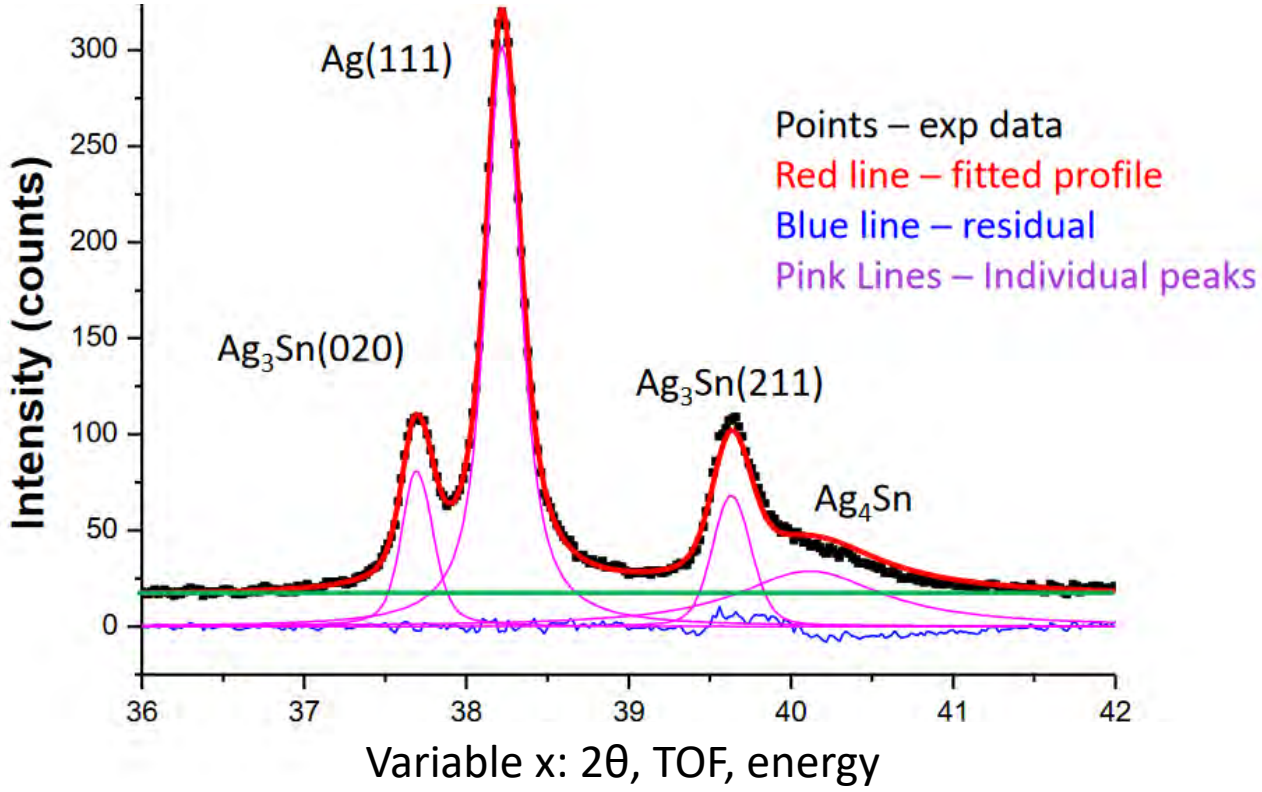
Refinement of a powder diffraction diagram



y_i is the intensity of the signal in the detector for each measured angle not I_{hkl}

→ how to extract I_{hkl} from the diffraction diagram ?

Decomposition of the diagram

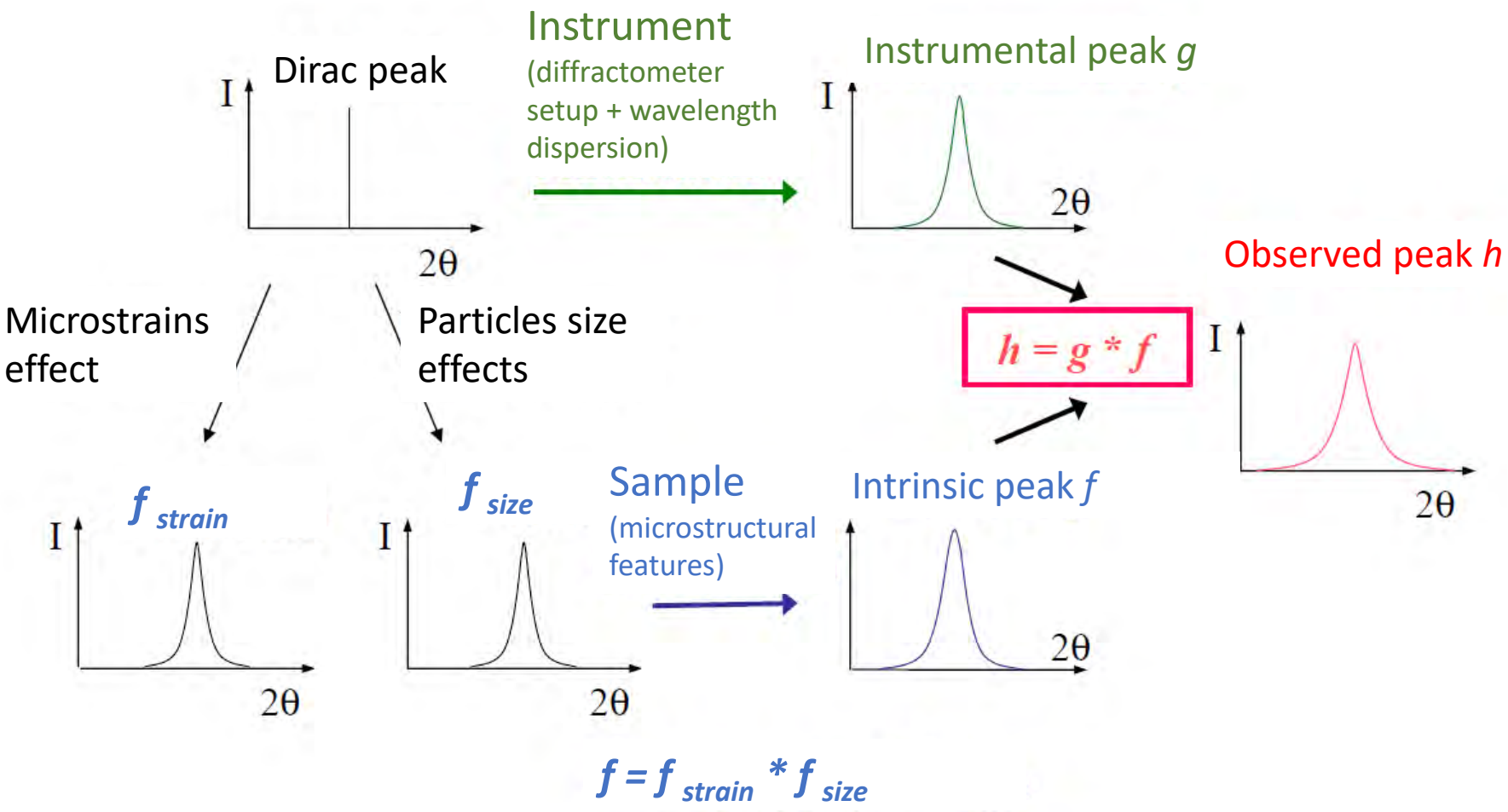


$$y_{calc}(x) = b(x) + \sum_k h_k(x)$$

With $h_k(x)$ Peak profile

→ Need to model the Profile (shape and width) of a Bragg Reflection for Extracting Intensities

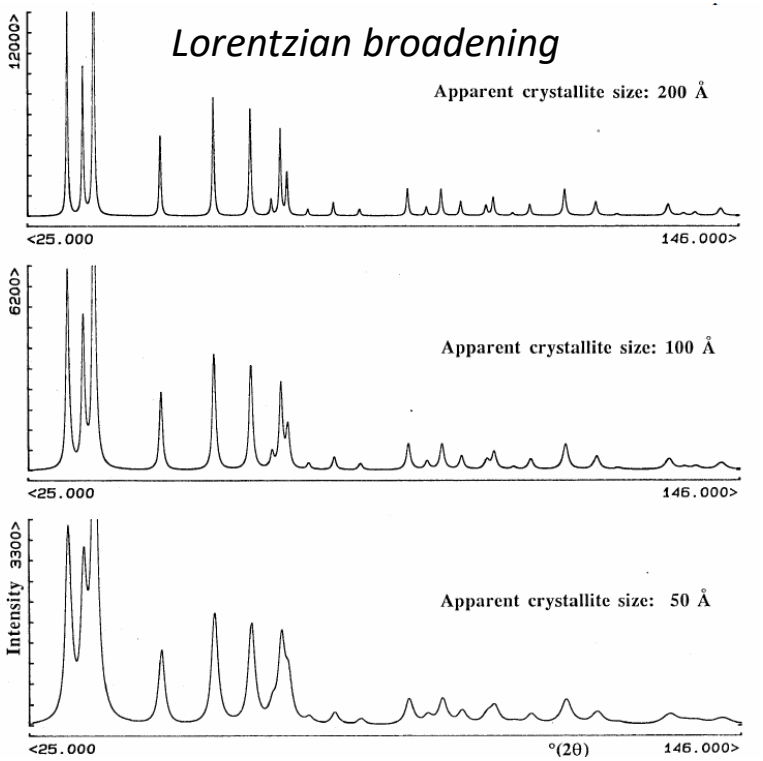
Profile of a Bragg Reflection



Sample line profile broadening

- Size effect

incomplete destructive interference at $\theta_{Bragg} \pm \Delta\theta$ for a finite (limited) number of lattice planes



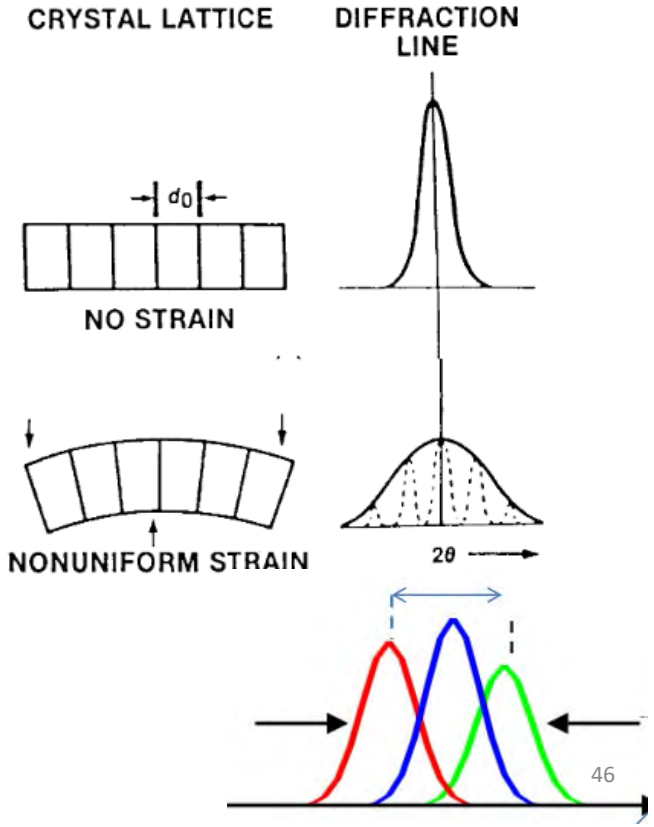
Ex: ZnO ($CuK_{\alpha 1}$)

- Strain effect

Distribution of deformations

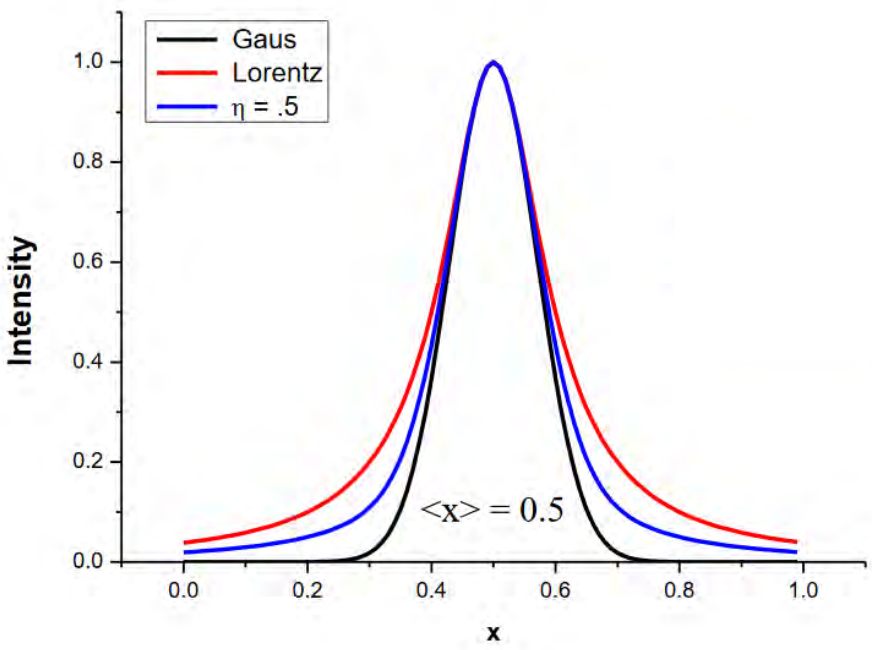
$$d_0 \pm \Delta d = d_0(1 \pm \varepsilon)$$

→ Overlap of diffraction profiles



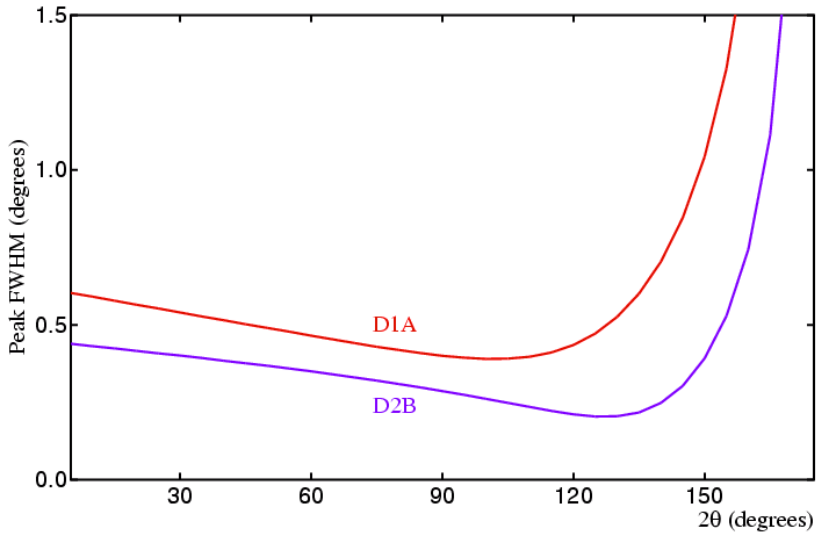
Profile modelisation: shape and width

Shape



Width

Angular dependence of H_G and H_L components



Pseudo-Voigt

$$pV(x) = \eta . L(x) + (1 - \eta) . G(x)$$

The profile function is characterized by its Full Width at Half Maximum: H

The Cagliotti law

$$H_G^2 = U \tan^2\theta + V \tan\theta + W + \frac{I_G}{\cos^2\theta}$$

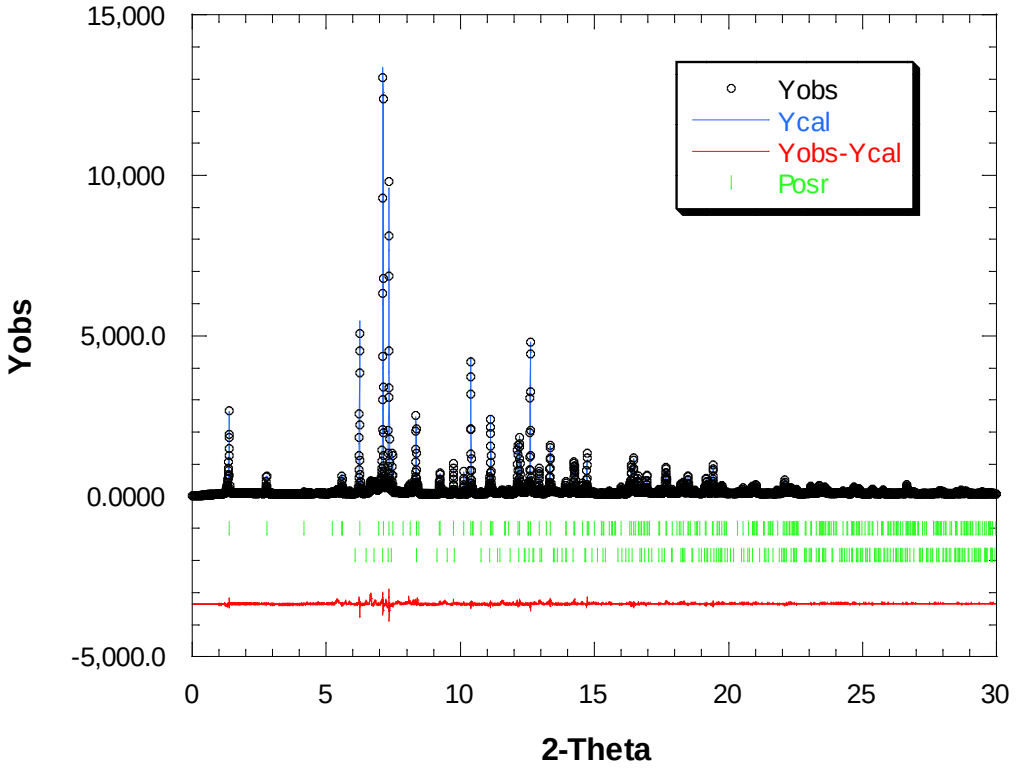
$$H_L = X \tan\theta + \frac{Y}{\cos\theta}$$

Rietveld refinement: a global refinement of the powder diagram with structural model

« A profile refinement method for nuclear and magnetic structures »
Rietveld, H.M., 1969. J. Appl. Crystallogr., 2, 65-71

$$yci = ybi + \sum_{\Phi=1}^{N} S_{\Phi} \sum_{k=k1}^{k2} j_{\Phi k} . Lp_{\Phi k} . O_{\Phi k} . M . \left| F_{\Phi k} \right|^2 . \Omega_{i\Phi k}$$

yci calculated intensity at pattern point i
ybi background intensity at pattern point i
Φ index for sample phases
k index for reflections contributing to point i
S_{Φ} scale factor for phase Φ
j_k multiplicity of reflection k
Lp_k Lorentz (polarisation) factor for reflection k
O_k preferred orientation correction for reflection k
M absorption correction
$|F_{\Phi k}|$ structure factor modulus for reflection k of phase Φ
Ω_{ik} profile function for reflection k of phase Φ calculated at pattern point i



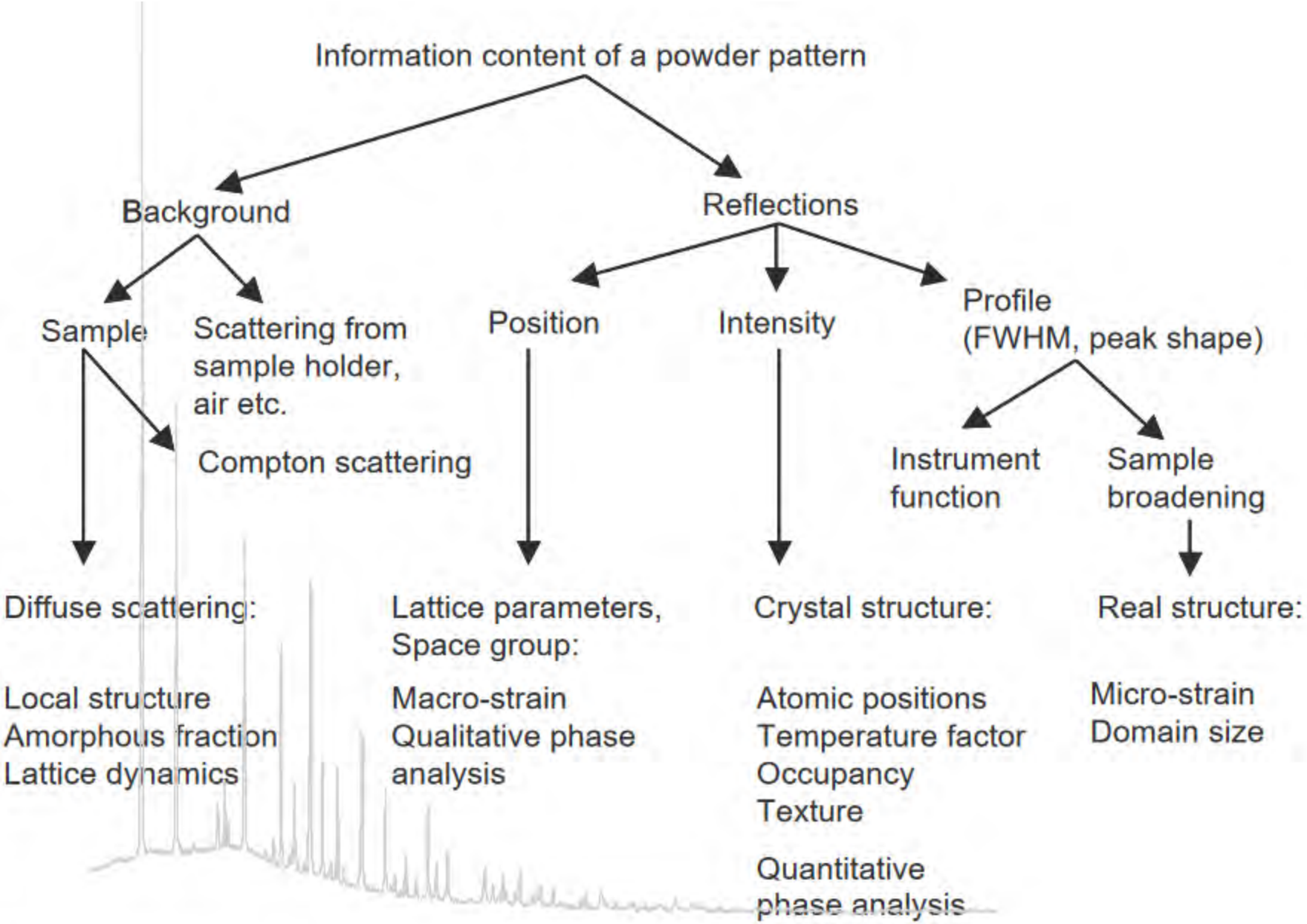


Figure 1 General information content of a powder diffraction pattern.

Phase identification

Phase quantification

Structure determination

Particle size

Particle strain

Microstructure

Type of studies:

Phase transition, cinetic

Crystallisation/amorphisation

Ionic migration

Polymorphism

Thermal expansion ….

X-ray vs Neutron diffraction

	X-Rays	Neutrons
Nature	Electromagnetic wave	Particle wave
	No mass, spin 1, no magnetic dipole moment	Mass, spin ½, Magnetic dipole moment
Scattered by	Electron cloud	Nuclei and magnetic moments of unpaired electrons
Scattering power	~ Z	independent
Q-dependence of scattering	yes	Nuclear: f is constant Magnetic: yes, strong
Resolution δd/d	Ultra-high (~10^{-4})	Medium (10^{-2}), High (10^{-3})

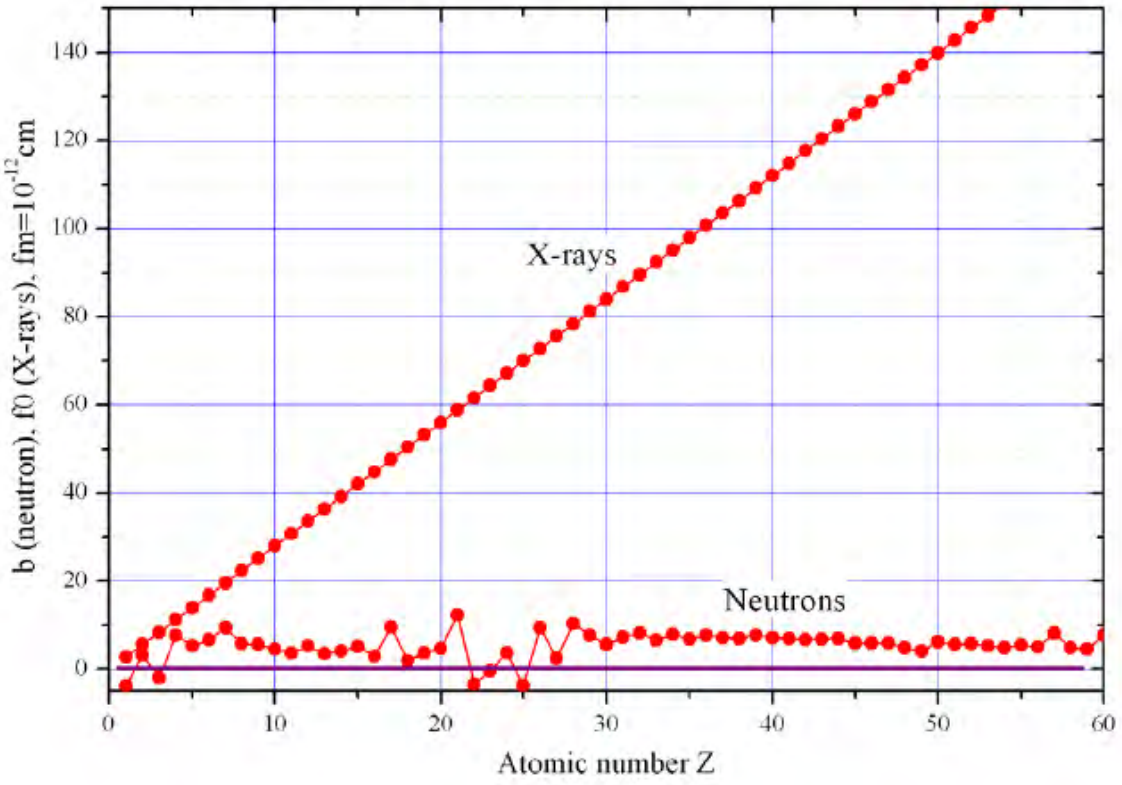
X-ray vs Neutron : Scattering power

- X-ray:

Atomic scattering factor
→ Large scattering power, ~Z

- Neutron:

Coherent scattering length
→ Low scattering power, independent of Z



X-ray vs Neutron : sample quantity

Neutron: low neutron flux, low scattering power

→ Large sample, typically few grams

→ Typical acquisition time: few minutes for high flux to few hours for high resolution

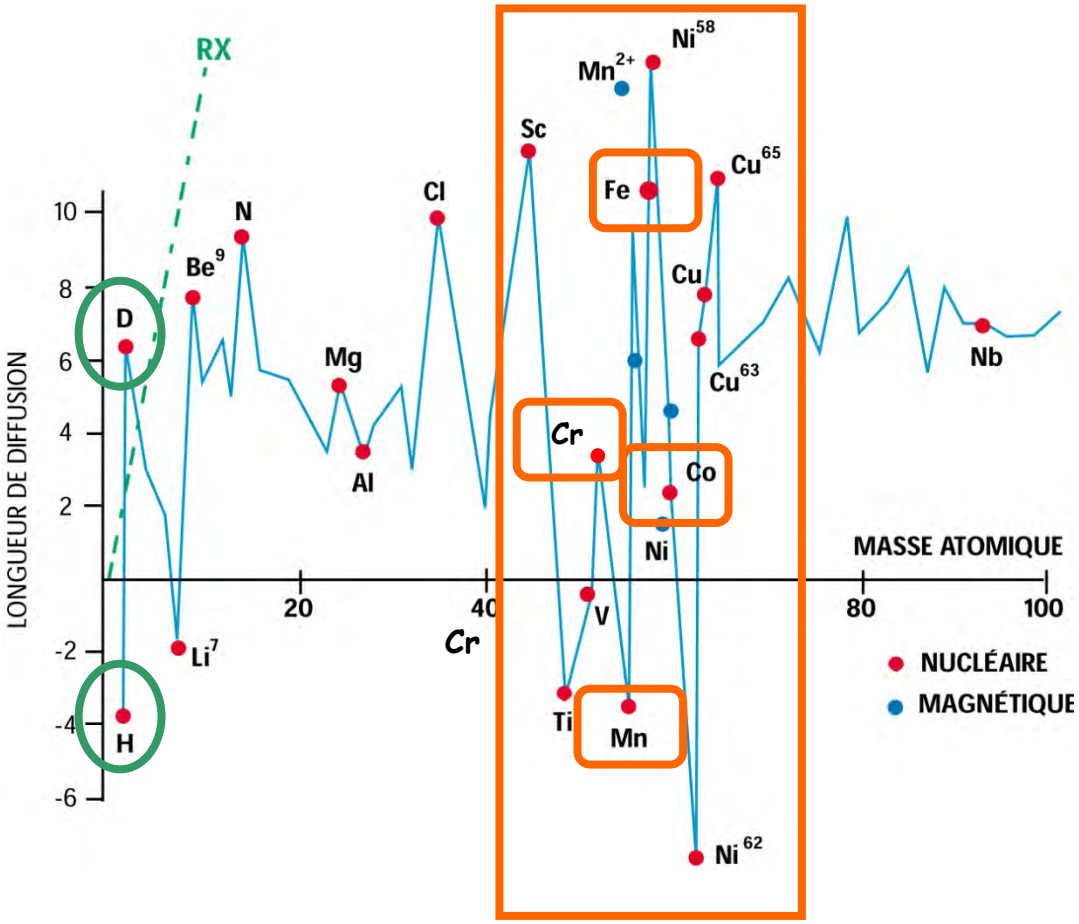
X-ray: high brilliance, high scattering power

→ Tiny samples

X-ray vs Neutron: Scattering power

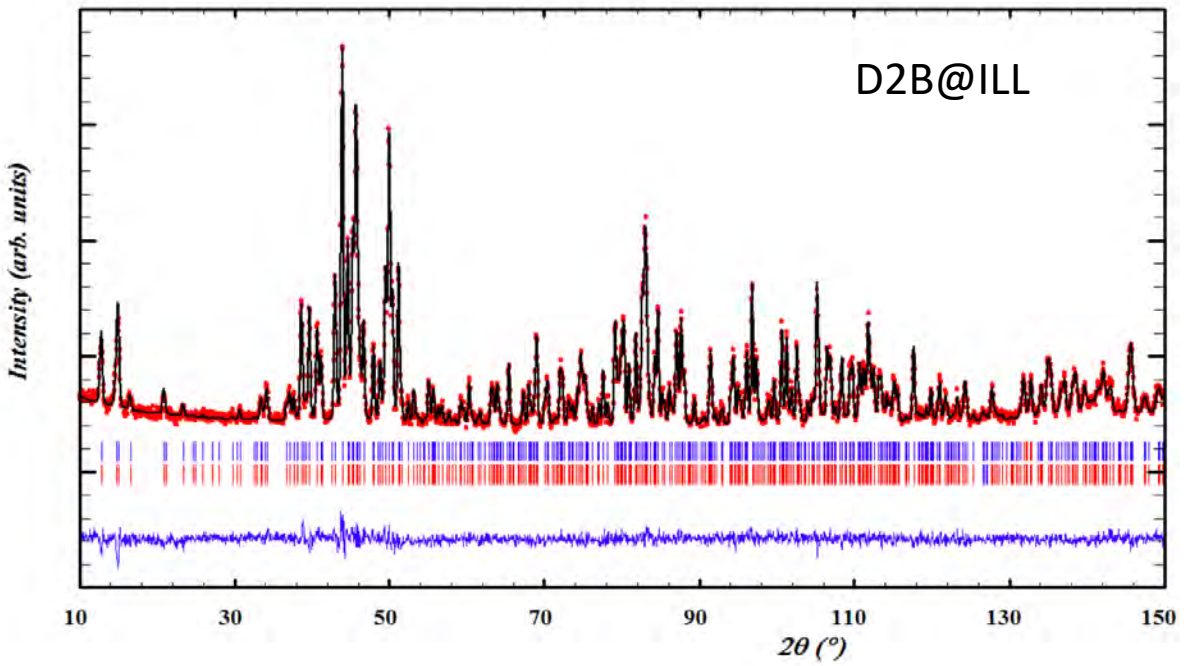
H	-0.374
D	0.667

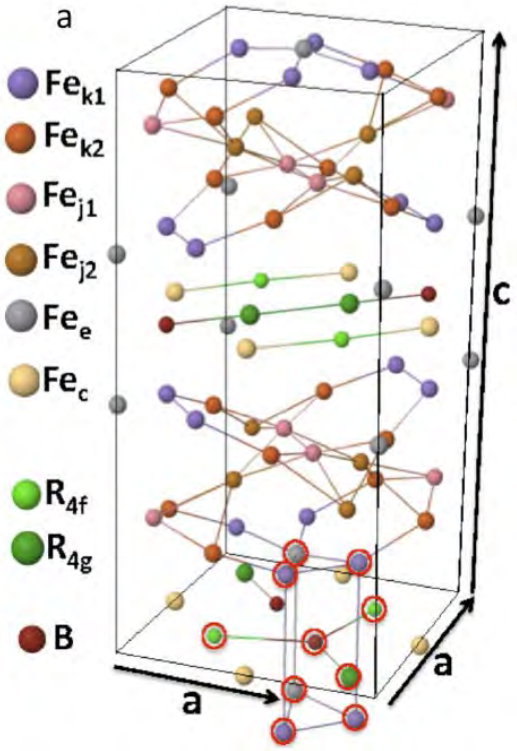
Cr	0.3635
Mn	-0.373
Fe	0.954
Co	0.253
Ni	1.03
^{58}Ni	1.44
^{60}Ni	0.28
^{62}Ni	-0.87



Neutron: contrast, light elements

Example: site-preference occupancy in (Nd-Ce)$_2$(Fe-Co)$_{14}$B hard permanent magnets



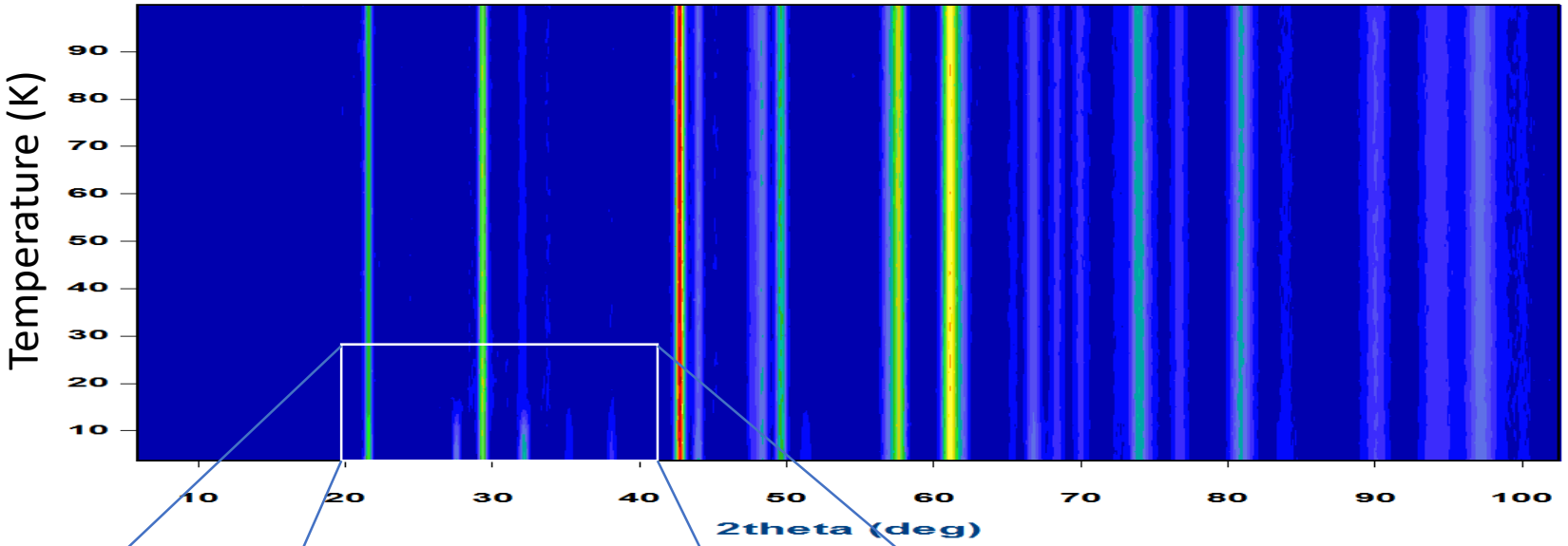


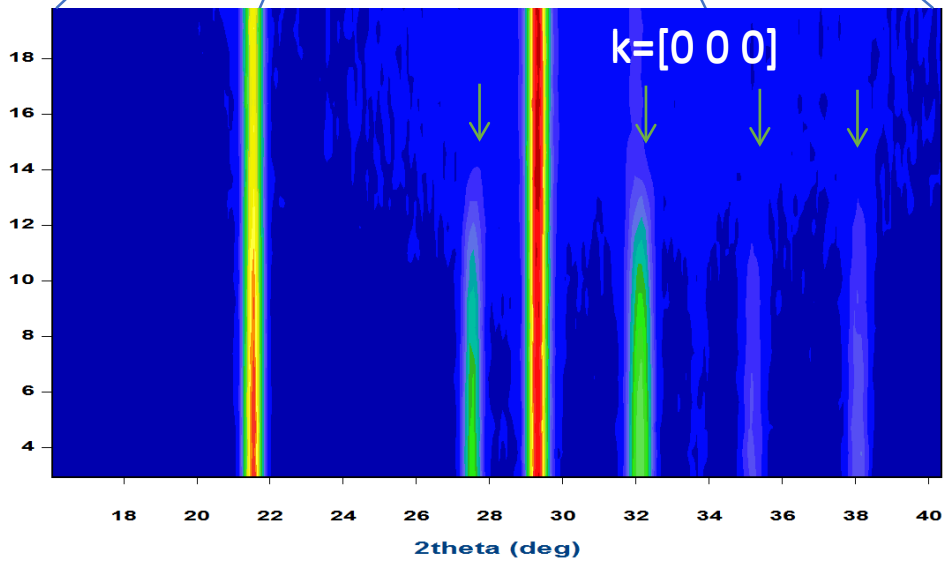
Fe/Co and Nd/Ce contrast allowed by neutron diffraction → site-preference → magneto-crystalline anisotropy

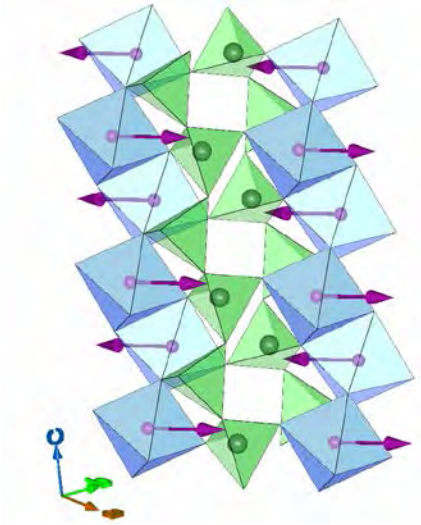
Colin, C. V. *et al. Appl. Phys. Lett.* **108**, 242415 (2016)

~~X-ray~~ vs Neutron: Magnetic structures

Exemple: Magnetic structure of $CaMnGe_2O_6$ magneto-electric pyroxene



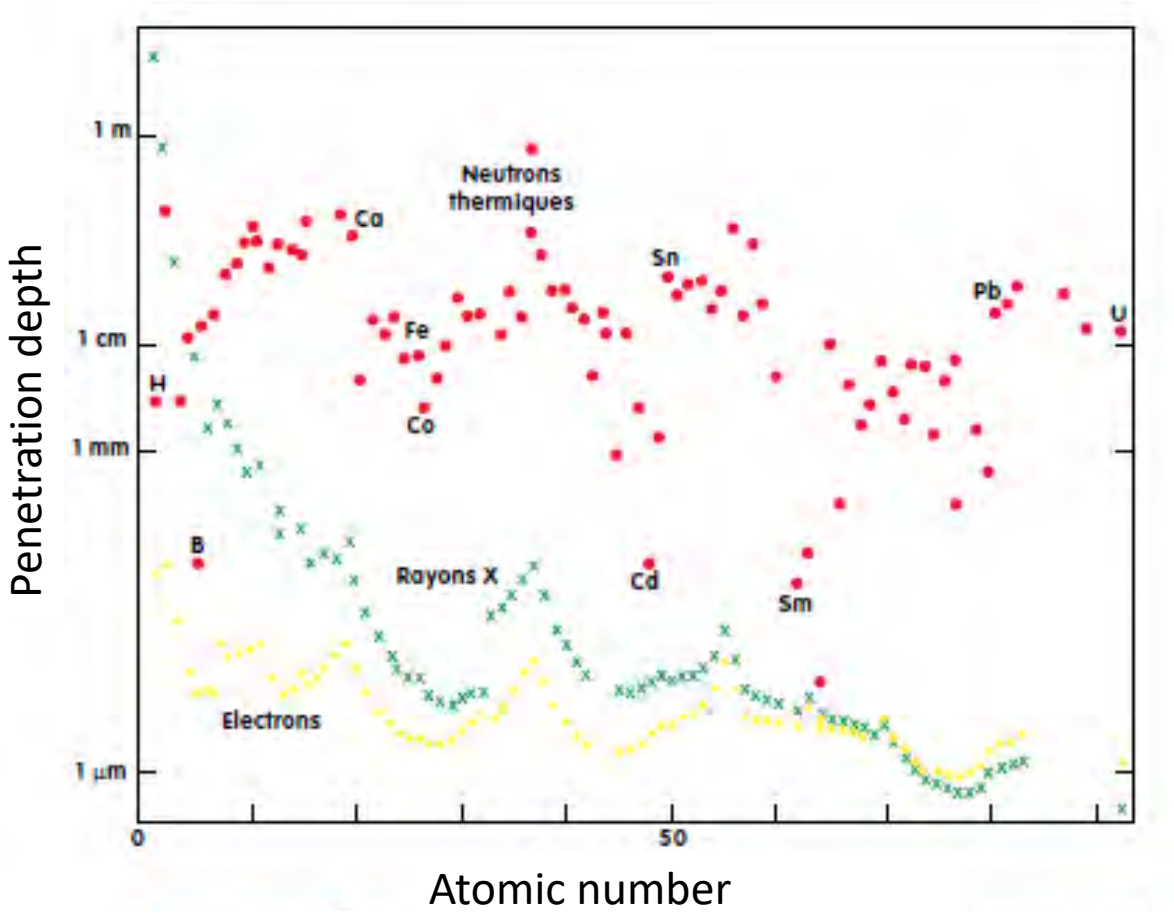




$CaMnGe_2O_6$
Magnetoelectric
Antiferromagnetic
Structure

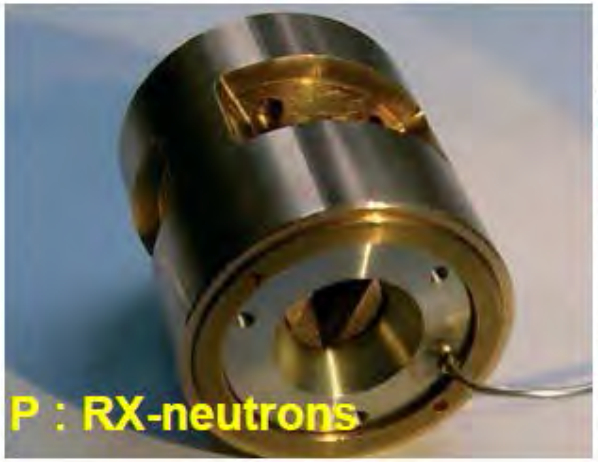
Ding, L. *et al. Phys. Rev. B* **93**, 064423 (2016).

X-Ray vs Neutron: Absorption



X-ray vs Neutron: Sample environment

* Champ Elect.
* Electrolyte
* …



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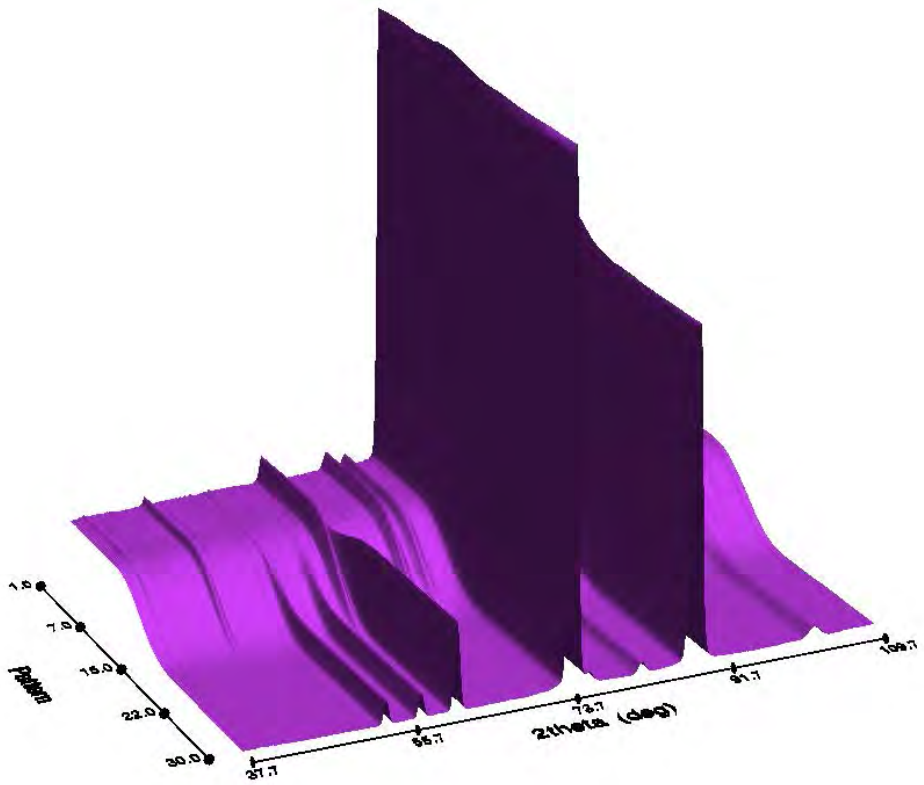
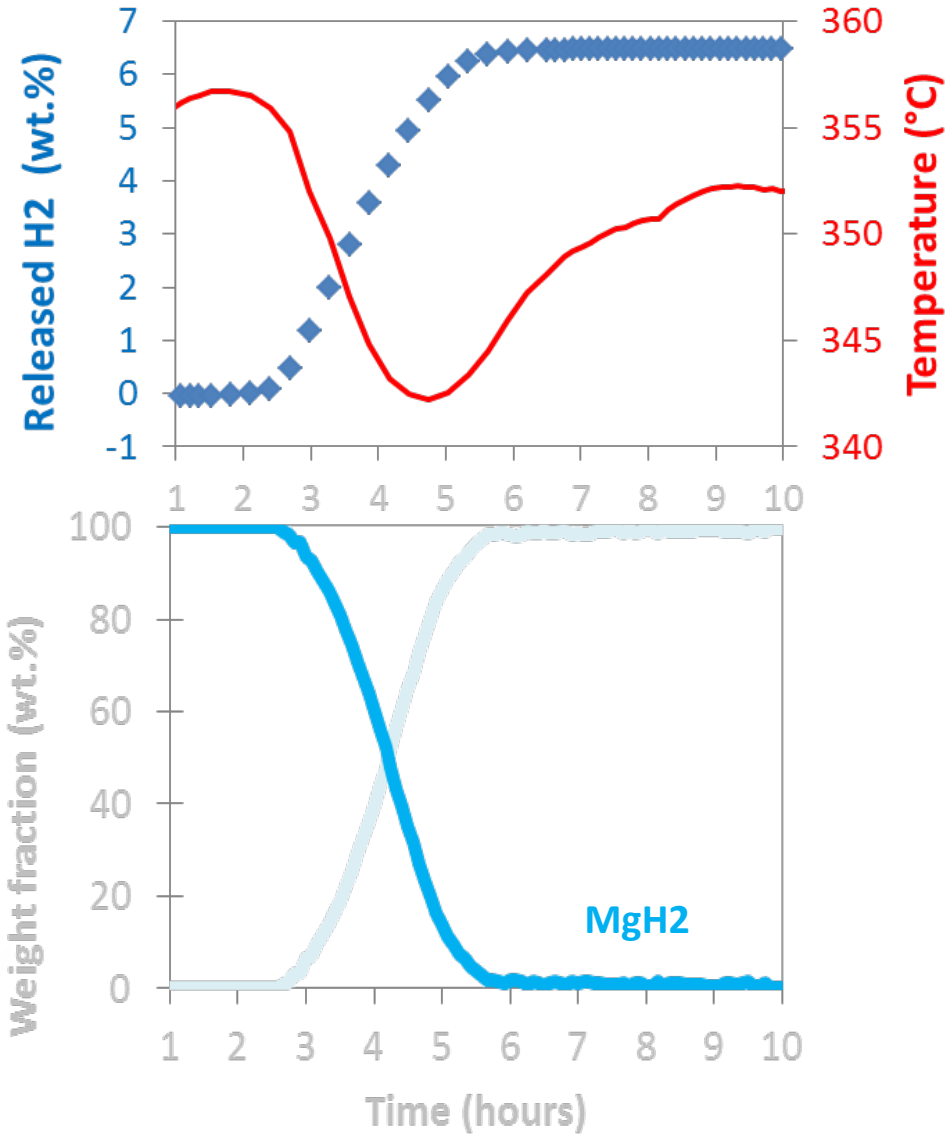
Exemple: Coupled H_2 Desorption Measurement, in-situ NPD

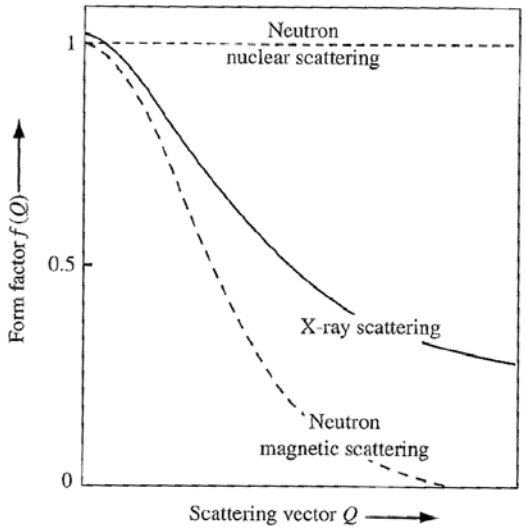
$MgH_2 \rightarrow Mg + H_2$

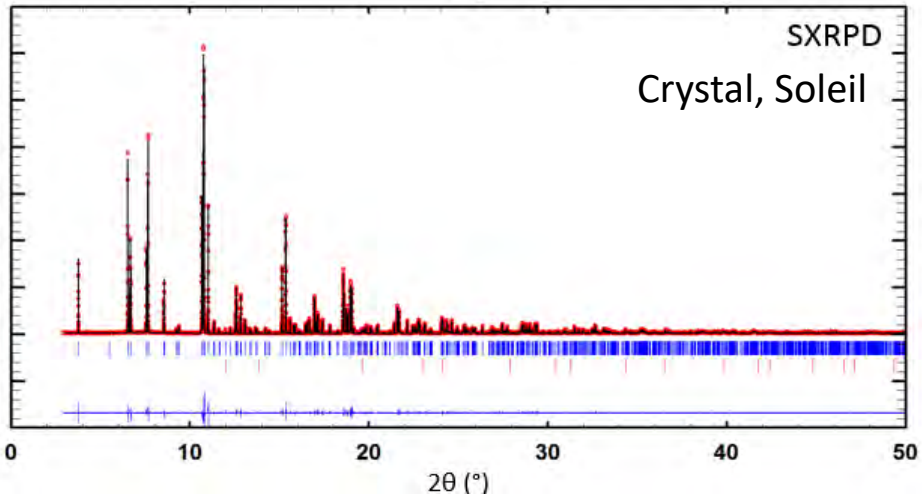
T= 350 °C, P = 200 mb

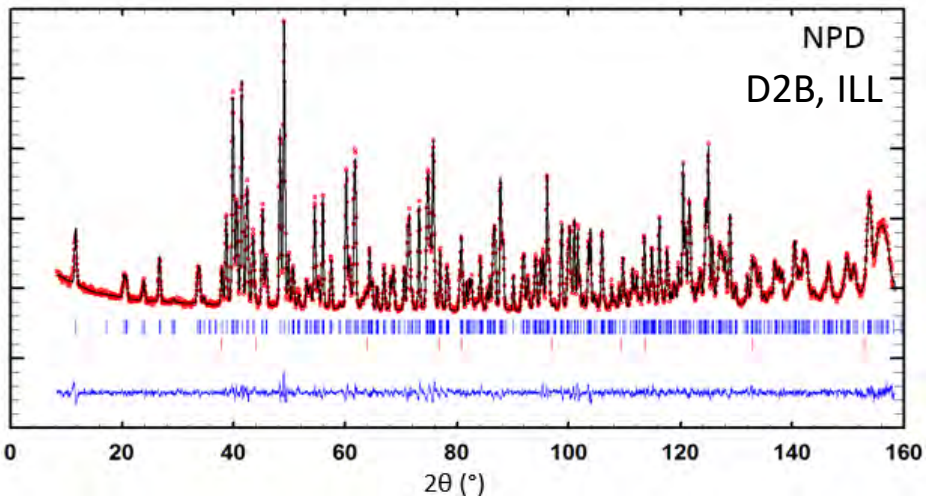




X-Ray vs Neutron: Q-dependence



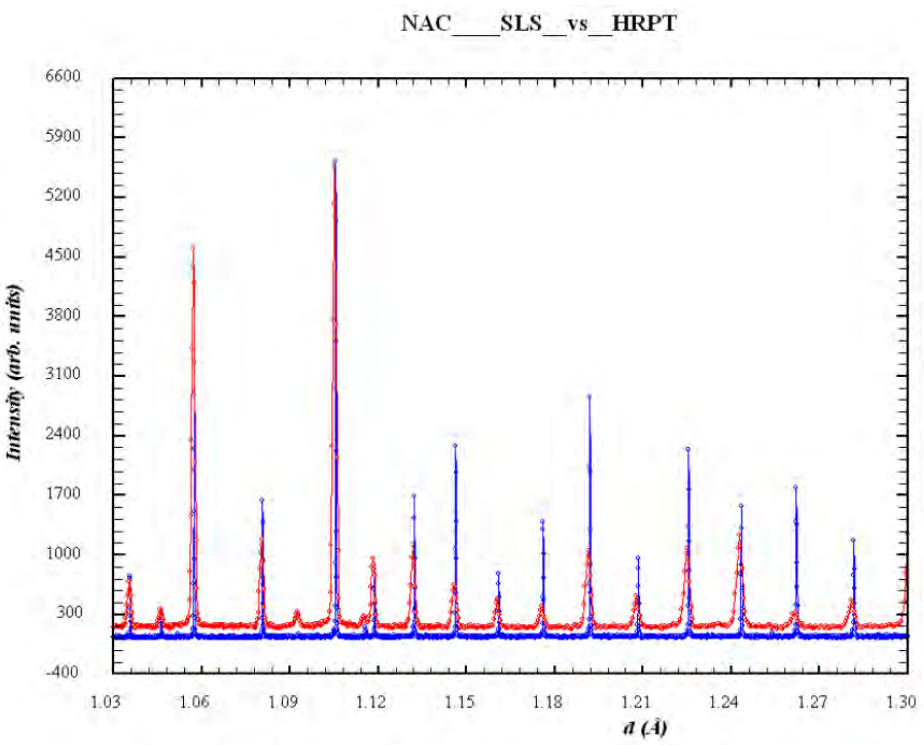


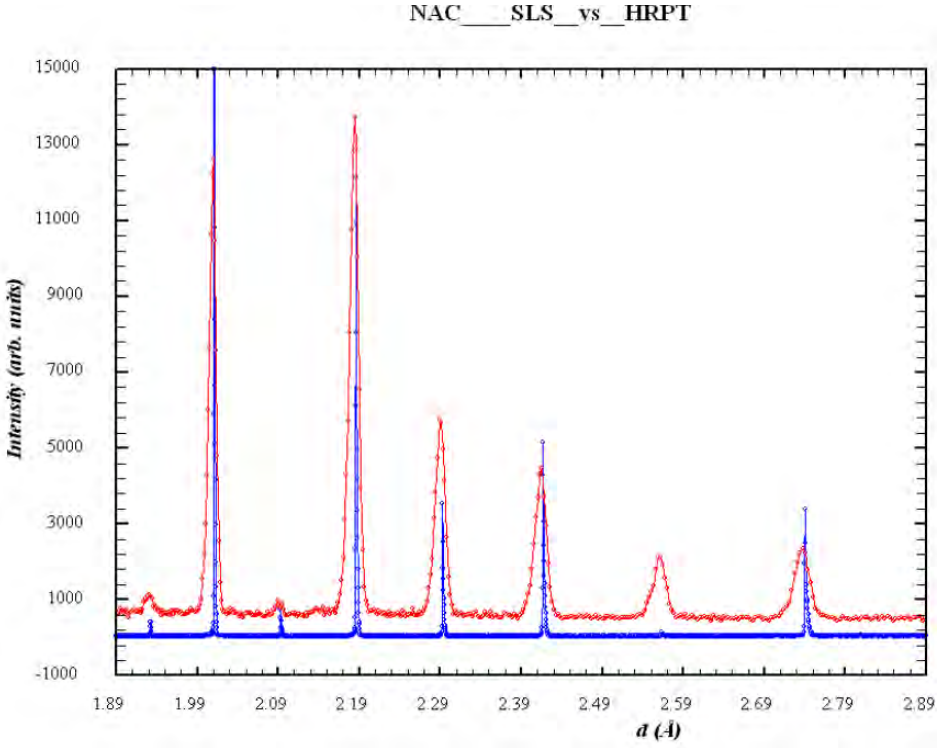


→ Better determination of Atomic Displacement Parameters (adp) by neutrons

X-ray vs Neutron: resolution

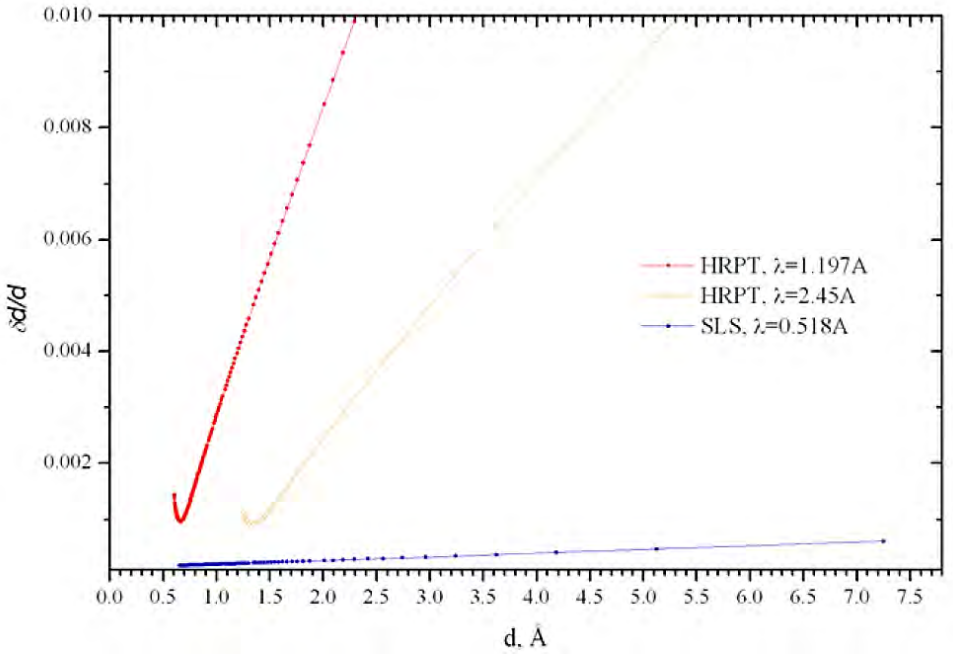
Comparison on a standard compound: $Na_2Al_2Ca_3F_{14}$

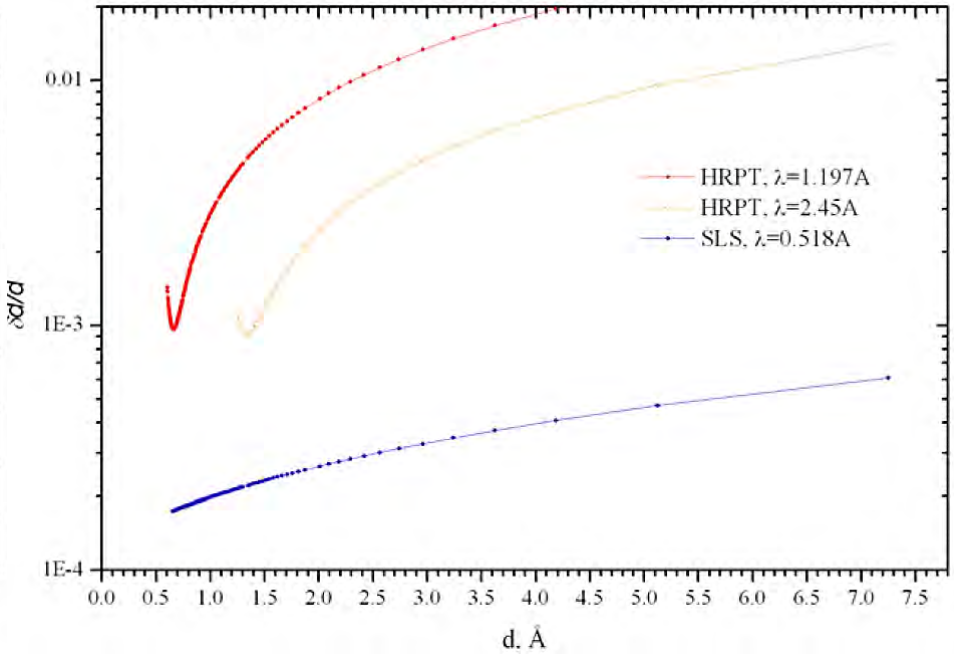




X-ray vs Neutron: resolution

Resolution function



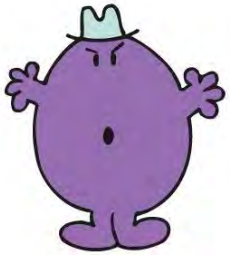


Obvious advantages of the synchrotron X-rays for:
-Unambiguous indexing
-Evaluation of the sample-related broadening effects

Neutron vs X-Ray diffraction

Neutrons

- Bulk
- Light elements
- Contrast (H/D, neighboring elements)
- Magnetic structures

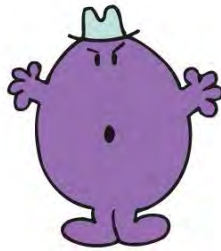


- Low availability
- Small flux, large sample
- Low resolution

X-Rays/synchrotron

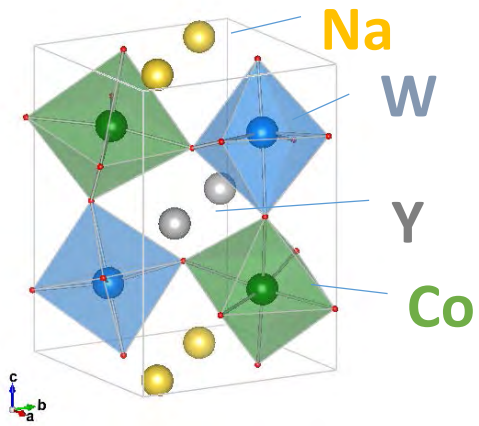
- (Extremely) brilliant source, small sample
- (Very) high resolution
- (Very) small volume probed
- High availability (lab sources)

- Neighbors and isotopes cannot be discriminated
- Light elements hard to detect
- Small volume probed (representative of your sample?)



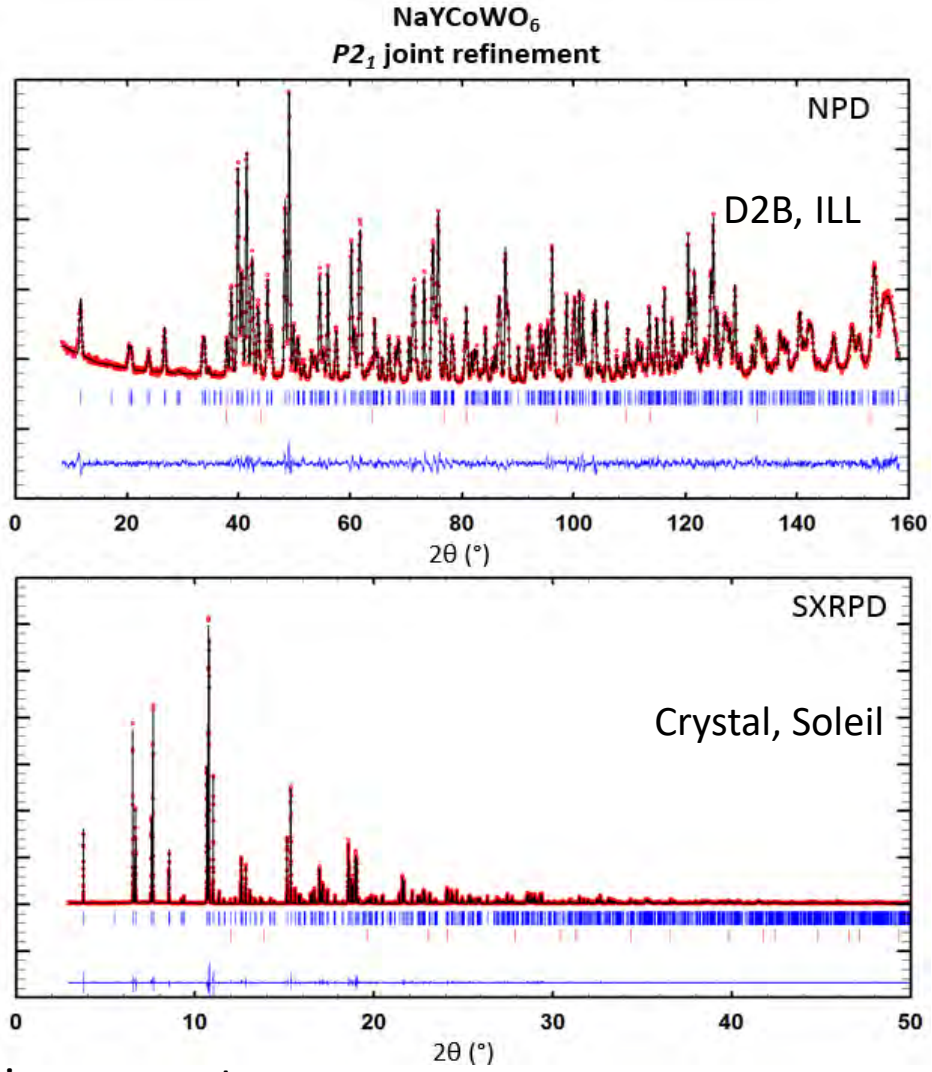
Adapted from F. Damay

X-Ray **AND** Neutron: joint refinement



$NaYCoWO_6$
Doubly ordered perovskite
with polar structure $P2_1$
pseudo-tetragonal

Zuo, P. *et al Inorg. Chem.* **56**, 8478–8489 (2017).



Combine the best of

X-ray: resolution → indexation, lattice parameters

Neutron: sensitive to light elements: oxygen positions, oxygen octahedral distortion

Thank you!