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Introduction to RIETVELD REFINEMENT &

Powder X-ray Diffraction Experimental setups

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Introduction to RIETVELD REFINEMENT

Jasper Plaisier

MCX beamline –Elettra Trieste

Outline

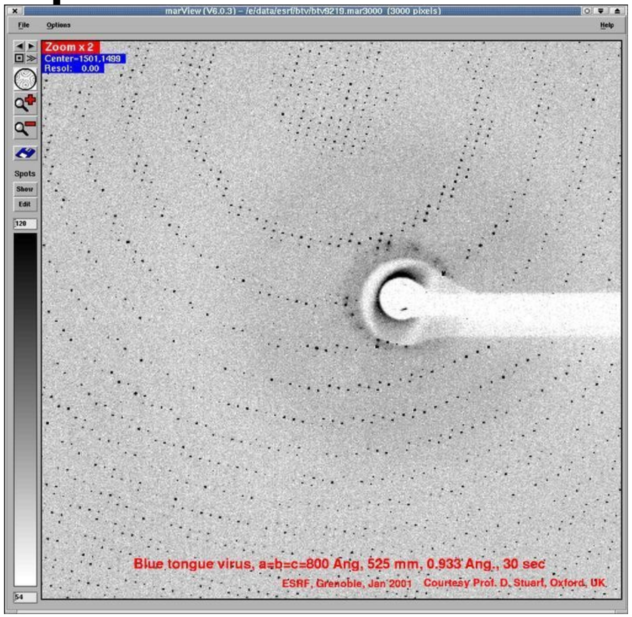
- Introduction
  - The method
  - The math
- Before you start refining
  - Indexing / unit cell, space group determination
  - Constructing a model
- Refinement
  - Important steps
  - Criteria of fit

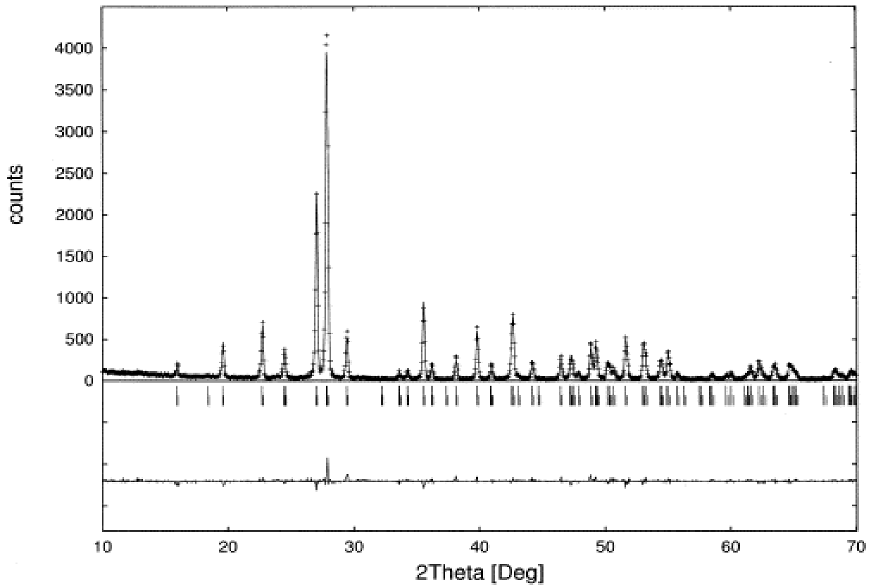
Introduction

- Hugo M. Rietveld (Den Haag, 1932)
- Structure determination from neutron powder diffraction
- Original software was written in 1969
- First reports on the application in XRD: 1977

Rietveld refinement

- Goal: get accurate structural parameters given a powder diffraction pattern.
- Peak intensities depend on structural parameters

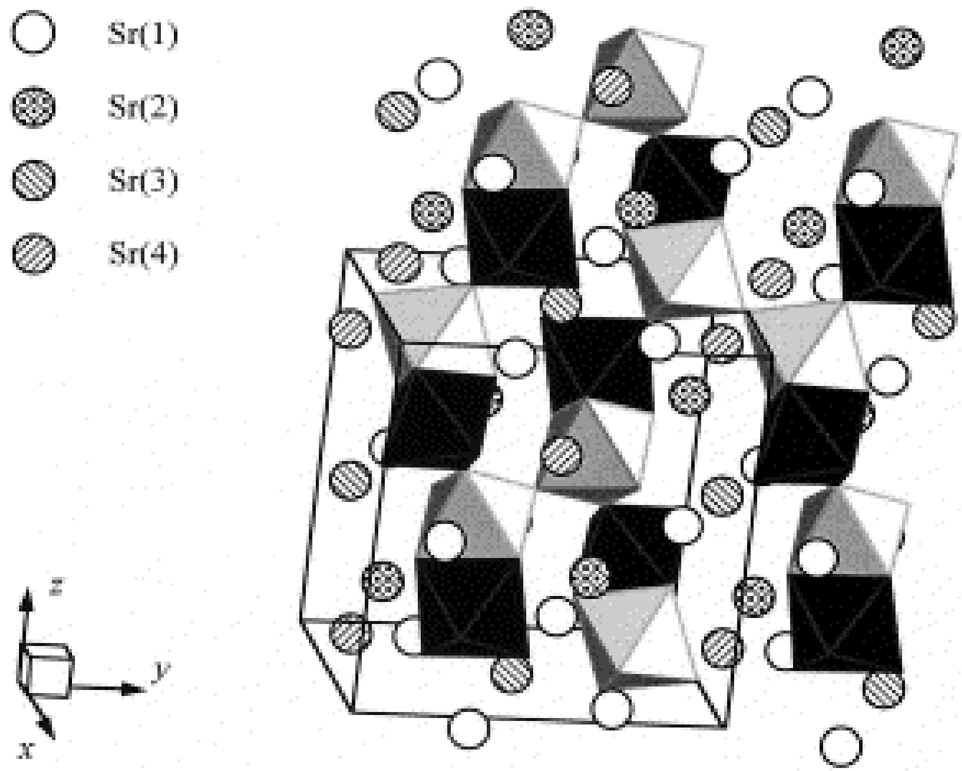




Crystal Structure

- Unit cell: regular repeating pattern of atoms that forms the crystal (defined by lattice parameters a, b, c, α, β, γ)
- Space group: Describes the symmetry of the atomic structure (eg. $P2_1/m$)
- Atomic positions within unit cell (x,y,z)

Crystal Structure



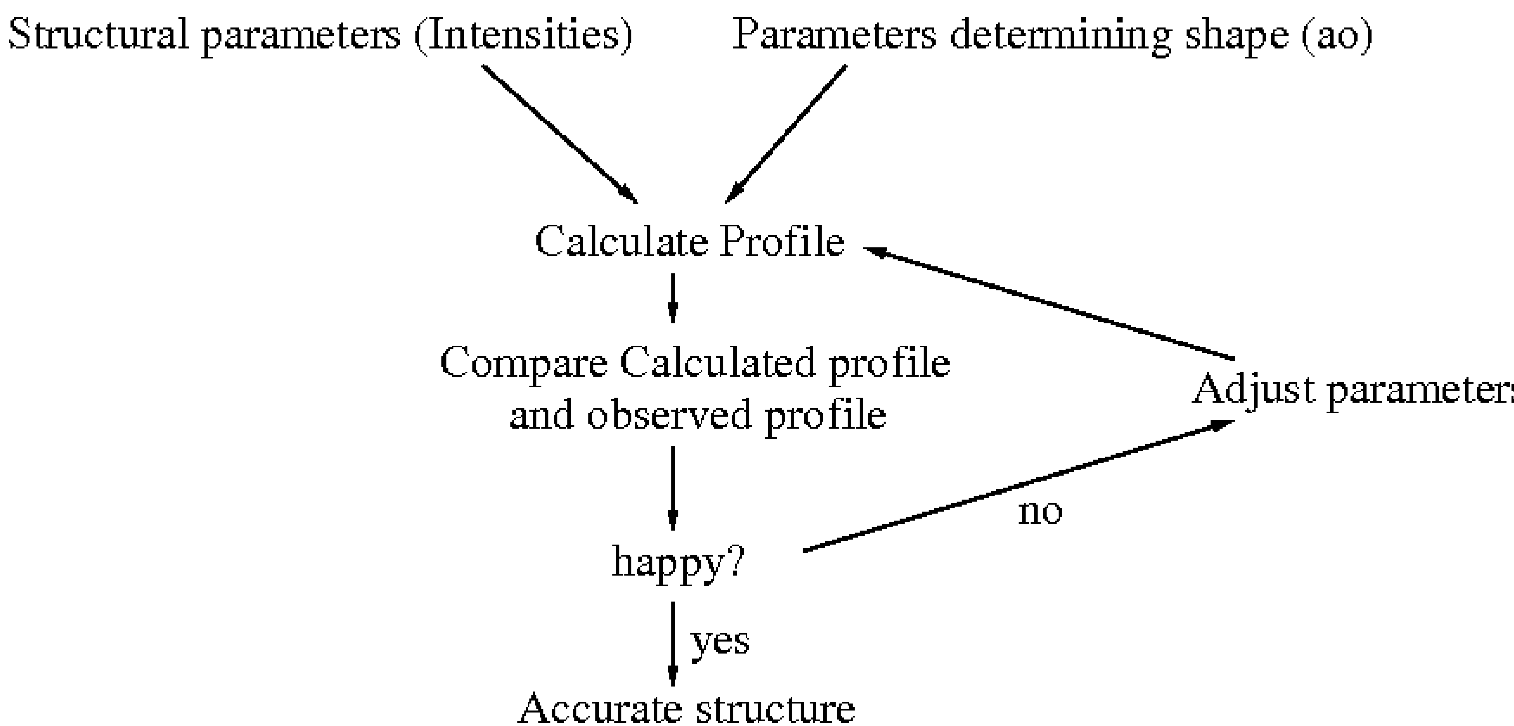
Peak intensities

- Integrated area of peak gives intensity
- Peak height is not a good estimate, shape must be taken into account
- Factors affecting peak shape: temperature absorption, particle size, instrument parameters

Rietveld method

- In the Rietveld method the parameters are refined using the least squares method until the best fit between the calculated pattern and the observed pattern is obtained

Rietveld method



Rietveld math

- Minimization of residual S_y

$$S_y = \sum_i w_i (y_i - y_{ci})^2$$

  – $W_i = 1/y_i$
  – Y_i = Observed intensity at the *i*th step
  – Y_{ci} = Calculated intensity at the *i*th step

Rietveld math

- Calculation of intensity y_{ic}

$$y_i = s \sum_K L_K |F_K|^2 \varphi(2\Theta_i - 2\Theta_K) P_{KA} + y_{bi}$$

- s_i = Scale factor
- K represents Miller indices, *hkl,* for a Bragg reflection
- L_K contains Lorentz, polarization and multiplicity factors
- φ is the reflection profile function
- P_K is the preferred orientation function
- A is the absorption factor
- F_K is the structure factor
- Y_{bi} is the background intensity at the *i*th step

Rietveld math

- Calculation of the structure factor

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

  - *hkl* Miller indices
  - x_j, y_j, z_j are the atomic position parameters of the jh atom in the unit cell
  - B_j = Temperature factor (thermal vibrations) of the *j*th atom
  - N_j site occupancy for the *j*th atom site
  - f_j scattering factor of the *j*th atom

Before we start refining

- Rietveld **refinement** requires a starting model that is close to the real model
- Starting values for instrument parameters can be determined using standard materials
- Necessary finding a reasonable estimate of
  - Unit cell parameters
  - Atomic positions
- Determine the correct space group

Finding unit cell parameters

- Unit cell parameters are related to the peak positions by Bragg's law:

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

- In case of a cubic cell : a=b=c, α=β=γ=90º

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

Simple cubic example

- a=4.0Å, space group Pm3m

2Θ	d	$1000/d^2$	h k l	$h^2+k^2+l^2$
22.21	4.00	62.5	1 0 0	1
31.61	2.83	125.0	1 1 0	2
38.97	2.31	187.5	1 1 1	3
45.31	2.00	250.0	2 0 0	4
51.01	1.79	312.5	2 1 0	5
56.29	1.63	375.0	2 1 1	6
66.00	1.41	437.5	2 2 0	8
70.58	1.33	500.0	3 0 0	9
			2 2 1	9

Finding unit cell parameters

- More complex unit cells make manual indexing difficult
- Indexing is usually done with a computer program (Dicvol, Treor, Ito)
- Input:
  - 20-30 accurately determined peak positions
  - Wavelength
  - Maximum cell volume
  - Error in peak positions

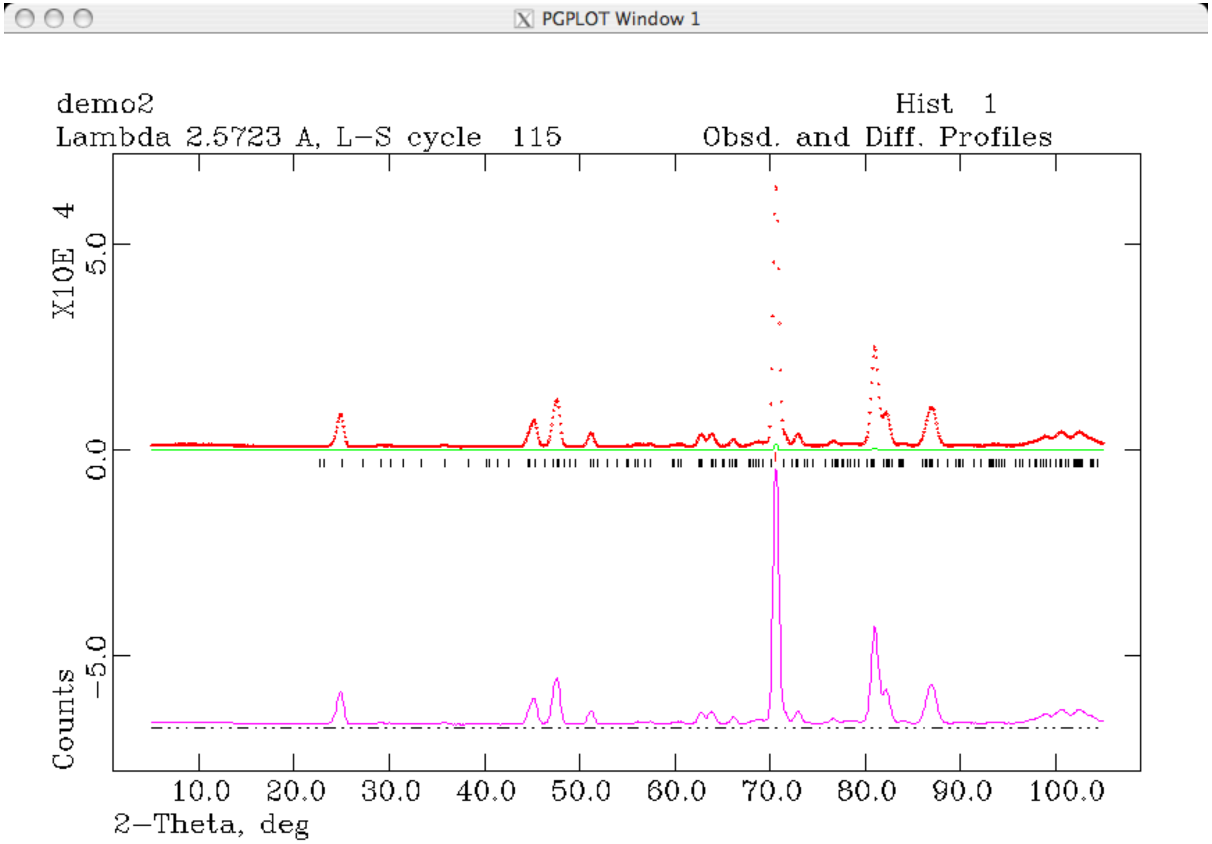
Finding space group

- Space group cannot be refined, must be right
- Some symmetry elements can be determined from systematic absences
- Often various refinements using different space groups are performed and their results compared

Starting model: atomic parameters

- Find in the database a known structure that is similar
- Determine a structure ab-initio using direct methods or modeling
  - Needs accurately estimated peak intensities
  - Small peak widths of synchrotron powder diffraction helps out a lot

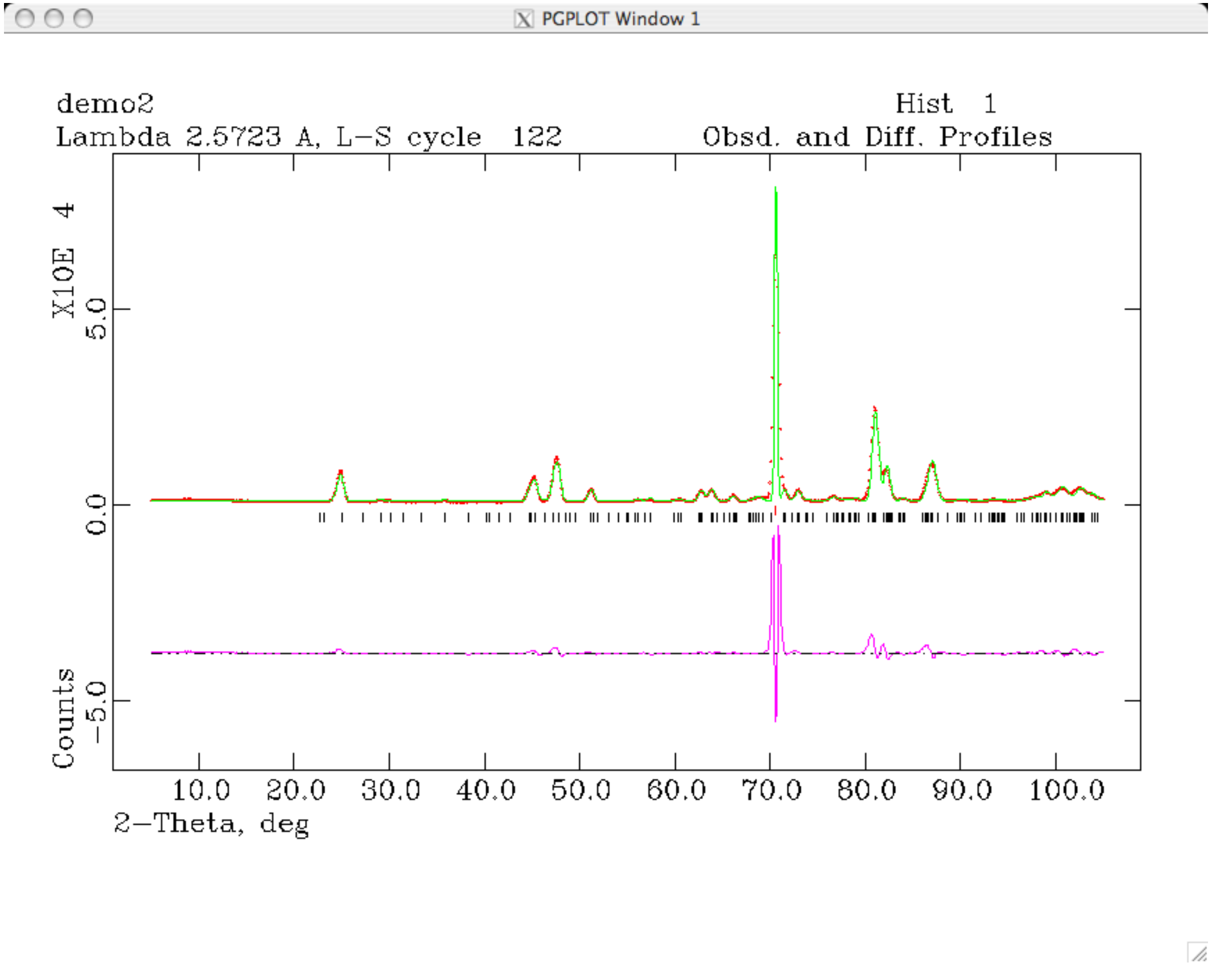
Refinement steps



Refinement steps

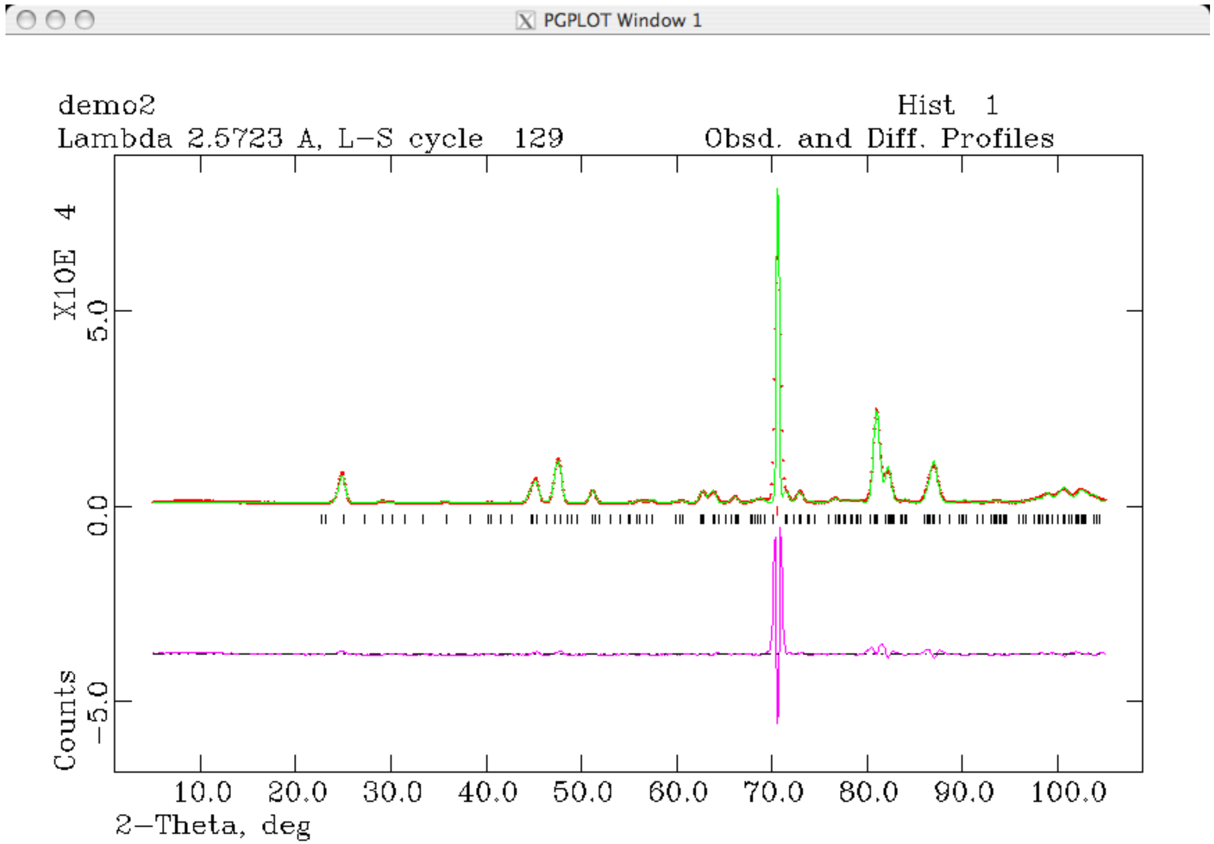
- Refining parameters to fit overall shape of diffraction pattern:
  - Scale factor
  - Background (function with 3-6 parameters)
  - Zero-point correction

Refinement steps



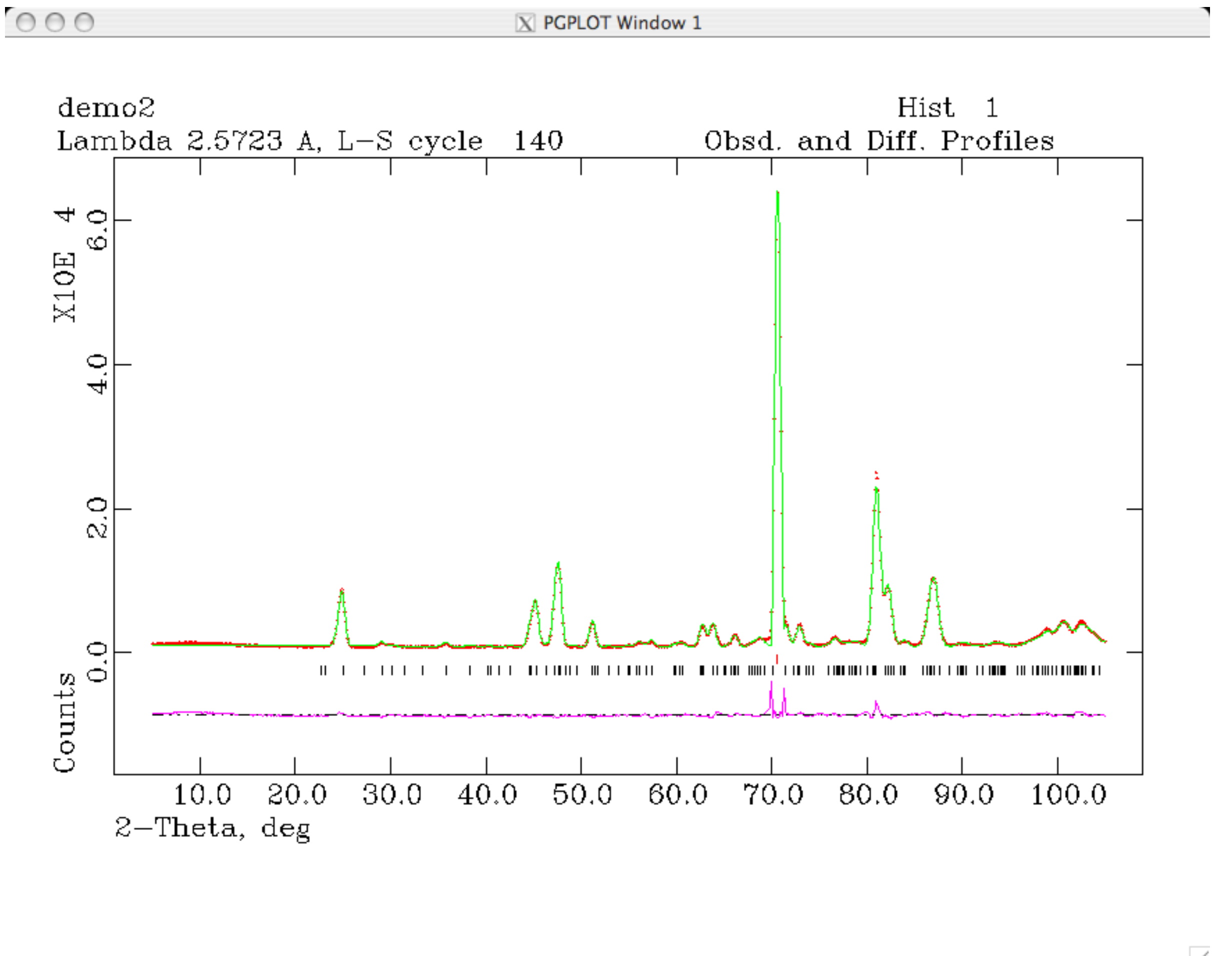
Refinement steps

- Get accurate peak positions by refinement of the unit cell parameters



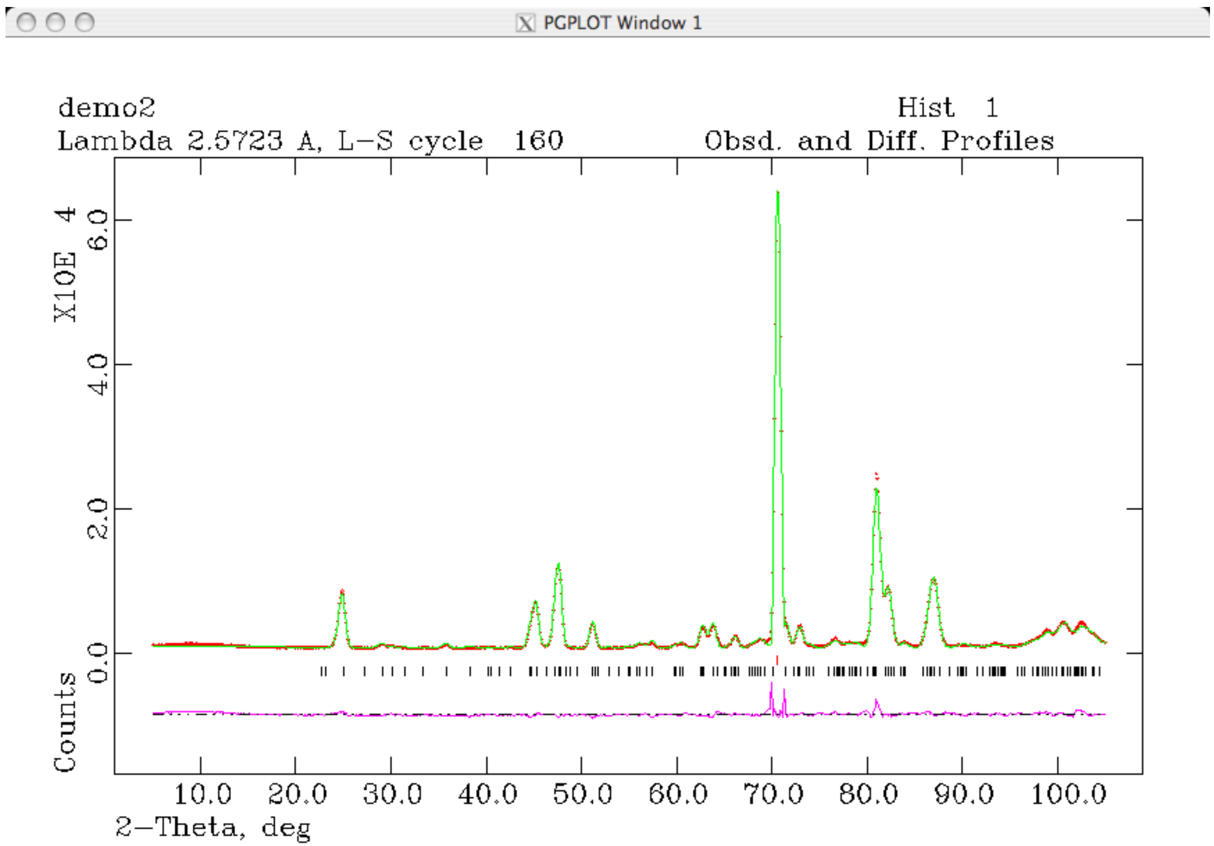
Refinement steps

- Peak shape parameters



Refinement steps

- Atomic parameters



Refinement steps

- Sequence of the parameters to be included in the refinement depends on the quality of the staring model
- Looking at the difference between the calculated and observed profile helps to decide the order in which to include the parameters

Criteria of fit

- Measure of the quality of the fit
- R-Bragg

$$R_B = \frac{\sum |I_K(obs) - I_K(calc)|}{\sum I_k(obs)}$$

- R-pattern

$$R_p = \frac{\sum |y_i(obs) - y_i(calc)|}{\sum y_i(obs)}$$

- R-weighted pattern

$$R_{wp} = \frac{\sum w_i(y_i(obs) - y_i(calc))^2}{\sum w_i(y_i(obs))^2}$$

Criteria of fit

- I_K is never directly observed.
- R-bragg is biased towards the model
- R_{wp} is directly related to the function that is minimized
- Don't forget to look at the patterns!!!

Powder X-ray Diffraction Experimental setups

Jasper Plaisier

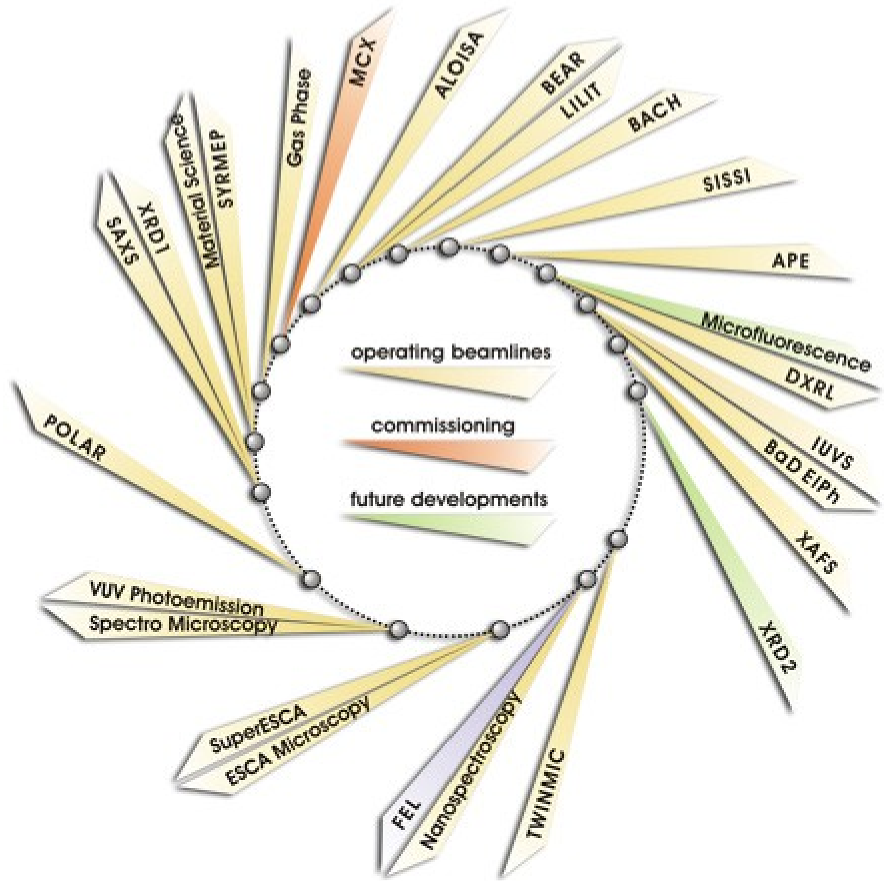
MCX beamline –Elettra Trieste

Outline

- Introduction
- Experimental techniques at MCX
- MCX Experimental setup
  - Beam line optics
  - Experimental hutch
- Experimental stations
  - Flat plate - reflection
  - Capillary - transmission

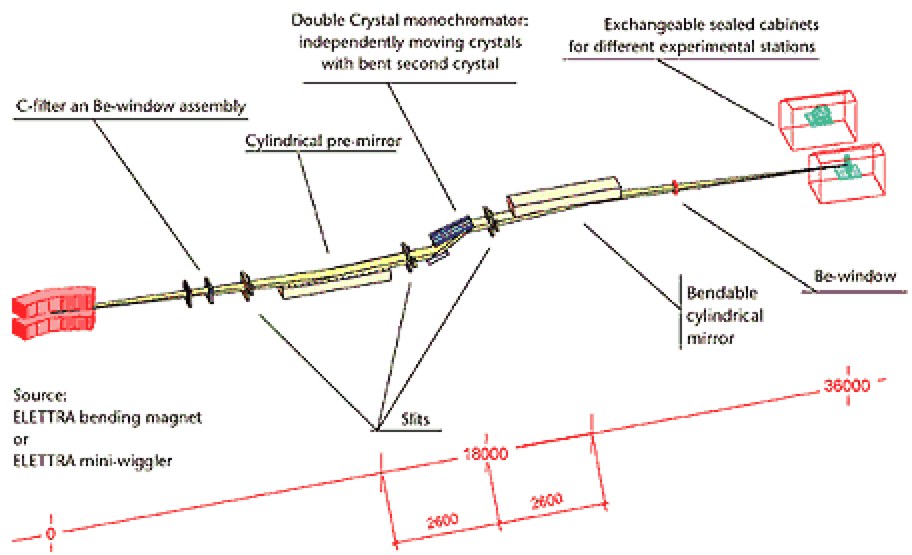
Introduction

- MCX is under construction

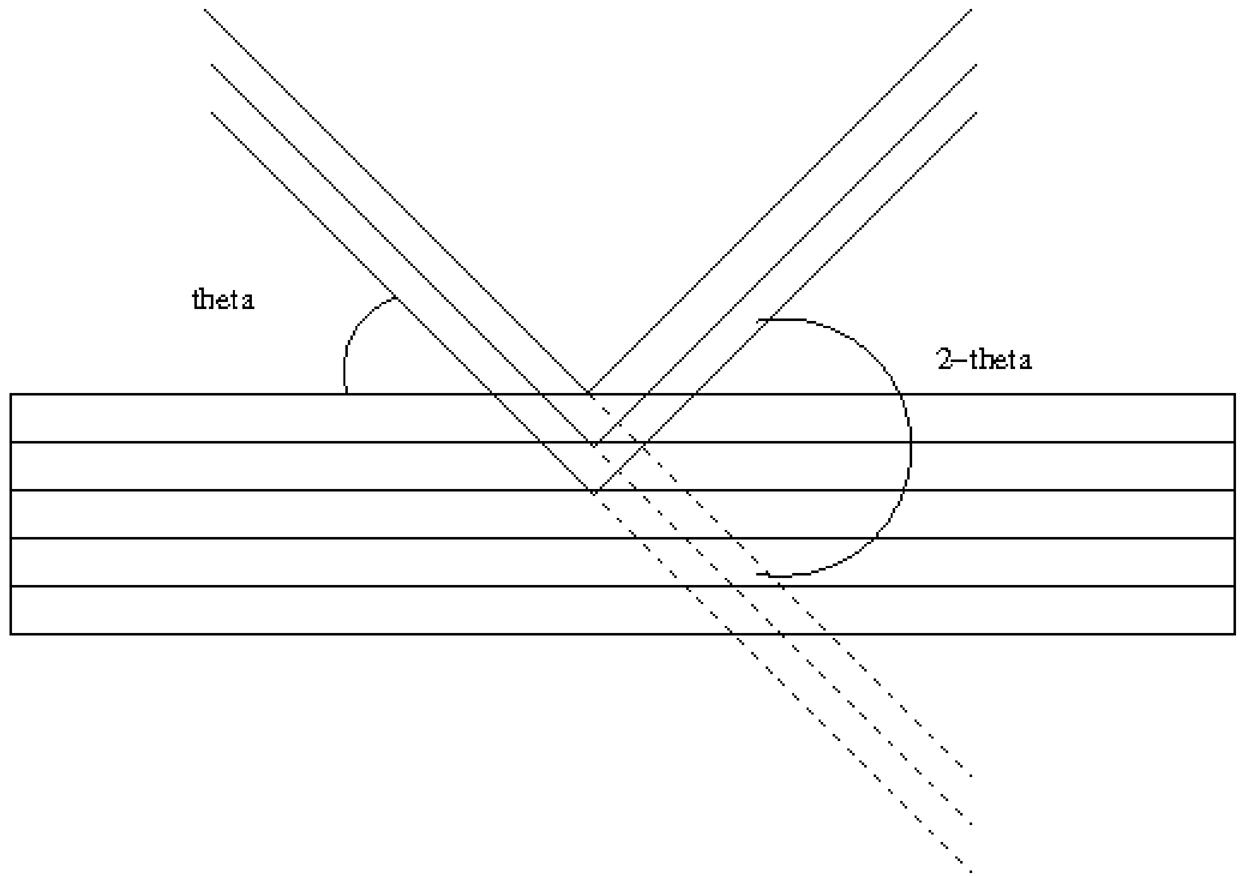


Introduction

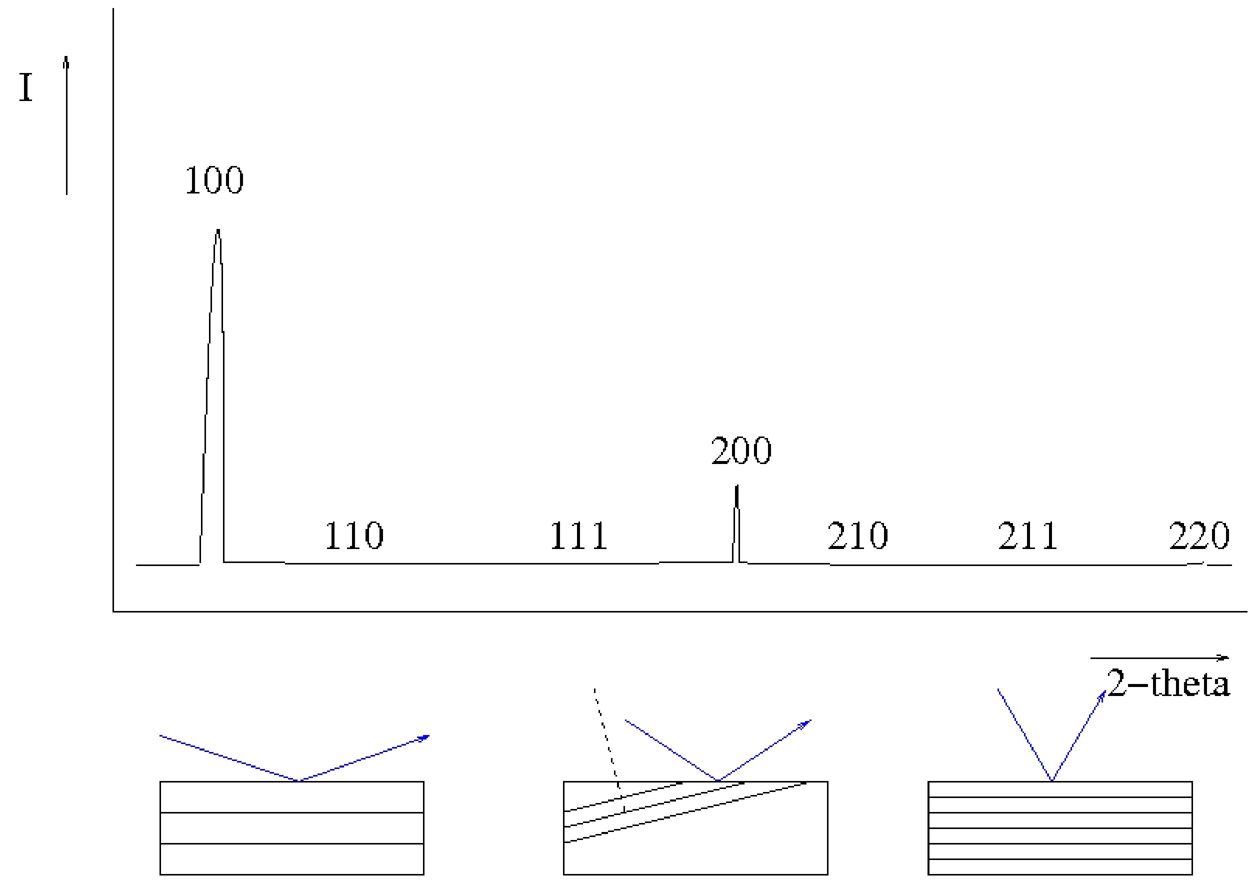
- <u>M</u>aterials <u>C</u>haracterization by <u>X</u>-rays



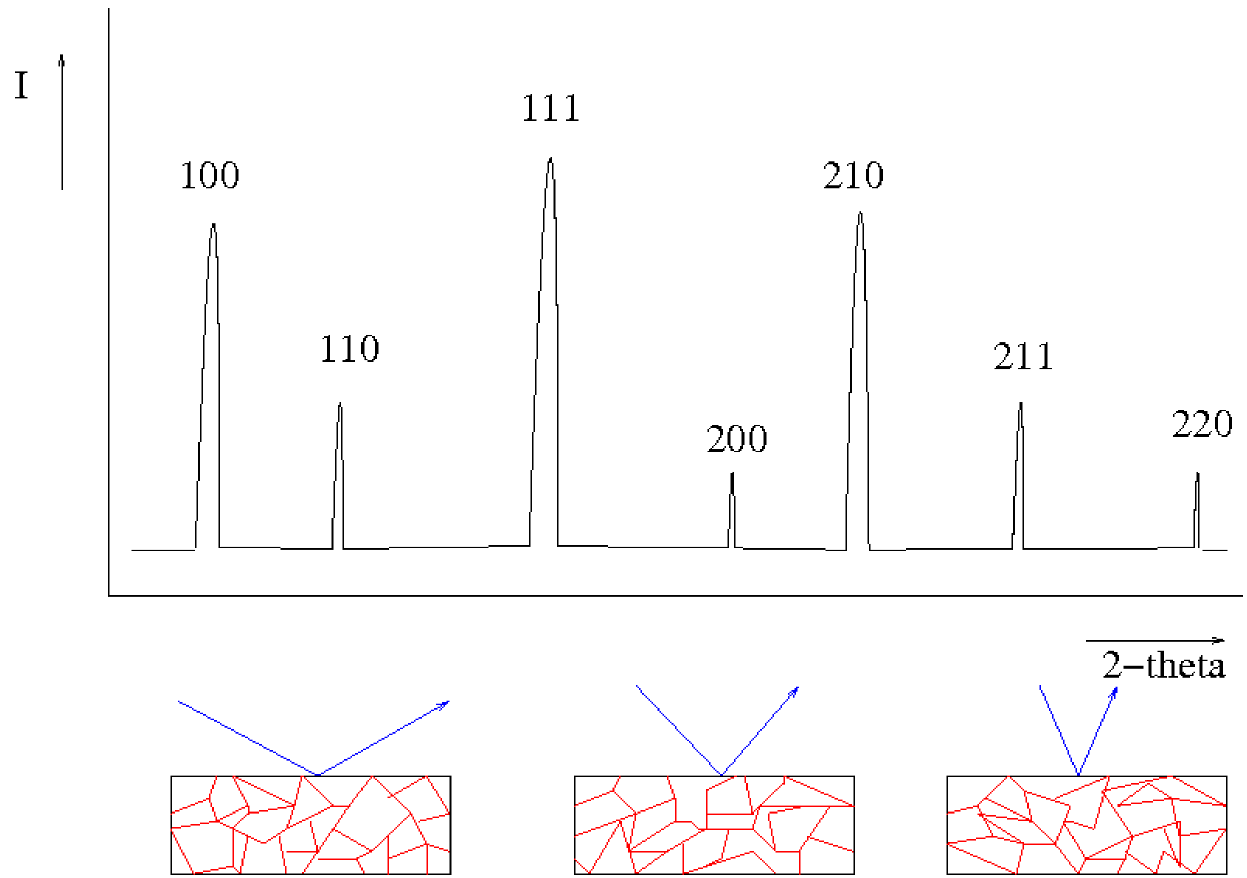
Introduction



Introduction



Introduction

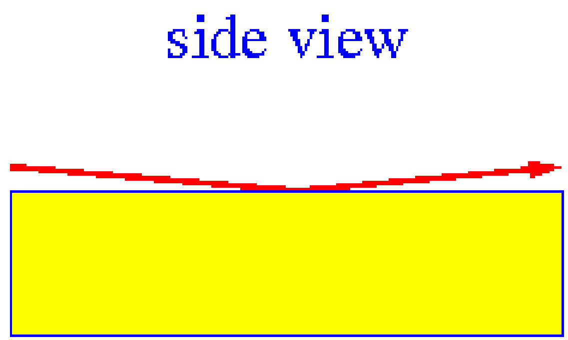


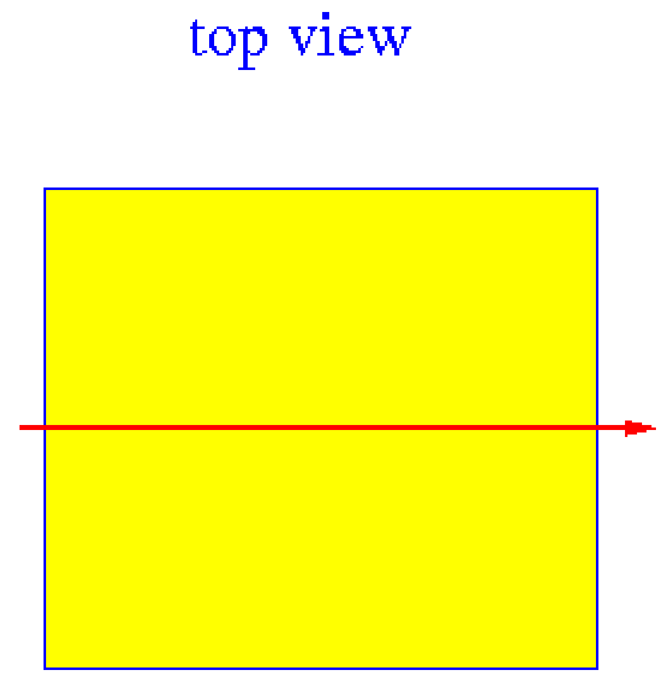
Experimental techniques at MCX
Grazing angle: reflectivity

- Based on total reflection of X-ray beam
- Study of:
  - Surface morphology
    - Roughness
    - Waviness
  - Composition
  - Structure of multilayer systems
- Layer thickness .5-400 nm,
- Needs difference of electron density in layers

Experimental techniques at MCX
Grazing angle: reflectivity

- The measurement:





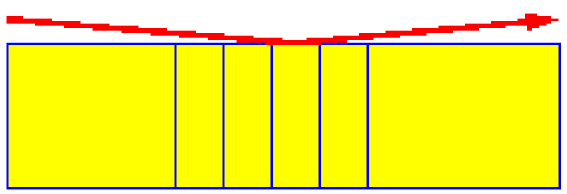
Experimental techniques at MCX Grazing angle: diffraction

- Based on Bragg diffraction in thin layer
- X-rays enter sample with small incident angle to limit penetration depth
- Study of:
  - Identification and study of monolayers
  - Differences in crystallinity surface/bulk
  - Surface residual stress and texture
  - Depth profiling

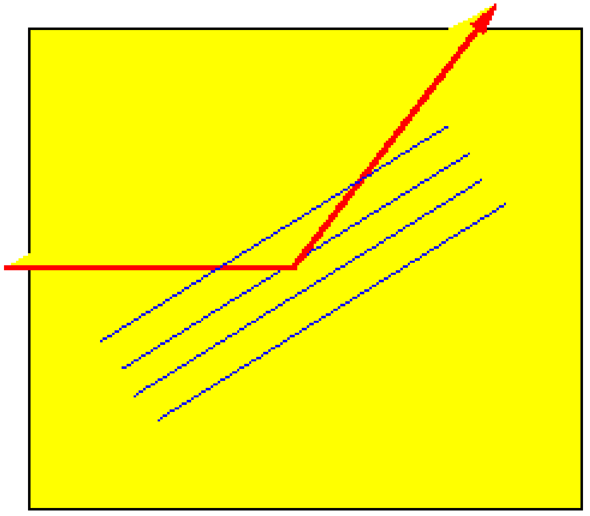
Experimental techniques at MCX
Grazing angle: diffraction

- Symmetric configuration

side view

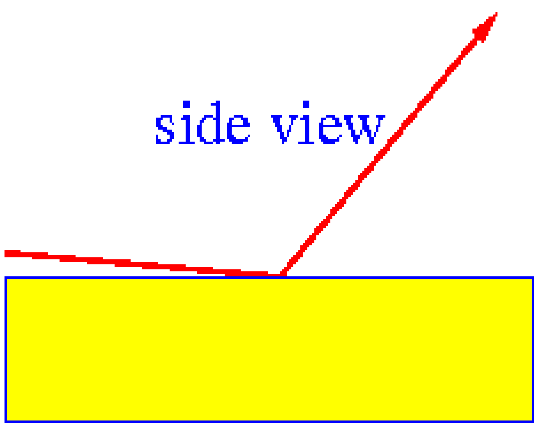


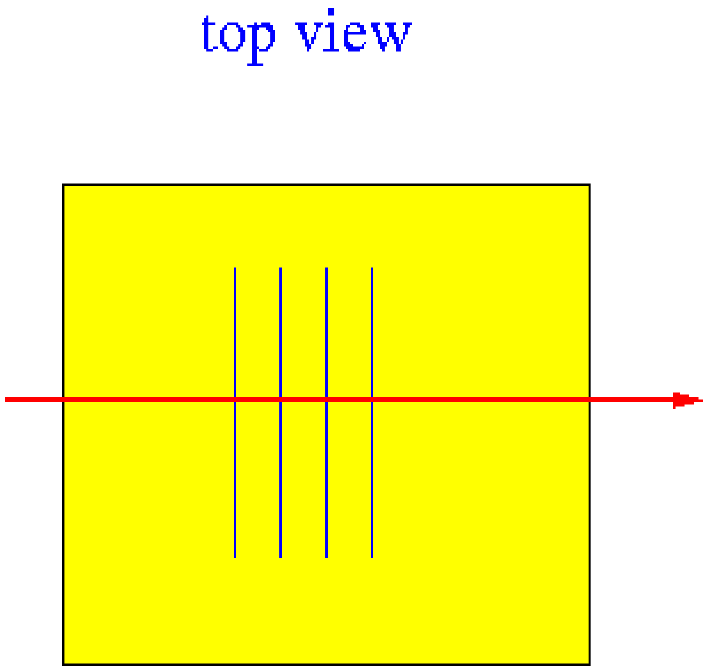
top view



Experimental techniques at MCX Grazing angle: diffraction

- Asymmetric configuration





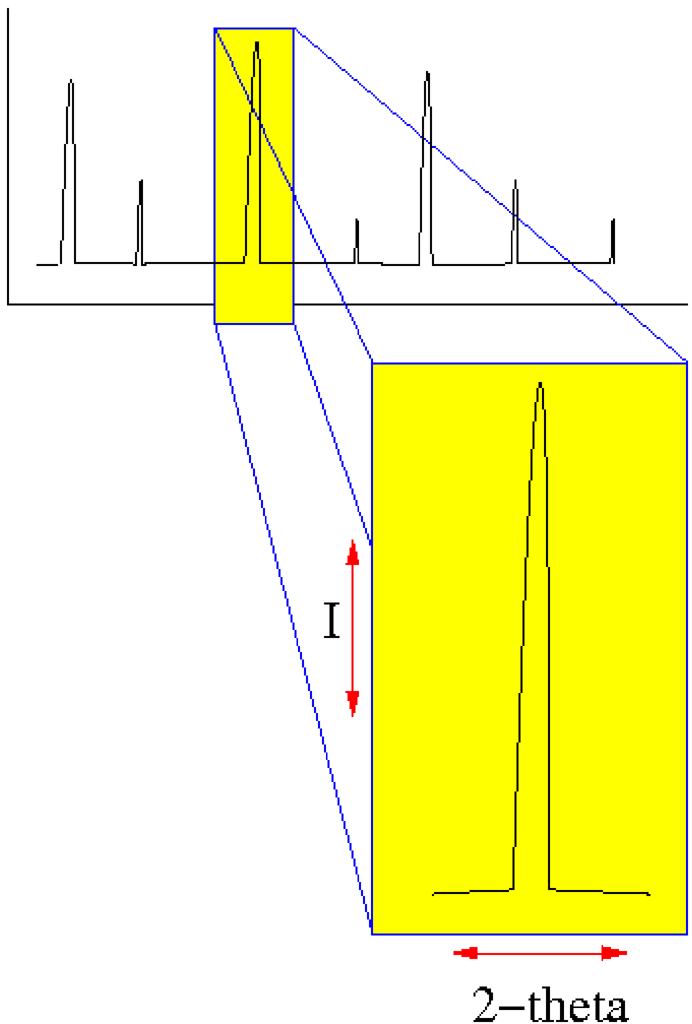
Experimental techniques at MCX Stress and texture analysis

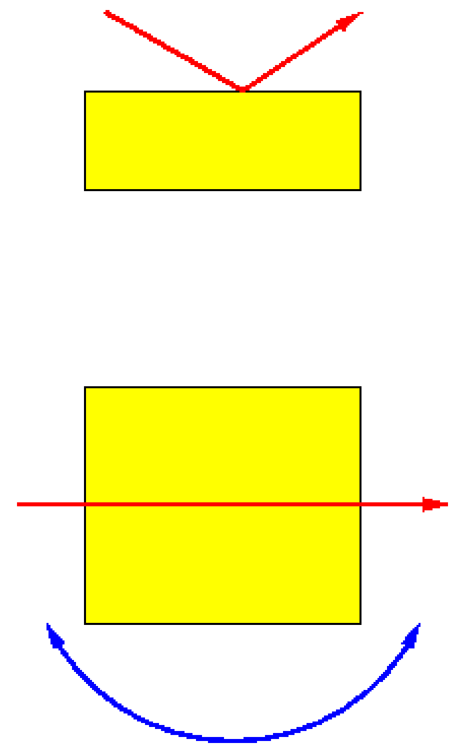
- Stress can be determined from precision lattice constant determination (diffraction peak shifts)
- Texture is the orientation distribution of the crystallites
- Texture is measured by rotating the sample while monitoring the intensity of a Bragg-reflection

Experimental techniques at MCX Elastic constants and mechanical properties

- Based on X-ray diffraction measurement while mechanical pressure is applied
- Elastic tensors can be determined by measuring different crystallographic directions

Experimental techniques at MCX Elastic constants and mechanical properties



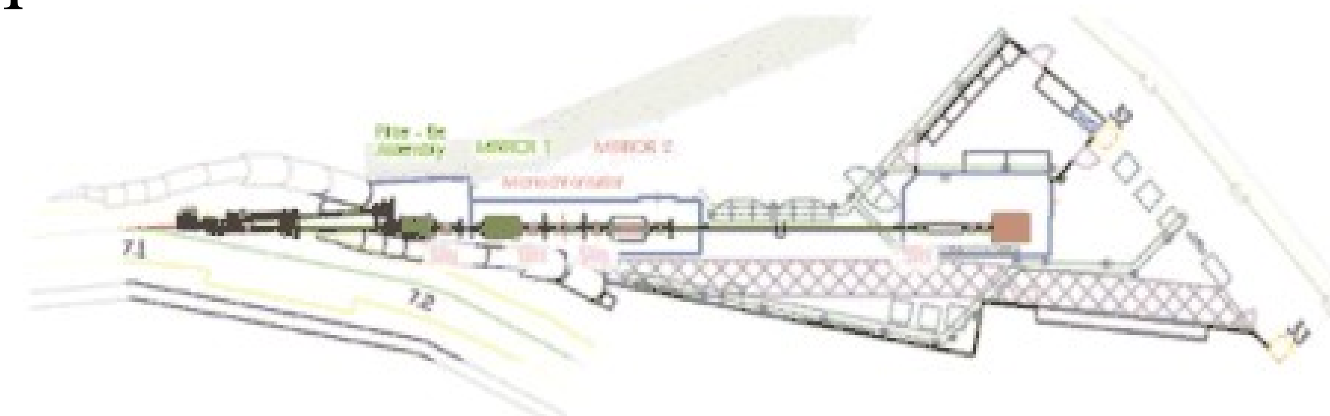


Experimental techniques at MCX Phase identification and profile analysis

- Phase identification by XRD fingerprint
- Quantitative phase analysis
- Structure solution and refinement
- Size and shape distribution
- Study of lattice defects

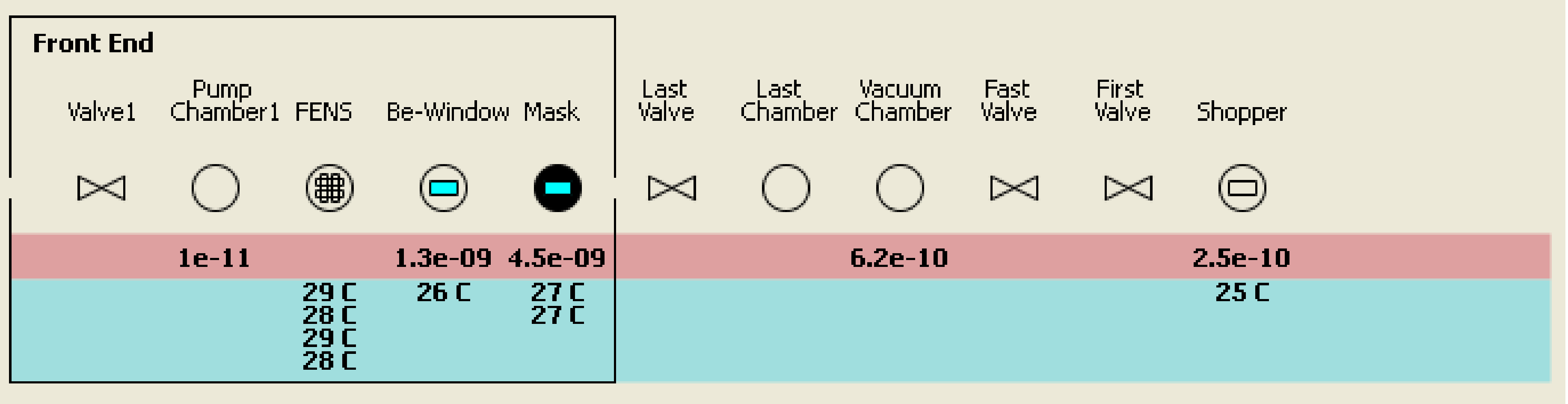
MCX Experimental setup

- Front end Hutch
- Beamline Optics Hutch
- Tube
- Experimental Hutch

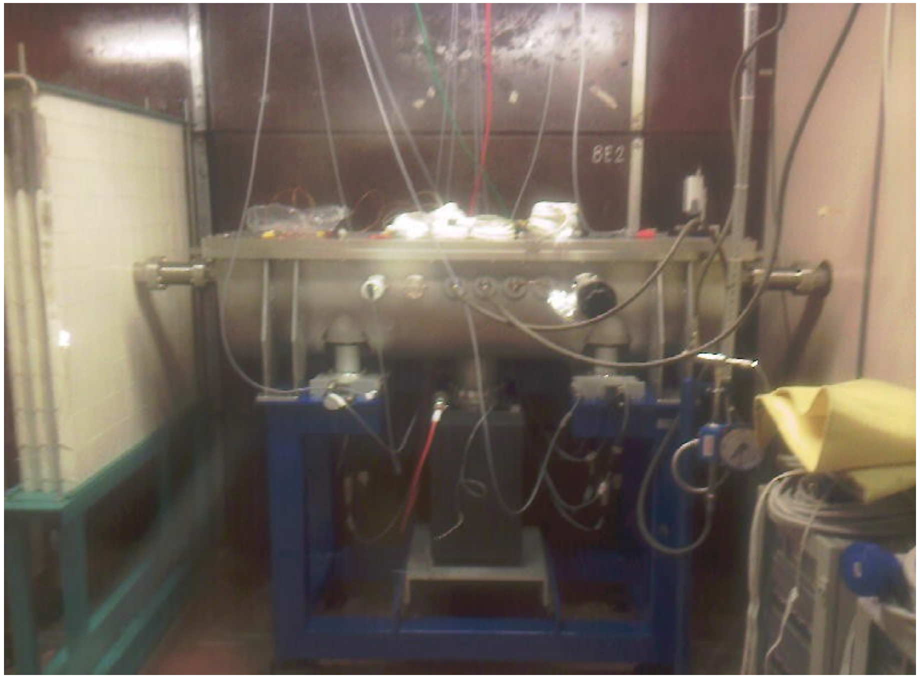


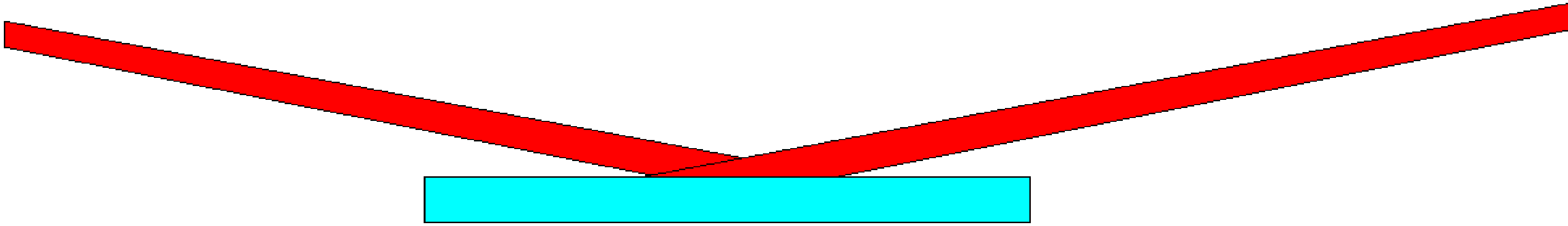
MCX Experimental setup
Front End Hutch

- Shopper
- Mask
- Be window
- First Entrance Slits
- Several valves

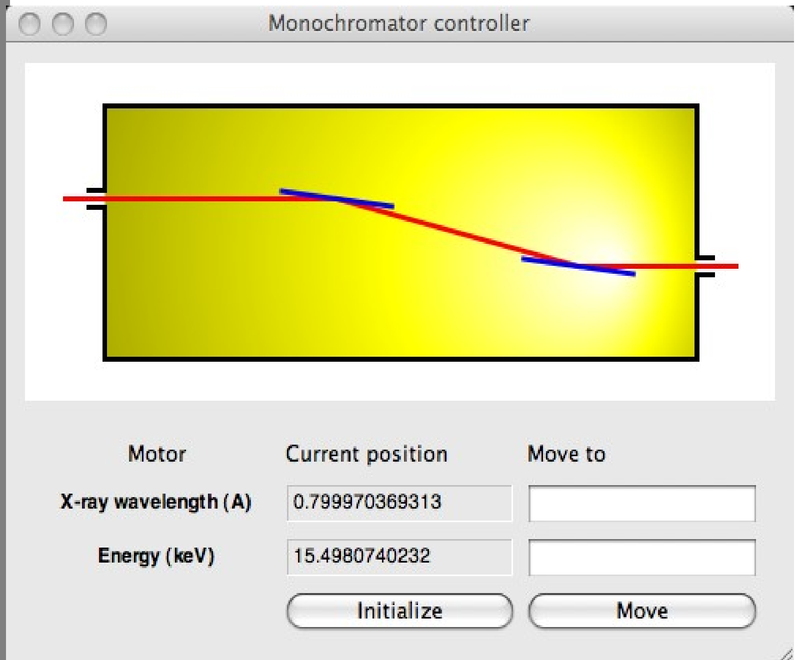


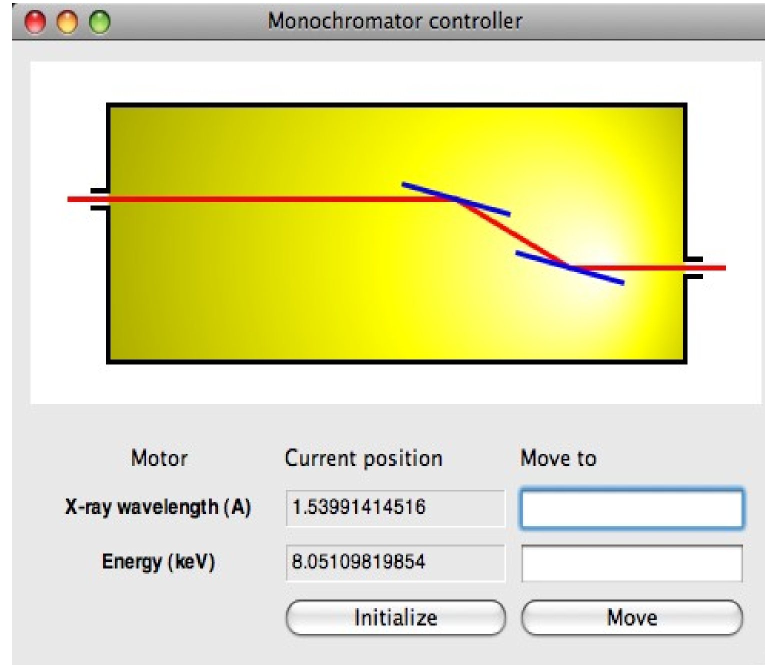
MCX Experimental setup
Optics – Mirror 1





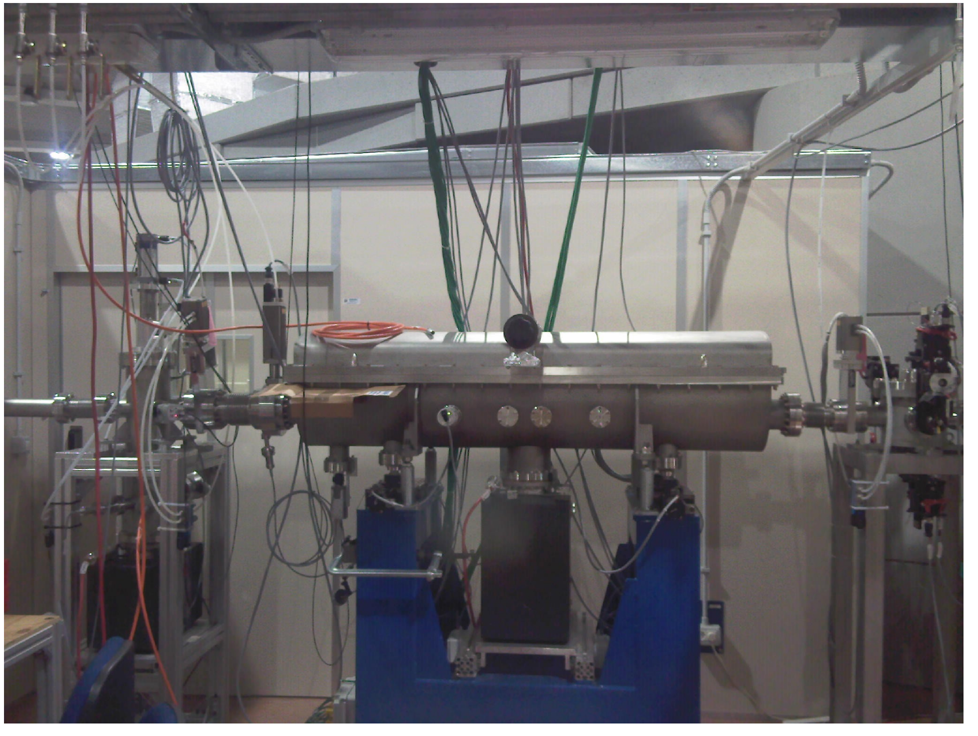
MCX Experimental setup
Optics – Monochromator



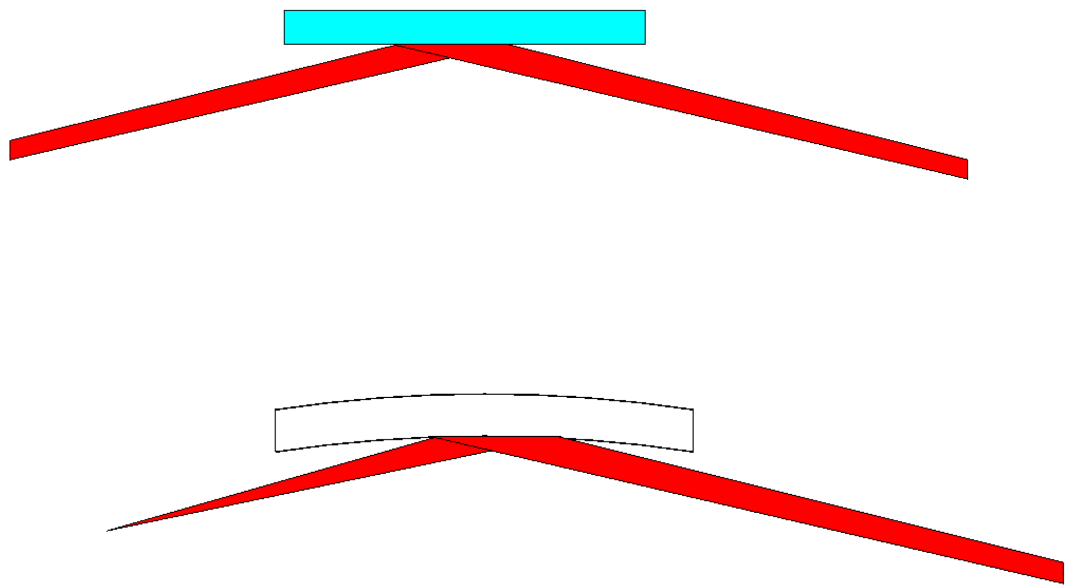


- Choice of wavelength of X-rays

MCX Experimental setup Optics – Mirror 2

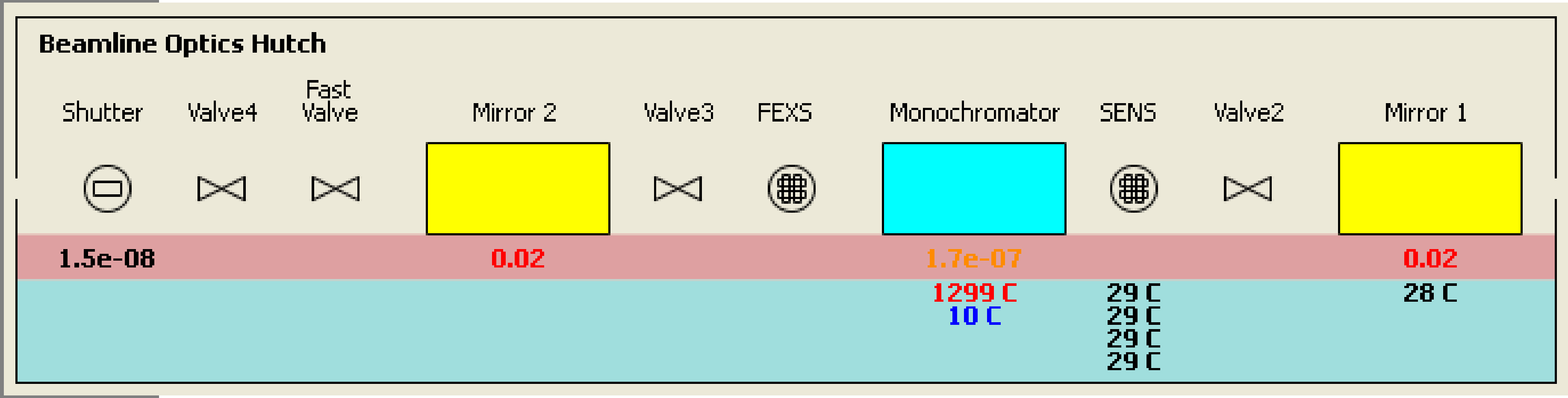


MCX Experimental setup
Optics – Mirror 2



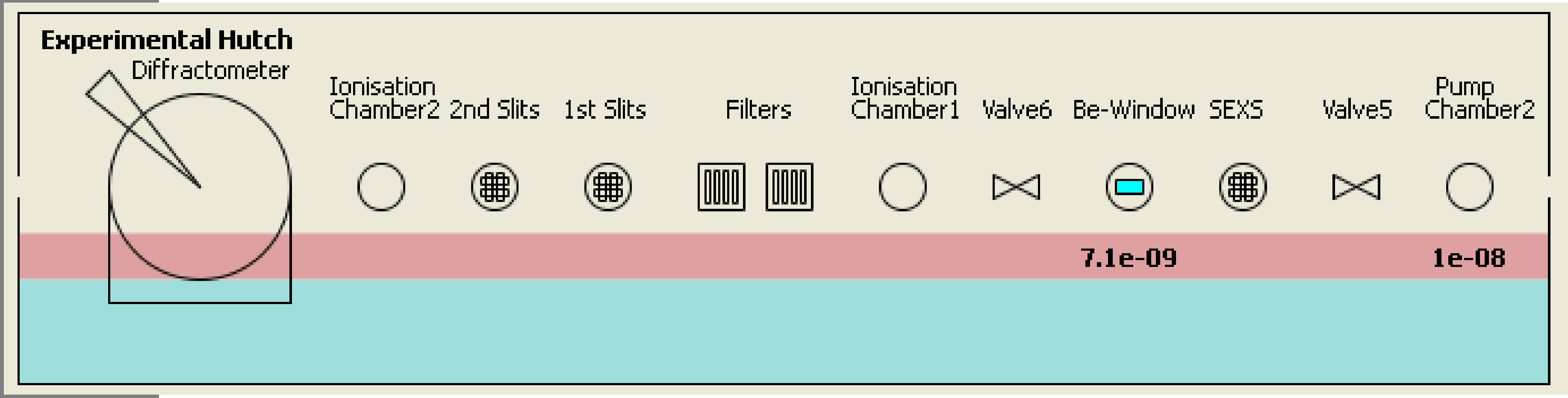
MCX Experimental setup
Beamline Optics Hutch

- Mirrors
- Monochromator
- Second entrance/First exit slits
- Shutter
- Several valves

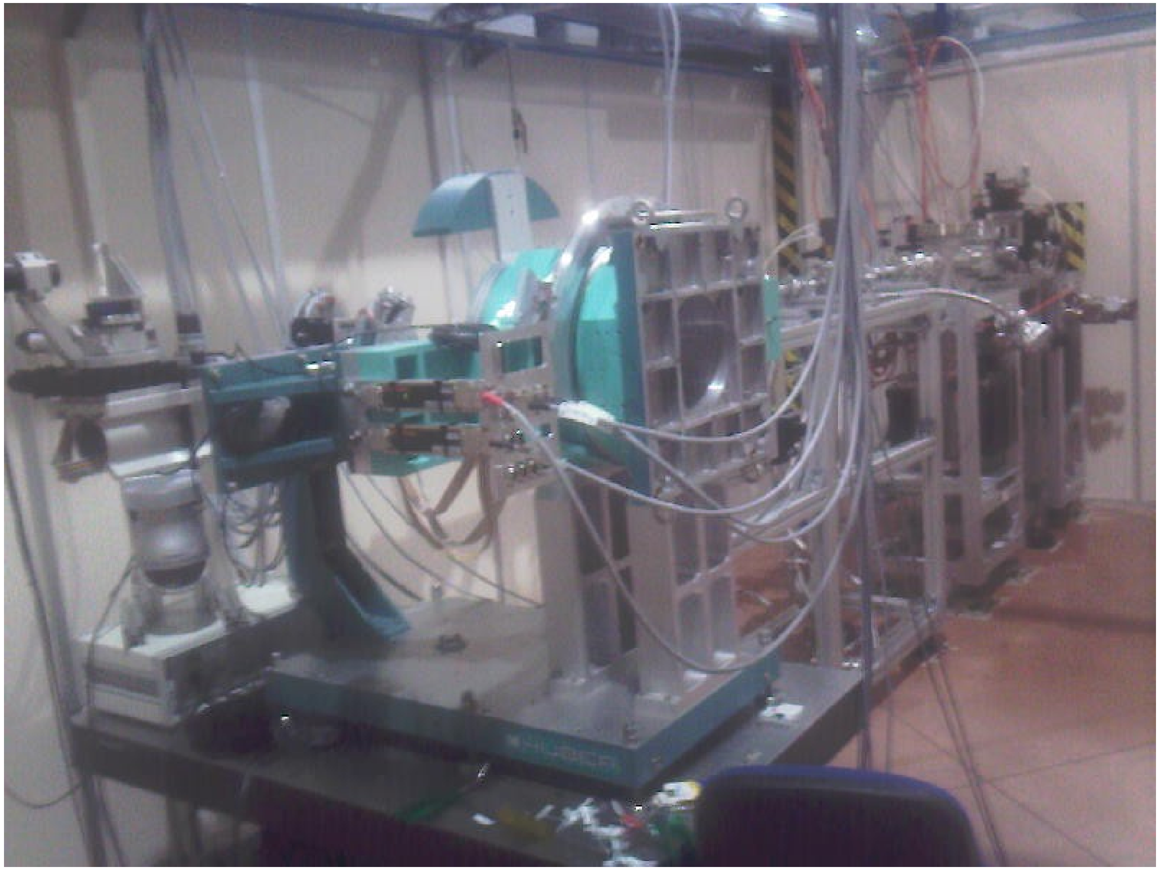


MCX Experimental setup Experimental Hutch

- Second exit slits
- Be-window
- filters
- slits
- Several valves
- Ionisation chambers

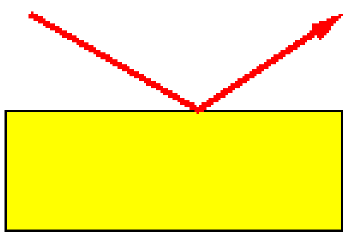


MCX Experimental setup
Experimental Hutch

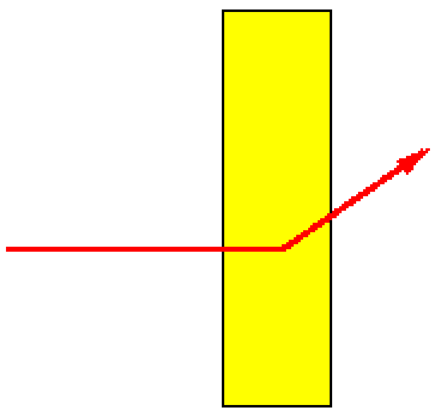


Diffraction geometry

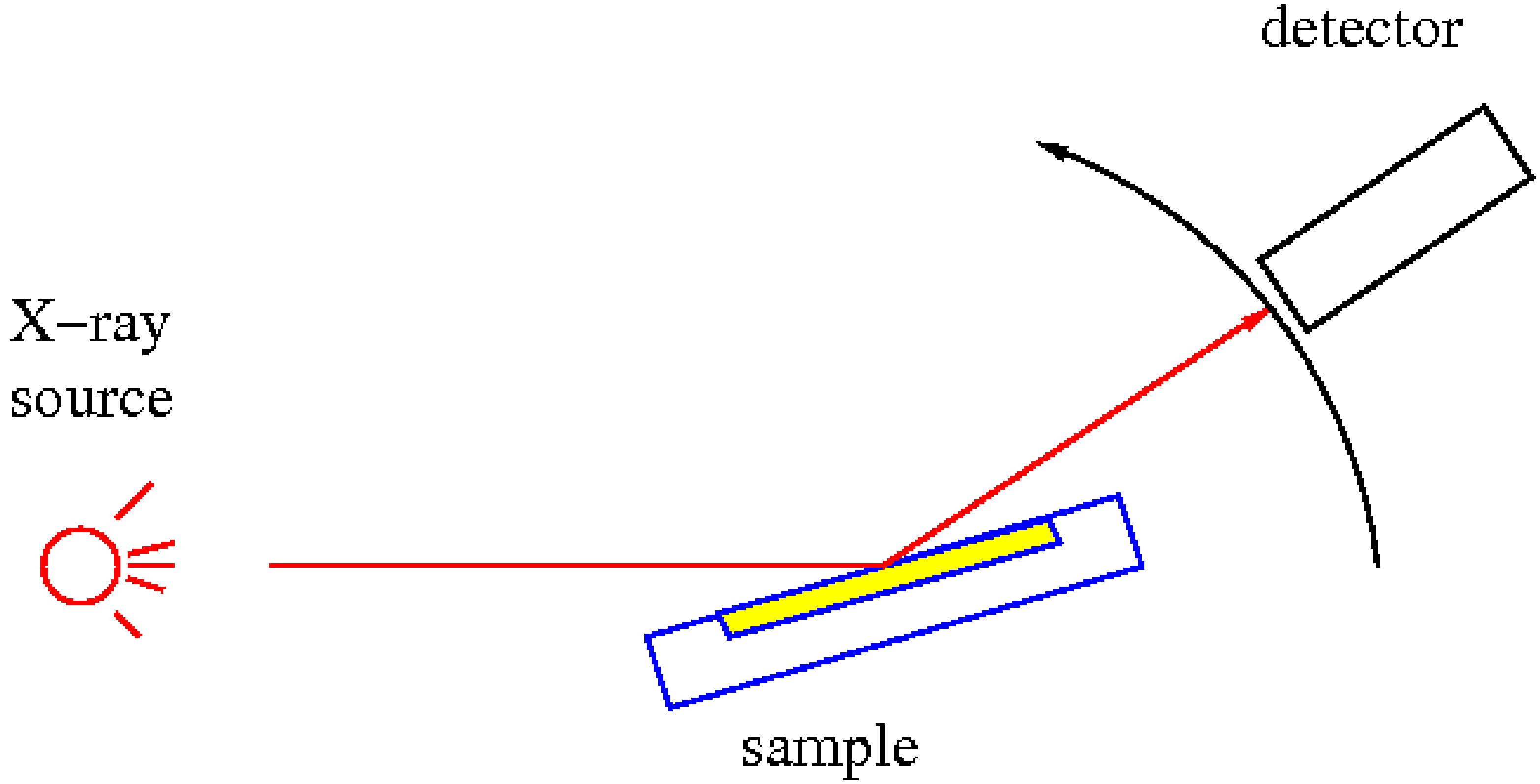
- Reflection geometry
  - Constant diffracting volume
  - Flat sample thick sample
  - Problem of preferred orientation



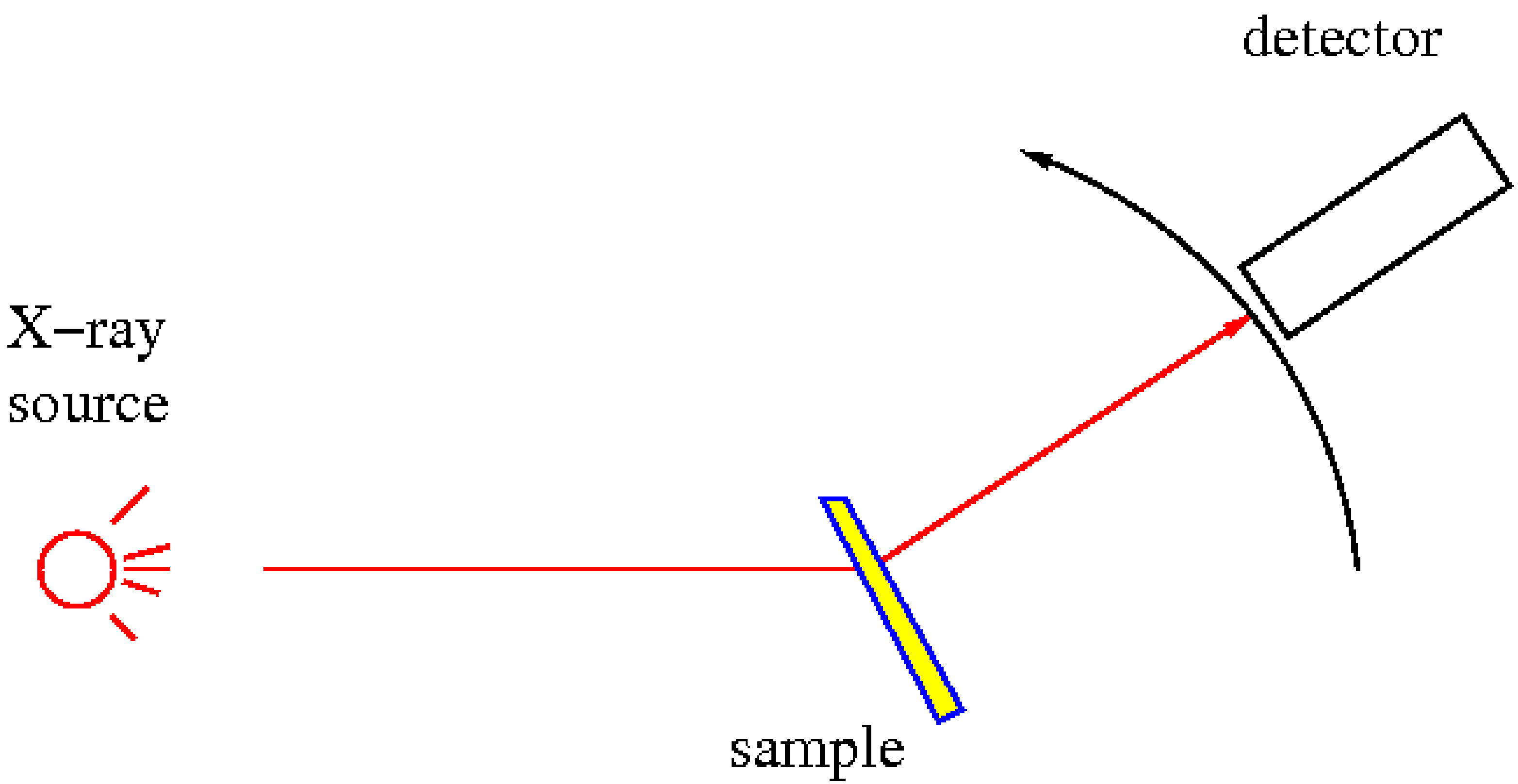
- Transmission geometry
  - Small sample volume
  - Lower signal background ratio



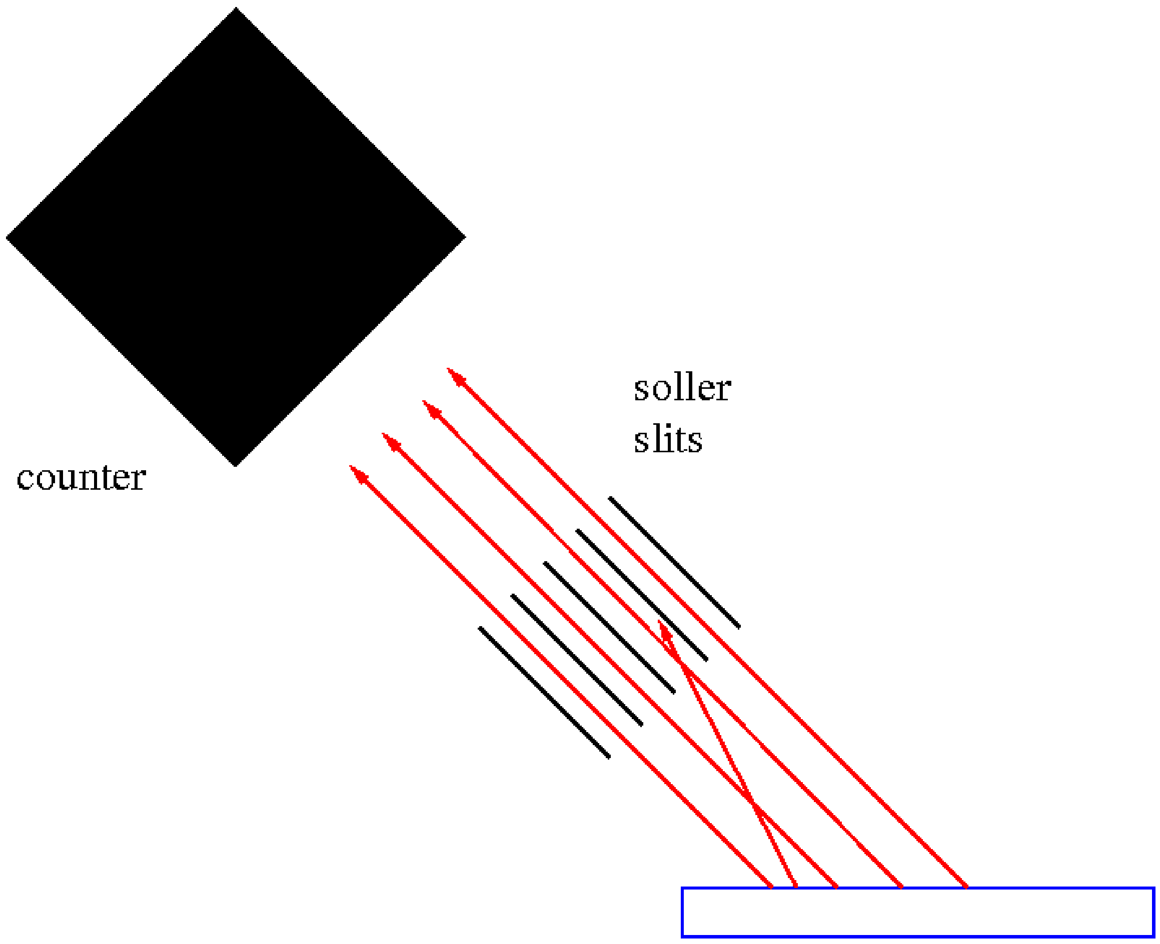
Bragg Brentano geometry



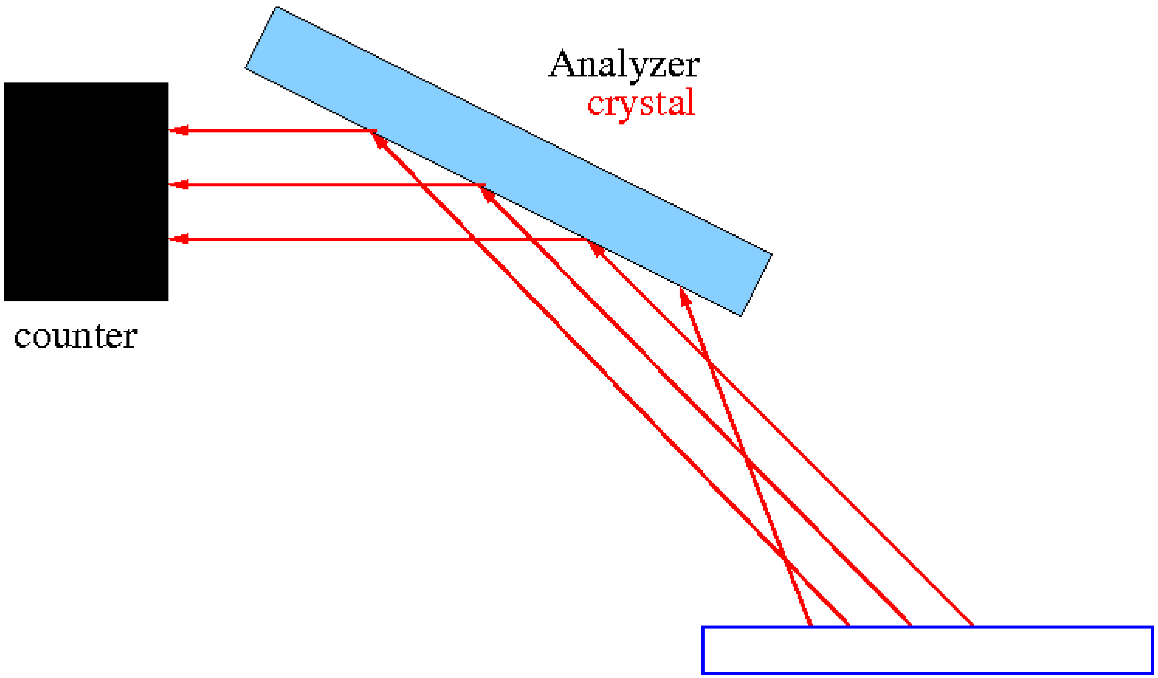
Debije-Scherrer geometry



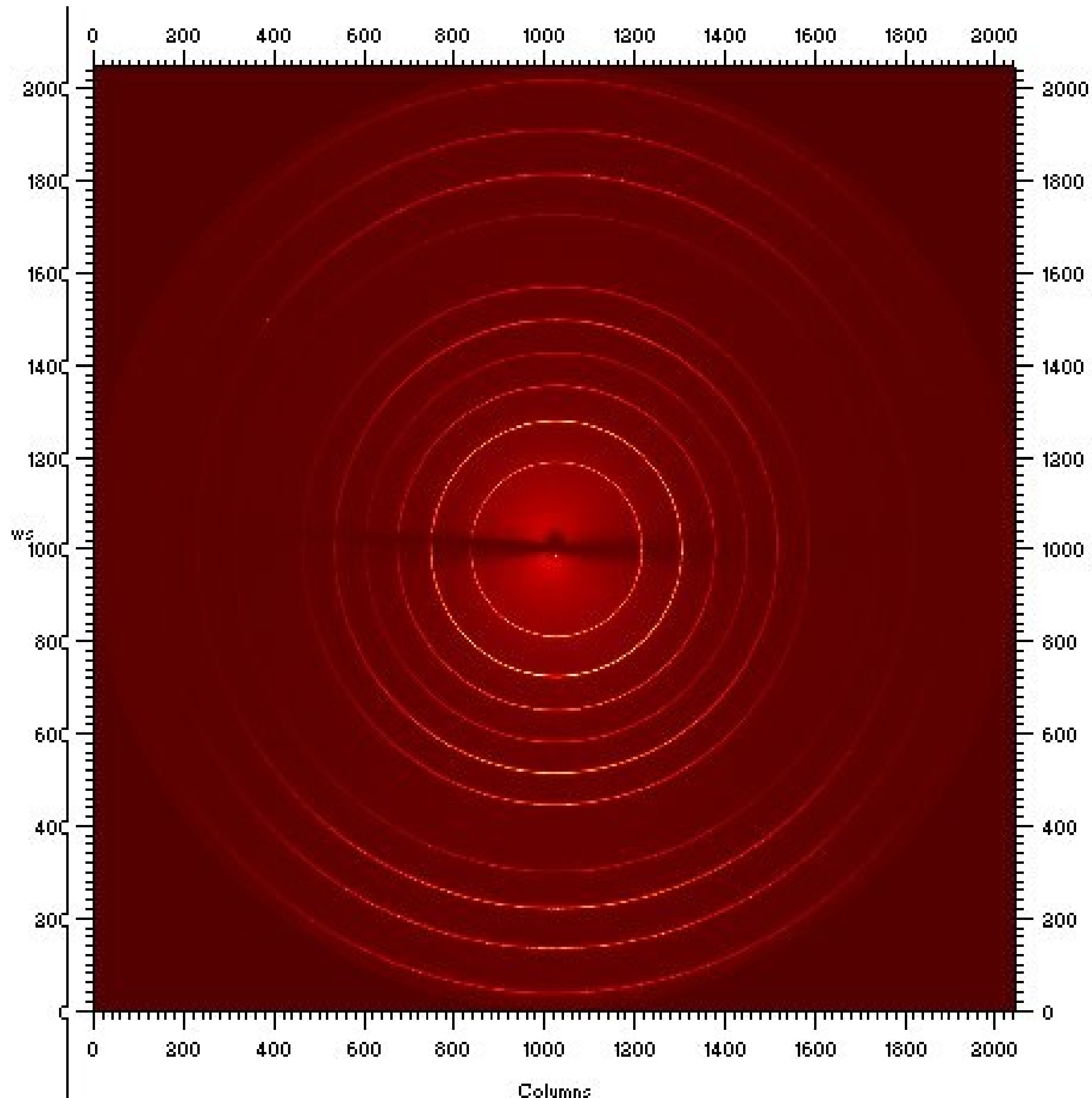
Detection system



Detection system



Using an 2D PSD

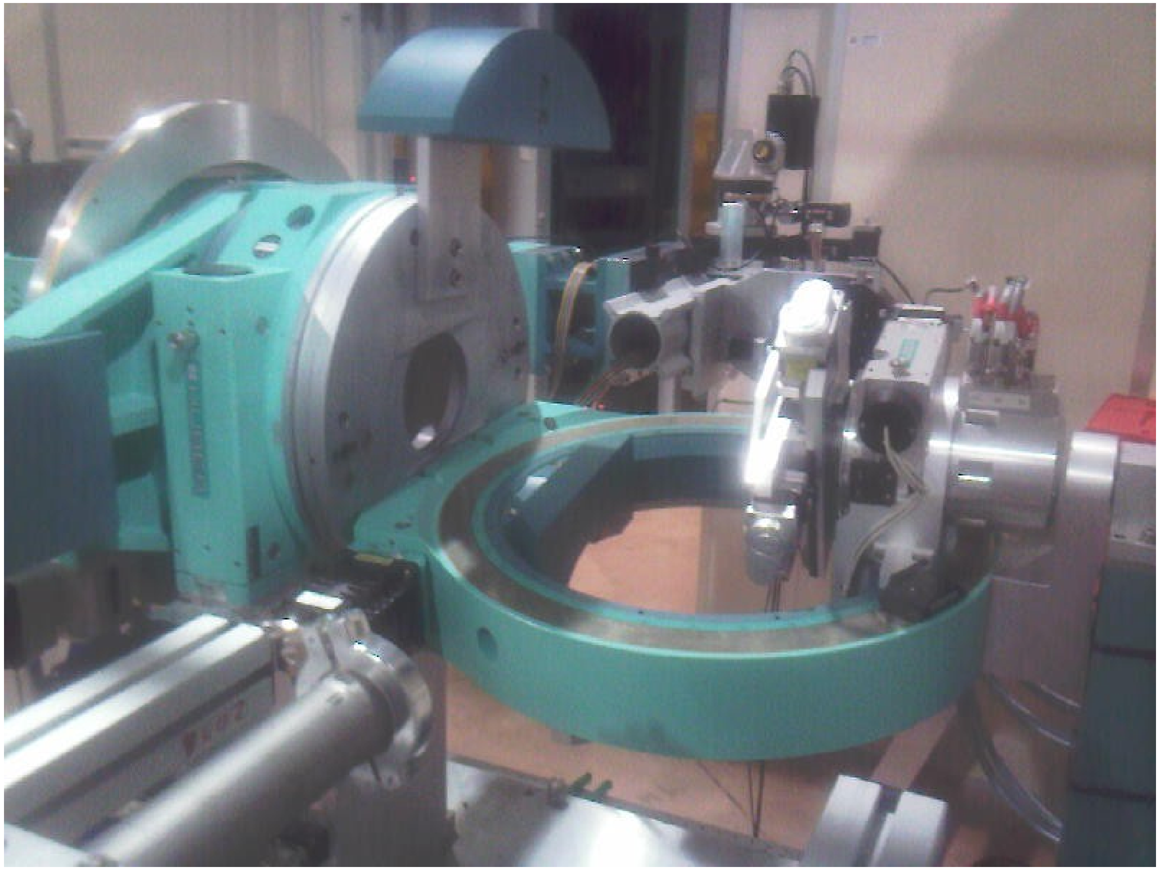


Multipurpose Diffraction System

- Must be suitable for various techniques
- MDS needs to be flexible
  - Support for different geometries
  - Space for in situ experimental chambers
- High precision control of movements required

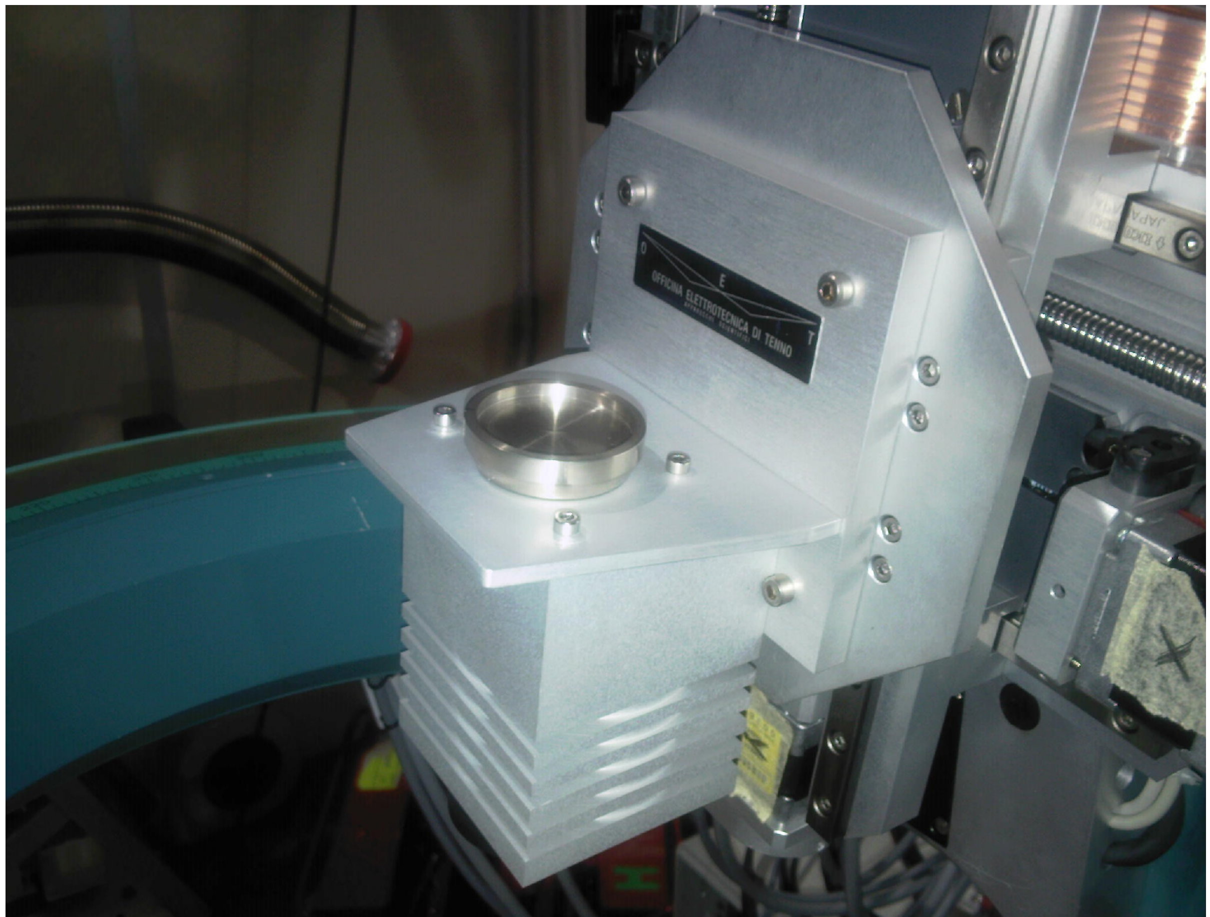
Experimental setup at MCX

- 4-circle goniometer



Experimental setup at MCX

- Sample holder



Experimental setup at MCX

- Detector