X-ray powder diffraction

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Sommary

- Lesson 1: Fundamental of powder diffraction
- Lesson 2: Collecting Quality Powder Diffraction Data
- Training : Phase ID and semi-quantitative analysis

X-ray powder diffraction

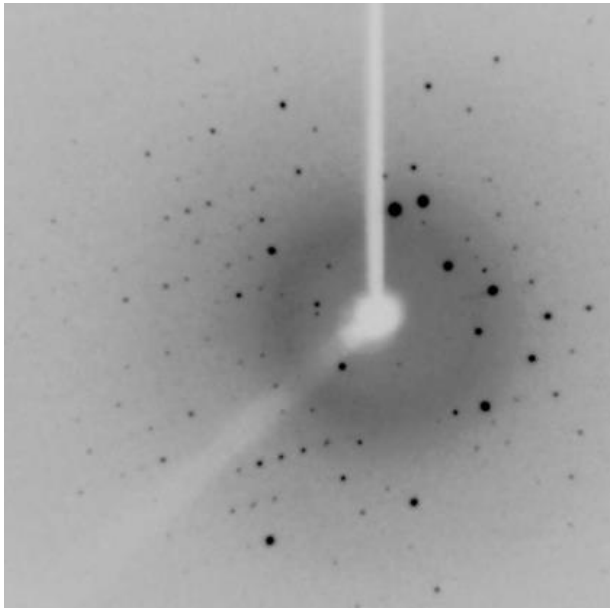
Lesson 1

Fundamantal on powder diffraction

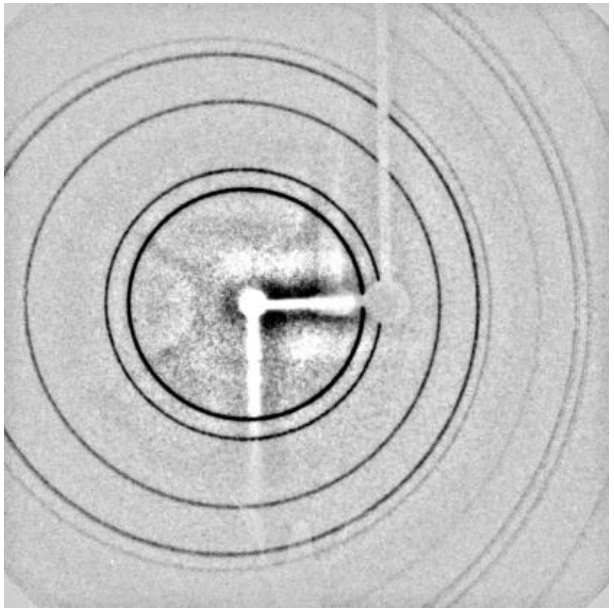
Fundamental of powder diffraction

Polycrystalline sample versus single-crystal

Single crystal diffraction pattern



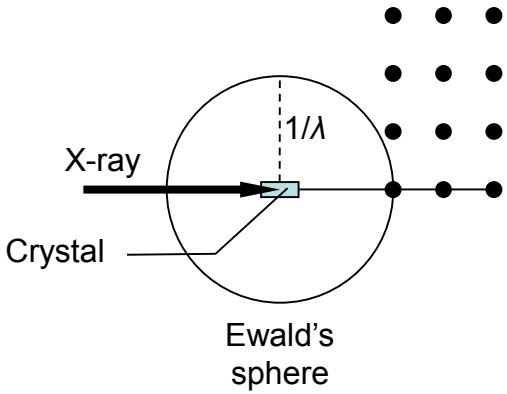
Polycrystalline (powder) diffraction pattern

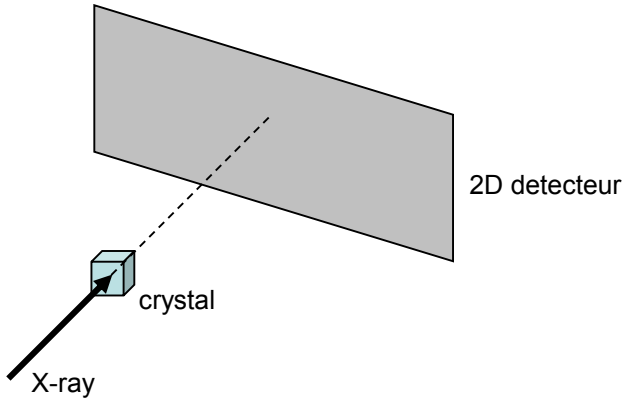


Fundamental of powder diffraction

Single crystal diffraction

- Only one reciprocal space



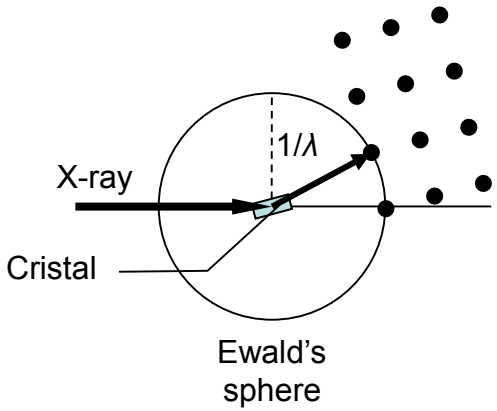


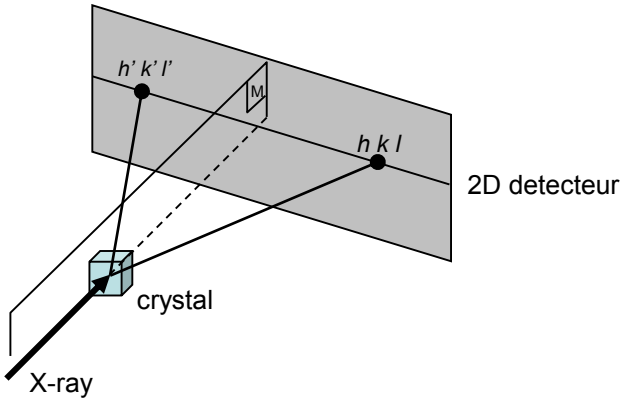
- X-rays will be diffracted by (*hkl*) atomic planes only if the correspondant points (nodes) of rows [*hkl*]* of the reciprocal lattice will coincide with the surface of the Ewald's sphere
- This an other translation of the Bragg law

Fundamental of powder diffraction

Diffraction par un monocristal

- Only one reciprocal space





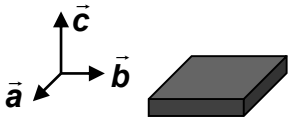
- X-rays will be diffracted by (*hkl*) atomic planes only if the correspondant points of rows [*hkl*]* of the reciprocal lattice will coincide with the surface of the Ewald's sphere
- This an other translation of the Bragg law

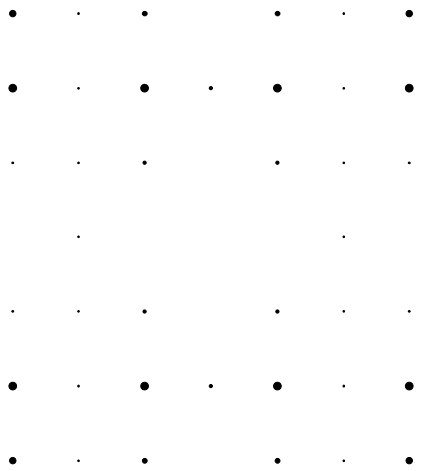
In case of single-crystal diffraction, the reconstruction of the reciprocal space is then possible

Fundamental of powder diffraction

Powder diffraction

✓ **Single-crystal**



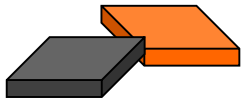


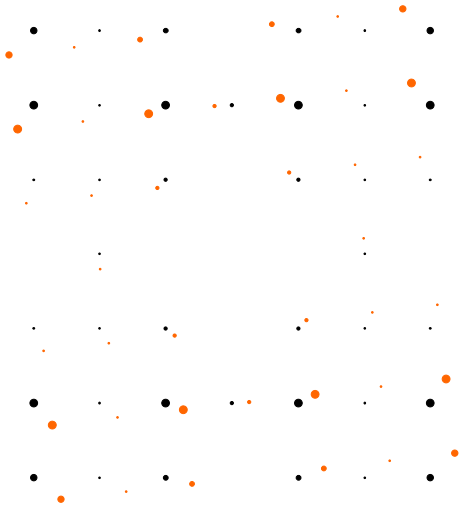
❑ **Only one reciprocal space**

Fundamental of powder diffraction

Powder diffraction

✓ **Two single-crystals**



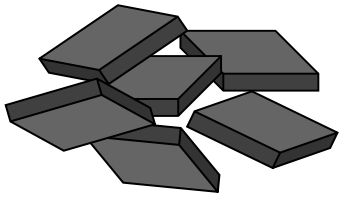


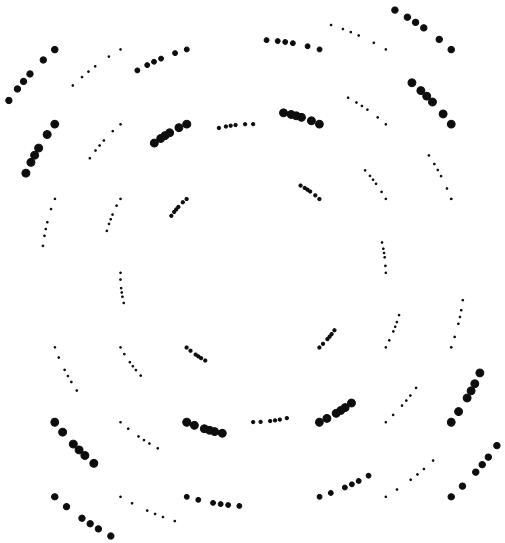
❑ **Two reciprocal spaces with the same origin O**

Fundamental of powder diffraction

Powder diffraction

✓ n single-crystals



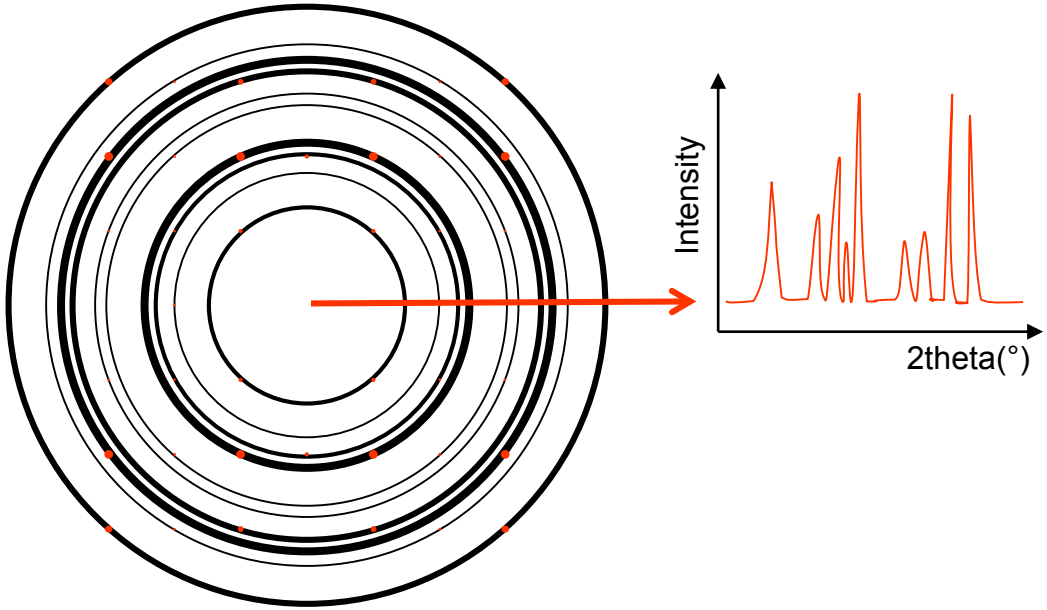


❑ n reciprocal spaces with the same origin O

Fundamental of powder diffraction

Powder diffraction

✓ 10^n single-crystal (crystallites) = polycristalline sample (powder)

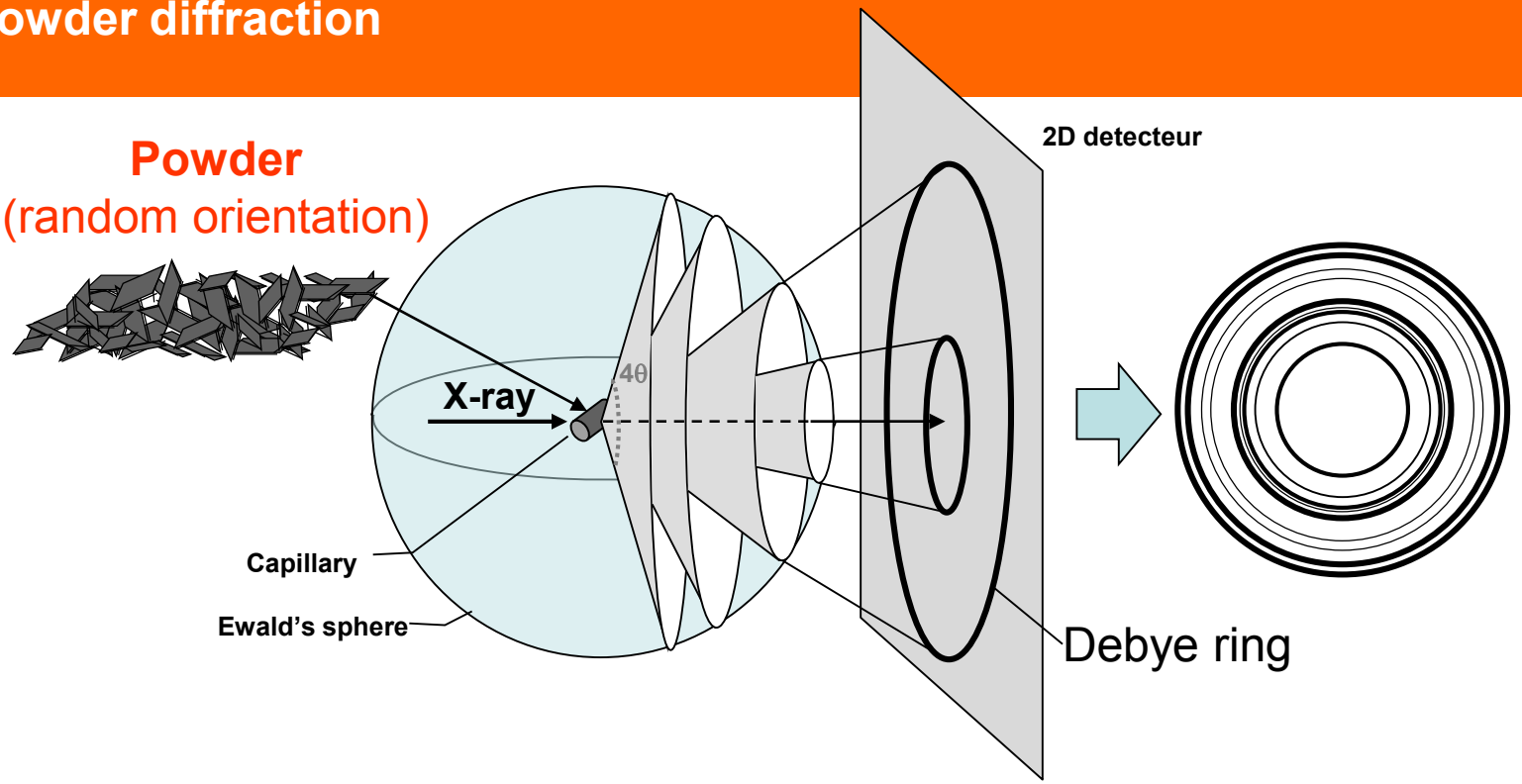


❑ 10^n reciprocal spaces with the same origin O

❑ **With a random orientation of the crystallites, points of the reciprocal space become circles**

Fundamental of powder diffraction

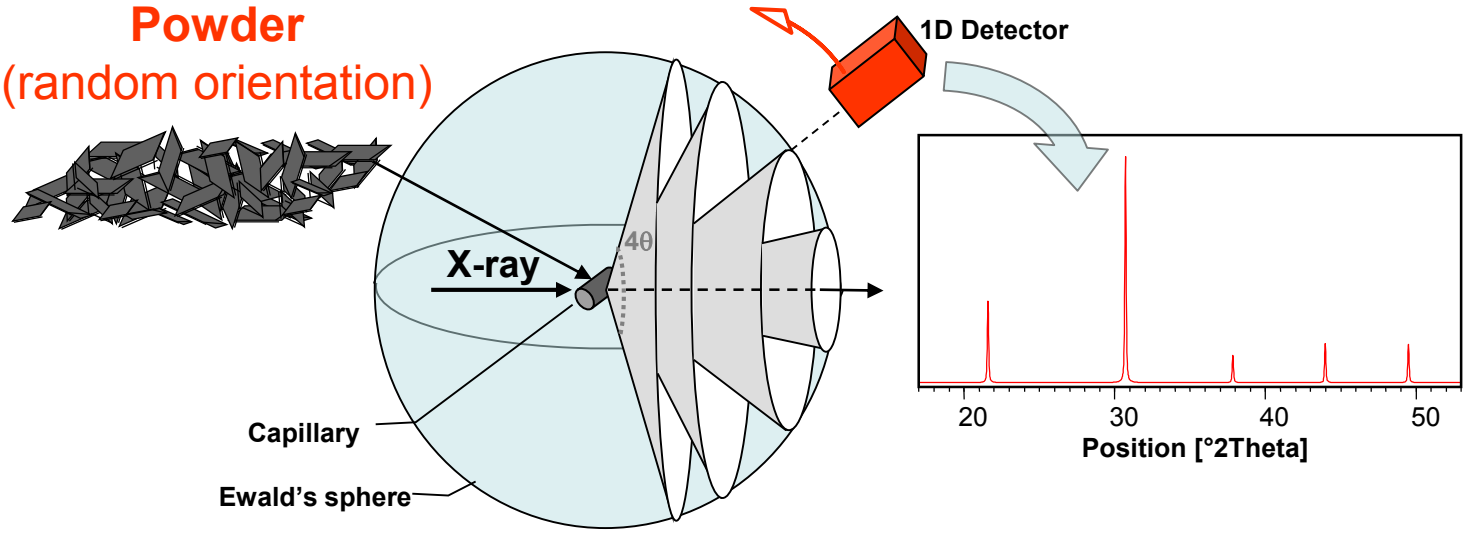
Powder diffraction



- The infinite number of randomly oriented identical reciprocal lattice vectors is the origin of the powder diffraction cones with opening angles 4θ
- These cones form circles with their ends placed on the surface of the Ewald's sphere
- Result = Debye rings on 2D detector

Fundamental of powder diffraction

Powder diffraction



- The infinite number of randomly oriented identical reciprocal lattice vectors is the origin of the powder diffraction cones with opening angles 4θ
- These cones form circles with their ends placed on the surface of the Ewald's sphere
- Result = powder pattern with 1D detector

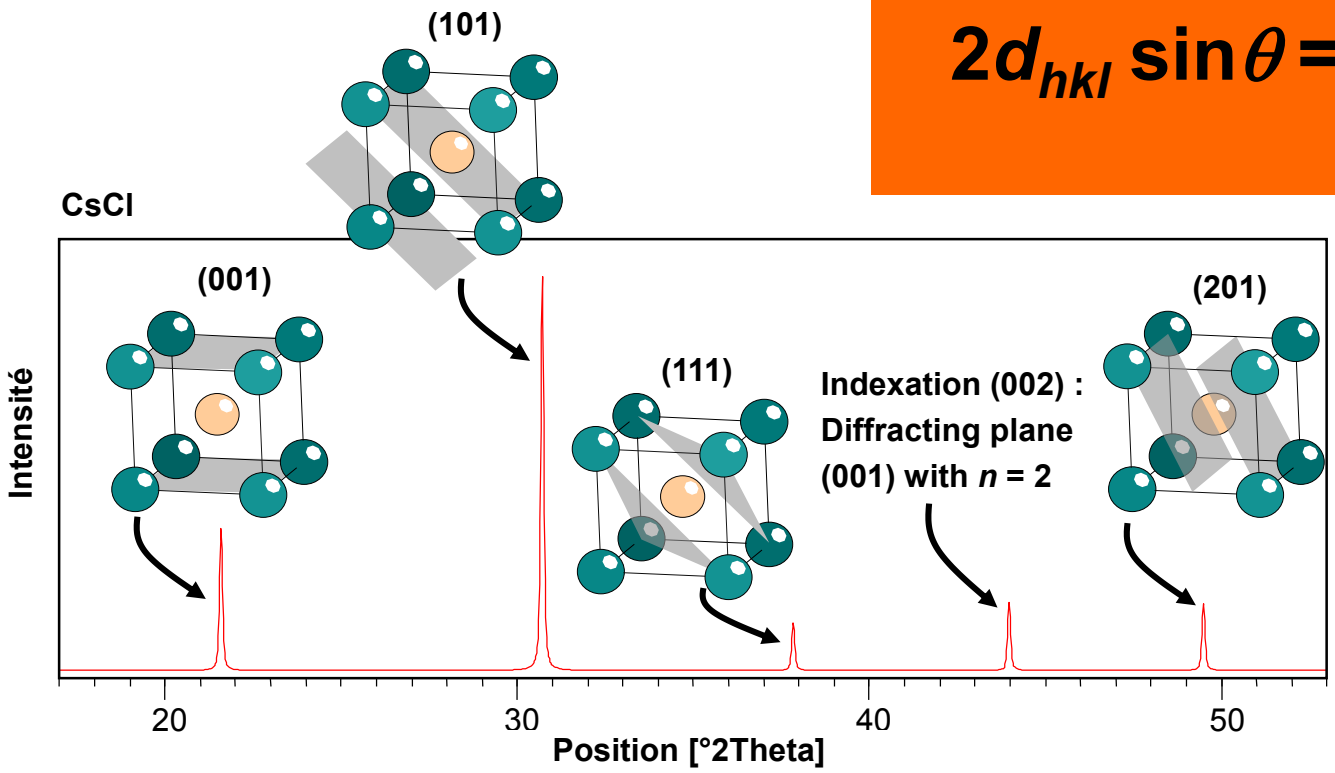
Fundamental of powder diffraction

Powder diffraction

- Peaks indexation

Bragg law

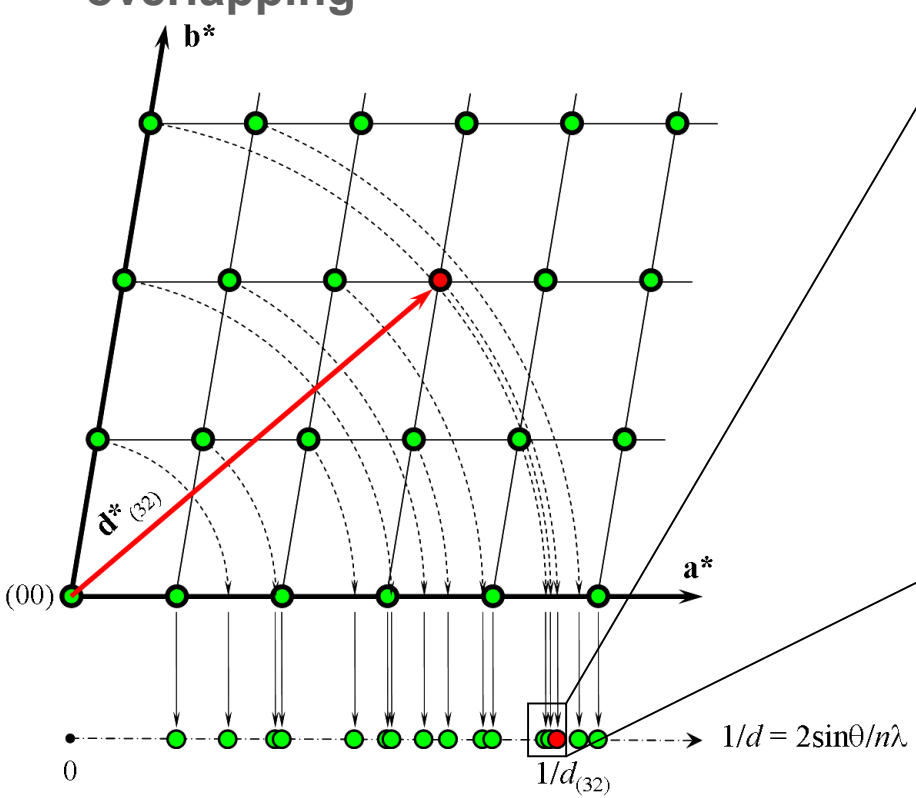
$$2d_{hkl}\sin\theta = n\lambda$$

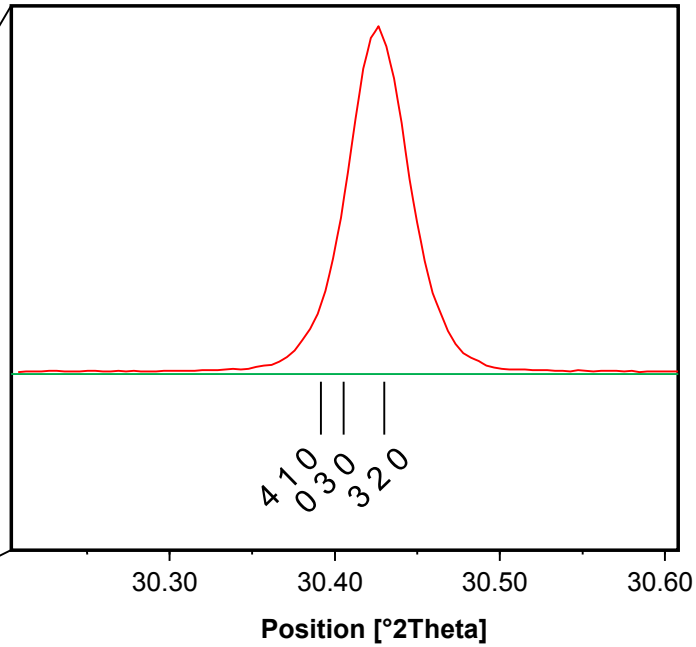


Fundamental of powder diffraction

Powder diffraction

- Projection of the 3D reciprocal space on a 1D direction = reflections overlapping



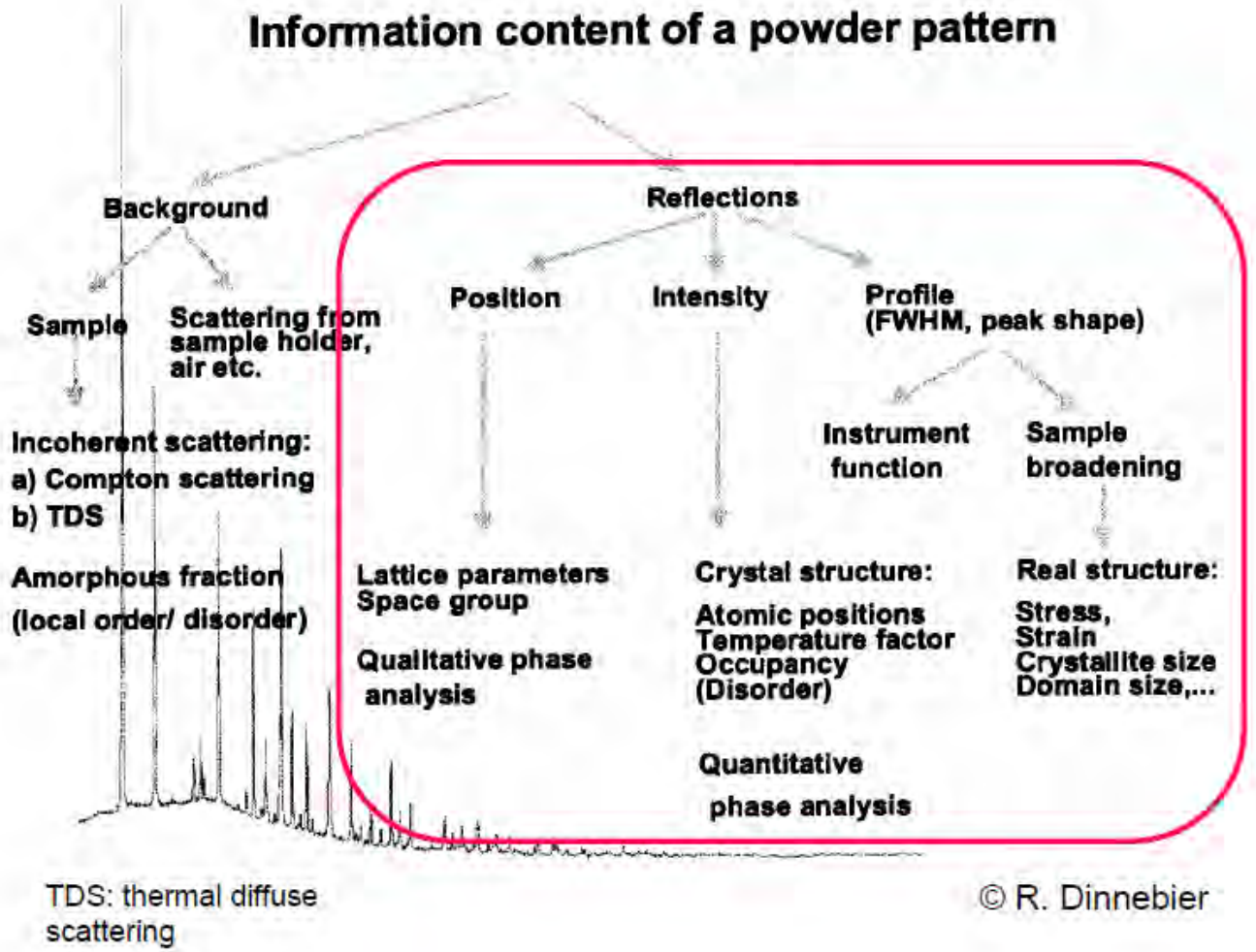


Powder pattern = 1D projection

- Since powder pattern = 1D projection
  - Reconstruction of the 3D reciprocal space no more possible
  - Difficulties to measure the peak intensities I_{hkl}

Fundamental of powder diffraction

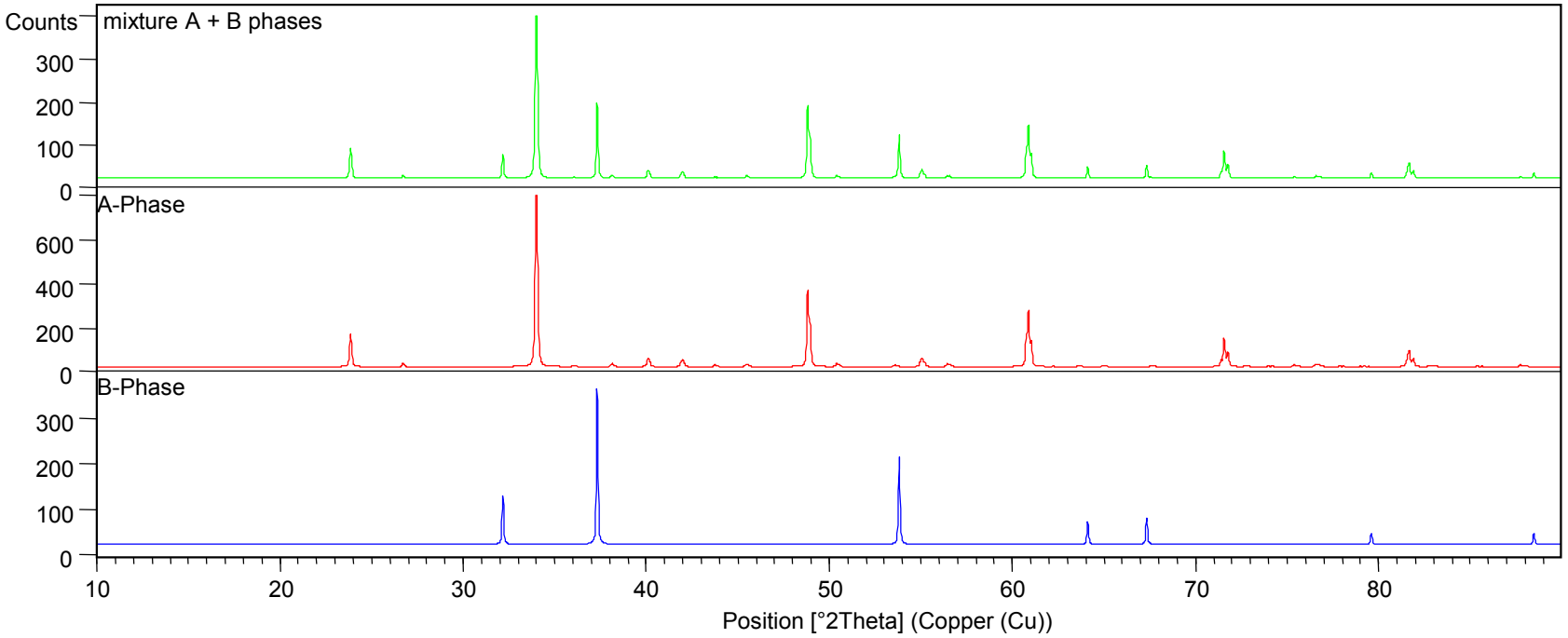
Powder diffraction



Fundamental of powder diffraction

Application: Phases identification

- Direct comparison of PXRD patterns



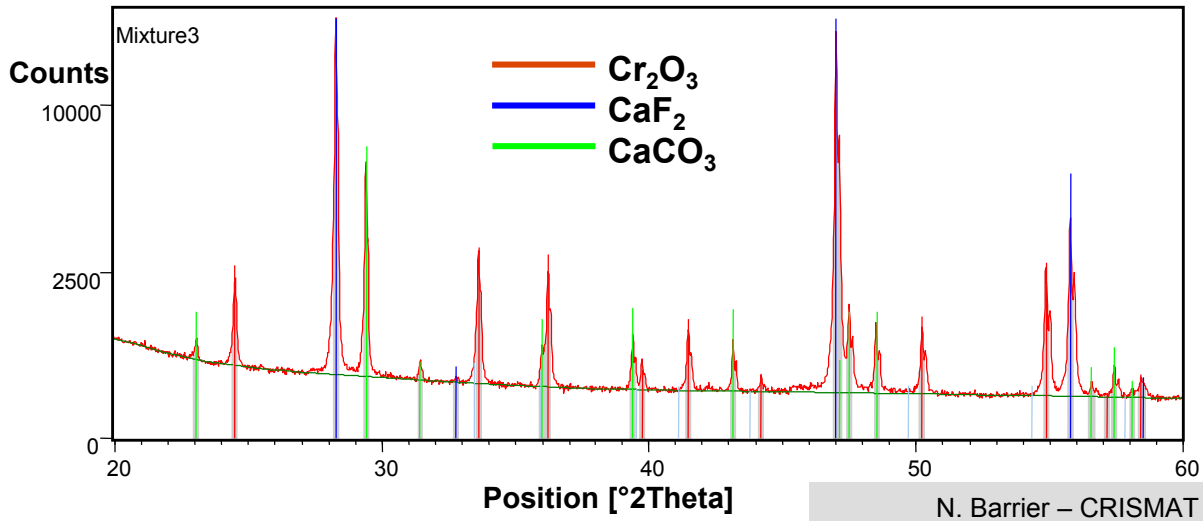
Fundamental of powder diffraction

Application: Phases identification

❑ Automatic phase analysis with data bases

- ✓ **PDF2 and PDF4+ ICDD** (International Centre for Diffraction Data)
- ✓ **COD: Free** (**http://www.crystallography.net/cod/new.html**)
- ✓ **ICSD FIZ Karlsruhe:** Inorganic Crystal Structure Database
- ✓ **CSD:** The Cambridge Structural Database
- ✓ **Yours**

Combines crystal and powder data and can be directly implimented in automatic search programs: HighScore, EVA, Match, Topaz, etc…



Fundamental of powder diffraction

Application: quantitative analysis

Peak list : SiO2

No.	*h*	*k*	*ℓ*	d [A]	2θ[°]	I [%]
1	1	0	0	4.25499	20.860	16.0
2	1	0	1	3.34347	26.640	100.0
3	1	1	0	2.45687	36.544	9.0
4	1	0	2	2.28149	39.465	8.0
5	1	1	1	2.23613	40.300	4.0
6	2	0	0	2.12771	42.450	6.0
7	2	0	1	1.97986	45.793	4.0
8	1	1	2	1.81796	50.139	13.0
9	0	0	3	1.80174	50.622	1.0
10	2	0	2	1.67173	54.875	4.0
11	1	0	3	1.65919	55.325	2.0
12	2	1	0	1.60827	57.235	1.0
13	2	1	1	1.54153	59.960	9.0

Name and formula

Chemical formula: **SiO2**

Crystallographic parameters

Crystal system: **Hexagonal** Z: **3,00**

a (Å) = 4.9134 **b (Å) = 4.9134** **c (Å): 5.4052**

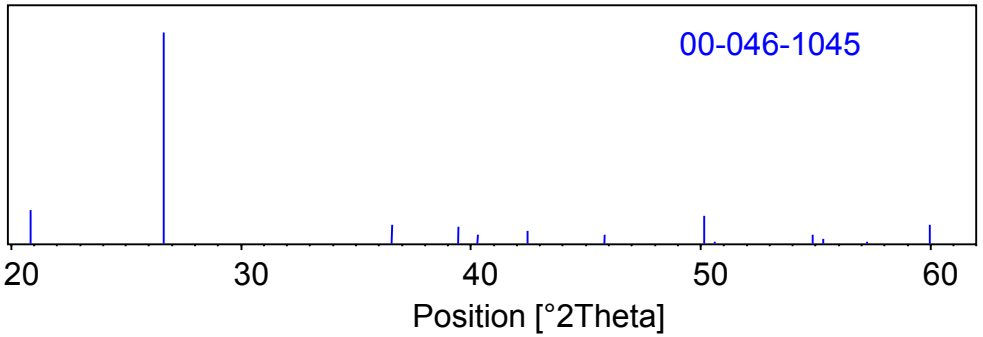
γ (°) = 120.0

Space group: **P3221** Space group number: **154**

Calculated density (g/cm^3): **2.65**

Volume of cell (10^6 pm^3): **113.01** RIR: **3.41**

Stick Pattern

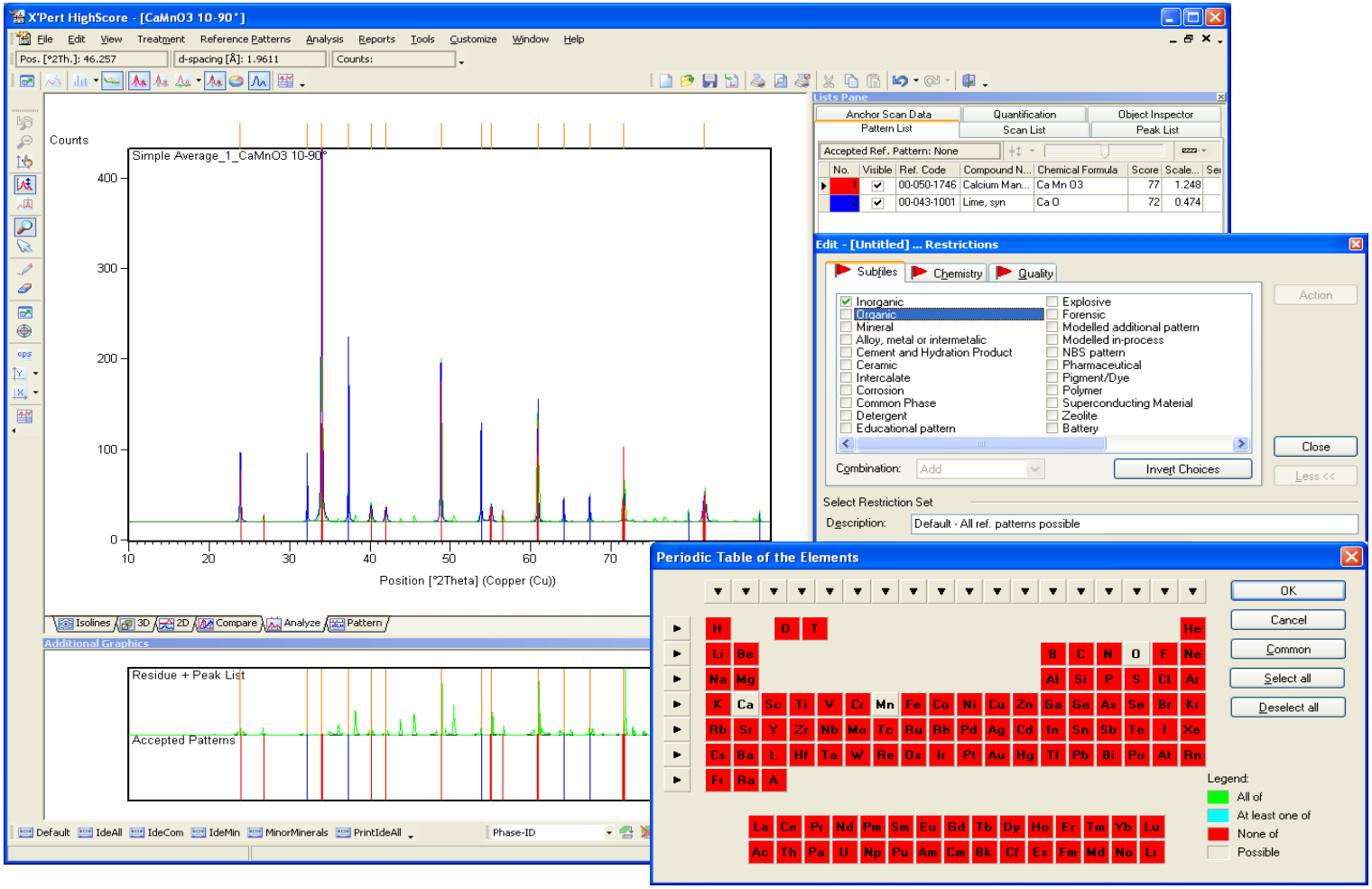


- If you find all those peaks in the XRD pattern it means that SiO_2 is present in the powder sample

Fundamental of powder diffraction

Application: Phases identification

- Automatic phase analysis with data bases

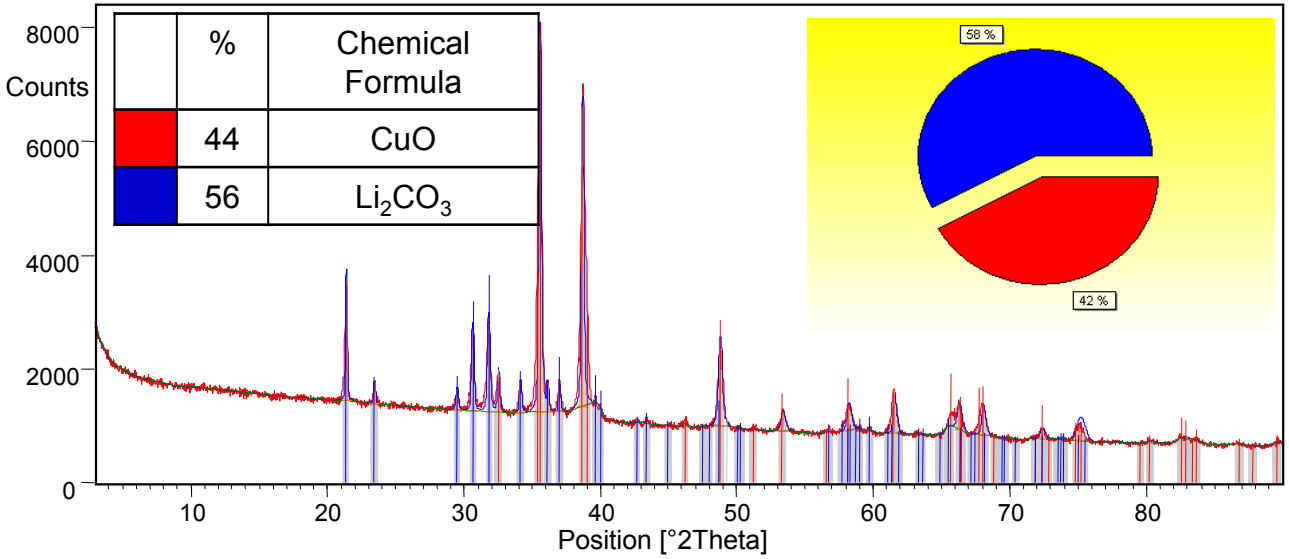


Fundamental of powder diffraction

Application: Semi-quantitative analysis

- Also available in all softwares for phase ID (HighScore, Eva, WinXpow, etc.)
- Simple principe : $I_i \propto C_i$
- To do a quantitative analysis it needs to introduced a standard sample (phase 0) in known quantity to calculate a ratio :

$$\frac{I_i}{I_0} = \frac{C_i}{C_0}$$



Fundamental of powder diffraction

Application: Semi-quantitative analysis

- We can do without standard sample :
  - Rietveld method (the most accurate but need more time)
  - Semi-quantitative method (less accurate but very fast and easy)
- To take into account the absorption phenomena in sample that affect the diffraction intensities we need to know for each cristalline phase the RIR factor (Reference Intensity Ratio)
- The RIR method scales all diffraction data to a standard : alpha-Al_2O_3
- For a mix of to phases we can write

$$\frac{C_i}{C_j} = \frac{RIR_j}{RIR_i}\frac{I_i}{I_j}$$

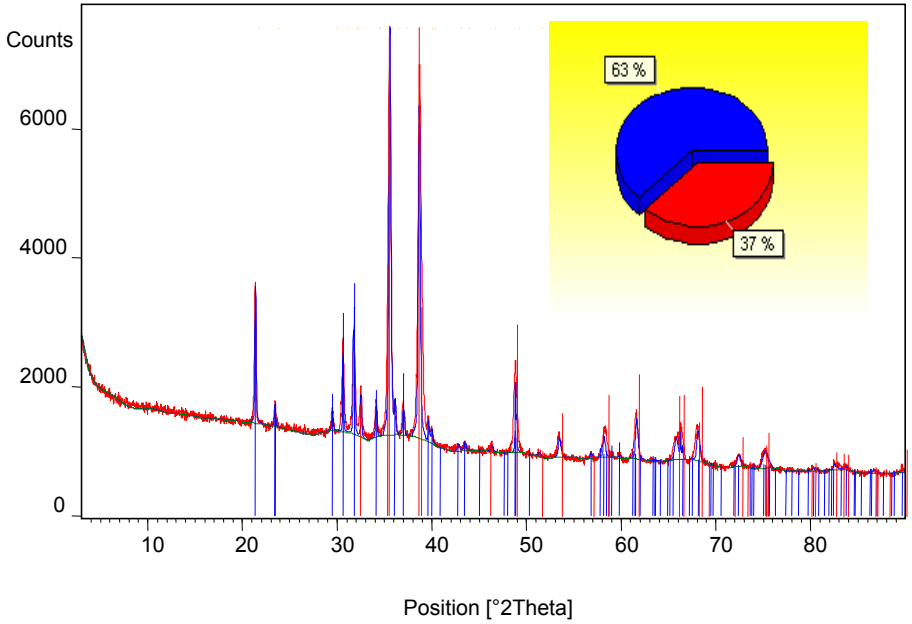
- We need to solve the following system of equations

$$\begin{cases} \frac{C_i}{C_j} = \frac{RIR_j}{RIR_i}\frac{I_i}{I_j} \\ C_i + C_j = 1 \end{cases}$$

Fundamental of powder diffraction

Application: Semi-quantitative analysis

- Example :



Semi-quantitative analysys of a mixture of CuO and LiCO3 by HighScore (PANalytical).

	Phase	Intensity (a.u.)	RIR
	CuO	1,180	4,98
	Li_2CO_3	0,309	0,76

$$\begin{cases} \dfrac{C_{CuO}}{C_{Li_2CO_3}} = \dfrac{RIR_{Li_2CO_3}}{RIR_{CuO}} \dfrac{I_{CuO}}{I_{Li_2CO_3}} \\ C_{CuO} + C_{Li_2CO_3} = 1 \end{cases}$$

$$\begin{cases} \dfrac{C_{CuO}}{C_{Li_2CO_3}} = \dfrac{0,76}{4,98} \dfrac{1,180}{0,309} = 0,5828 \\ C_{CuO} + C_{Li_2CO_3} = 1 \end{cases}$$

$$\begin{cases} C_{CuO} = 0,37 \\ C_{Li_2CO_3} = 0,63 \end{cases}$$

For 1 g of powder sample, we have 0,37 g of CuO and 0,63 g of Li_2CO_3

X-ray powder diffraction

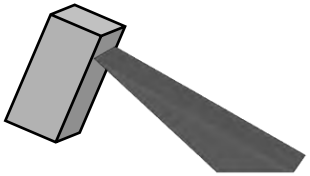
Lesson 2

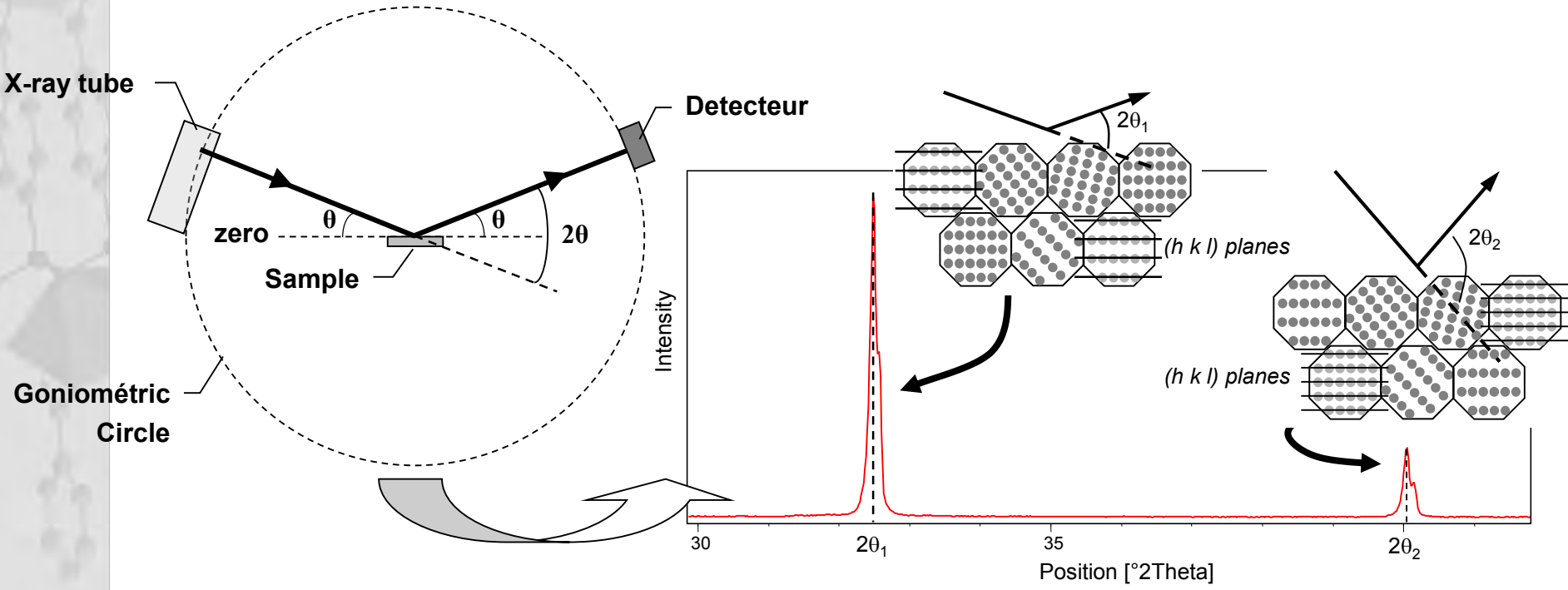
Collecting Quality Powder Diffraction Data

PXRD pattern measurement

Geometries of X-ray lab diffractometers

- **Bragg – Brentano**
  - linear and divergent incident beam
  - large area irradiated on the sample surface at low angle
  - flat sample and its surface is tangent to the diffractometer axis
  - Only the (*hkl*) planes parallel to the surface will give rise to diffraction

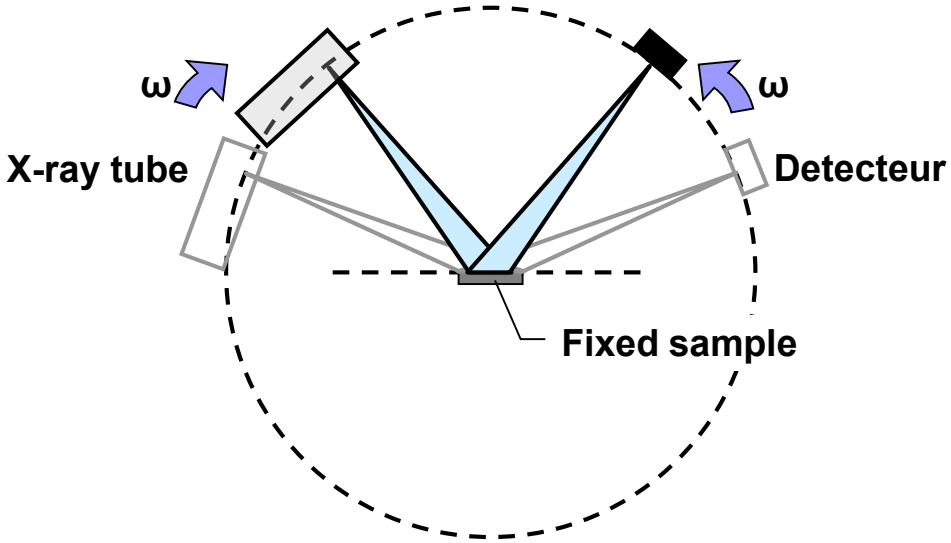




PXRD pattern measurement

Geometries of X-ray lab diffractometers

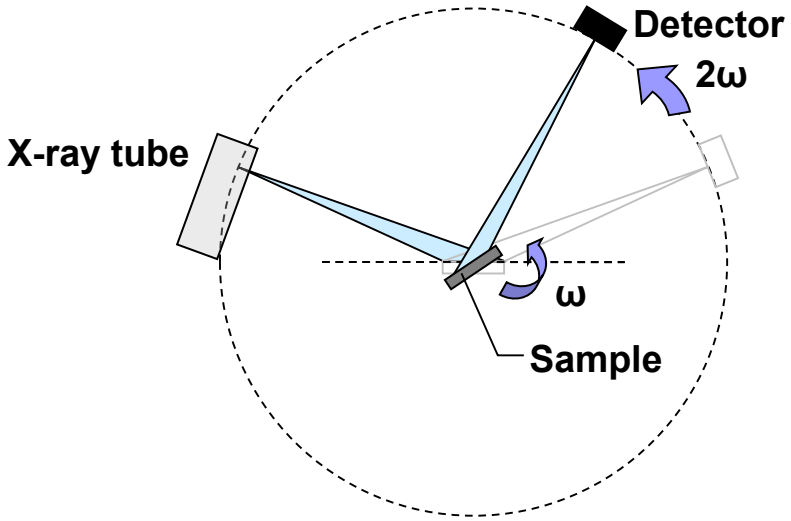
- **Two Bragg – Brentano configurations (reflection mode)**
  - **Theta – theta**
    - ✓ Fixed flat sample in a horizontal position
    - ✓ X-ray tube and detector rotate simultaneously in opposite directions at a constant and adjustable speed $\varpi = d\theta/dt$.



PXRD pattern measurement

Geometries of X-ray lab diffractometers

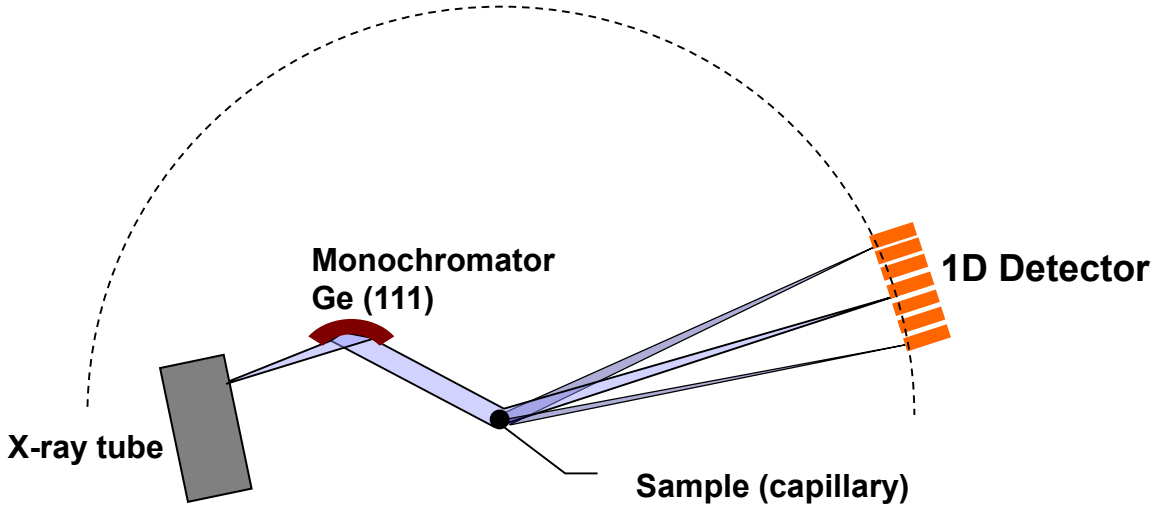
- **Two Bragg – Brentano configurations (reflection mode)**
  - **Theta – 2theta**
    - ✓ Fixed X-ray tube
    - ✓ The sample and the detector rotate simultaneously in the same direction with different speeds, respectively ϖ and 2ϖ ($\varpi = d\theta/dt$)

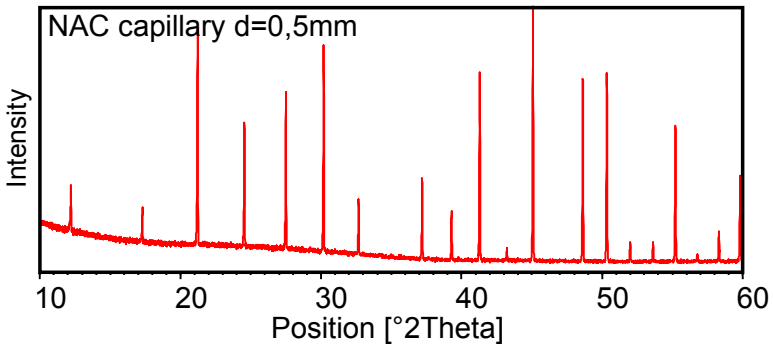


PXRD pattern measurement

Geometries of X-ray lab diffractometers

- Debye-Scherrer (transmission mode)
  - Focused beam on the detector via a mirror or a monochromator
  - Sample in a capillary in the centre of the diffractometer

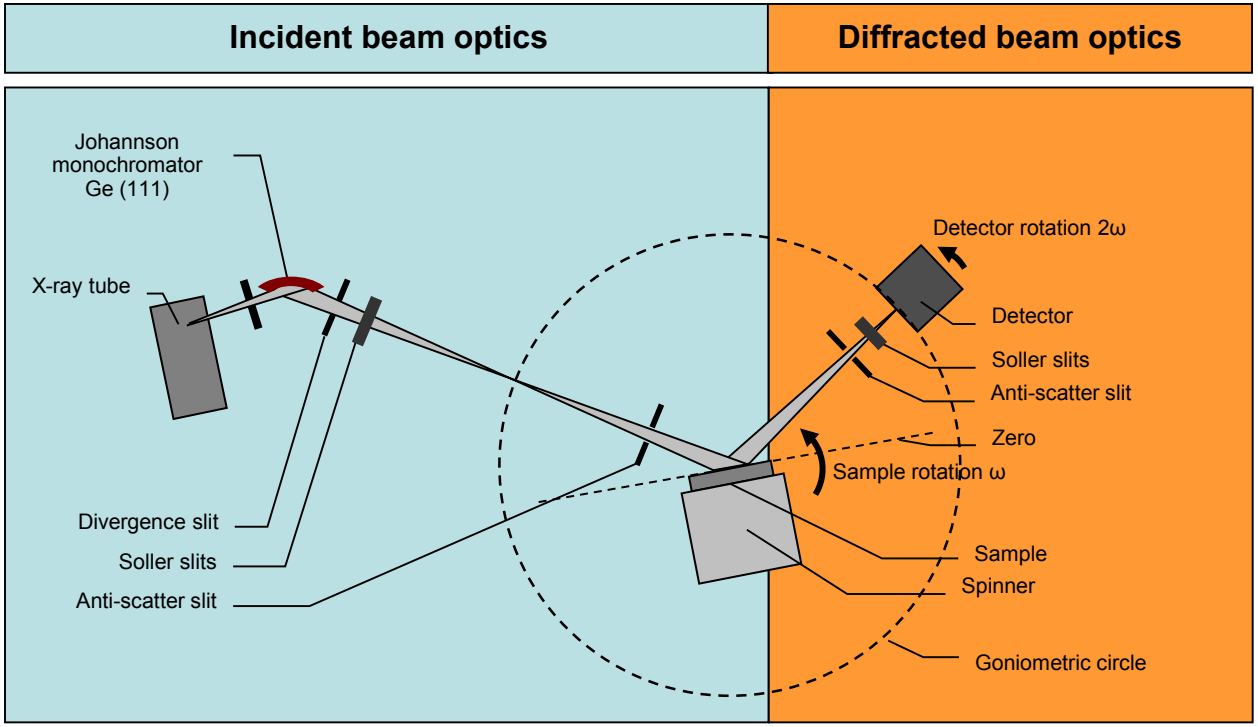


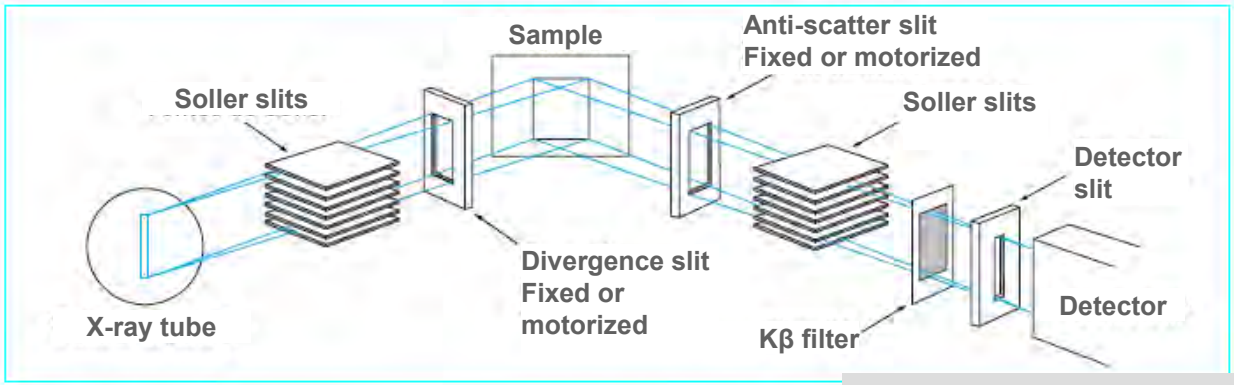


FWHM ~ 0.05°(2θ)

PXRD pattern measurement

Optics of X-ray lab diffractometers

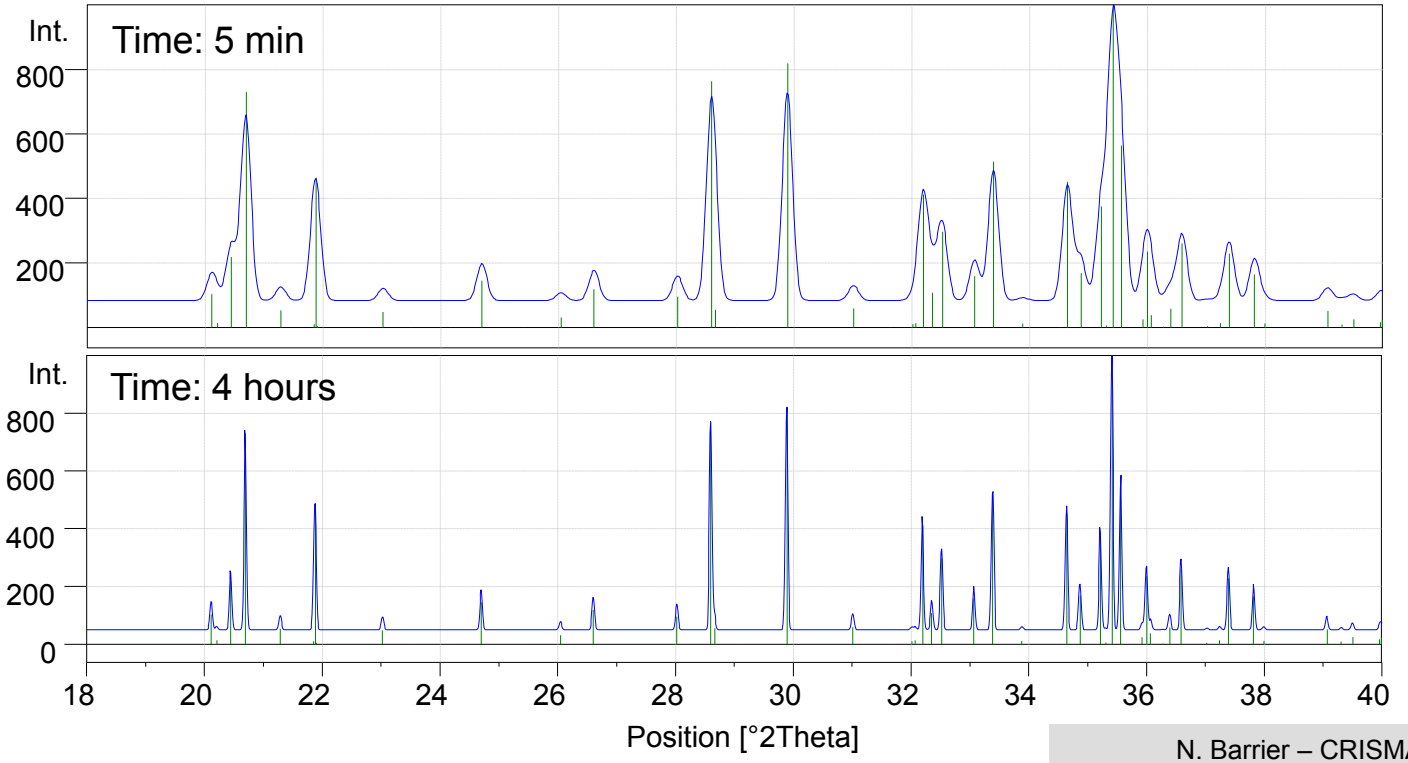




PXRD pattern measurement

Optics of X-ray lab diffractometers

- **Be smart ! Adapt optics to what you want to do with your data**
  - **Phase analysis**
    - ✓ High flux for rapid scan = **large opening slits** and low resolution
  - **Rietveld refinement**
    - ✓ High resolution to separate reflections = **small opening slits** and low flux



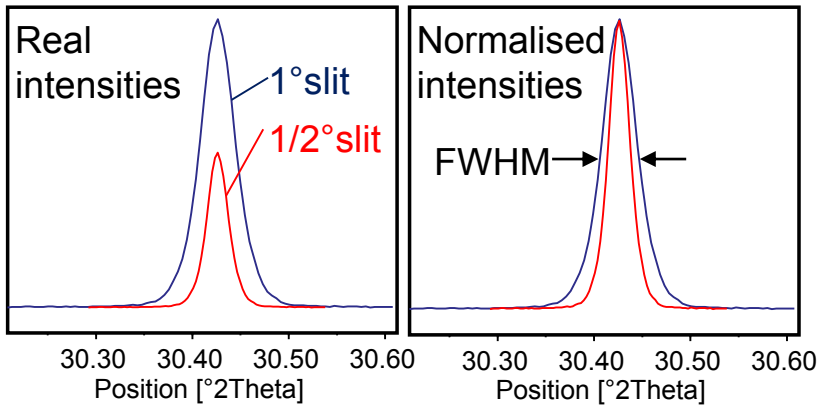
Phase analysis

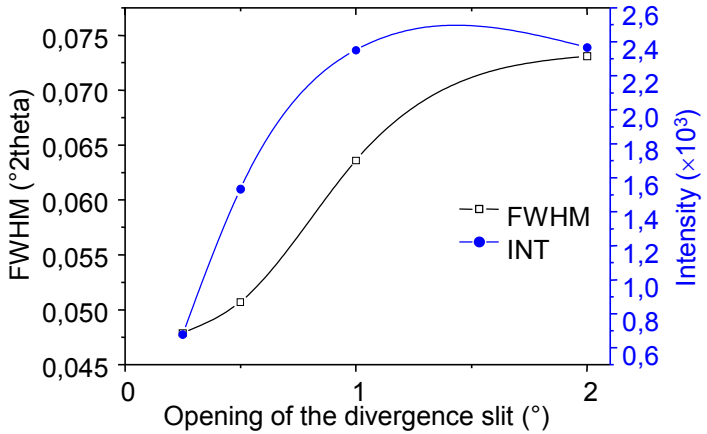
Rietveld refinement

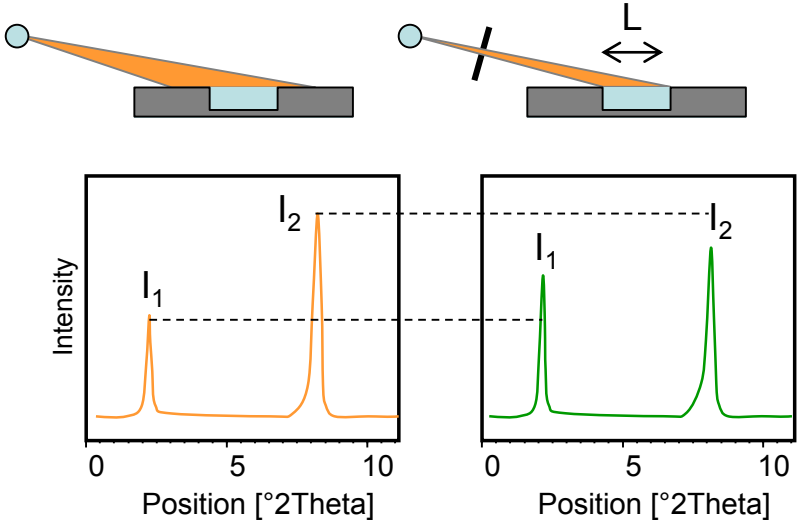
PXRD pattern measurement

Optics of X-ray lab diffractometers

- **Divergence slit**
  - Reduce the in plane divergence of the beam
  - Reduce the Full Width at Half Maximum (FWHM) of the peaks
  - Avoid over-irradiation of the sample at low angles (beam larger than the sample)







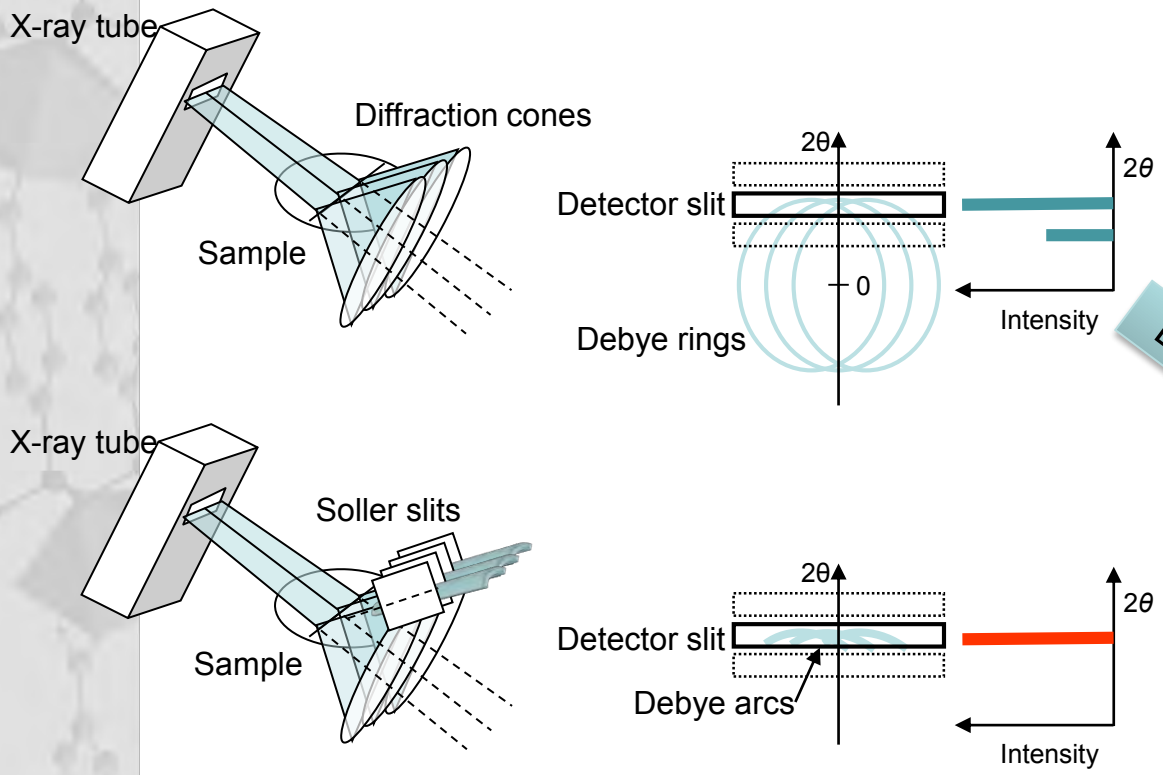
False I_1/I_2 ratio **Good I_1/I_2 ratio**

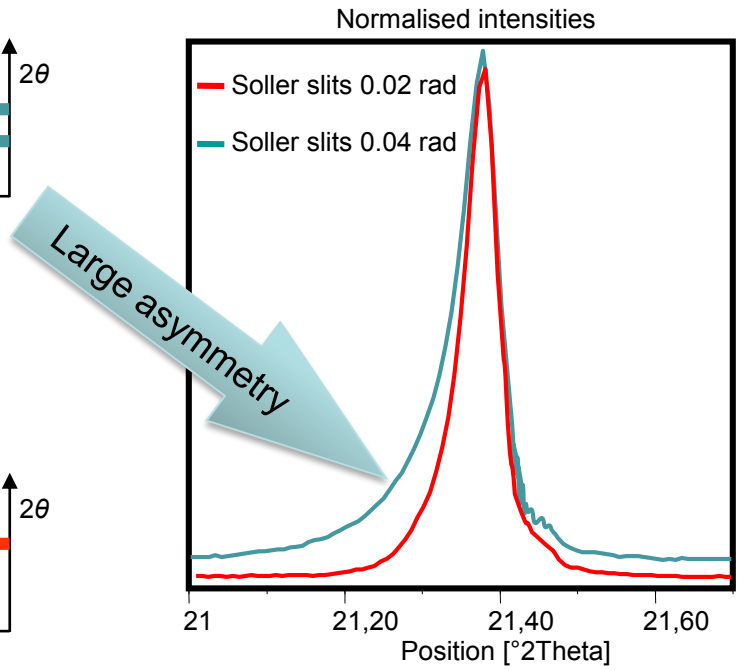
$$L=\frac{2R\cdot sin\theta\cdot\tan(\frac{\alpha}{2})}{sin^2\theta-con^2\theta\cdot tan^2(\frac{\alpha}{2})}$$

PXRD pattern measurement

Optics of X-ray lab diffractometers

- **Soller slits**
  - Reduce the peak asymmetry at low angles

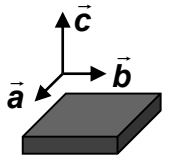




PXRD pattern measurement

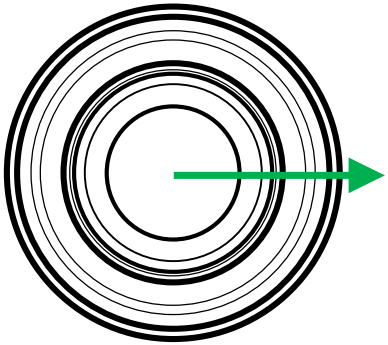
Sample preparation

- Ideal size of the cristallites : 1 < Ø < 10 µm
- Try to avoid preferential orientation of the crystallites

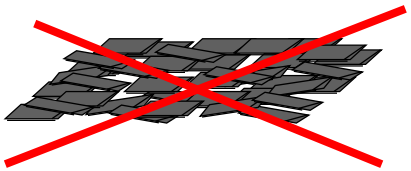


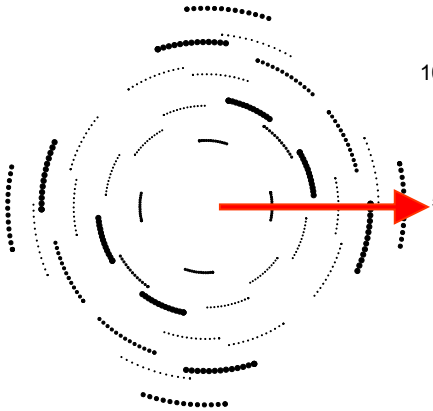
Crystallite

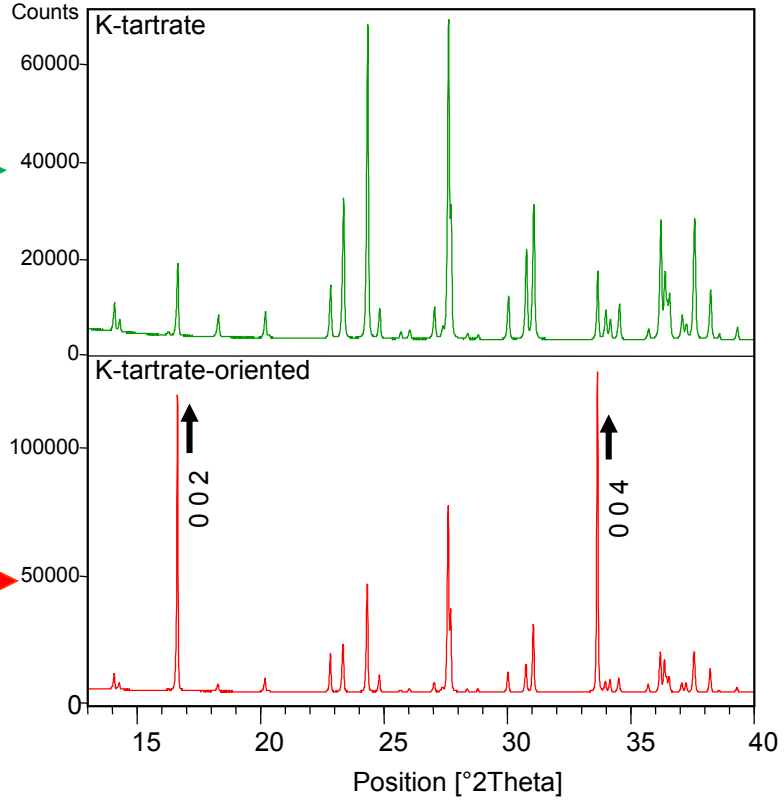
Powder
(random orientation)



Powder
(oriented cristallites)

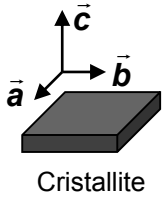


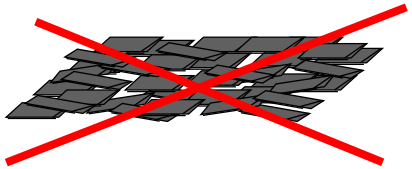




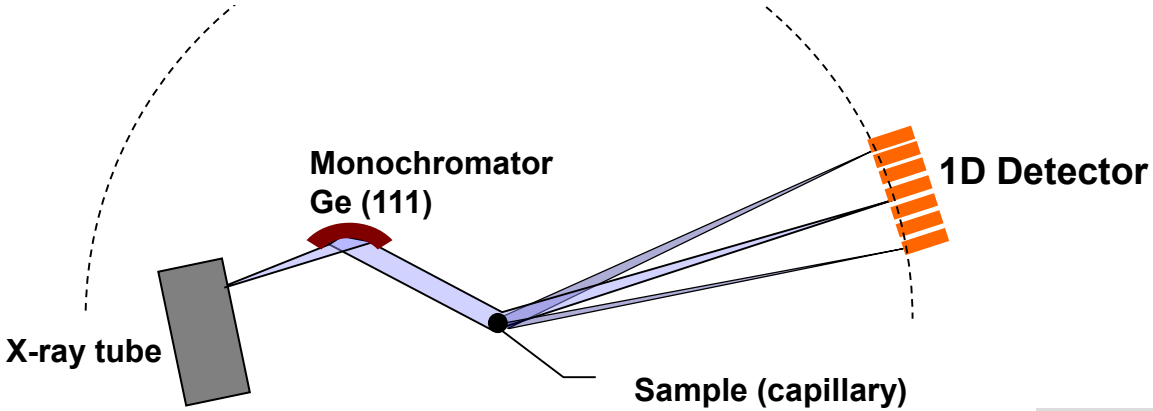
PXRD pattern measurement

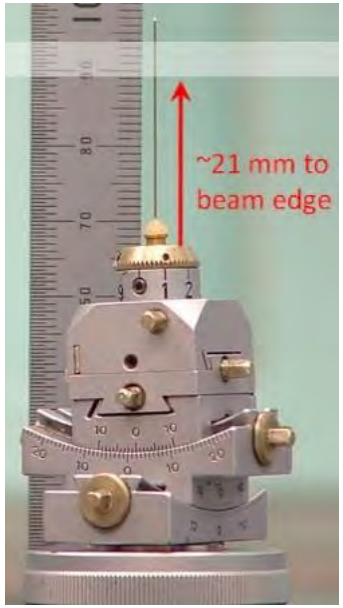
Sample preparation





- **Various tips to limit the preferential orientation**
  - The most efficient: use of capillary (Debye Scherrer geometry)
    - Small quantity of powder
    - Useful for air-sensitive samples
    - Not suitable for absorbent materials

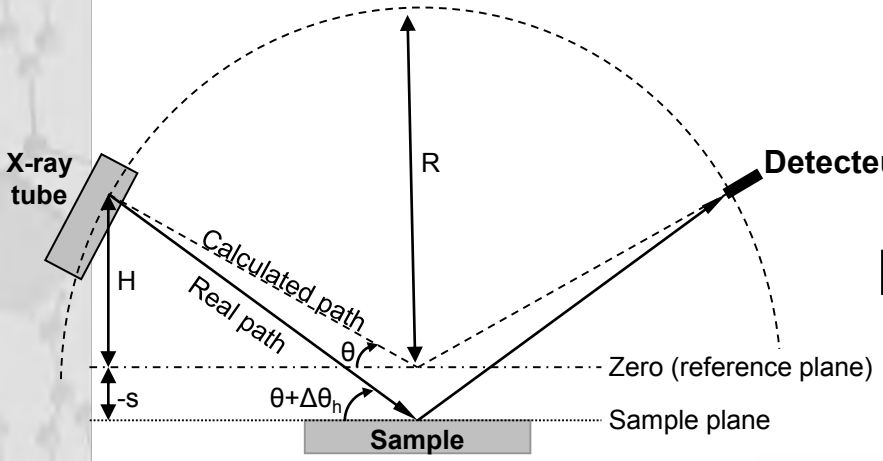


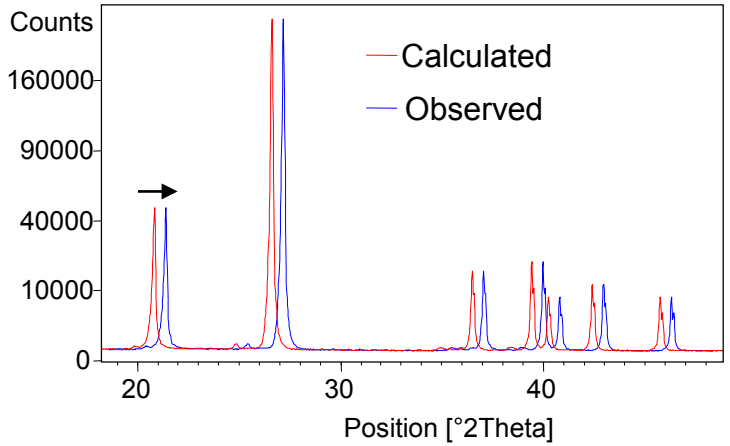


PXRD pattern measurement

Sample preparation

- Sample height: avoid over- or under-thickness of the sample

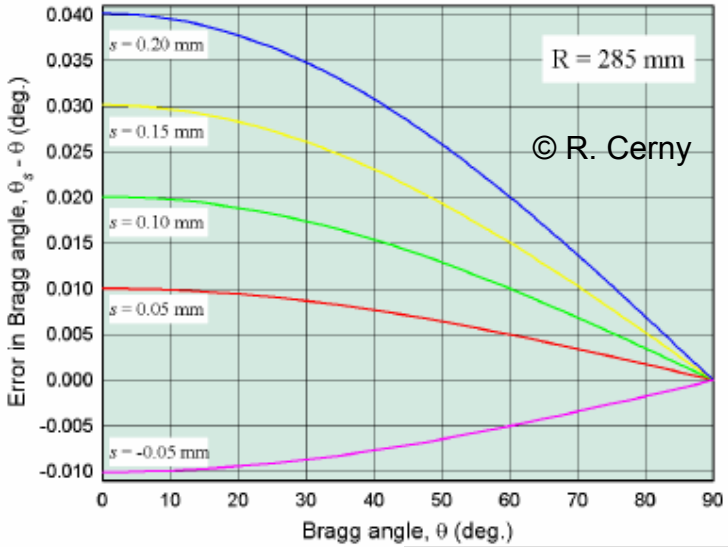




$$\Delta 2\theta(rad) = 2\theta_{obs} - 2\theta_{calc} = -\frac{2s\cos\theta}{R}$$

s: height offset from the centre of the diffractometer (zero)

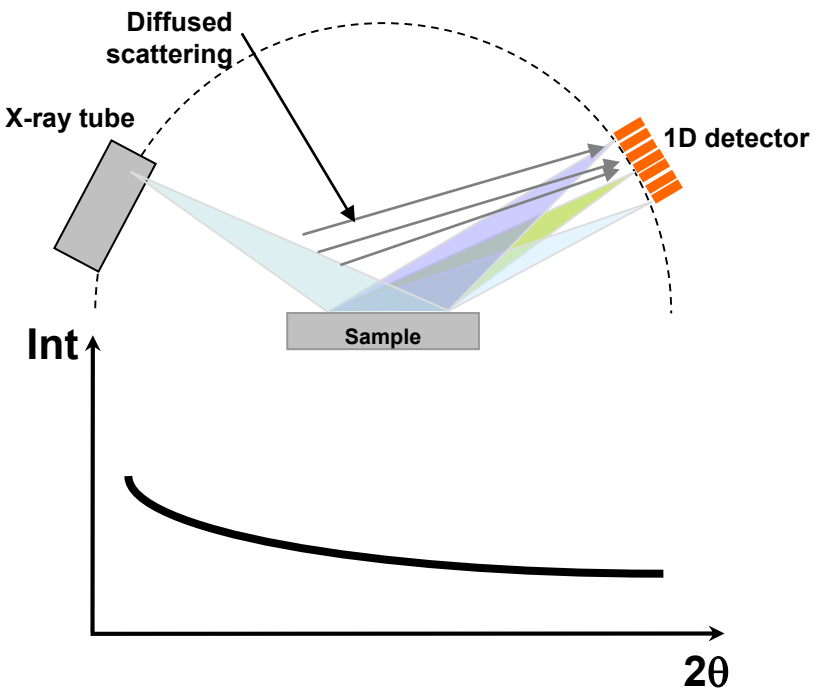
R: goniometer radius

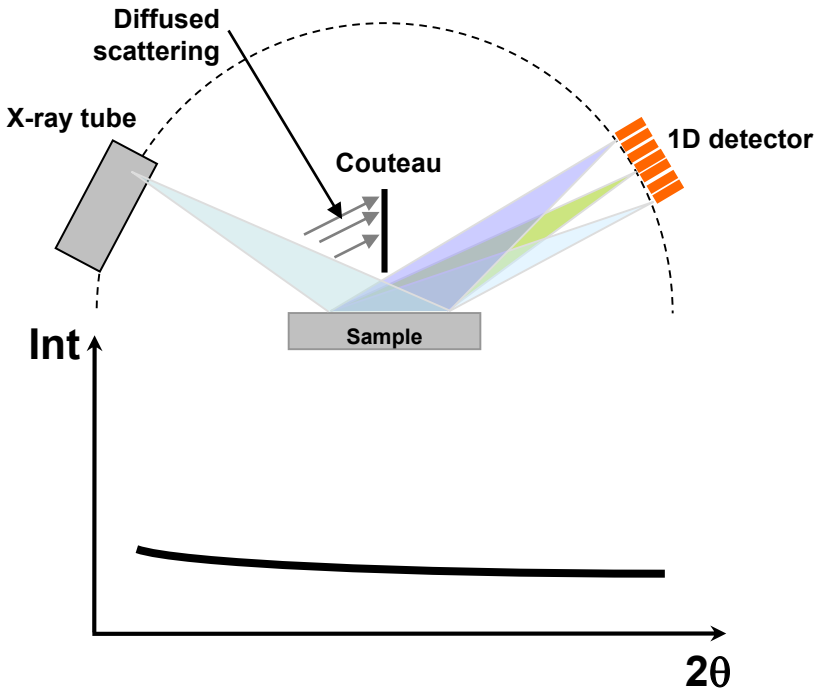


PXRD pattern measurement

Optics of X-ray lab diffractometers

- Anti-scatter systems: slits and knife
  - reduces the background at low angles
  - improves the signal-to-noise ratio

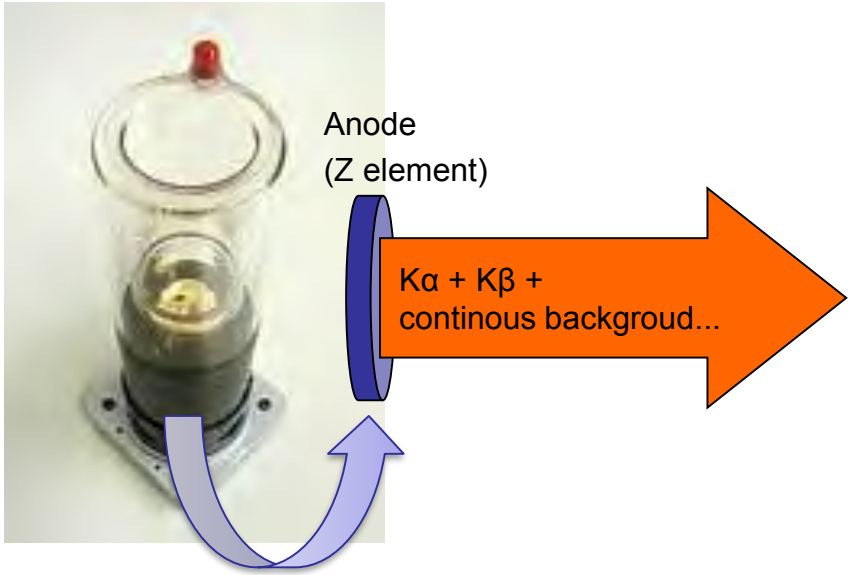


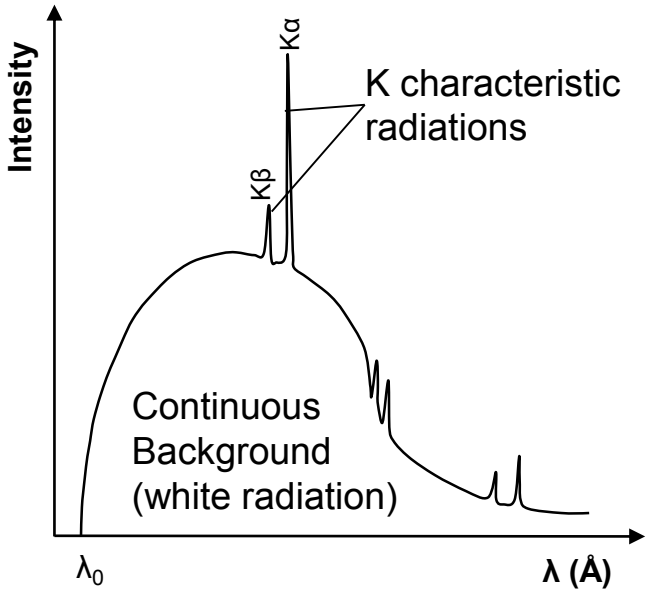


PXRD pattern measurement

Optics of X-ray lab diffractometers

- **Monochromatization**
  - Reduces the intensity of white radiation, and eliminating the undesirable characteristic wavelengths from the X-ray spectrum
  - Reduces the intensity of the fluorescence radiations coming from the sample

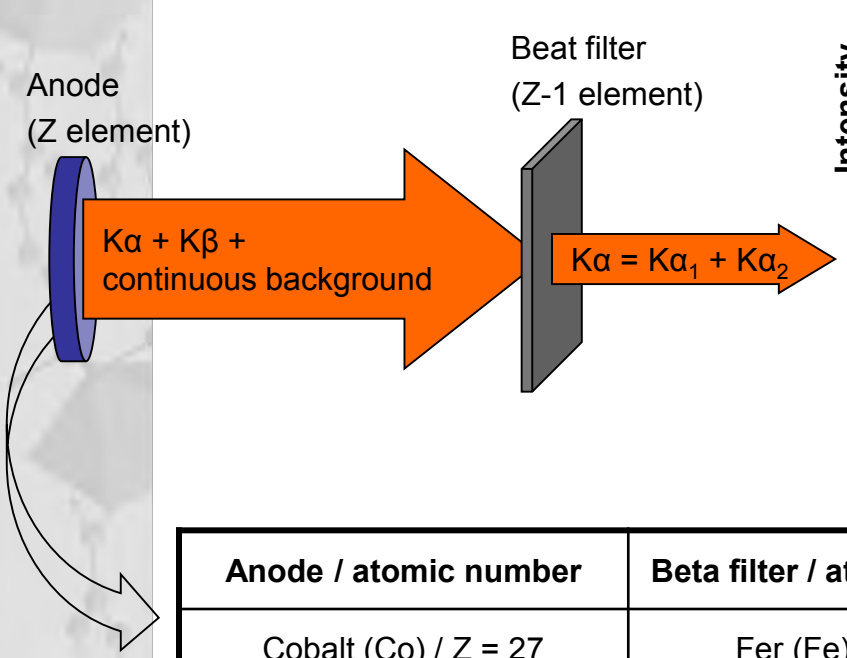


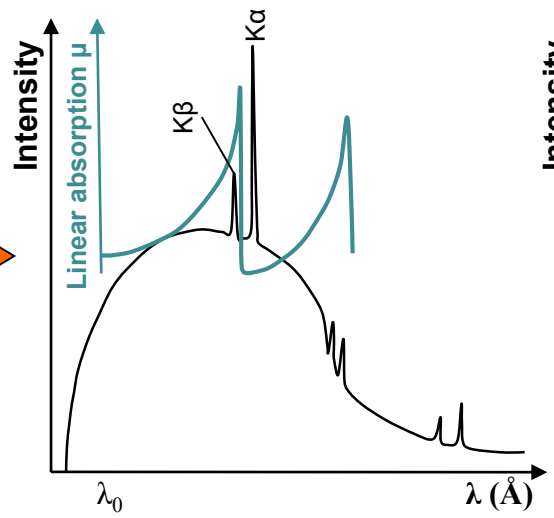


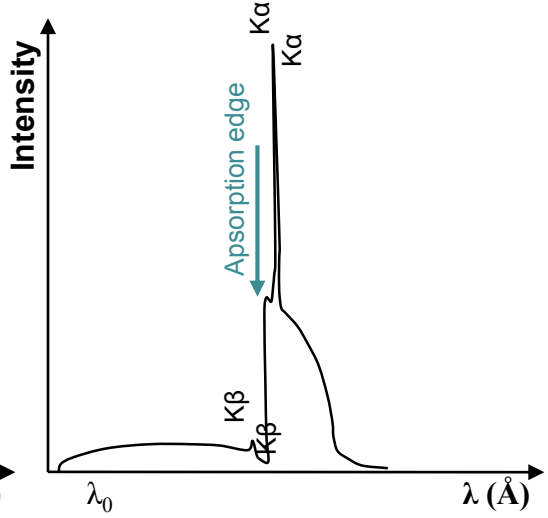
PXRD pattern measurement

Optics of X-ray lab diffractometers

- **Monochromatization**
  - **Beta filter**
    - ✓ Selective absorption of the Kβ radiation and transmit the $K\alpha_1$ and $K\alpha_2$ parts of the X-ray spectrum
    - ✓ A least after filtration the $I_{K\beta}/I_{K\alpha} = 0{,}01$





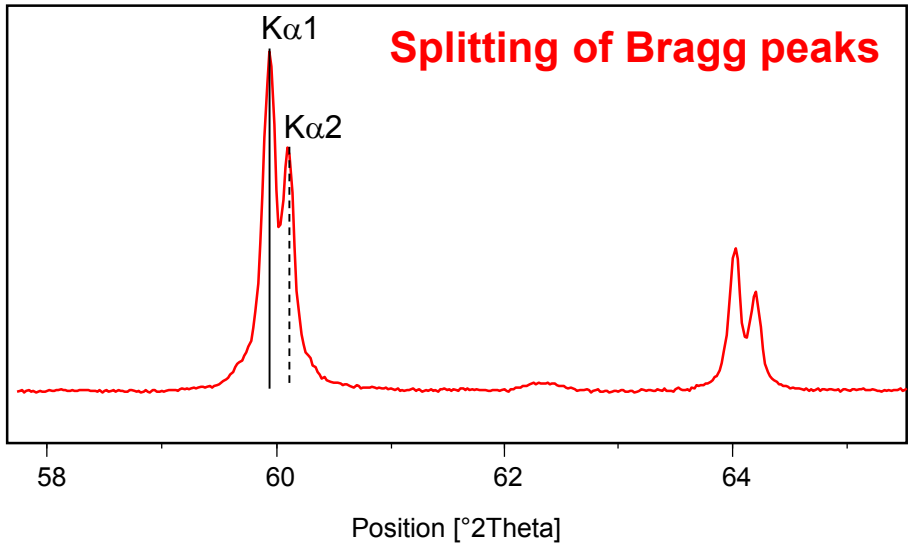


Anode / atomic number	Beta filter / atomic number
Cobalt (Co) / Z = 27	Fer (Fe) / Z = 26
Cuivre (Cu) / Z = 29	Nickel (Ni) / Z = 28

PXRD pattern measurement

Optics of X-ray lab diffractometers

- **Monochromatization**
  - **Disadvantages of the beta filter**
    - ✓ $K\alpha_2$ radiation still present, X-ray beam not totally monochromatic = splitting of the Bragg peaks
    - ✓ Presence of $K\alpha_3$ and $K\alpha_4$ radiations
    - ✓ Presence of « step » in the background just before high intensity reflection due to the Ni-absorption edge
  - **Advantages : cheap whithout complicated adjustment**



Copper radiations

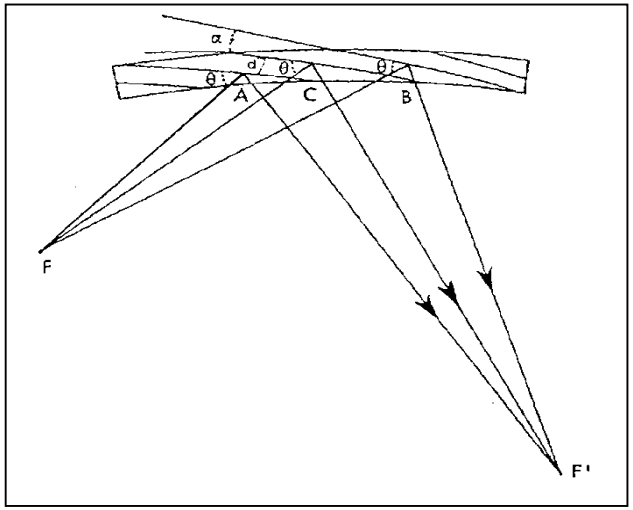
- **$K\alpha_1$ (λ = 1.54060 Å) : $I_{K\alpha1}$ = 100%**
- **$K\alpha_2$ (λ = 1.54460 Å) : $I_{K\alpha2}$ ~ ½ $I_{K\alpha1}$**

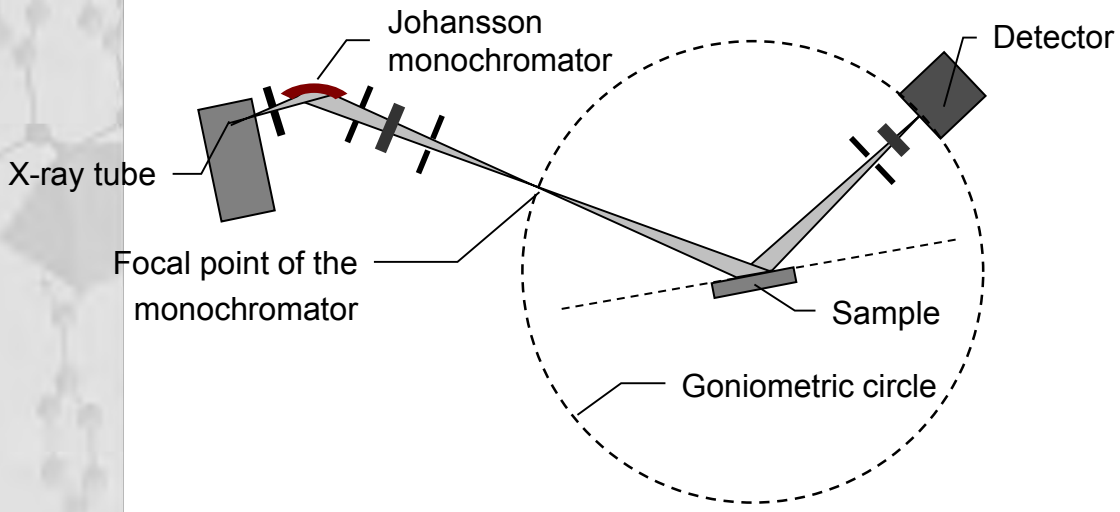
PXRD pattern measurement

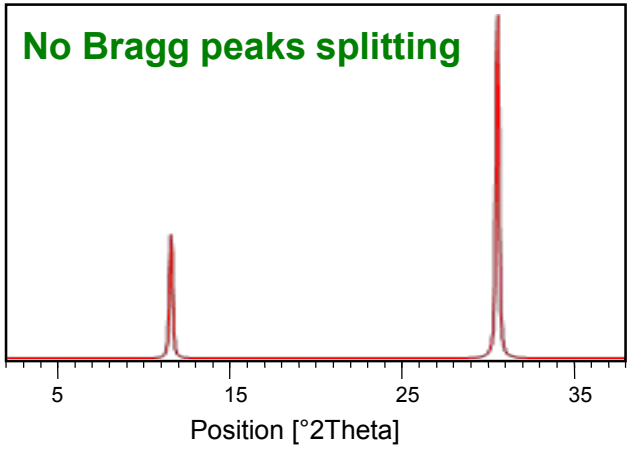
Optics of X-ray lab diffractometers

- **Monochromatization**
  - **Johannson monochromator**
    - ✓ Provides pure Kα1 radiation
    - ✓ Placed in the incident beam
    - ✓ **Avantages: no Bragg peaks splitting**
    - ✓ **Disadvantage: flux divided by 10 compare to the beta filter**

Asymmetric and curve crystal



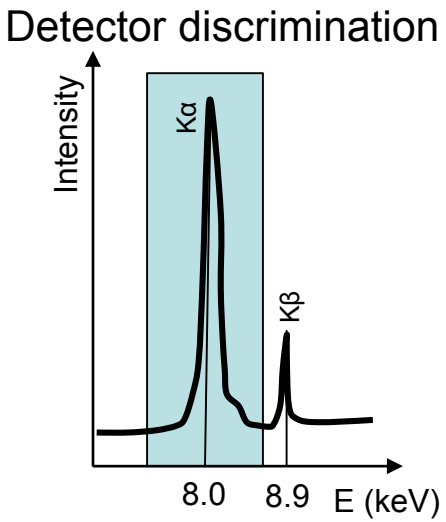


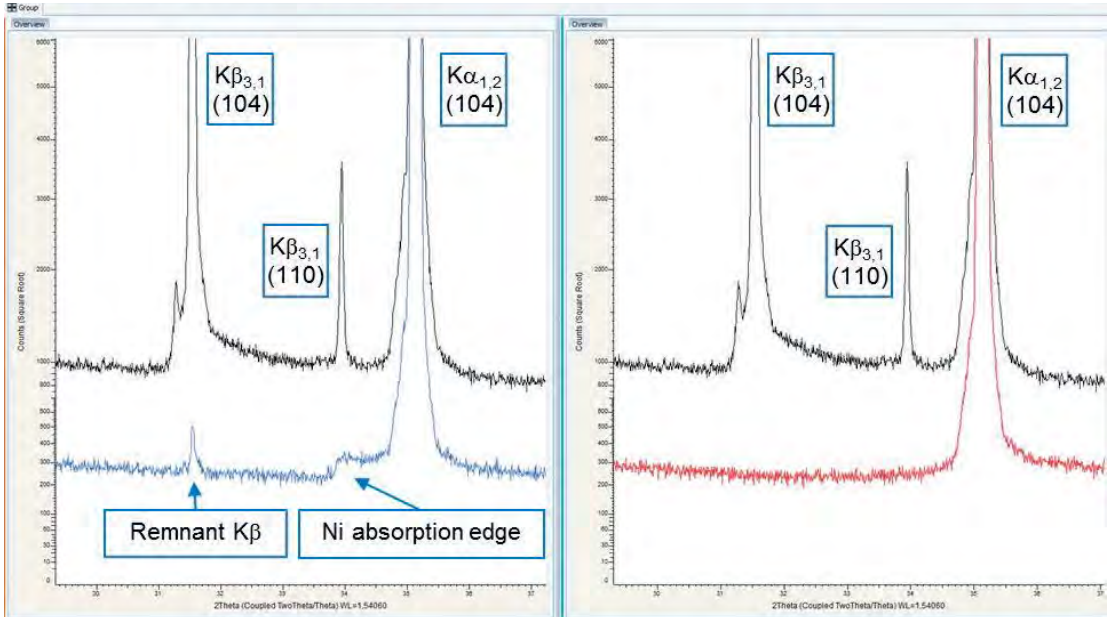


PXRD pattern measurement

Optics of X-ray lab diffractometers

- **Monochromatization**
  - **Solid state detector : Bruker Lynx Eye XE-T B**
    - ✓ Energy resolution better than 380 eV for the Cu radiation
    - ✓ **Avantages: No needs of Kß filters, suppress the Kß radiation and the Ni adsorption edge**
    - ✓ **Disadvantage: Bragg peak splitting ($K\alpha_1$ + $K\alpha_2$)**



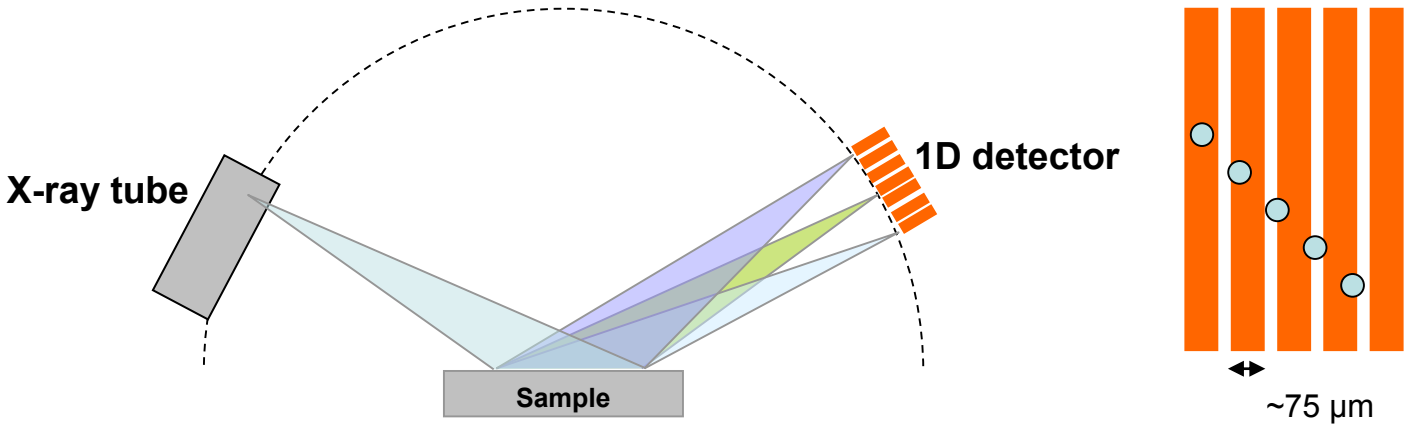


--- filter mode disabled
--- filter mode disabled plus Ni-filter
--- filter mode enabled

PXRD pattern measurement

Optics of X-ray lab diffractometers

- Solid state real time multiple strip detectors
  - Multiple silicium strips : each strip = 1 point detector
  - Between 190 and 250 strips / detector = angular range ~ 3,5°(2θ)



- **Advantages:**
  - ✓ High-speed data acquisition up to 450 times faster than a conventional point detector system
  - ✓ Good energy resolution = reduction of the fluorescence radiation coming from the sample
  - ✓ Very good resolution: intrinsic minimum FWHM ~ 0,02°(2θ)

PXRD pattern measurement

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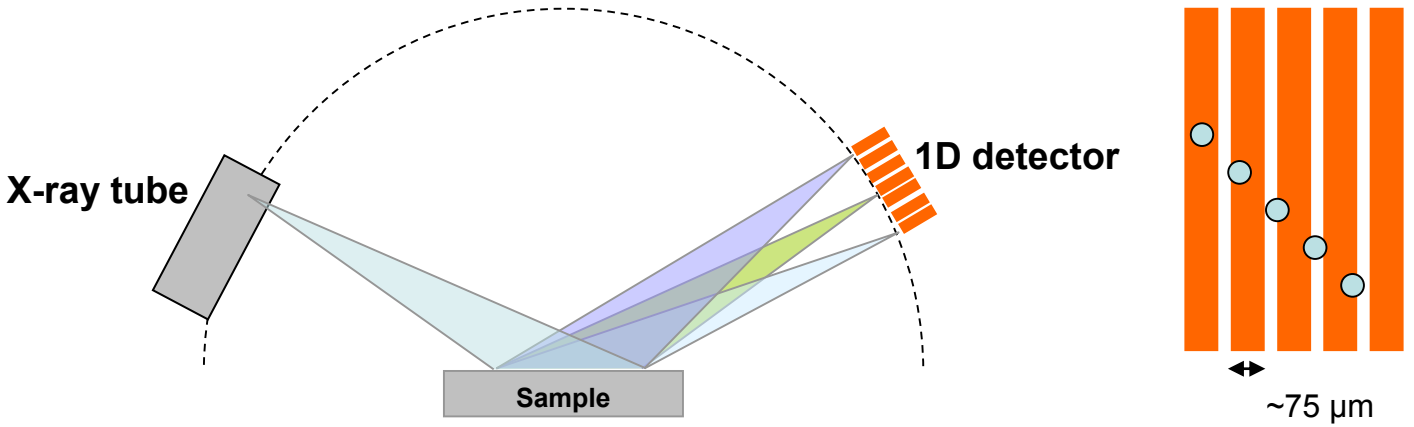

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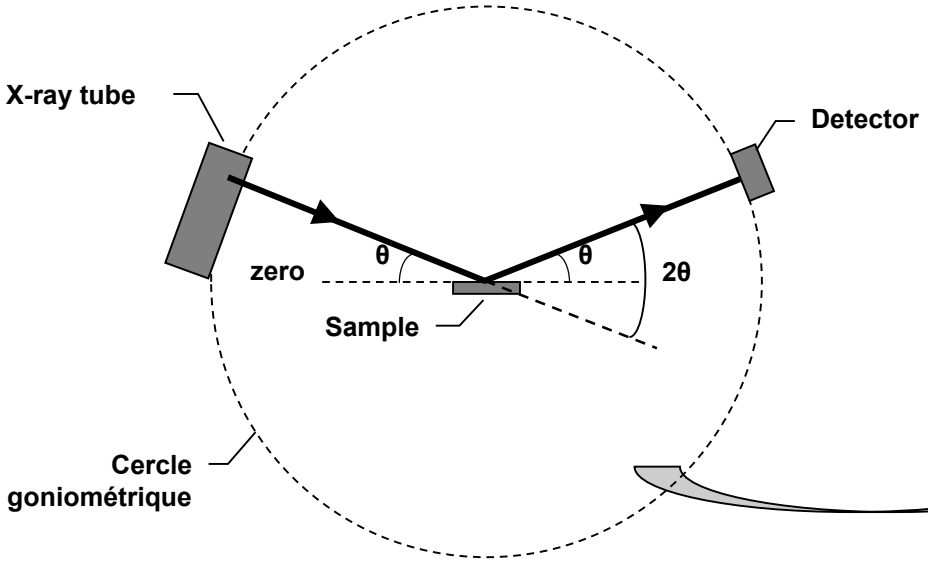
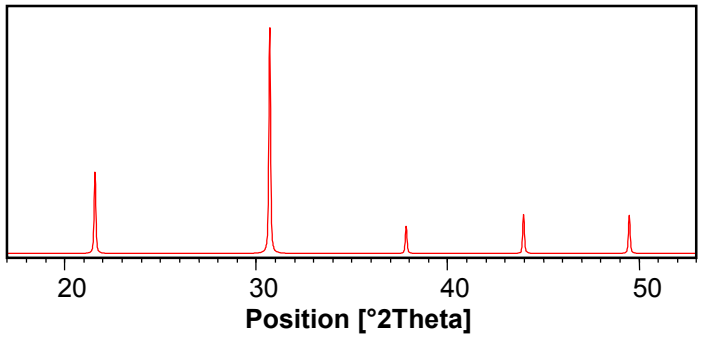
PXRD pattern measurement

Before reccording data

- **Setting the zero shift of the goniometer to avoid the shift of the reflections**
  - Calibration with a reference sample (Si or Al_2O_3 from NIST, …)
- **Determination of the instrumental parameters:**
  - Calibration with a reference sample (LaB_6-NIST,…) before refinements (Fullprof, HighScore, …)
  - Direct refinements with Fundamental Parameter method (Topas, JANA2006)





X-ray powder diffraction

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