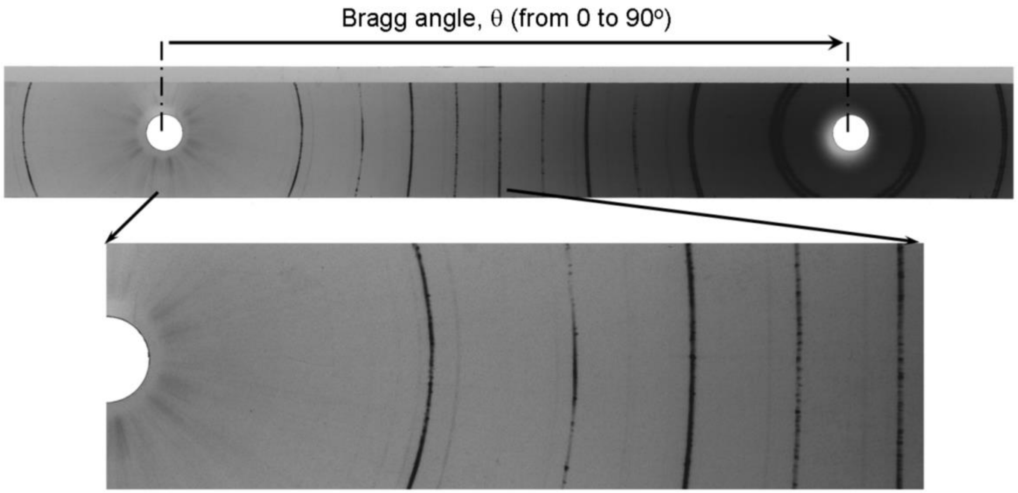
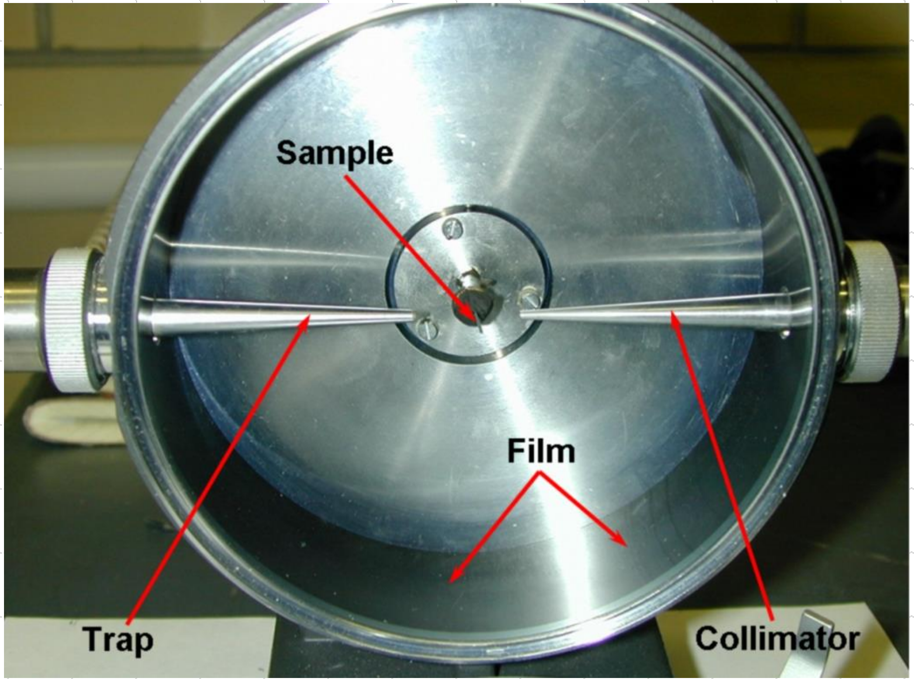
Diffractometer

Geometry
Optics
Detectors

Diffractometers

- Debye Scherrer Camera





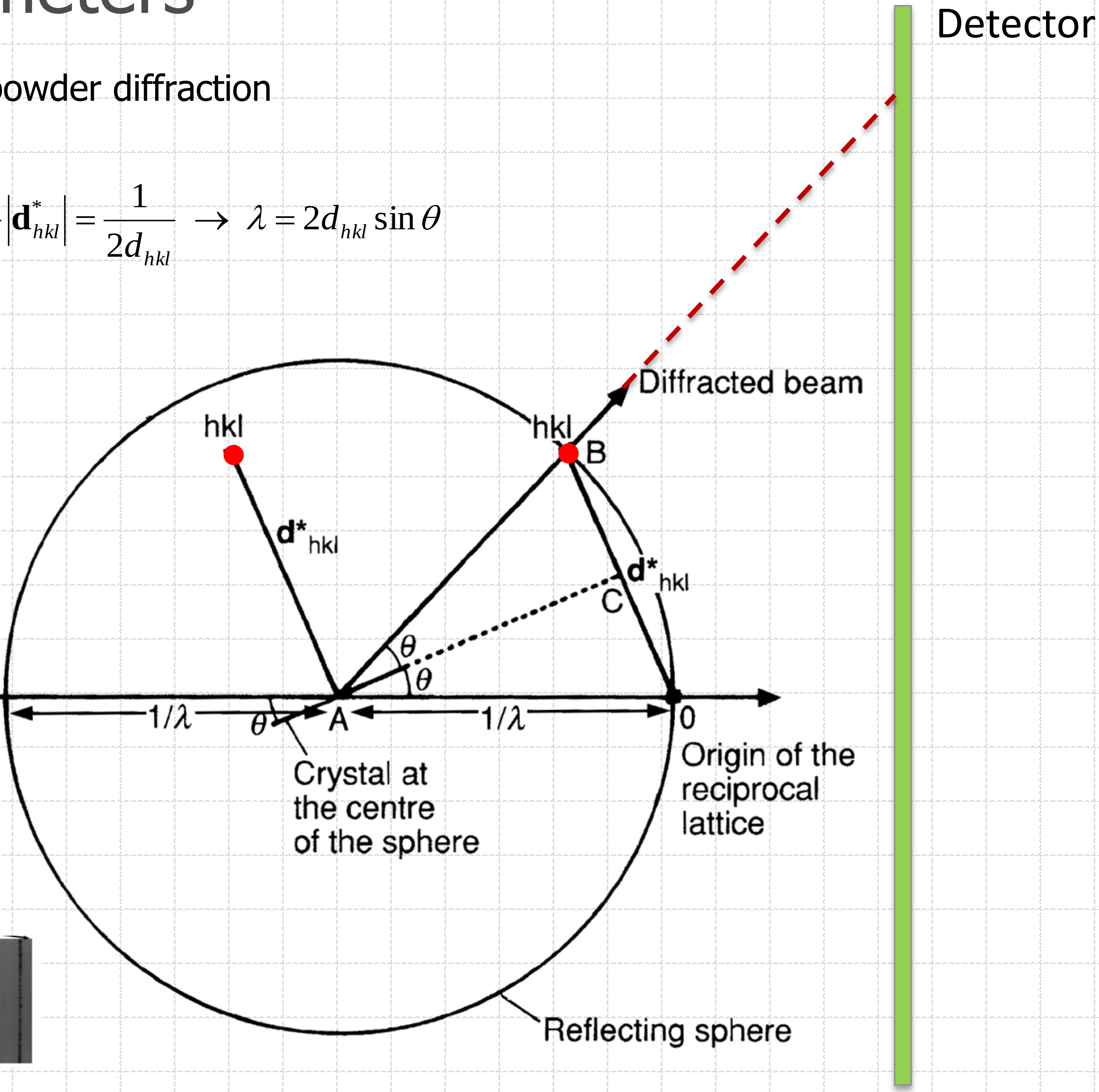
V.K. Pecharsky and P.Y. Zavalij "Fundamentals of Powder Diffraction and Structural Characterization of Materials".

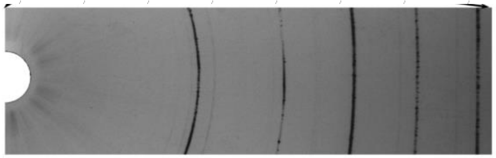
Diffractometers

- Ewald sphere and powder diffraction

$$|\mathbf{OC}| = \frac{1}{\lambda}\sin\theta = \frac{1}{2}\left|\mathbf{d}^*_{hkl}\right| = \frac{1}{2d_{hkl}} \rightarrow \lambda = 2d_{hkl}\sin\theta$$

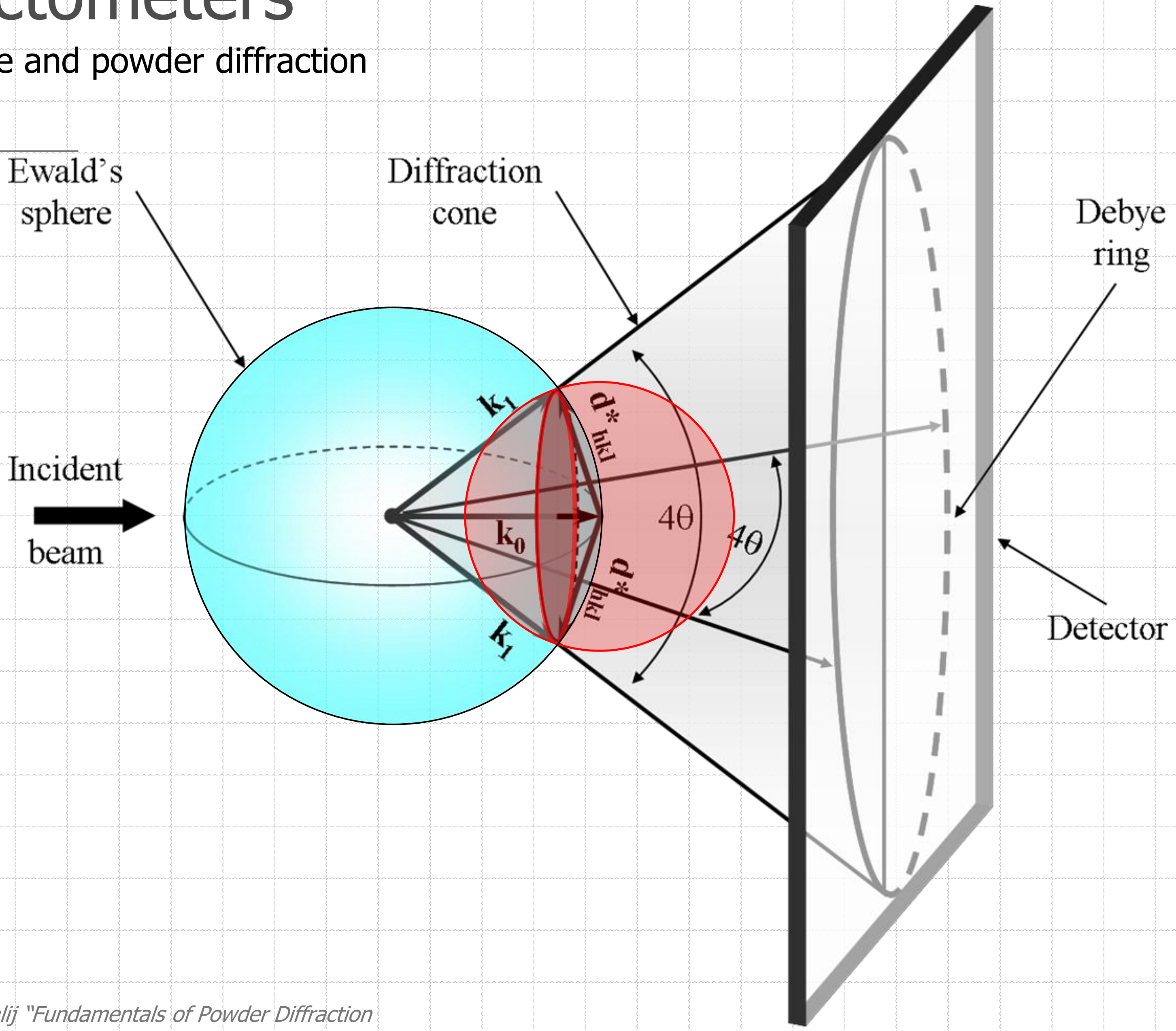
$$|\mathbf{OB}| = \mathbf{d}^*_{hkl}$$





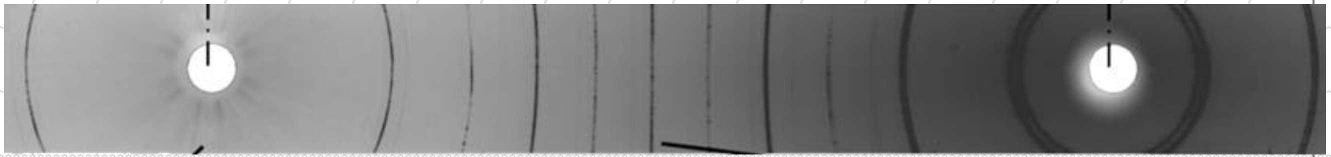
Diffractometers

- Ewald sphere and powder diffraction

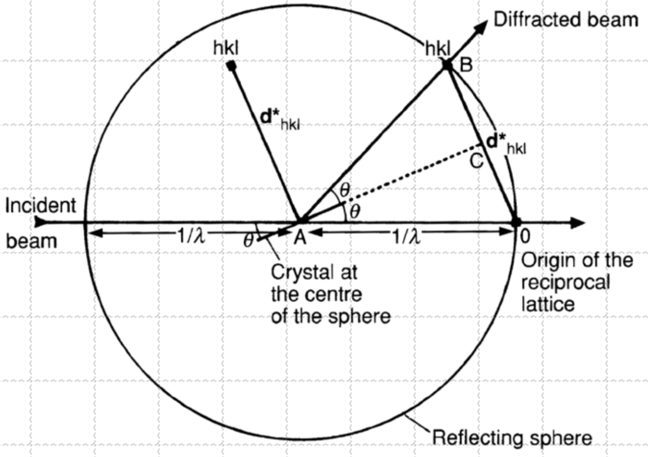


V.K. Pecharsky and P.Y. Zavalij "Fundamentals of Powder Diffraction and Structural Characterization of Materials".

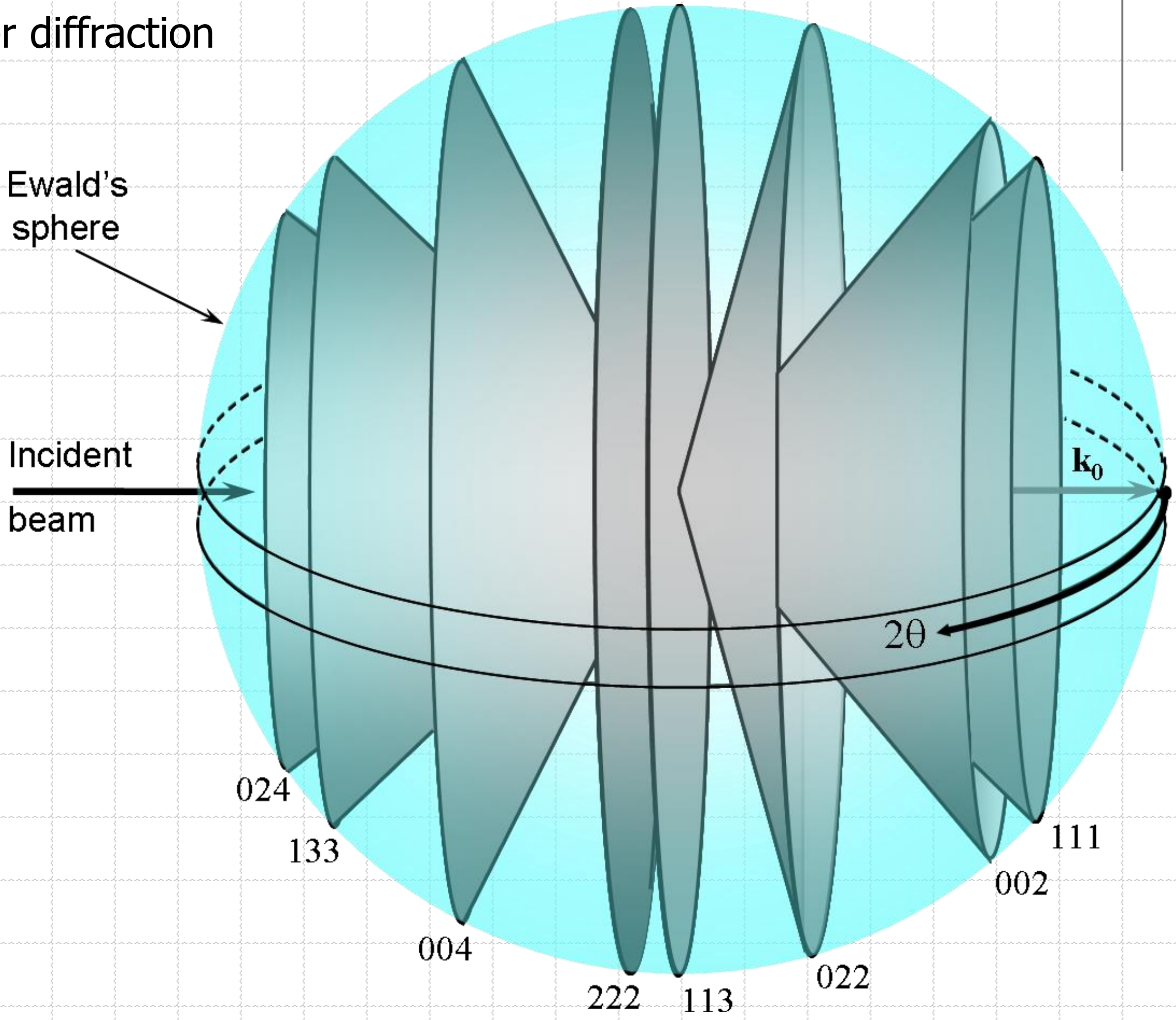
Diffractometers



- Ewald sphere and powder diffraction



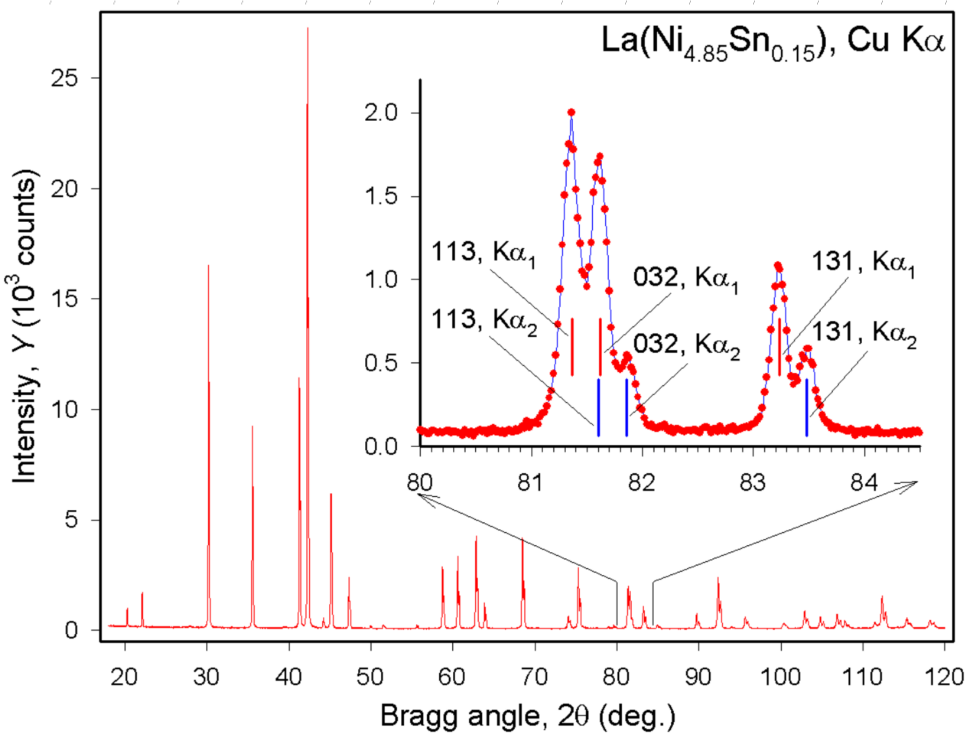
$$|\mathbf{OC}| = \frac{1}{\lambda}\sin\theta = \frac{1}{2}\left|\mathbf{d}^*_{hkl}\right| = \frac{1}{2d_{hkl}} \rightarrow \lambda = 2d_{hkl}\sin\theta$$

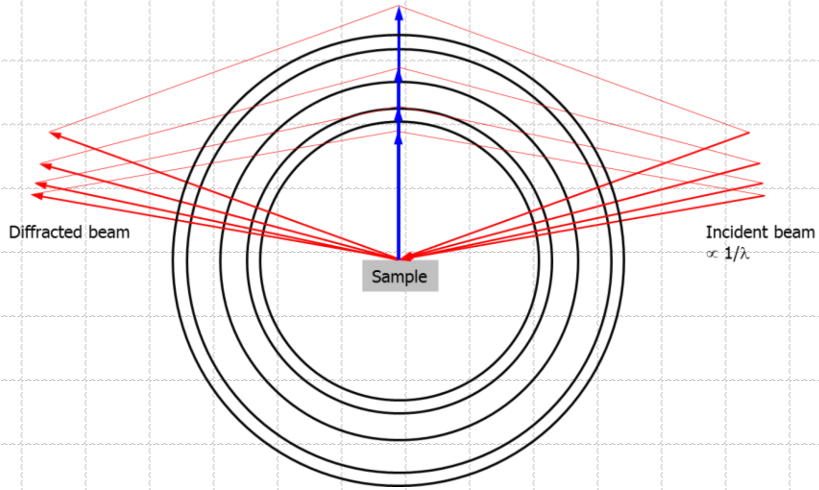


V.K. Pecharsky and P.Y. Zavalij "Fundamentals of Powder Diffraction and Structural Characterization of Materials".

Diffractometers

- Powder Diffractometer

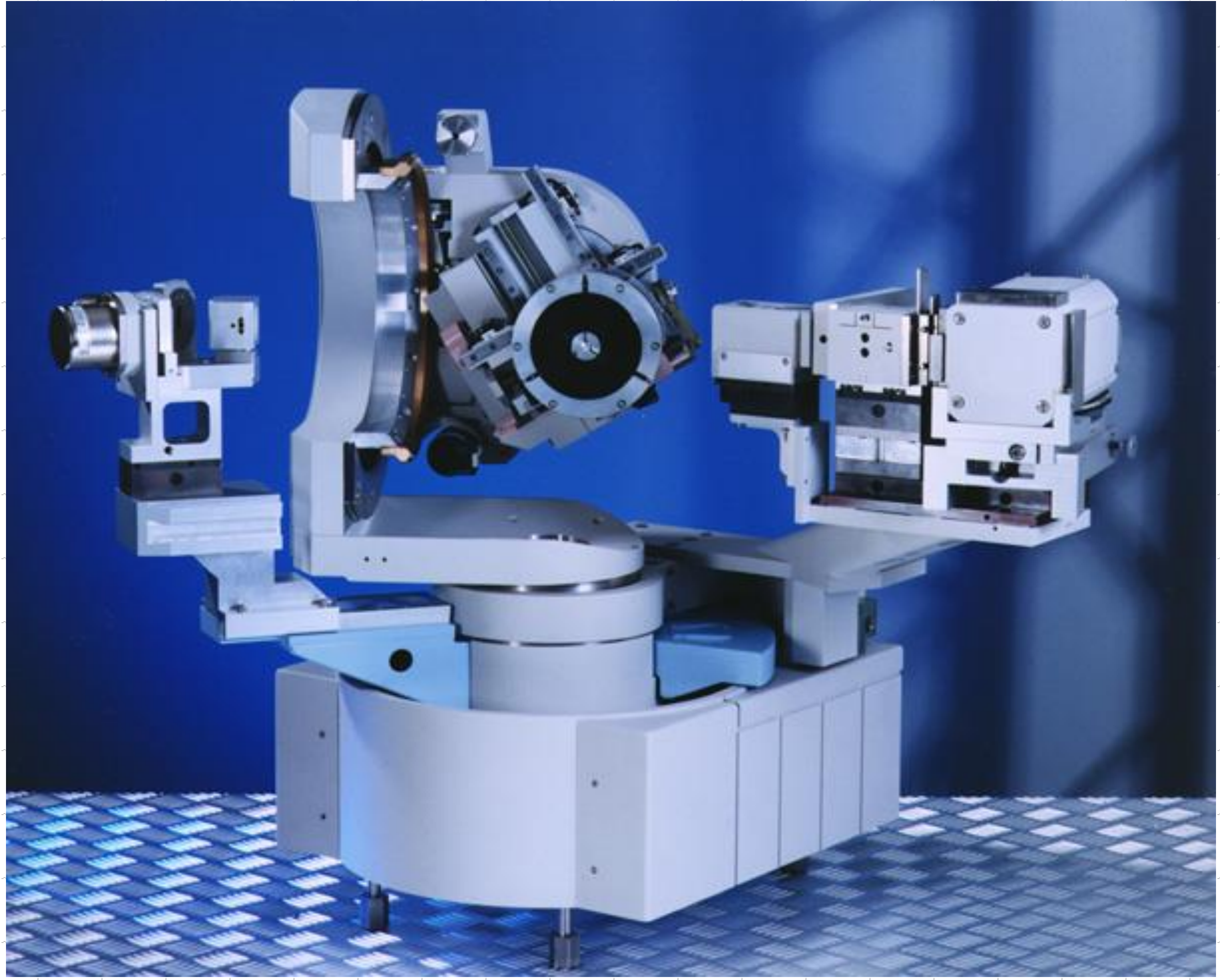




V.K. Pecharsky and P.Y. Zavalij "Fundamentals of Powder Diffraction and Structural Characterization of Materials".

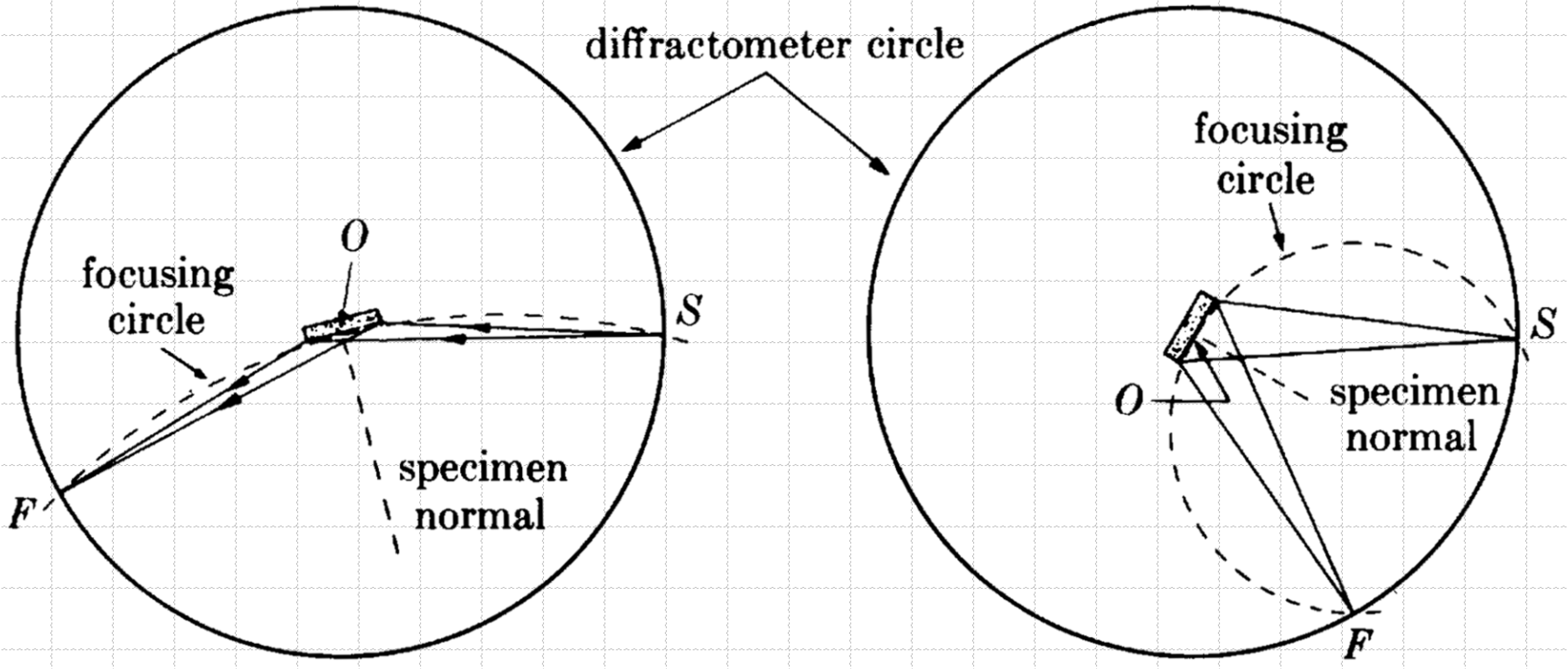
Diffractometers

- PANalytical X’Pert Materials Research Diffractometer



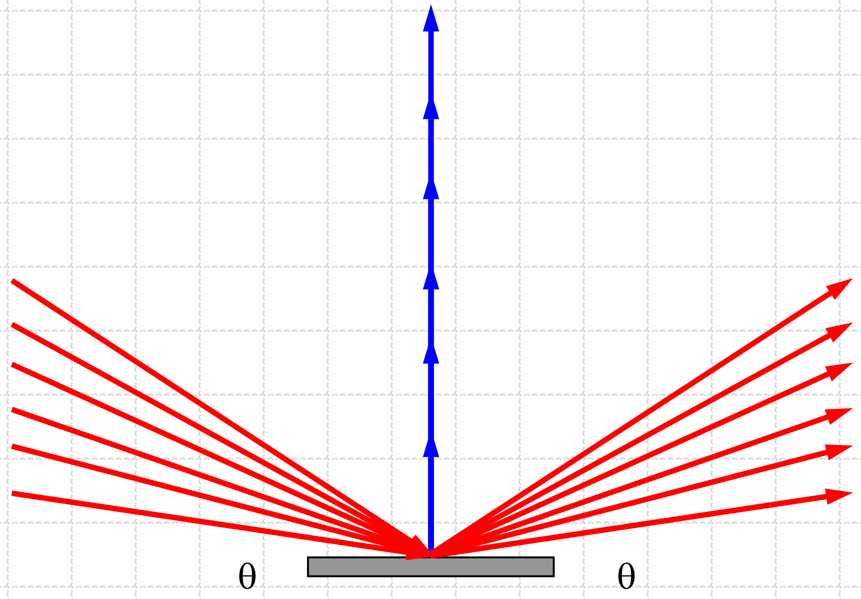
X-ray Powder Diffractometer

- Powder diffractometers working in the Bragg-Brentano (θ-2θ) geometry utilize a parafocusing geometry to increase intensity and angular resolution



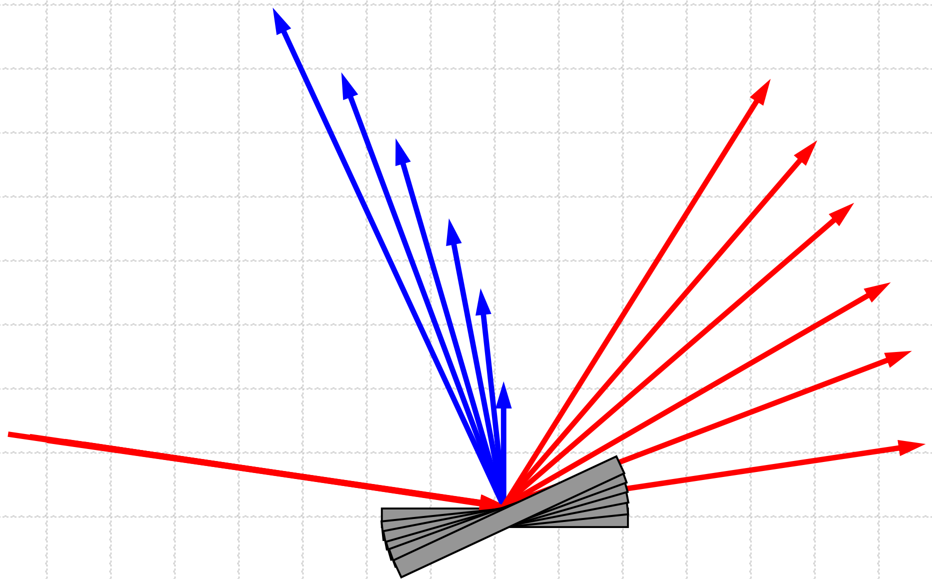
Diffractometers

- Goniometer for Powder Diffraction – θ-θ scan



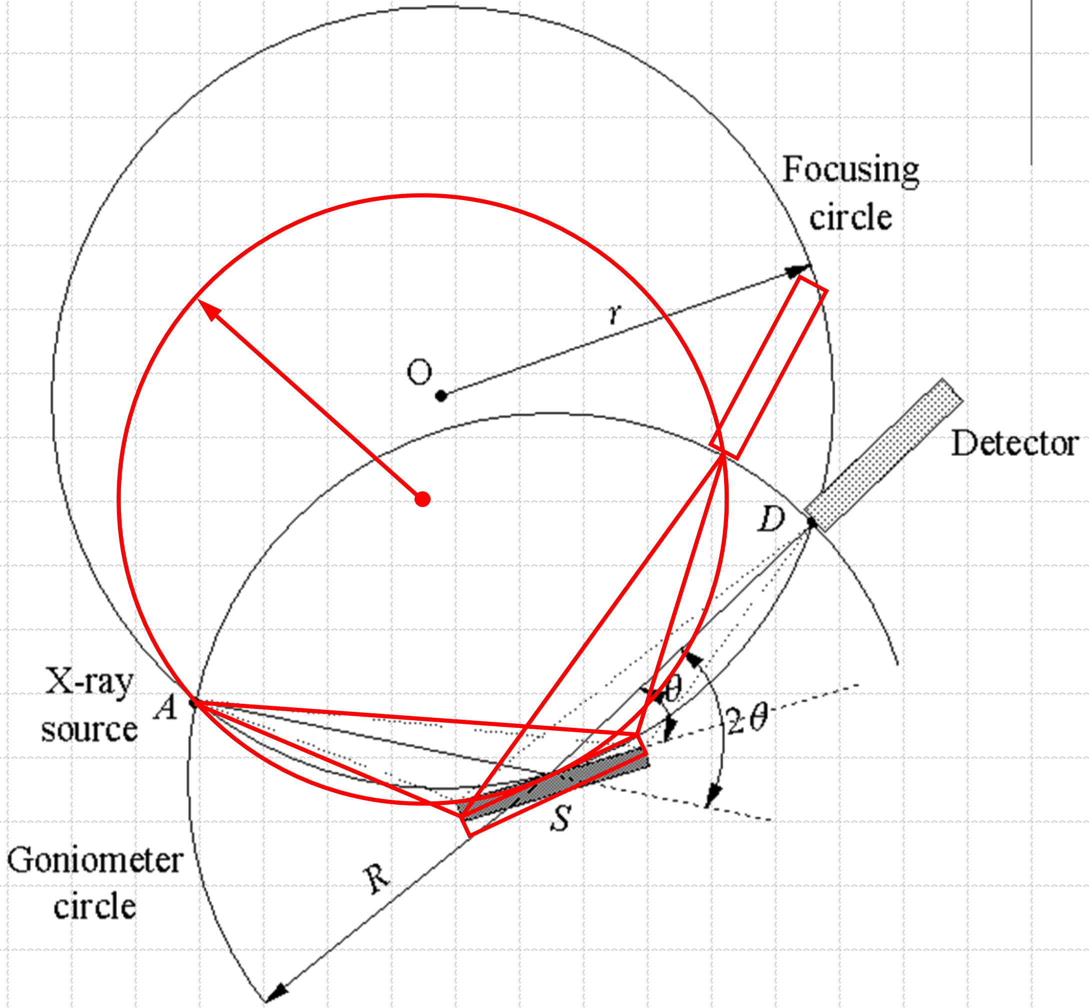
Diffractometers

- Goniometer for Powder Diffraction – θ-2θ scan



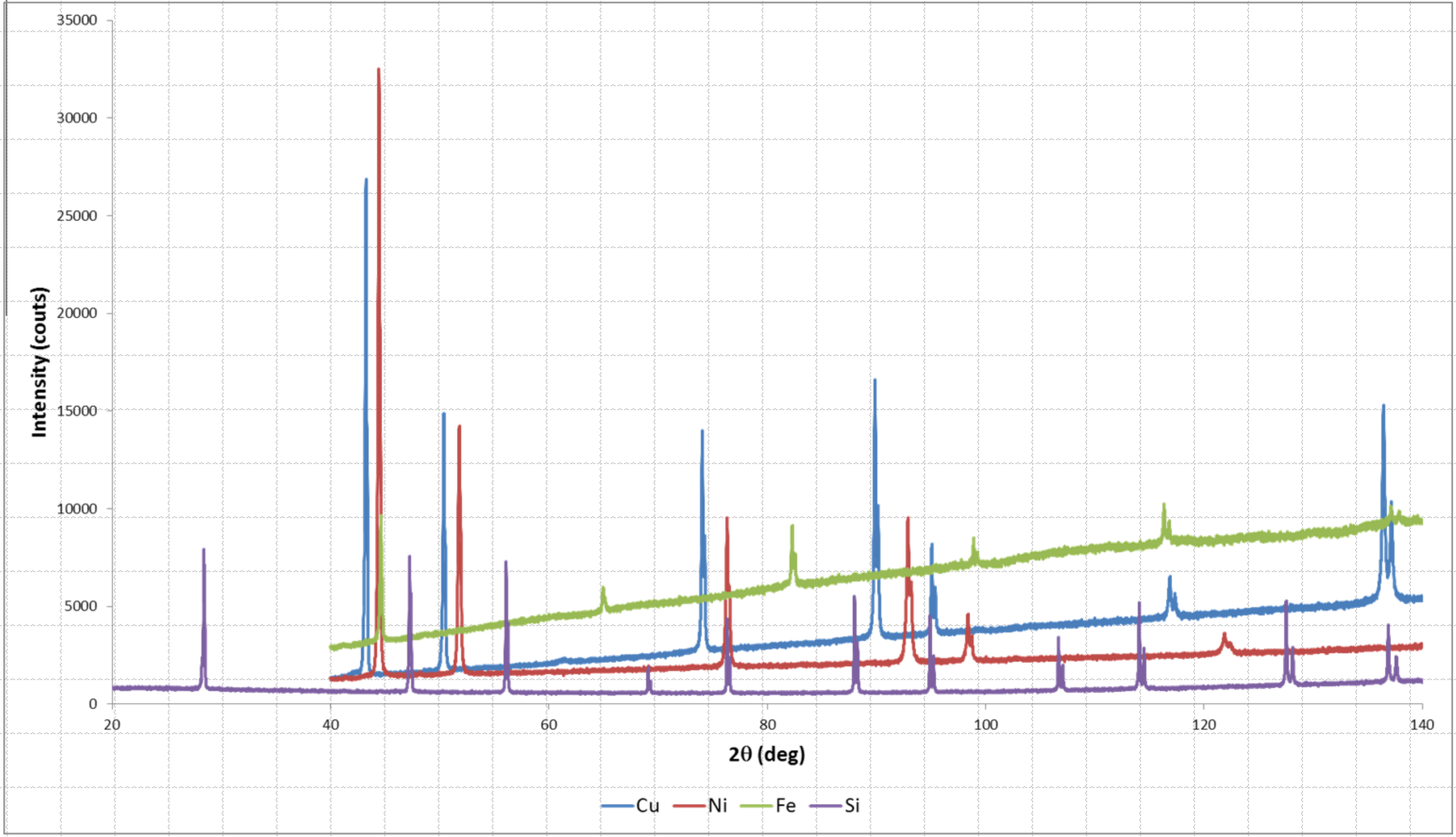
X-ray Powder Diffractometer

- Parafocusing geometry of the Bragg-Brentano diffractometer. *S* is the sample, *R* is the radius of the goniometer circle, *r* is the radius of a focusing circle and *θ* is the Bragg angle. The x-ray beam is emitted from point *A* and is focused at the detection point *D*.



X-ray Powder Diffractometer

- Powder Diffraction of Cu, Ni, Fe and Si.



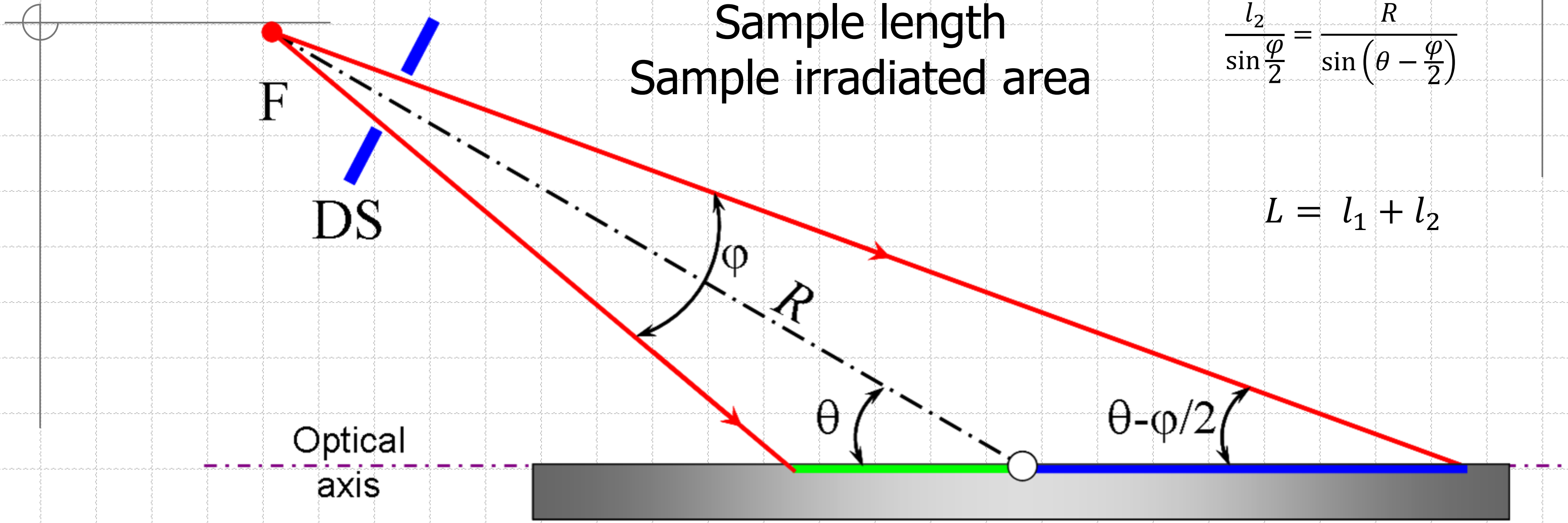
X-ray Powder Diffractometer

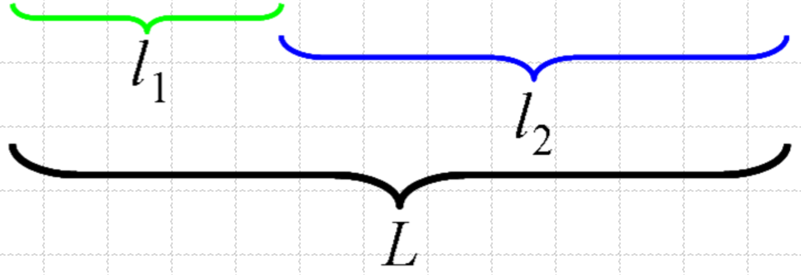
$$\frac{l_1}{\sin\frac{\varphi}{2}} = \frac{R}{\sin\left(\theta+\frac{\varphi}{2}\right)}$$

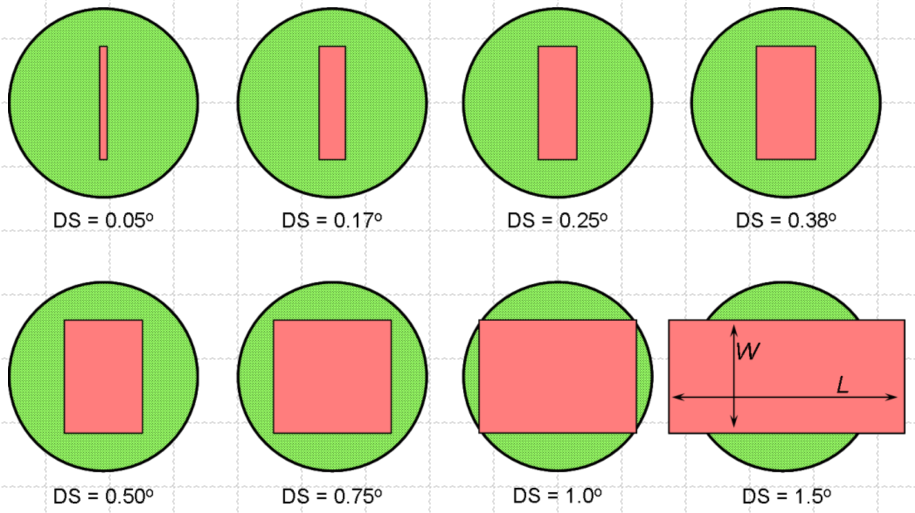
$$\frac{l_2}{\sin\frac{\varphi}{2}} = \frac{R}{\sin\left(\theta-\frac{\varphi}{2}\right)}$$

$$L = l_1 + l_2$$

Sample length
Sample irradiated area





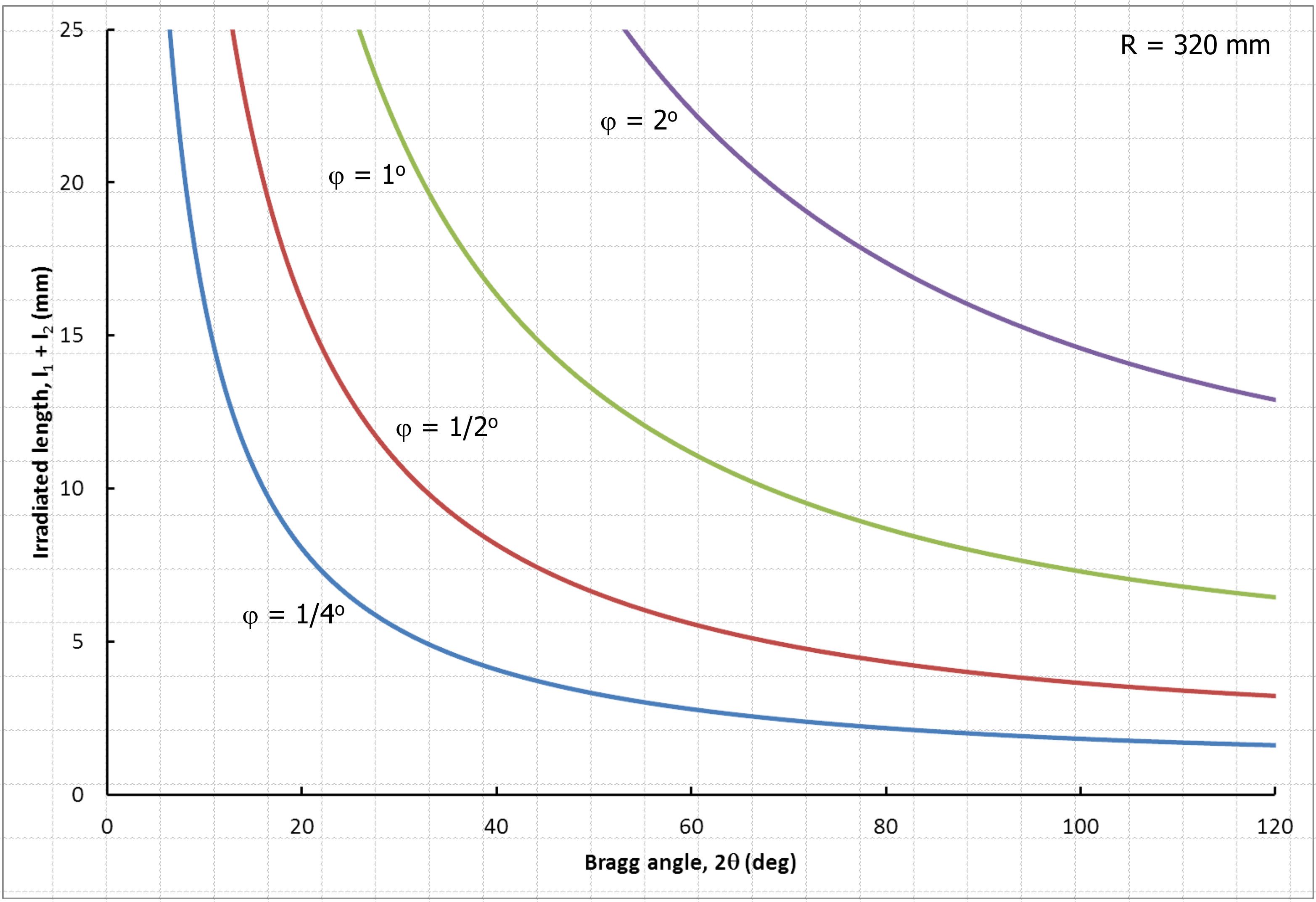


DS = 0.05°
DS = 0.17°
DS = 0.25°
DS = 0.38°
DS = 0.50°
DS = 0.75°
DS = 1.0°
DS = 1.5°

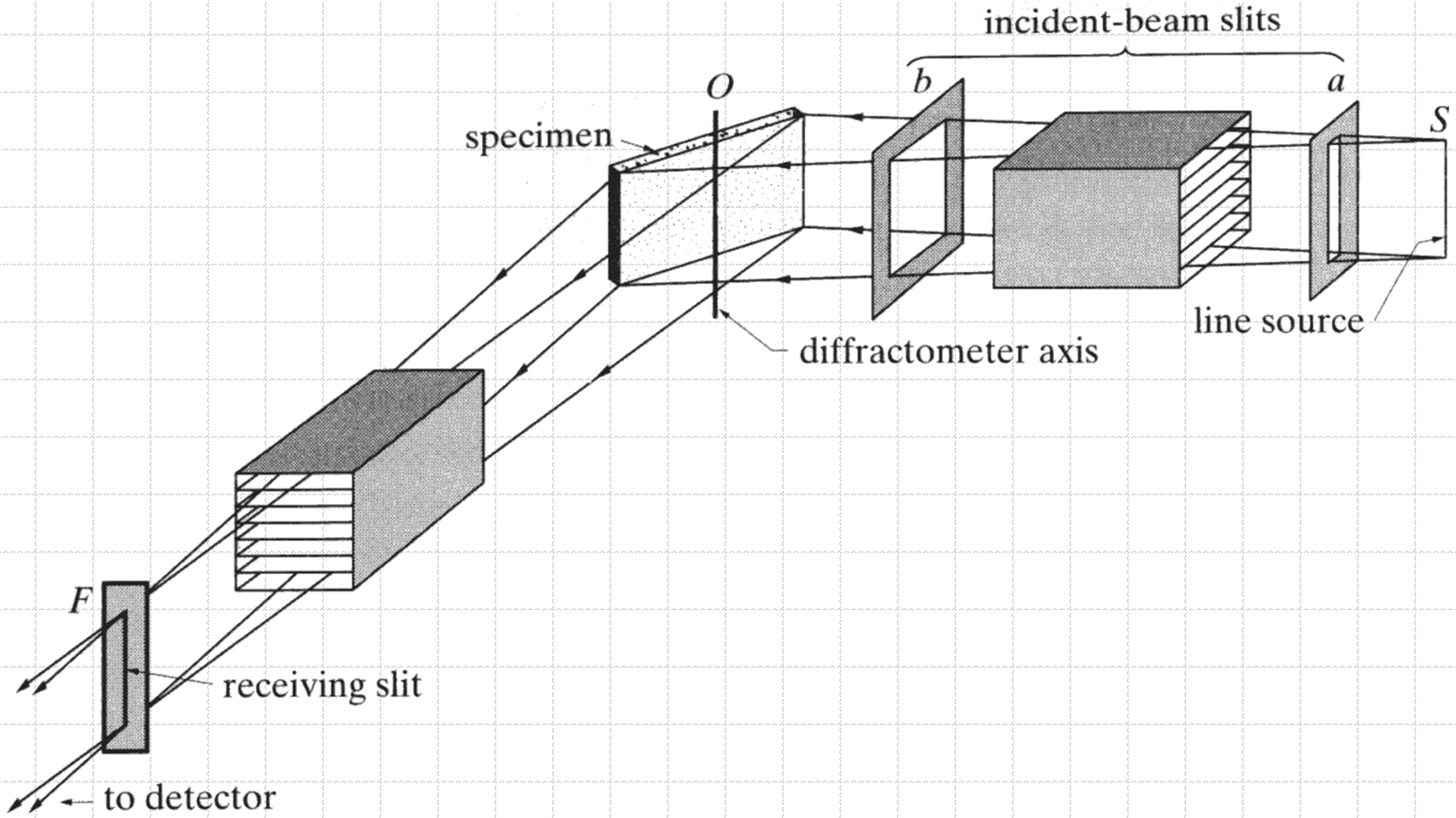
X-ray Powder Diffractometer

Sample length

Sample irradiated area



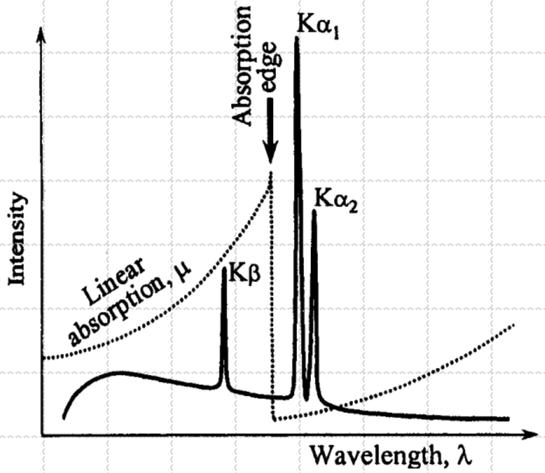
X-ray Optics

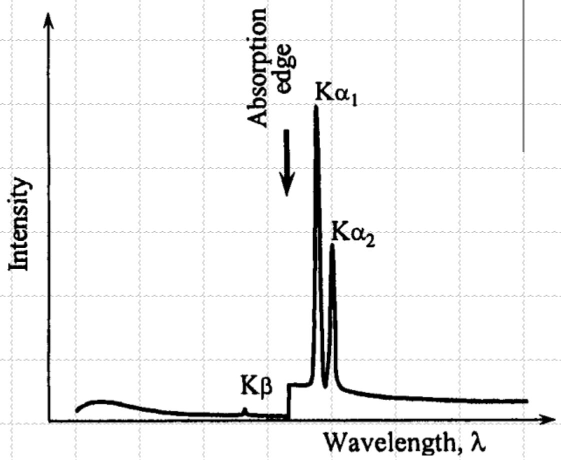

incident-beam slits
O
b
a
S
specimen
line source
diffractometer axis
F
receiving slit
to detector

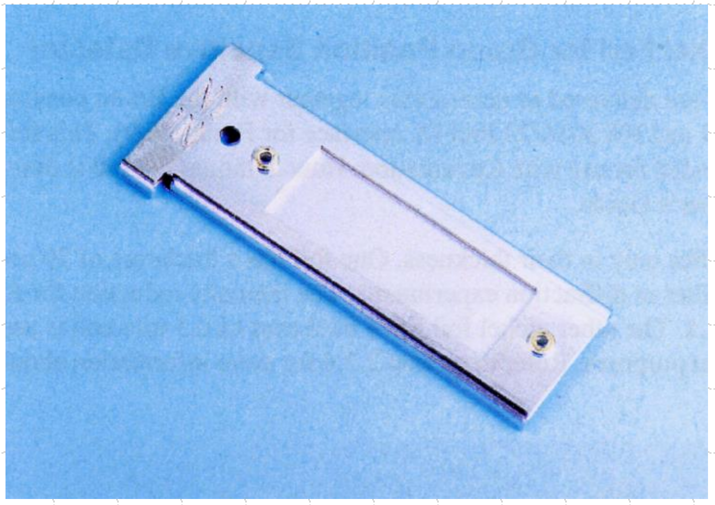
Beta-filters

$$I_t = I_0 \exp(-\mu x)$$

- A beta-filters are used to keep as much as possible of the characteristic *K*α radiation from the tube whilst suppressing *K*β and white radiation.



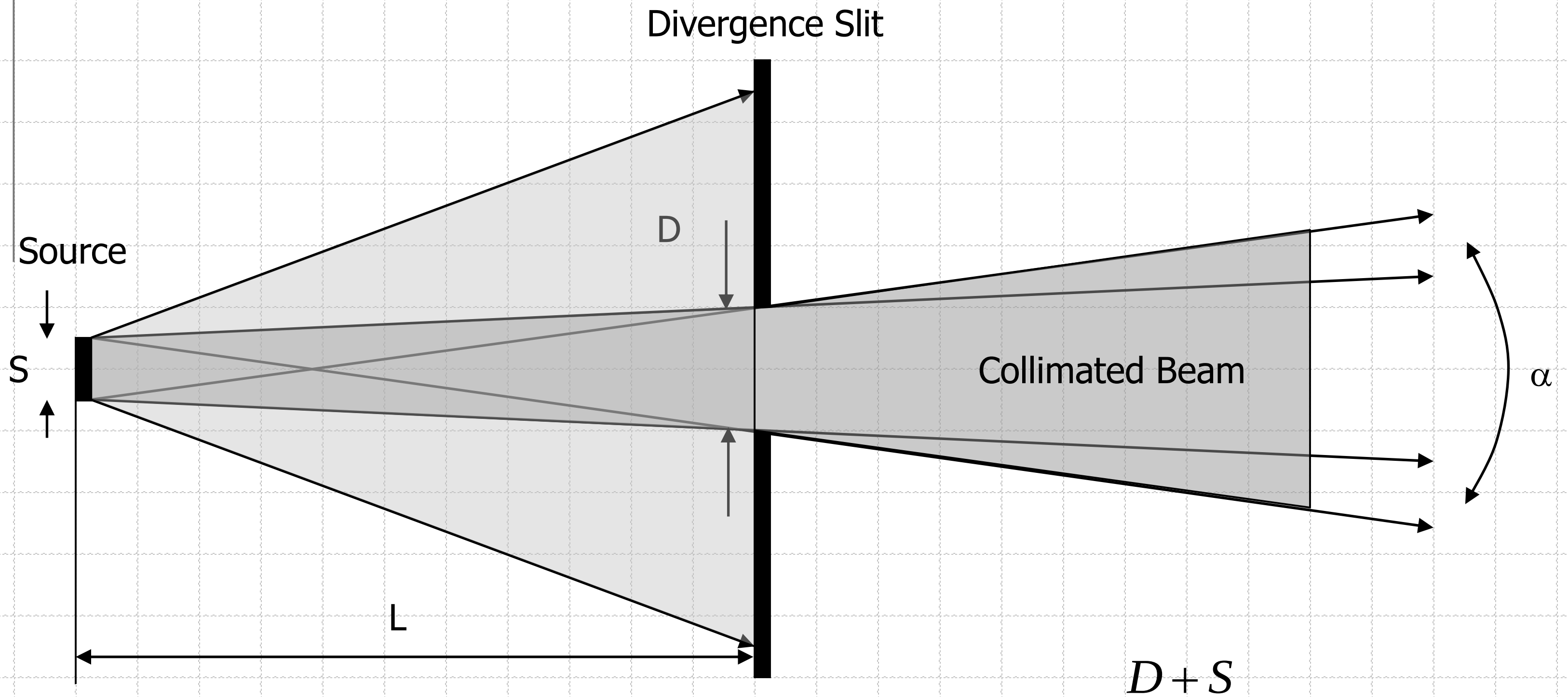




Tube anode material	Beta-filter material	Thickness [μm]	$K\beta$ intensity reduction [%]	$K\alpha$ intensity reduction [%]
Mo	Zr	75	97	54
Cu	Ni	20	99	58
Co	Fe	16	99	51
Cr	V	13	98	45

Collimators

- Simplest collimation is achieved by placing a slit between x-ray source and the sample

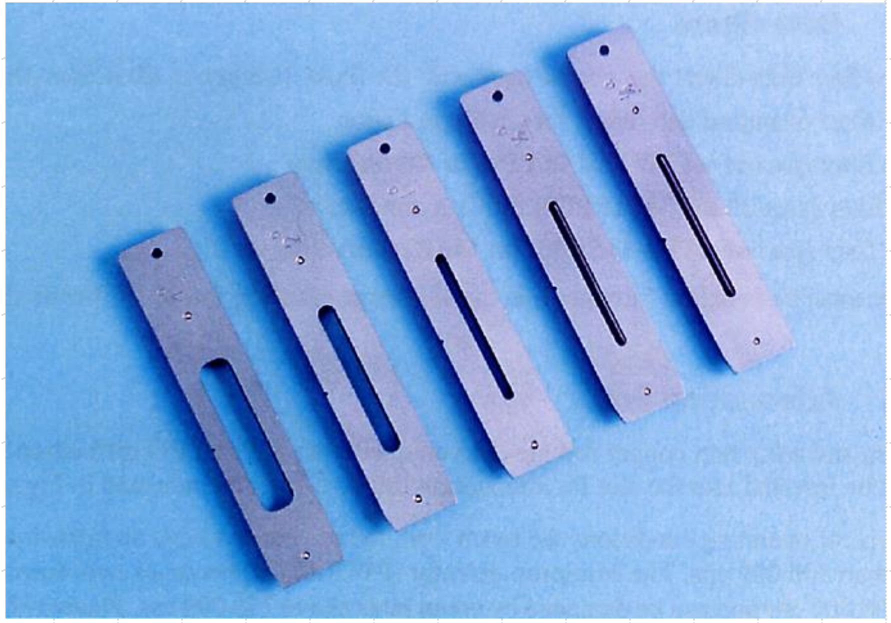


$$\alpha \approx \frac{D+S}{L}$$

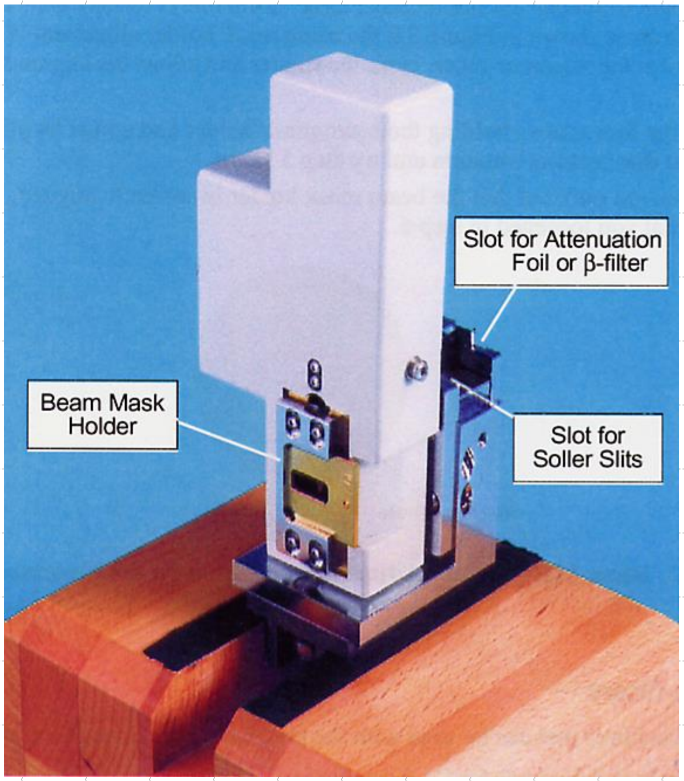
if $L >> D$

Divergence Slits

- Divergence slits are fitted in the incident beam path to control the equatorial divergence of the incident beam, and thus, the amount (length) of the sample that is irradiated by the incident x-ray beam.



Fixed divergence slit



Programmable divergence slit

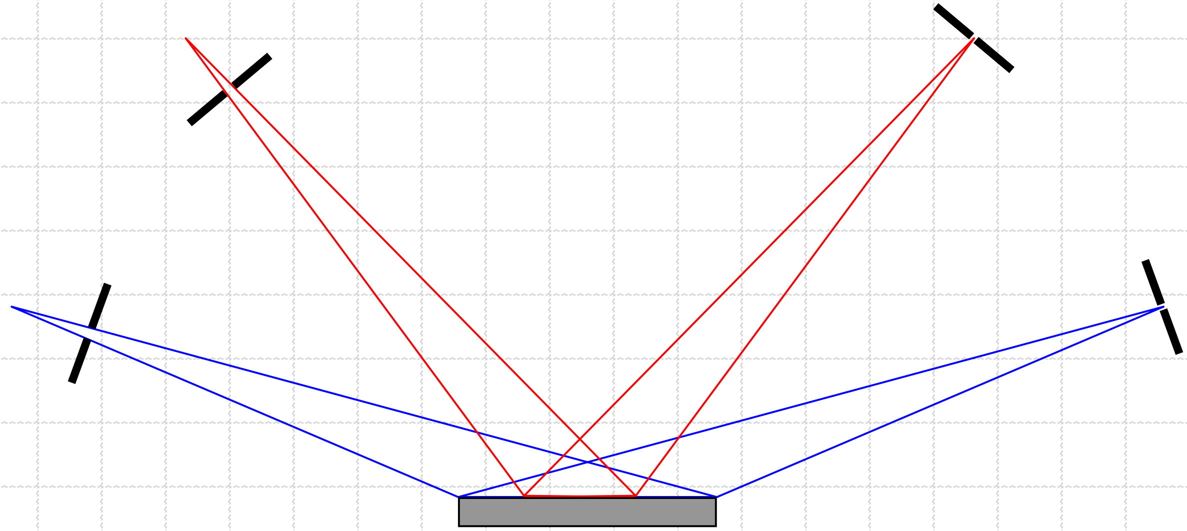
Diffractometers

- Fixed Slits

Divergence Slit:
- Match the diffraction geometry and sample size
- At any angle beam does not exceed sample size

$$\alpha \approx \frac{L \sin\theta}{R} \text{ (rad)}$$

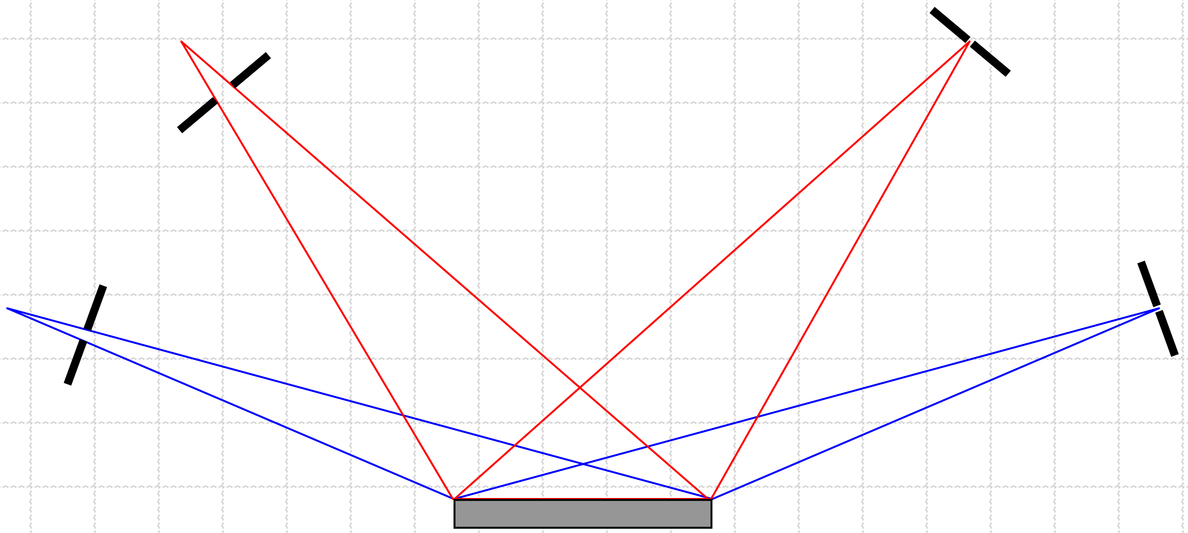
Receiving Slit:
- As small as possible to improve the resolution
- Very small slit size reduces diffracted beam intensity



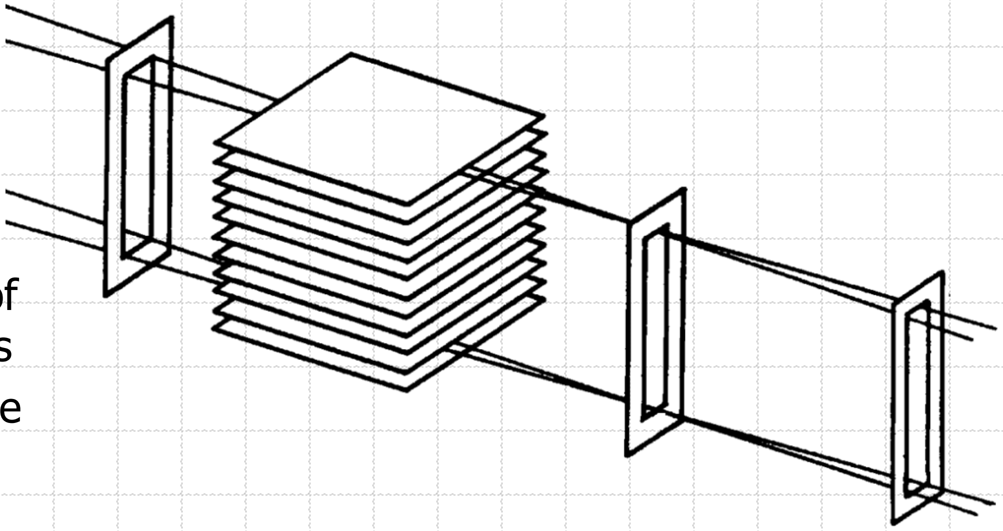
Diffractometers

Variable Slits

- Vary aperture continuously during the scan
- Length of the sample is kept constant

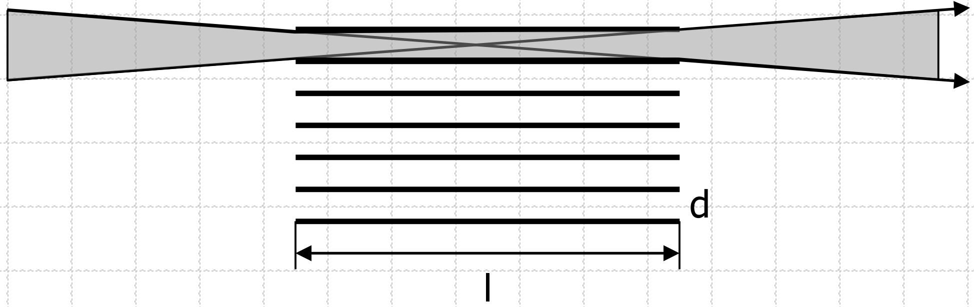


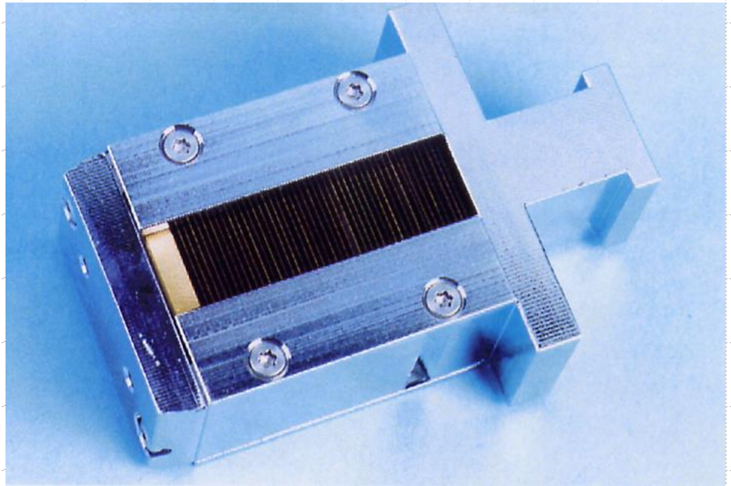
Soller Slits



- Soller slits used to limit the axial (vertical / out-of-plane) divergence of the incident & diffracted X-ray beams
- Using soller slits improves peak shape and the resolution in 2θ-type scans, especially at low scattering angles.

$$\alpha \approx \frac{2d}{l}$$

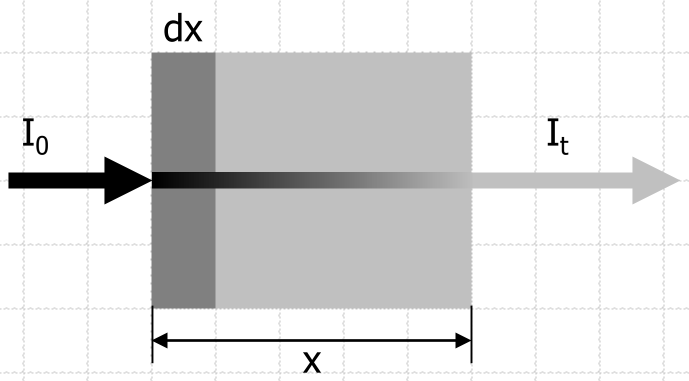


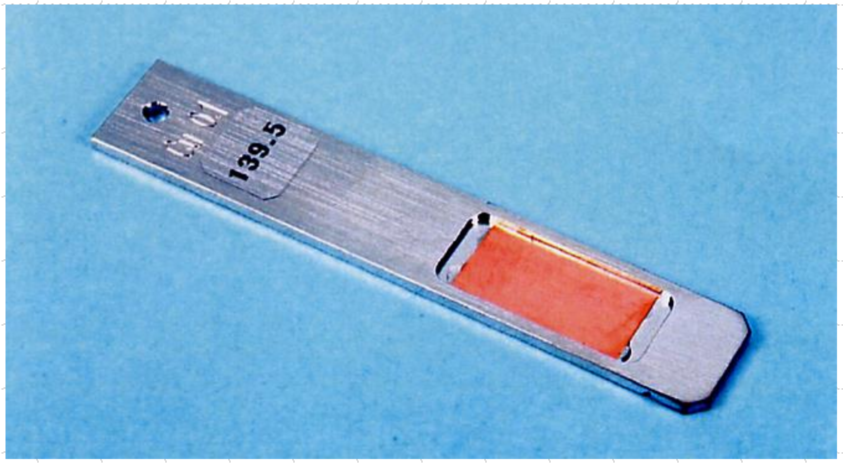


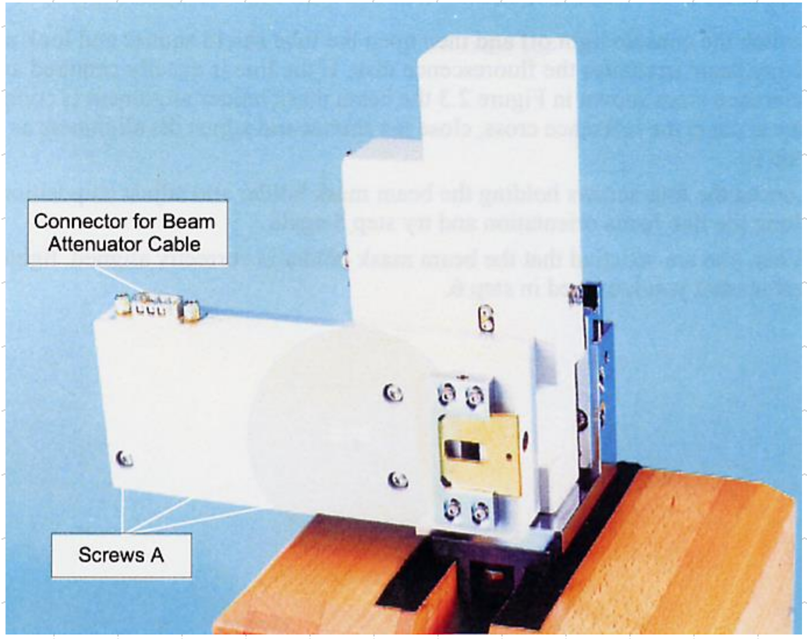
Beam Attenuators

- The beam attenuator is an absorber which is placed in the x-ray beam to reduce its intensity by a specific factor.
- Attenuation factors:
  - Copper (0.1 mm) ≈ 100
  - Combined copper + nickel (0.2 mm / 0.02 mm) ≈ 10,000

$$I_t = I_0 \exp(-\mu x)$$



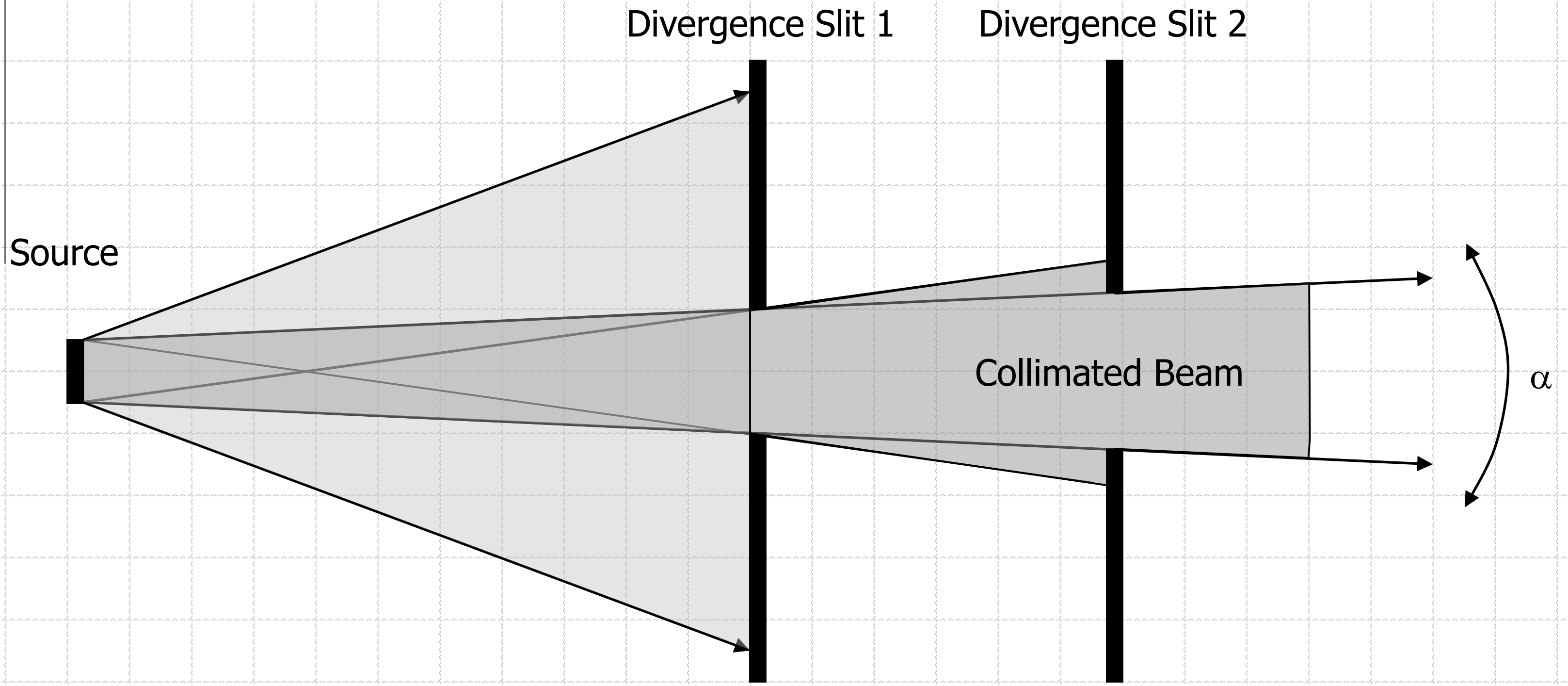




Automatic beam attenuator

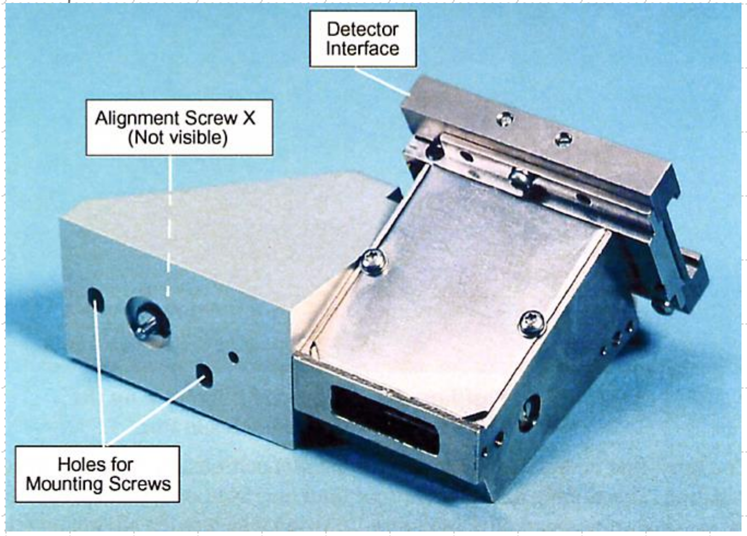
Collimators

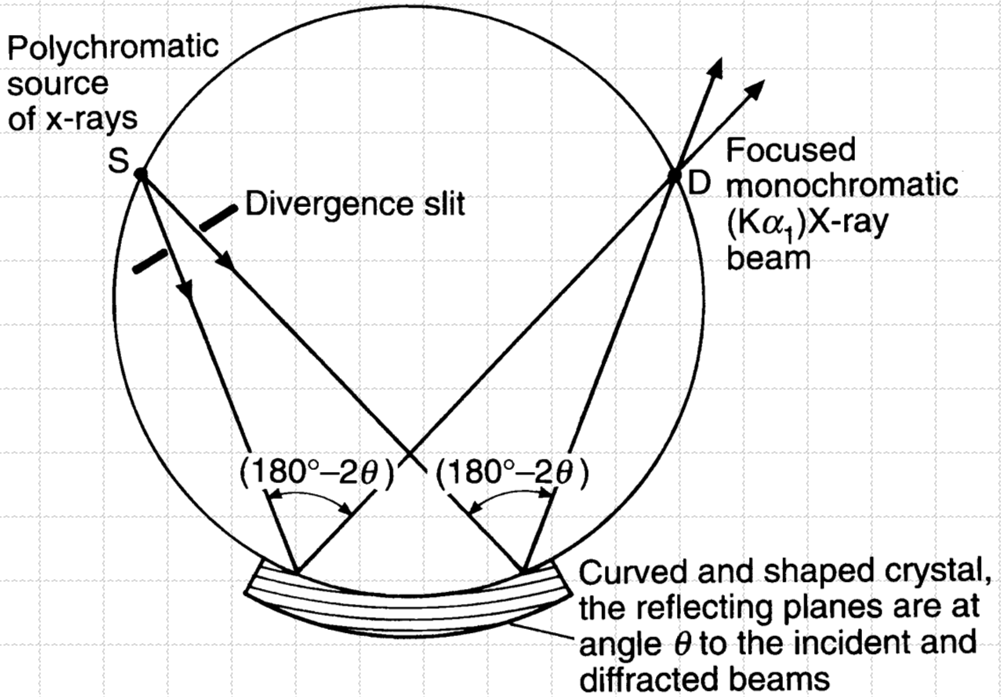
- Second slit can be added to provide additional collimation



Curved Crystal Monochromator

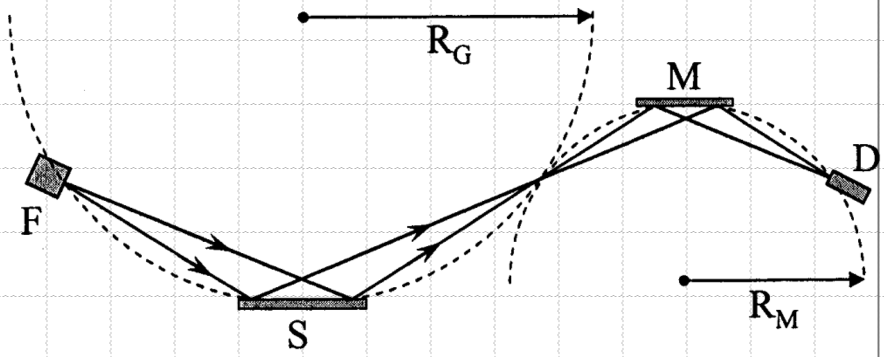
- The focusing geometry can be used to provide a monochromatic source of x-rays.
- Used in Bragg-Brentano geometry and consist of a curved (Johann) pyrolitic graphite crystal.

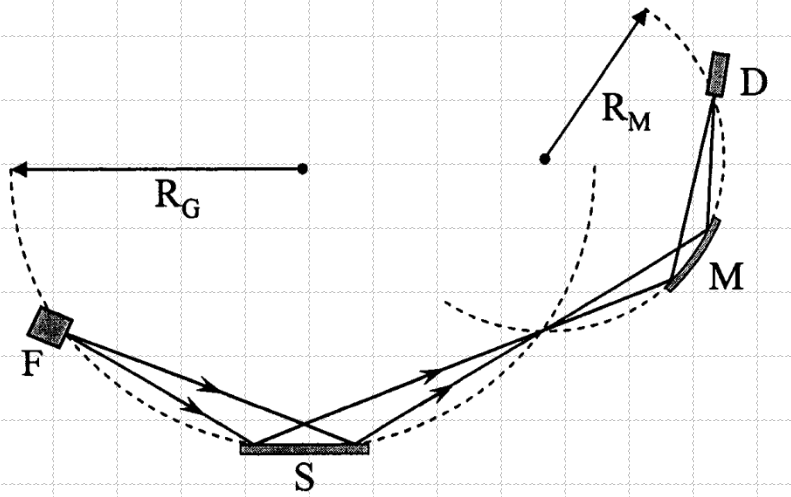


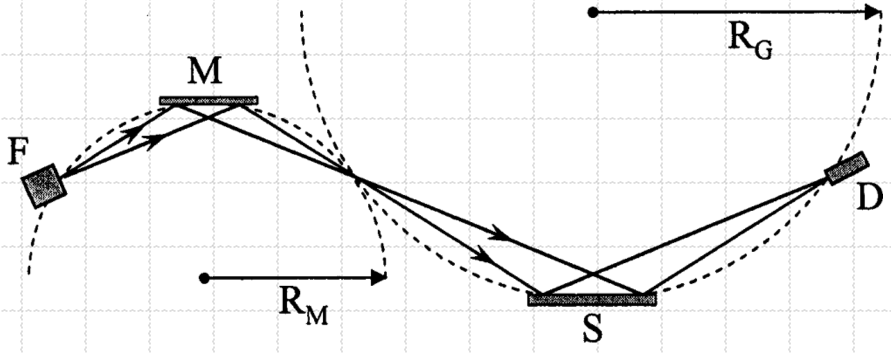


Crystal Monochromator

- Three different sample-monochromator geometries used in powder diffraction:
  - Flat diffracted beam monochromator
  - Curved diffracted beam monochromator
  - Flat primary beam monochromator



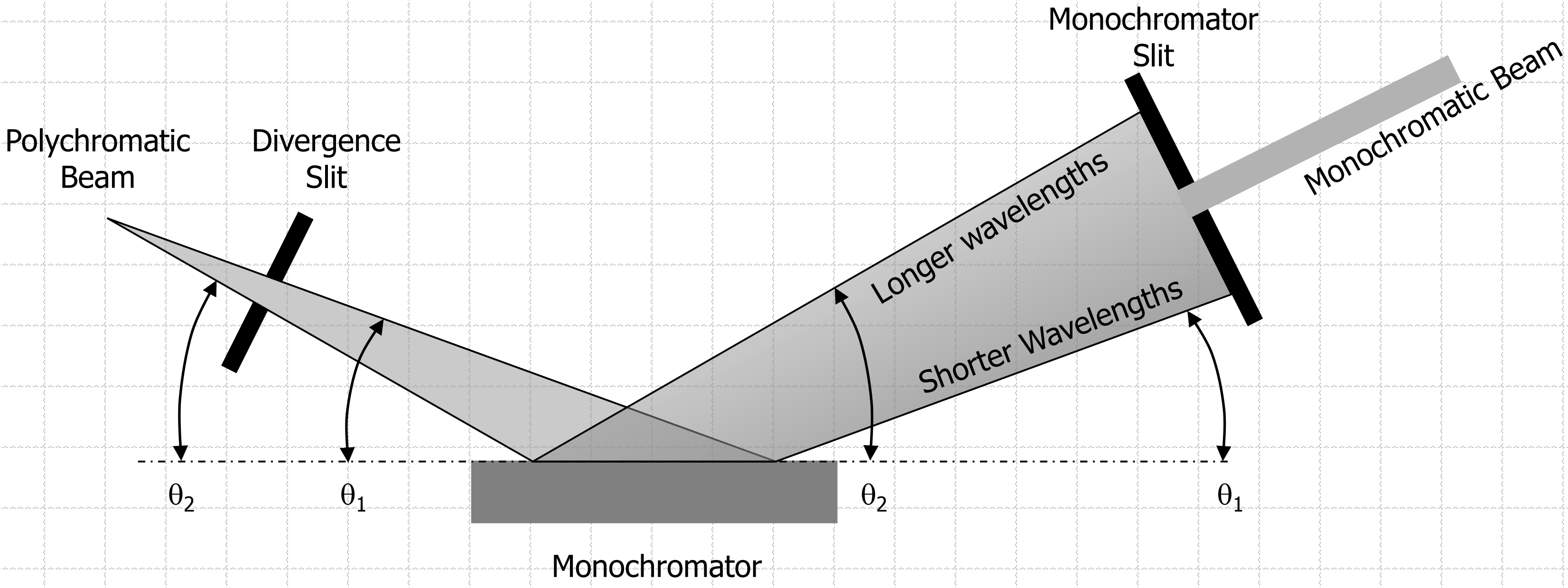




Crystal Monochromator

- X-ray beam monochromatization can be achieved by diffraction from single crystals: Si, Ge, LiCl, and graphite.

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

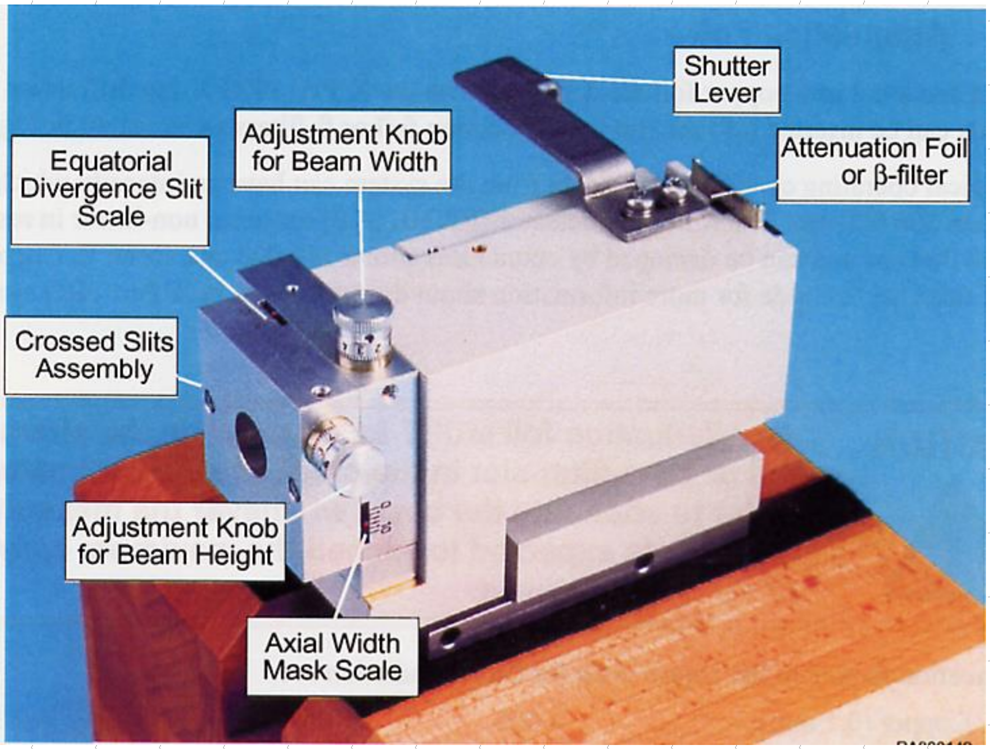


- Sufficient to separate Kα and Kβ
- Not sufficient to separate Kα_1 and Kα_2

Point Source Geometry

- An incident beam collimator is a device that combines a divergence slit and a beam width mask in one optical module. It is used in combination with the point focus x-ray tube.

- Main applications:
    - Texture analysis
    - ψ-stress analysis



Crossed slits collimator

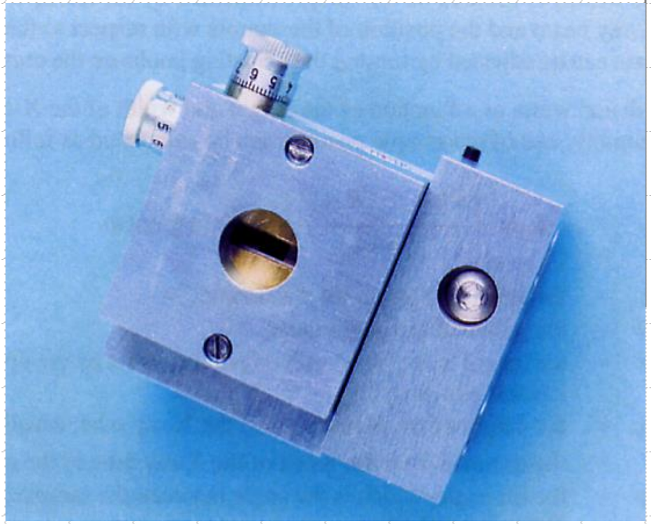
Point Source Geometry

$$L = \left\{ \frac{Rh + p_h(R - f)}{f \sin\omega} \right\} + W \sin\psi \cot\omega$$

where L = the irradiated length on the sample,
R = the radius of the goniometer,
h = the height of the incident X-ray beam, as set by the divergence slit on the crossed slits assembly,
p_h = the height of the point focus of the X-ray tube, usually 1.2 mm,
f = the distance from the focus of the X-ray tube to the crossed slits,
ψ = the tilt angle, which is the angle between the sample surface normal and the equatorial plane,
ω = the angle between the incident beam and the sample surface.

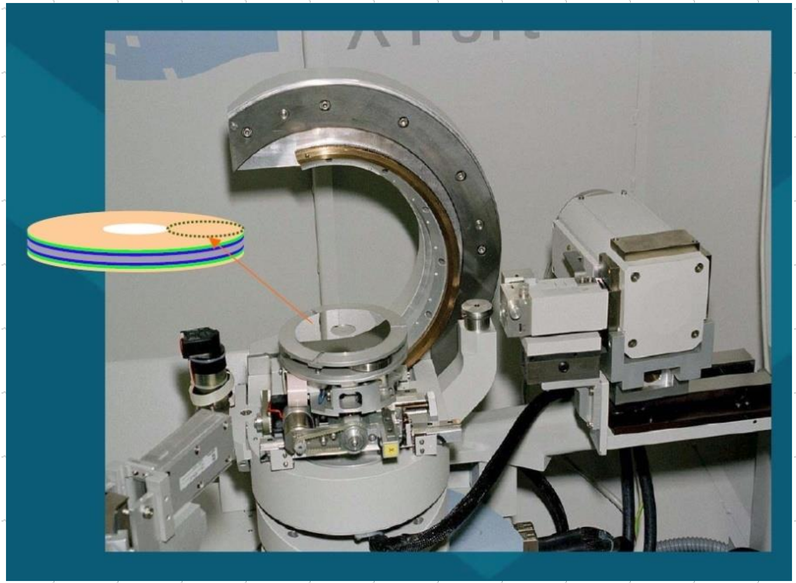
$$W = \frac{Rw + p_w(R - f)}{f \cos\psi}$$

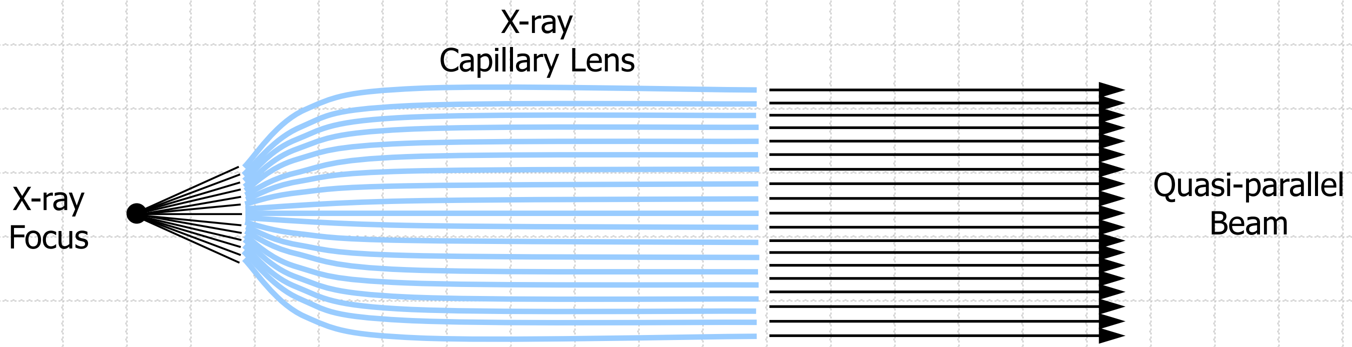
where W = the irradiated width on the sample,
R = the radius of the goniometer,
p_w = the width of the point focus of the X-ray tube, usually 0.4 mm,
w = the width of the incident X-ray beam, as set by the axial mask on the crossed slits assembly,
f = the distance from the focus of the X-ray tube to the crossed slits,
ψ = the tilt angle, which is the angle between the sample surface normal and the equatorial plane.



Point Source Geometry

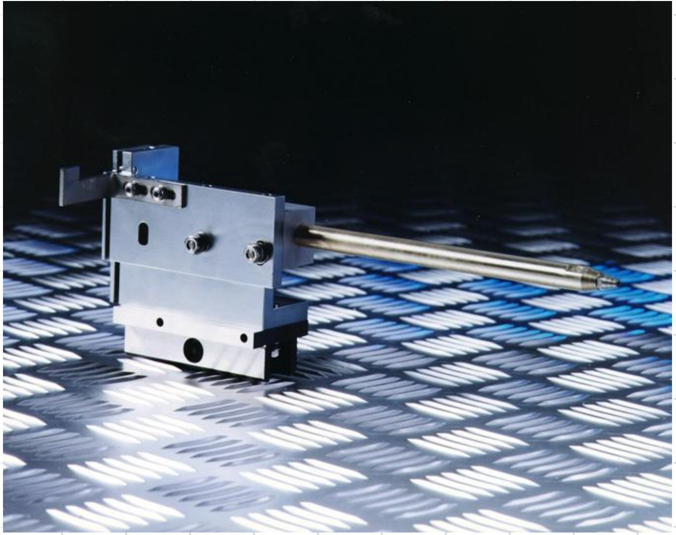
- X-ray Lens

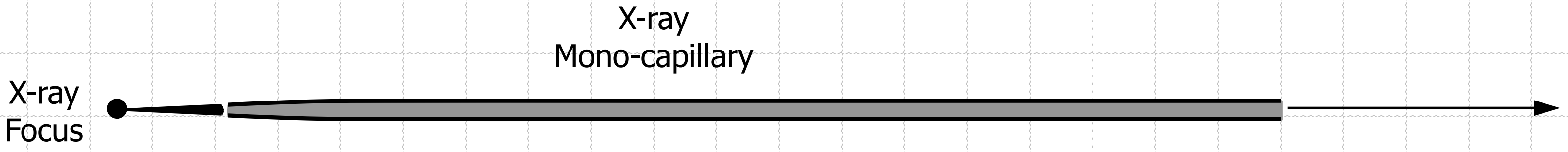




Point Source Geometry

- X-ray Mono-capillary
  - Used for microdiffraction
  - Beam sizes 1 mm – 10μm

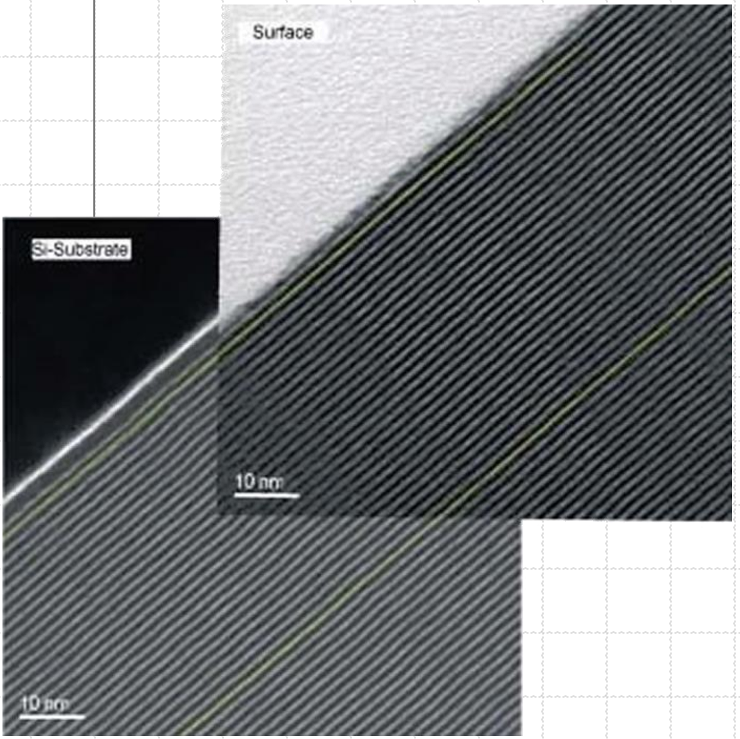




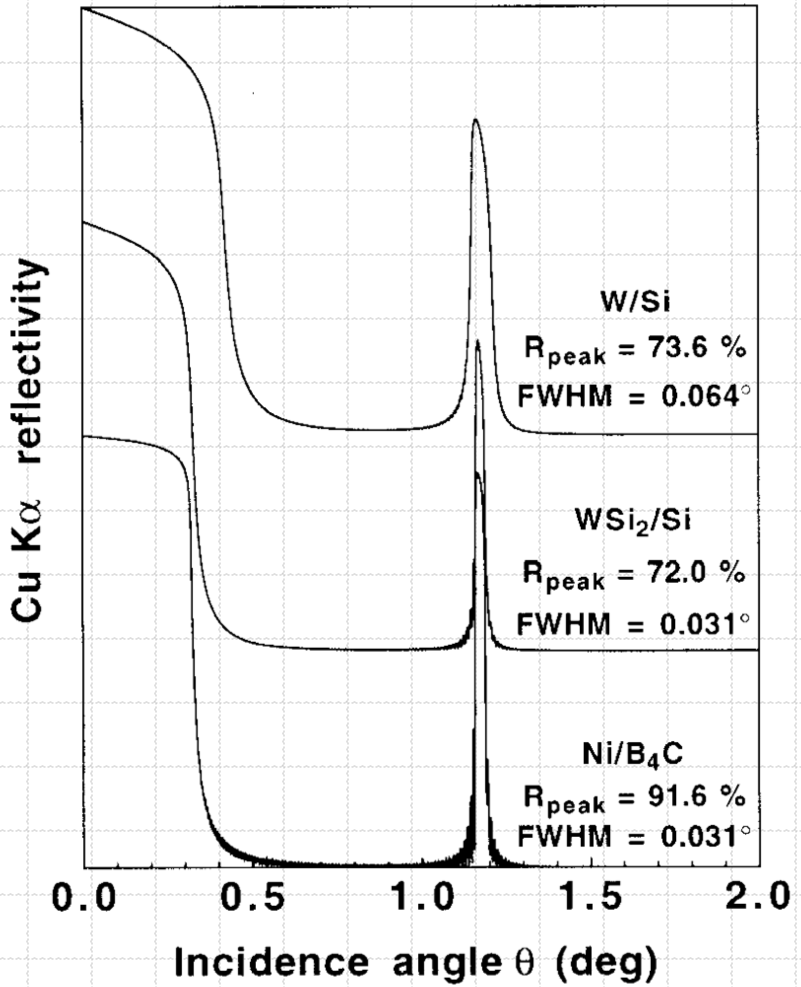
Multilayer X-ray Mirrors

Materials:
W/Si, W/B_4C, WSi_2/Si, Ni/Mg and Ni/B_4C

- Göbel Mirrors

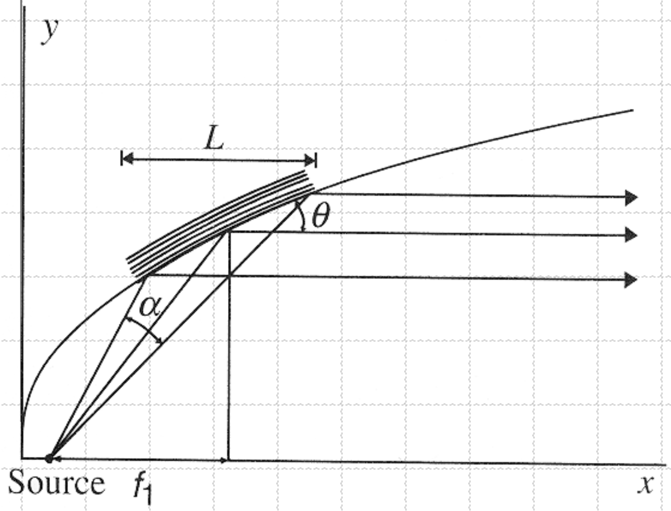


TEM micrograph of a multilayer mirror Mo/B_4C with a *d*-spacing of 1.4 nm and 500 pairs

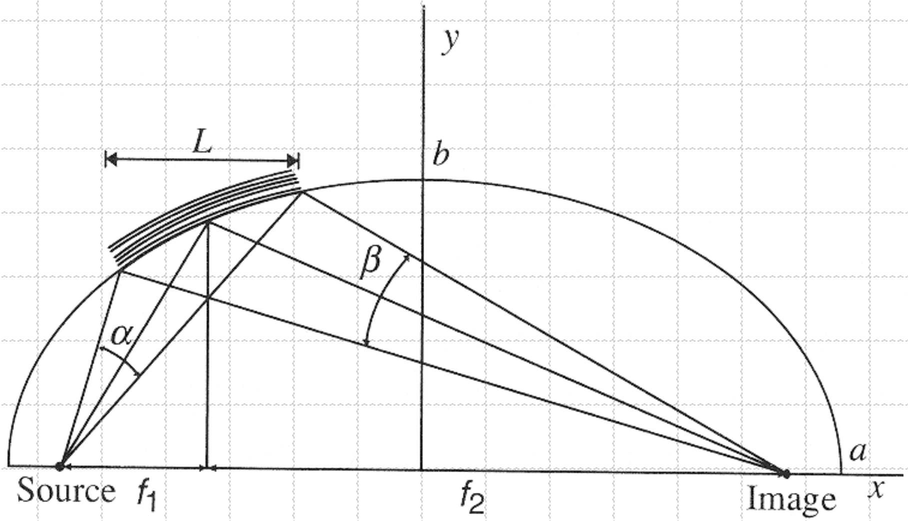


Calculated Cu Kα reflectivity vs. incidence angle for W/Si, WSi_2/Si and Ni/B_4C multilayers (100 layer pairs, 4 nm period.

Multilayer X-ray Mirrors



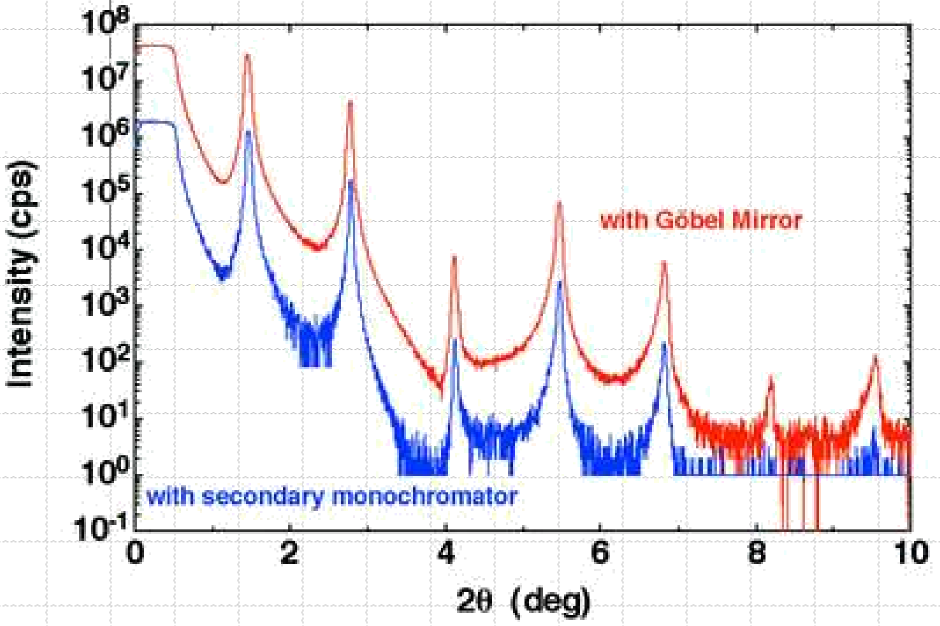
Parabolic Mirror

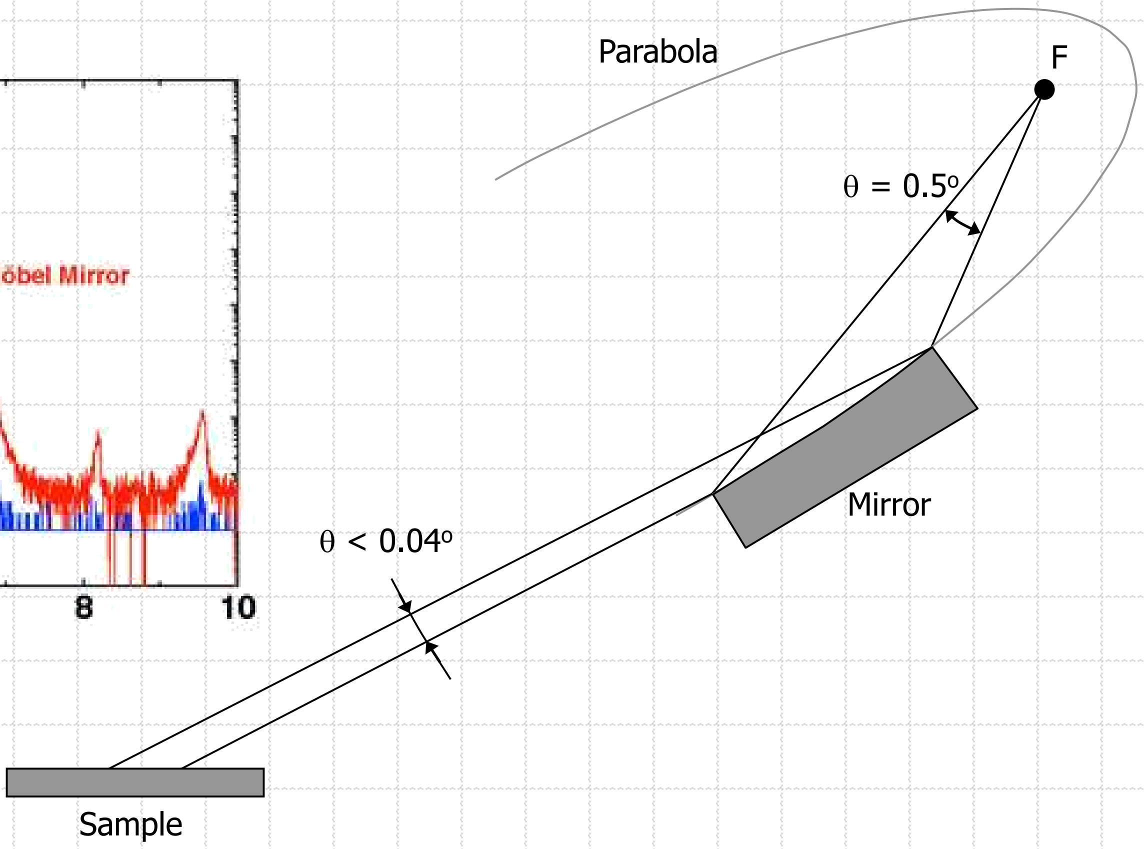


Elliptical Mirror

Parallel Beam Geometry

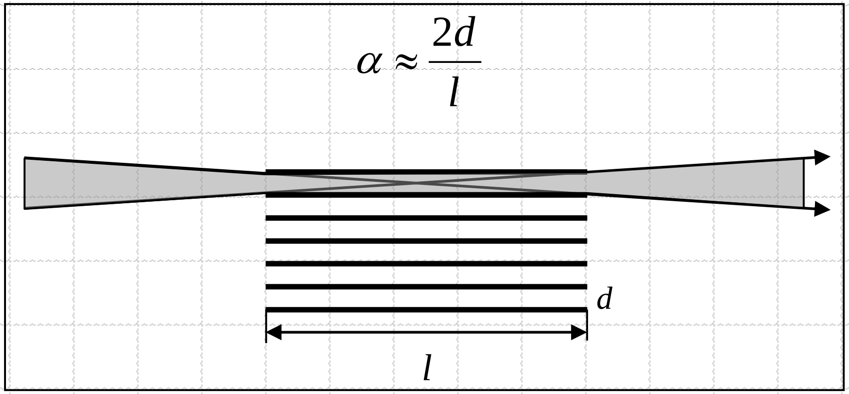
- Incident Beam:
  - X-ray Göbel Mirror



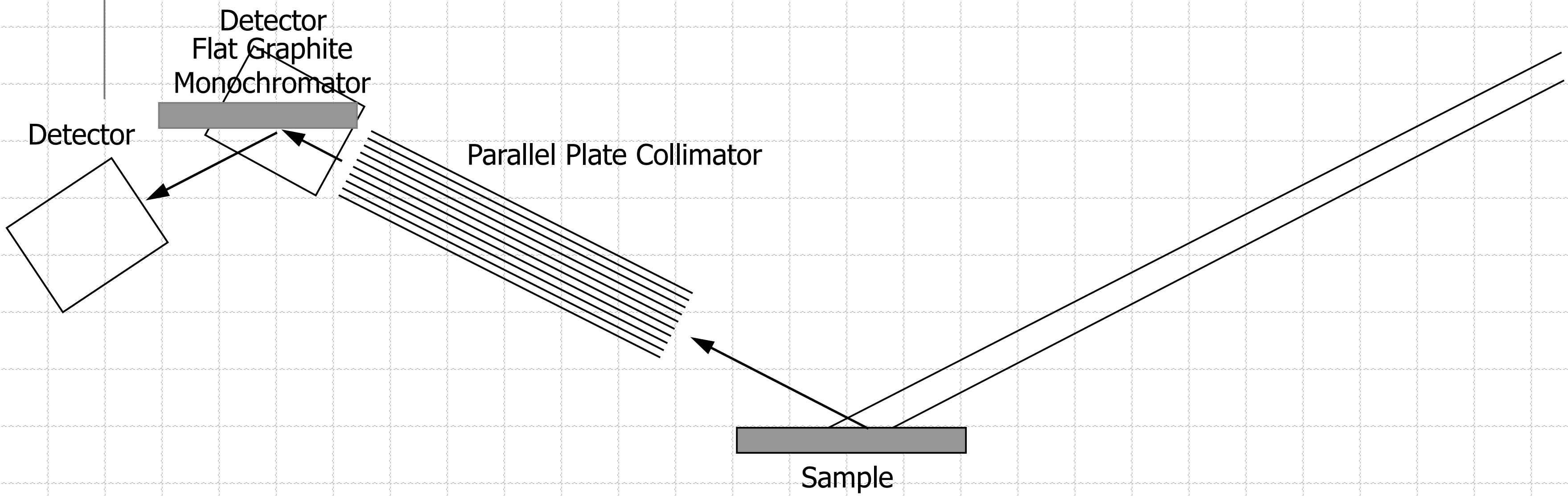


Parallel Beam Geometry

- Incident Beam:
    - X-ray Mirror



$$\alpha \approx \frac{2d}{l}$$



Detector

Flat Graphite Monochromator

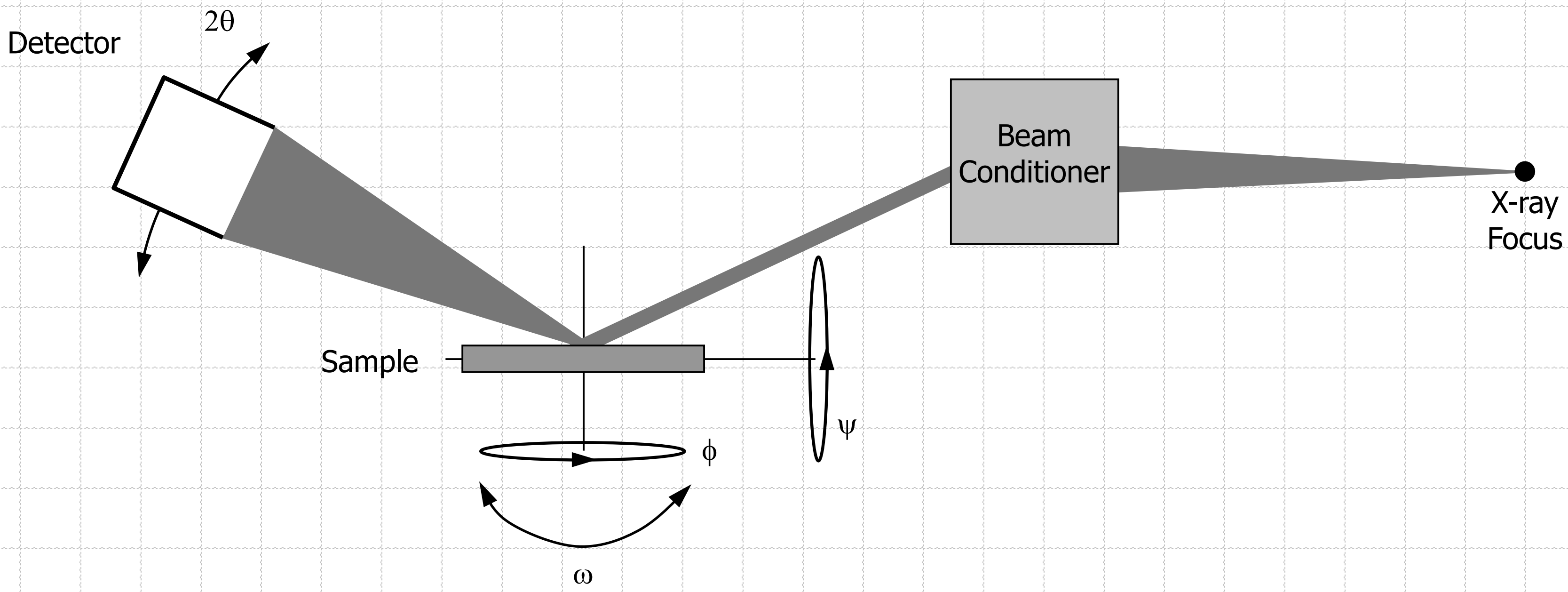
Detector

Parallel Plate Collimator

Sample

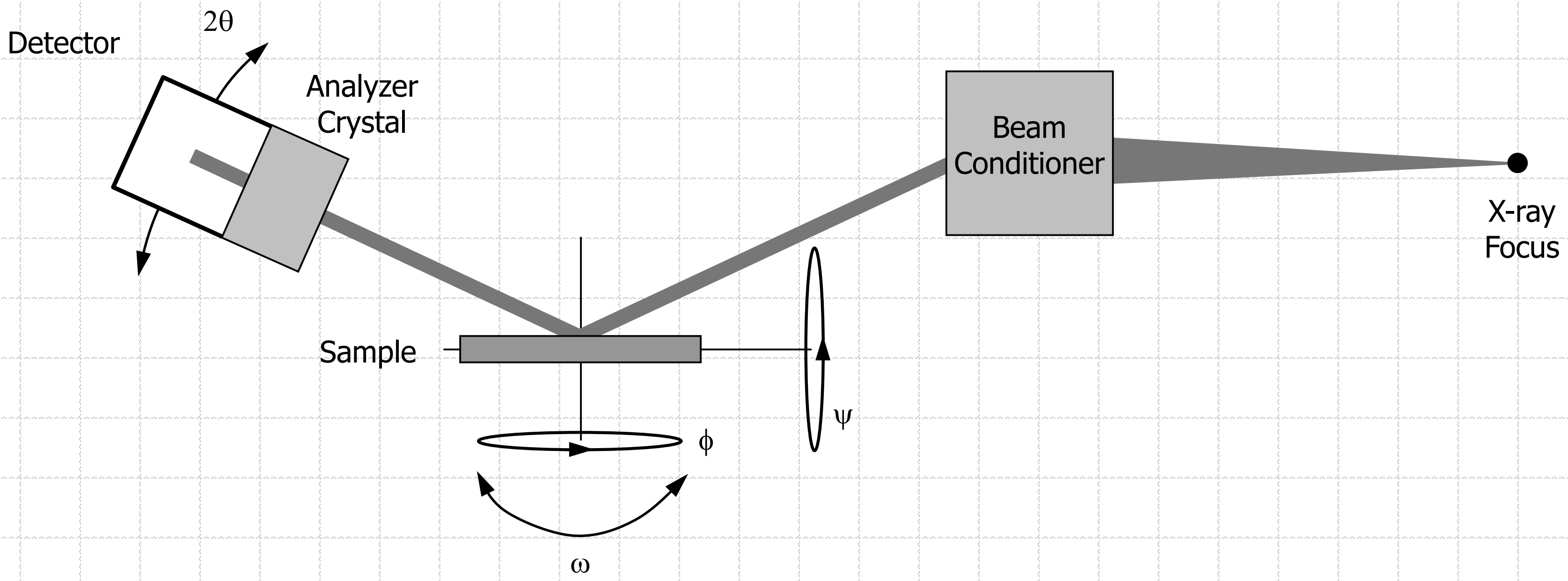
High Resolution Geometry

- High resolution double-axis diffractometer:
  - Open detector mode



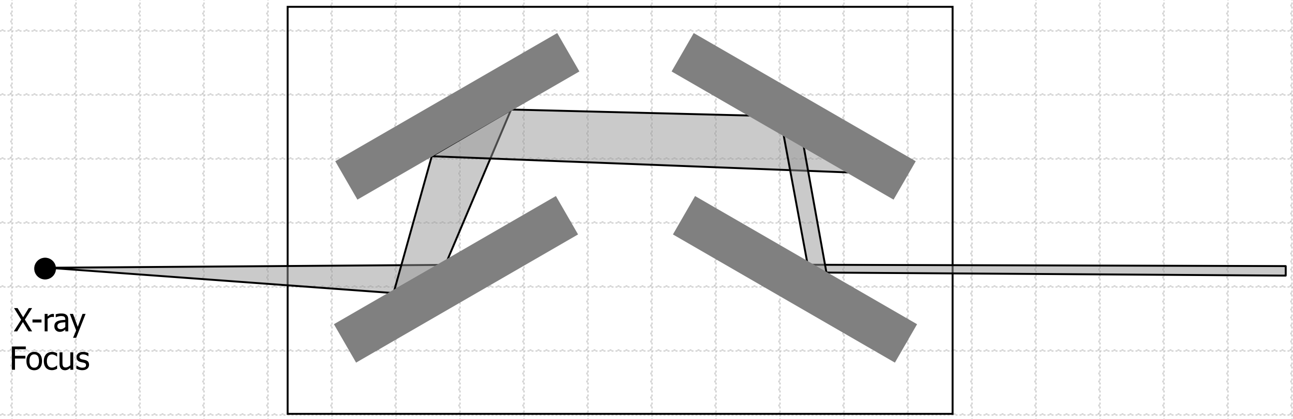
High Resolution Geometry

- High resolution triple-axis diffractometer:



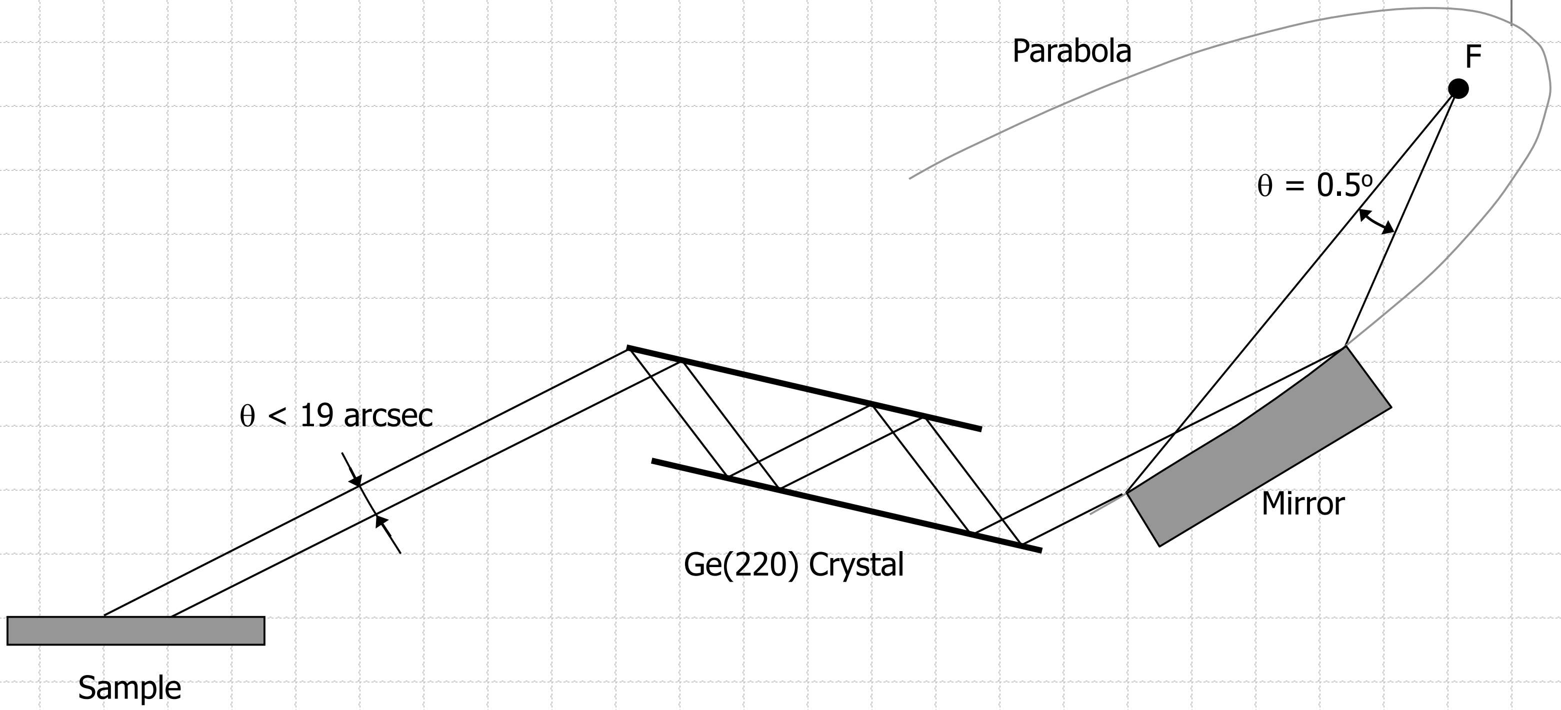
High Resolution Geometry

- Bartels Monochromator



High Resolution Geometry

- Incident Beam:
    - X-ray Hybrid Monochromator



Detectors

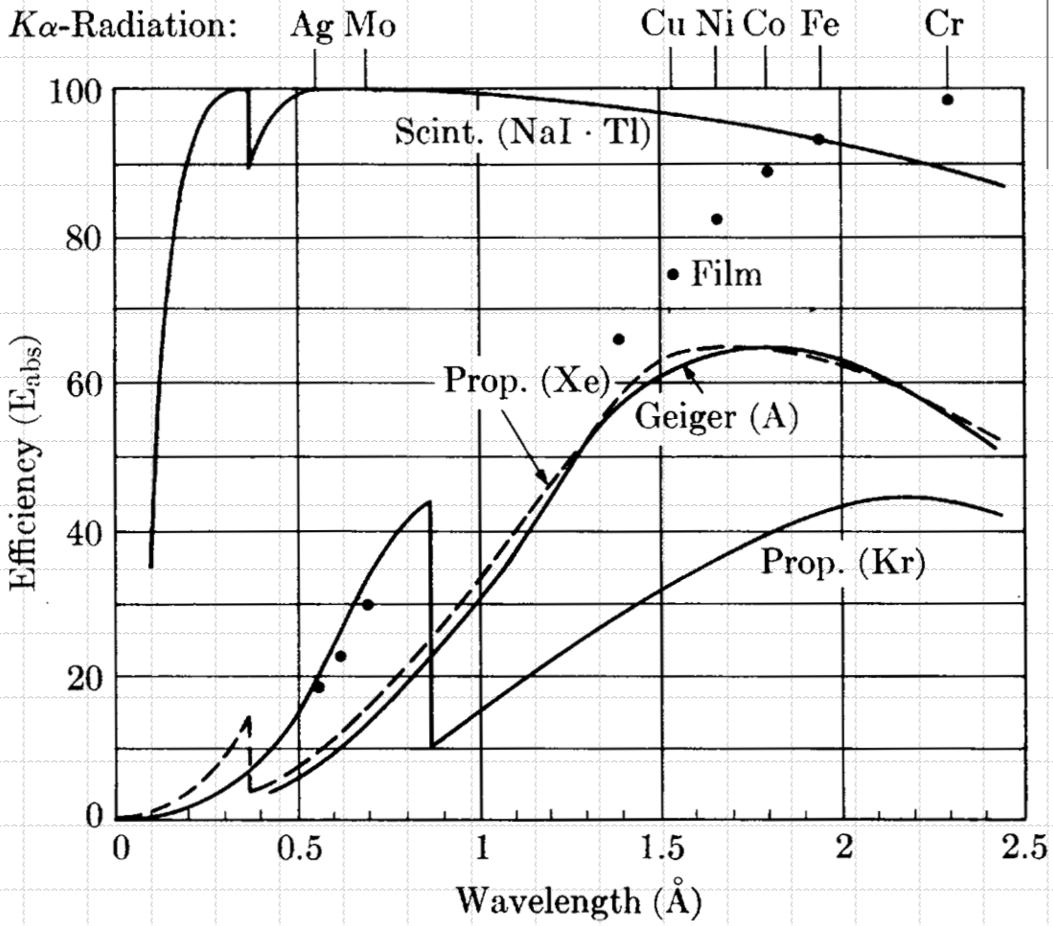
- The x-ray detector is the last item in the x-ray beam path.
- It is used to count numbers of photons, that is, the intensity of the diffracted beam at a certain 2θ position of the goniometer

- single photon detectors
  - scintillation detectors
  - (gas-filled) proportional counters
  - semiconductor detectors
- linear (position-sensitive) detectors
  - gas-filled (wire) detectors
  - charge-coupled devices (CCD's)
- area detectors
  - 2-D wire detectors
  - CCD area detectors
- X-ray film (should be obsolete)

Desired Properties of X-ray Detectors

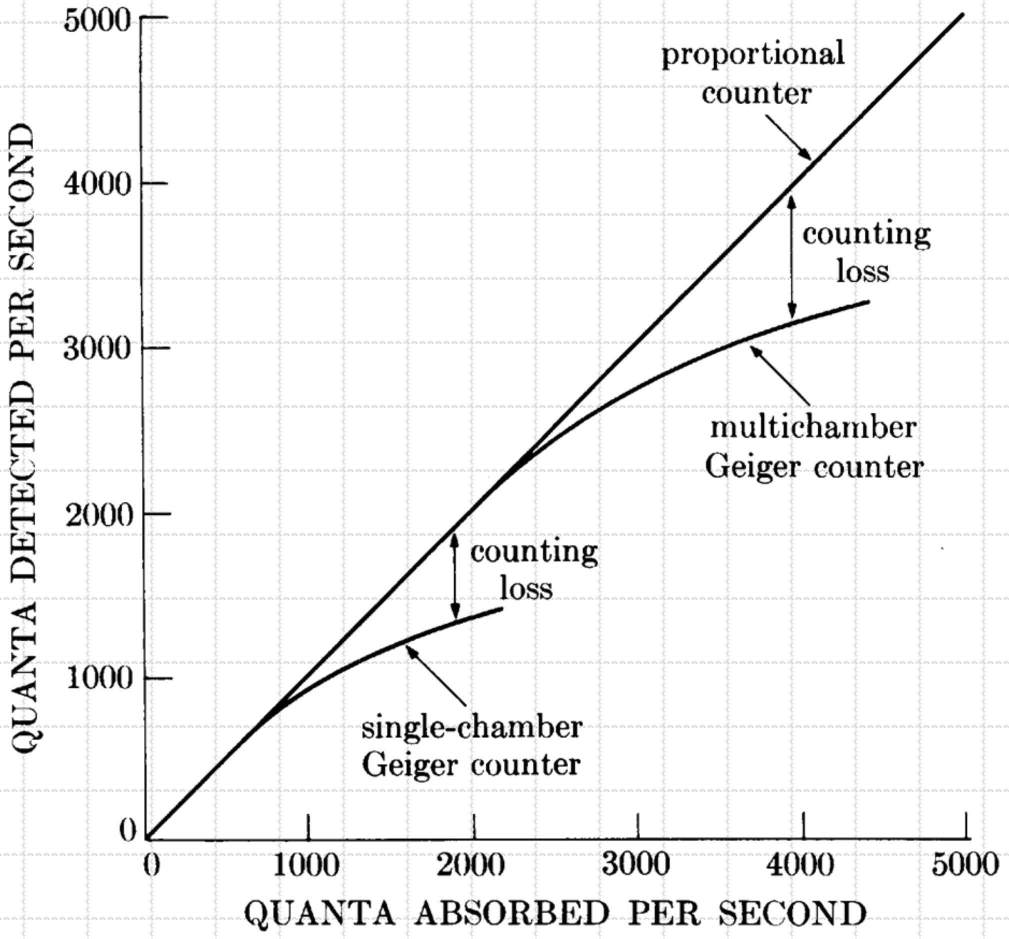
- **Quantum counting efficiency** – number of photons detected by the detector to the number of photons entering the detector.

$$
\begin{aligned}
E &= E_{abs}E_{det} \\
&= \left[\left(1-f_{abs,w}\right)\left(f_{abs,d}\right)\right]\left[1-f_{losses}\right]
\end{aligned}
$$



Desired Properties of X-ray Detectors

- **Linearity** – the ability of the detector to provide an output that is in direct proportion to the intensity of the x-ray beam (number of x-ray photons entering the detector).

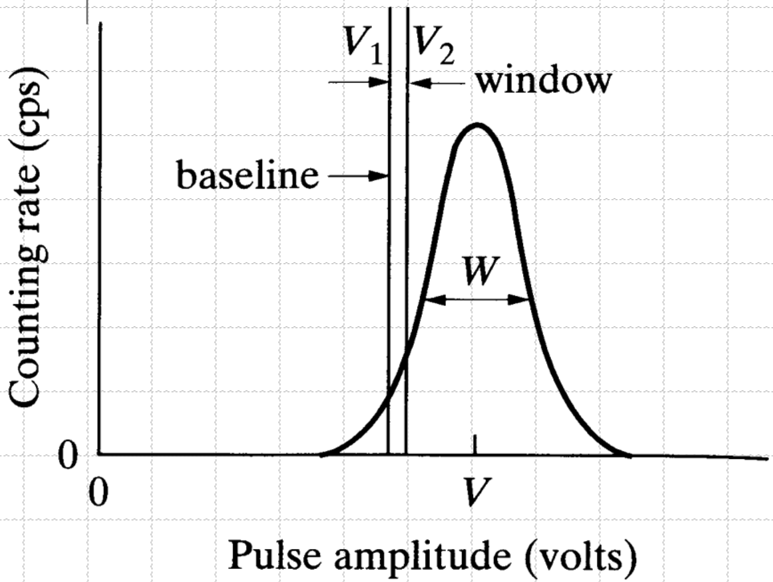


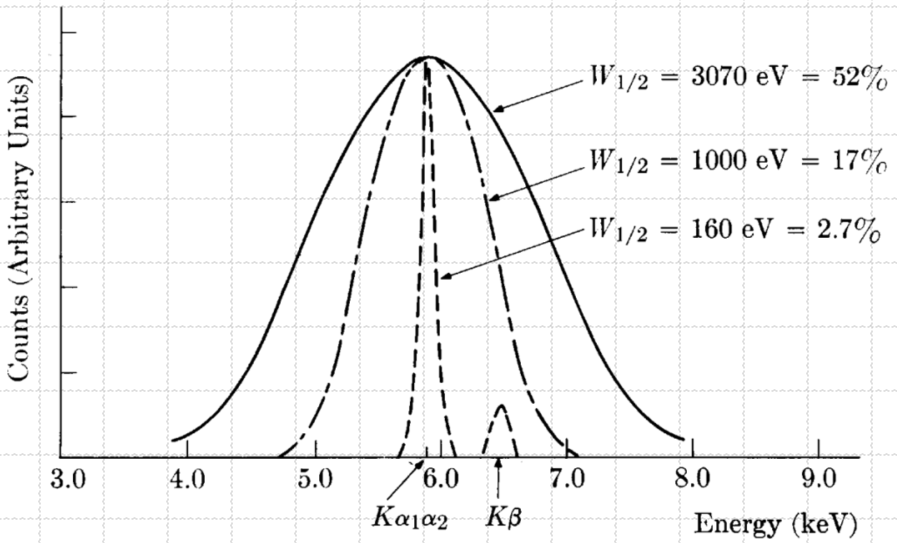
Desired Properties of X-ray Detectors

- **Energy resolution** – the ability of the detector to distinguish between energies.
  - resolution → input photon of energy E produces an output pulse of height V ±δ V

$$R = \frac{W}{V}$$

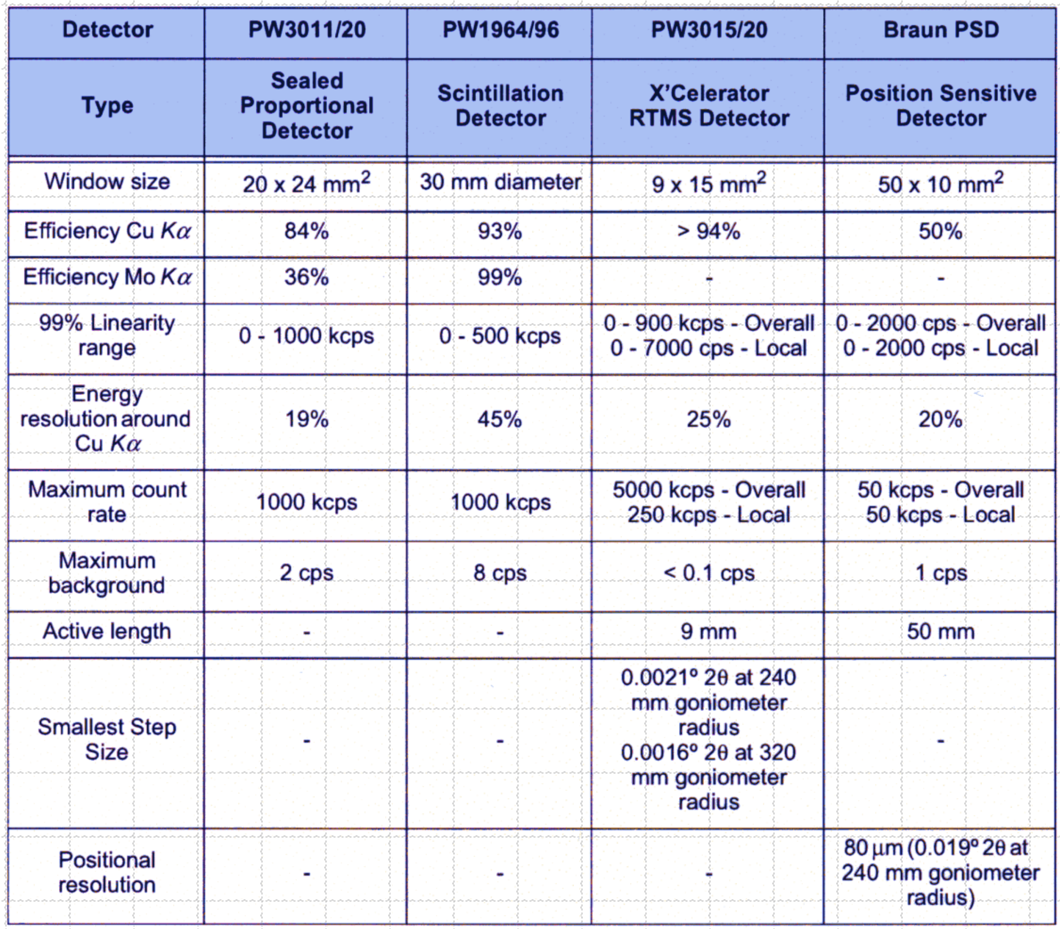
Smaller R better resolution





Desired Properties of X-ray Detectors

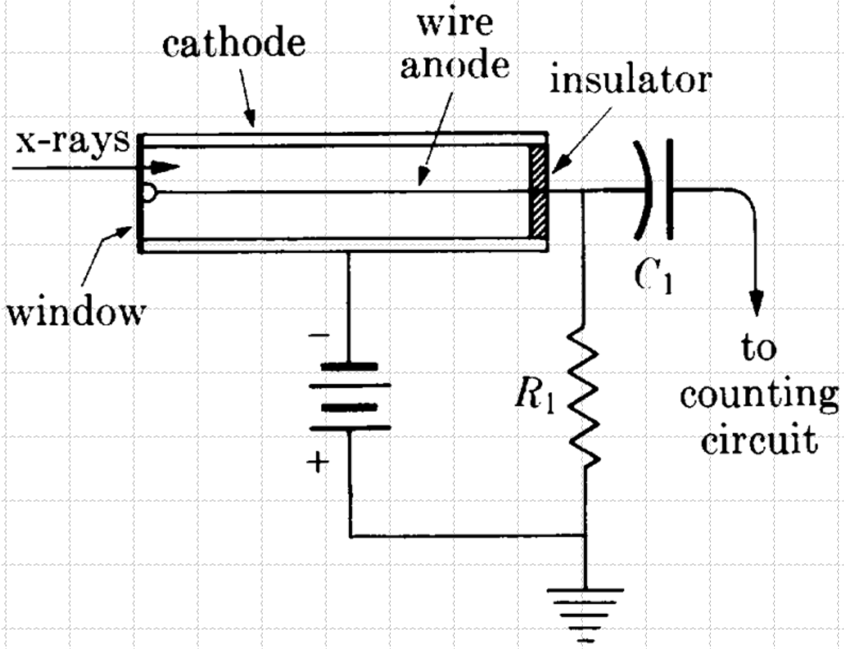
- **Energy proportionality** – the ability of the detector to produce a pulse with a height proportional to the energy of the x-ray photon detected.
- **Sensitivity** – the ability of the detector to detect low intensity levels.



Detector	PW3011/20	PW1964/96	PW3015/20	Braun PSD
Type	Sealed Proportional Detector	Scintillation Detector	X'Celerator RTMS Detector	Position Sensitive Detector
Window size	20 x 24 mm^2	30 mm diameter	9 x 15 mm^2	50 x 10 mm^2
Efficiency Cu $K\alpha$	84%	93%	> 94%	50%
Efficiency Mo $K\alpha$	36%	99%	-	-
99% Linearity range	0 - 1000 kcps	0 - 500 kcps	0 - 900 kcps - Overall 0 - 7000 cps - Local	0 - 2000 cps - Overall 0 - 2000 cps - Local
Energy resolution around Cu $K\alpha$	19%	45%	25%	20%
Maximum count rate	1000 kcps	1000 kcps	5000 kcps - Overall 250 kcps - Local	50 kcps - Overall 50 kcps - Local
Maximum background	2 cps	8 cps	< 0.1 cps	1 cps
Active length	-	-	9 mm	50 mm
Smallest Step Size	-	-	0.0021° 2θ at 240 mm goniometer radius 0.0016° 2θ at 320 mm goniometer radius	-
Positional resolution	-	-	-	80 µm (0.019° 2θ at 240 mm goniometer radius)

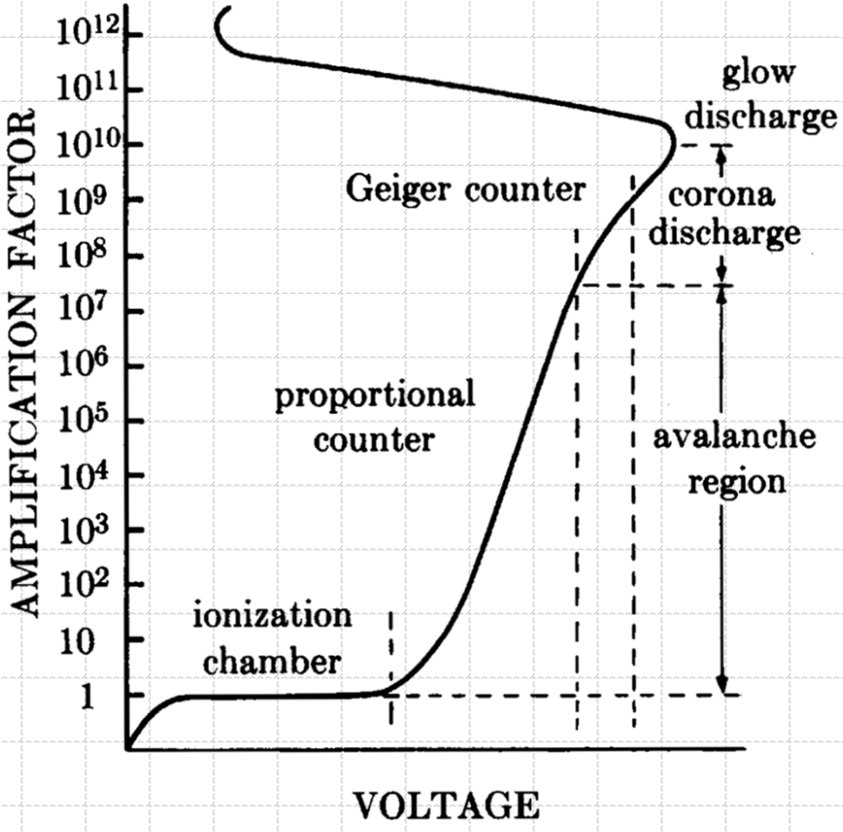
Gas-filled Proportional Counter

- A proportional counter consists of the following main components:
  - a gas-filled cylindrical envelope (usually Ar, Kr, or Xe)
  - a central anode wire
  - a grounded coaxial cylinder (the cathode)
  - an X-ray transparent window



Gas-filled Proportional Counter

- When an X-ray photon ionizes a gas molecule, the ejected photoelectrons are accelerated to the anode
    - low voltages – photoelectrons don’t have enough energy to ionize other molecules
    - intermediate voltages – gas amplification occurs (photo-electrons ionize gas molecules on the way to the anode
    - high voltages – discharge occurs throughout the gas volume



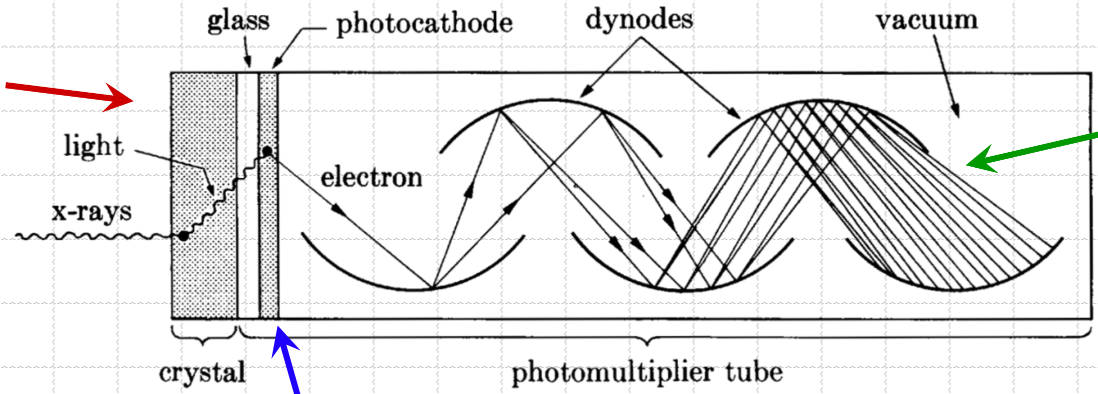
Aspects of Proportional Counters

- Proportional counter
  - Each X-ray photon causes multiple ionizations (29 eV for argon → >300 ion/electron pairs with CuKα)
  - In the gas amplification regime (gain of 10^3 to 10^5), a pulse of a few millivolts is produced
  - Pulse amplitude proportional to photon energy
  - Much better energy resolution (15% to 20%) than scintillation detectors

- Geiger-Müller counter
  - no longer proportional – entire chamber "light up" with UV
  - large pulse amplitude (~volts) so no amplification needed; good for survey meters
  - slow to relax, so maximum count rate is limited

The Scintillation Detector

- The detector has two basic elements:
    - a crystal that fluoresces visible light (scintillates) when struck by X-ray photons
    - a photomultiplier tube (PMT) that converts the light to electrical pulses



NaI(Tl) scintillator (very sensitive to moisture) – emits around 4200Å

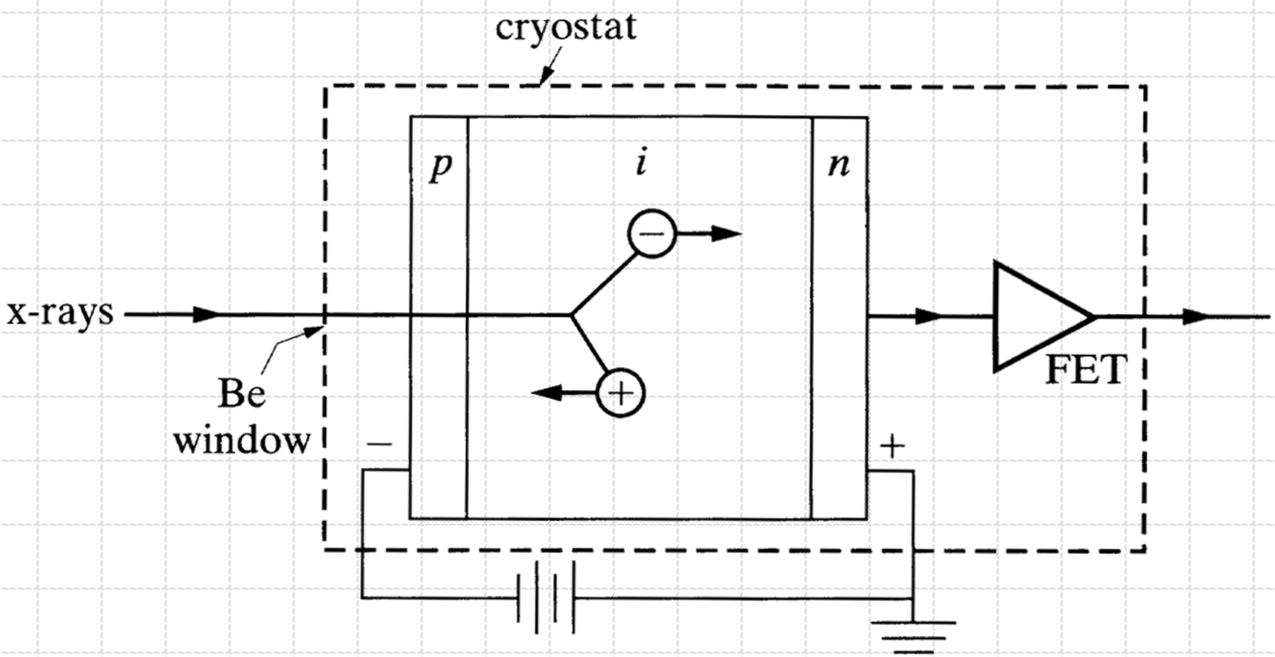
gain ~5× per dynode (total gain with ten dynodes is $5^{10} \approx 10^{7}$)

CsSb photocathode – ejects electrons

Aspects of Scintillation Detectors

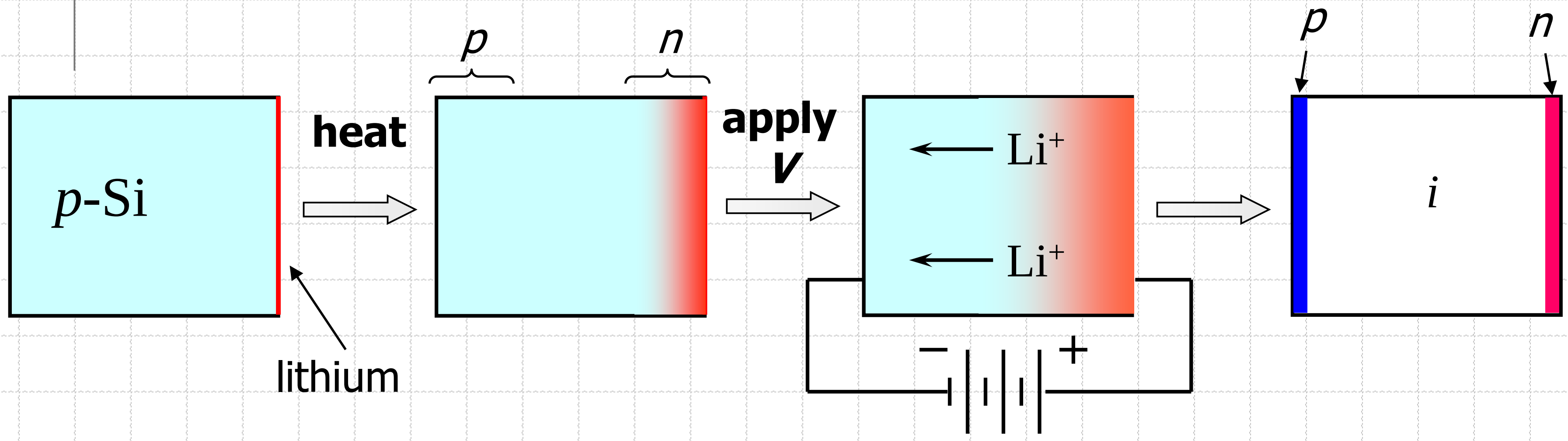
- Relatively inexpensive (~$1500) and rugged
- All necessary electronics are "off the shelf"
- Scintillator crystal can develop "dead spots" over time
- NaI is very hydroscopic and needs careful encapsulation
- Sealed from ambient light with thin Be window
- Energy resolution is poor (~50%)
- Typical noise of < 1 count/sec; advanced detectors can be linear in excess of 10^6 counts/sec

Aspects of Semiconductor Detectors



Semiconductor Detectors

- Semiconductor detectors are solid-state proportional counters – each photon produces electron-hole (e/h) pairs
- The detection of e/h pairs would not be possible if the semiconductor has free carriers (n-type or p-type) so it must be intrinsic – this can be done by “lithium drifting”



lightly *p*-doped Si has Li plated

heat to have the Li diffuse

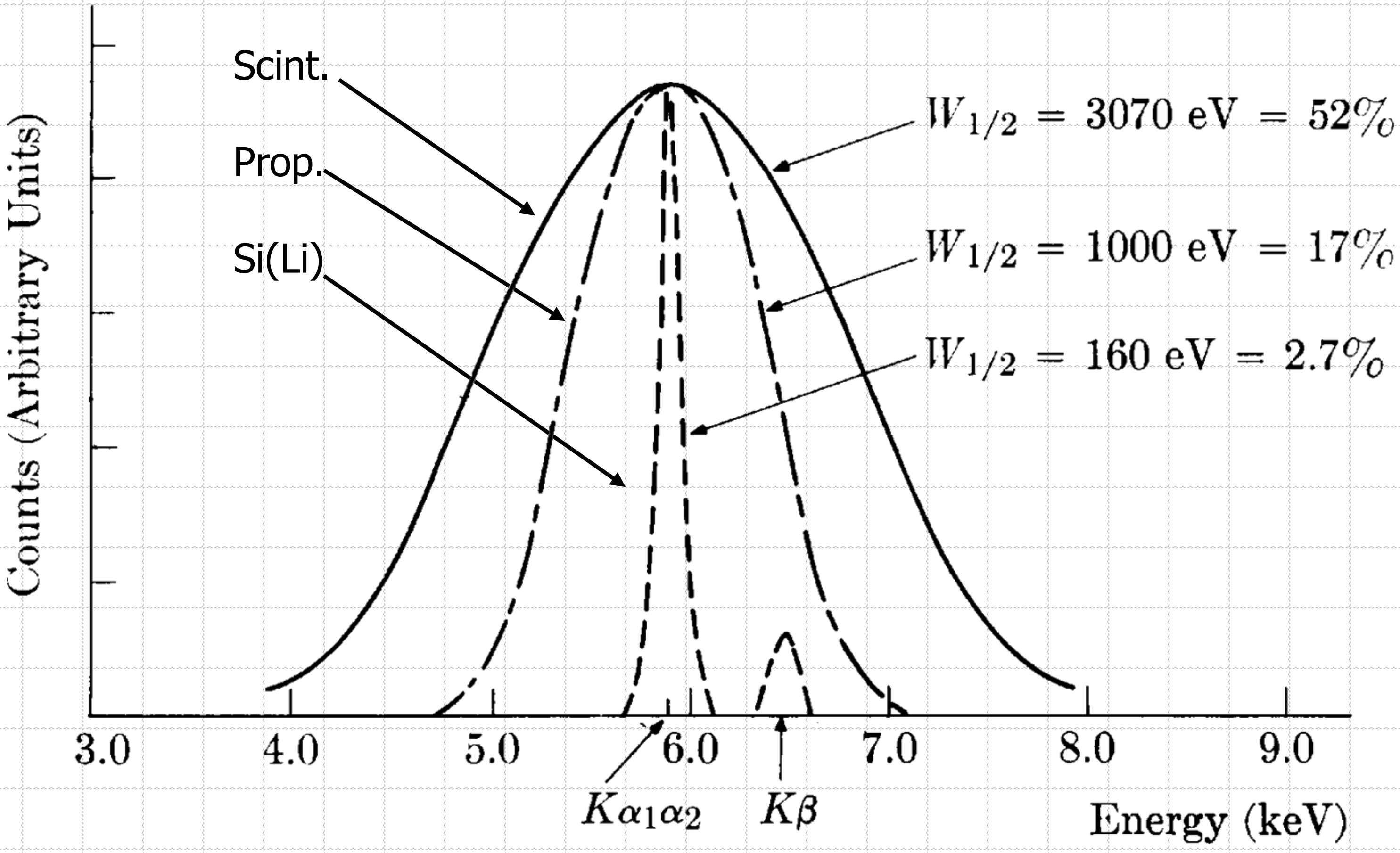
apply a reverse bias to cause Li⁺ ions to “drift

a wide central intrinsic region is formed

Aspects of Semiconductor Detectors

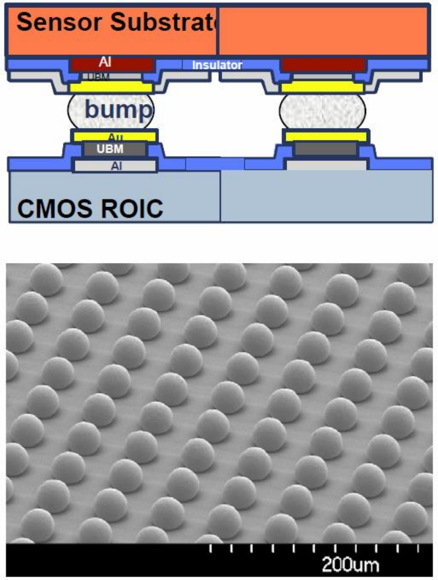
- Originally: Si(Li) and Ge(Li) – “silly” and “jelly”
- Now intrinsic Si and intrinsic Ge are available (Ge better due to higher absorption and better energy resolution)
- Energy resolution about 2%
- Small signal requires a charge-sensitive preamp integrated with the detector
- due to thermal e/h generation and noise in the preamp, cooling to 77K is needed
- New detectors use Si p-i-n photodiodes and large bandgap materials (CdTe and CdZnTe) for room-temperature operation

Detectors

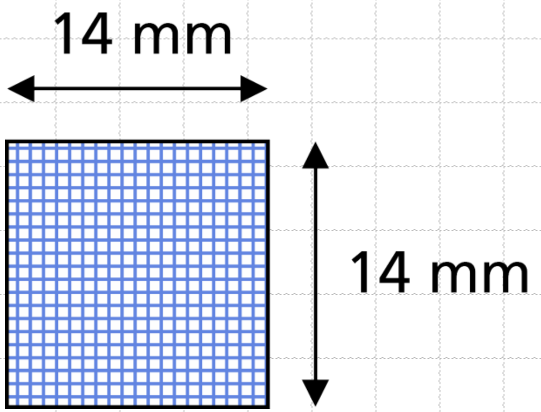

Scint.
Prop.
Si(Li)
$W_{1/2}$ = 3070 eV = 52%
$W_{1/2}$ = 1000 eV = 17%
$W_{1/2}$ = 160 eV = 2.7%
Counts (Arbitrary Units)
3.0
4.0
5.0
6.0
7.0
8.0
9.0
$K\alpha_1\alpha_2$
$K\beta$
Energy (keV)

PIXcel Detector

- Resolution better than 0.04° 2Theta
- Efficiency: > 94 % for Cu radiation
- Maximum count rate: > 25,000,000 cps
- Detector noise: < 0.1 cps
- Scan range: from 1° to more than 160° in 2Theta
- Large active length: ~2.5° 2Theta
- Can be used for "static" measurements

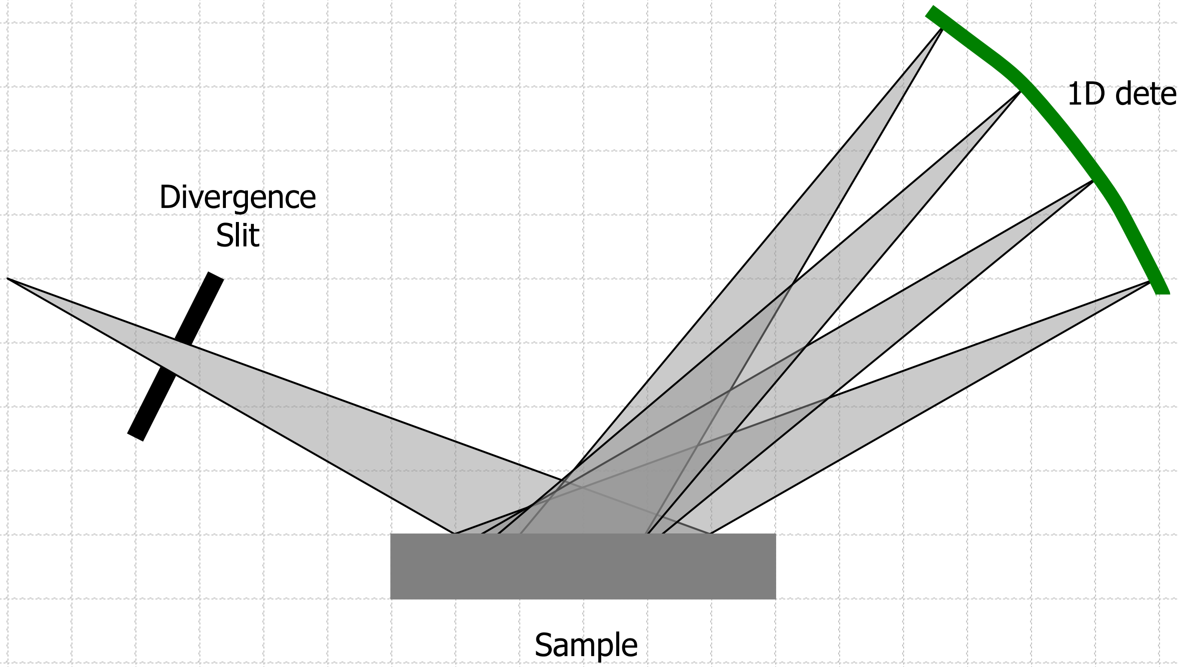


Schematic of pixel detector

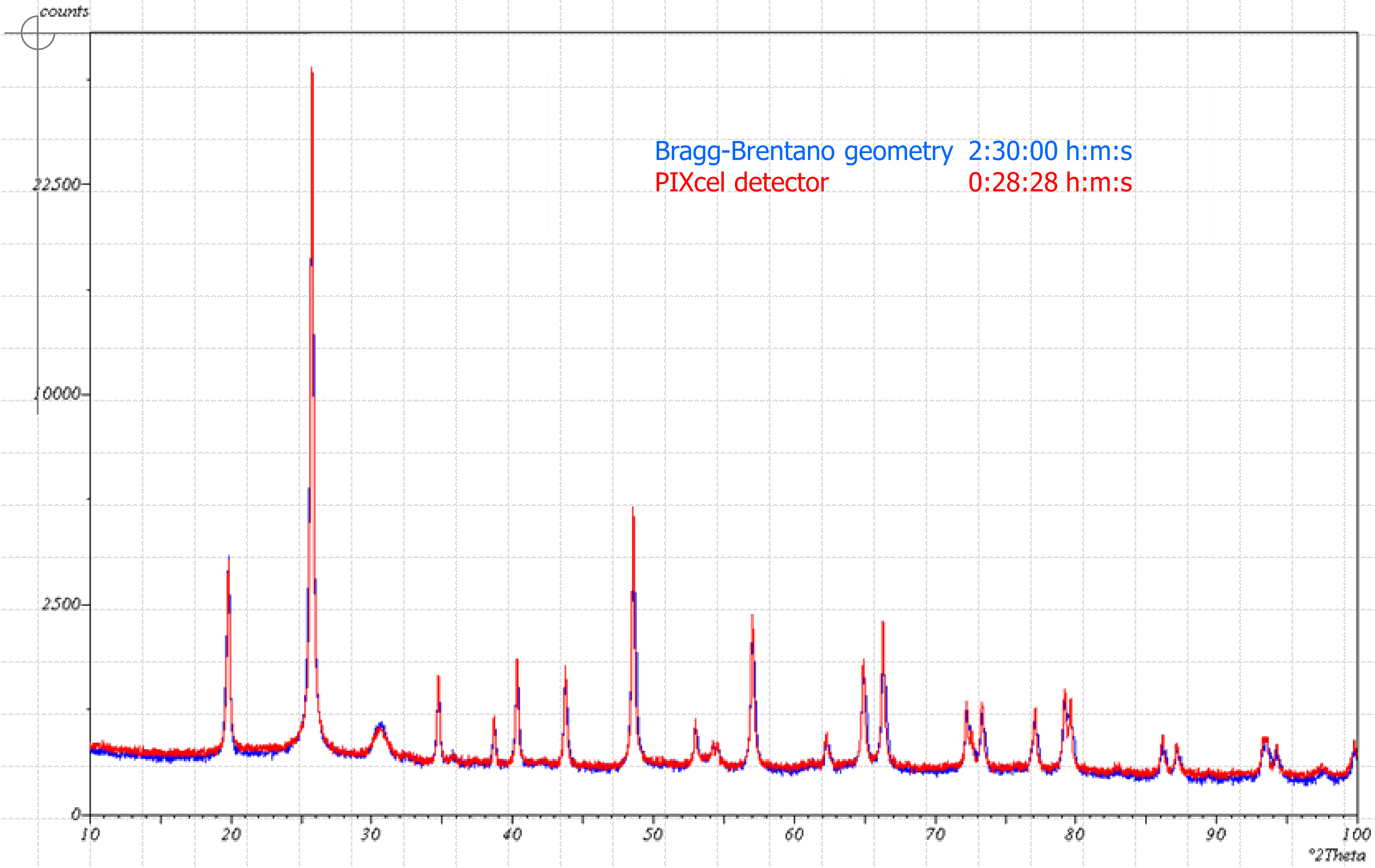


- 256 x 256 = 65536 pixels
- 55 micron x 55 micron
- 97% count rate linearity up to 100,000 cps per pixel: > 25,000,000 cps per "strip"
- Static measurements possible with all detectors
- 2D possible

PIXcel Detector



PIXcel Detector



Two Dimensional Detector