# X-ray Diffraction (XRD)
# X-ray Diffractometer

Pecharsky Chapter 6

Cullity Chapter 1

Krawitz Chapter 3

Jenkins & Snyder – Chapter 1, 4, 5, 6



## Q's



- Why do we (have to) use XRD?
- What is XRD? What is X-ray diffractometer?
- How to collect raw data of XRD?
- What kind of information can we get from XRD pattern?
- How can we get more accurate/precise results?

## Elemental analysis vs. Phase analysis



- ➢ Elemental analysis
  - ✓ Optical spectroscopy
    - ▪ Probes the outer electronic structure of atoms
      - – Optical emission (e.g. ICP OES*)
      - – Atomic absorption spectrometry (AAS)
  - ✓ X-ray fluorescence spectroscopy (XRF)
    - ▪ Probes the inner electronic structure of atoms
- ➢ Phase analysis
  - ✓ X-ray diffraction (XRD)

- ➢ Qualitative analysis
- ➢ Quantitative analysis

- ➢ Qualitative elemental analysis
- ➢ Quantitative elemental analysis
- ➢ Qualitative phase analysis
- ➢ Quantitative phase analysis

* inductively coupled plasma optical emission spectrometry

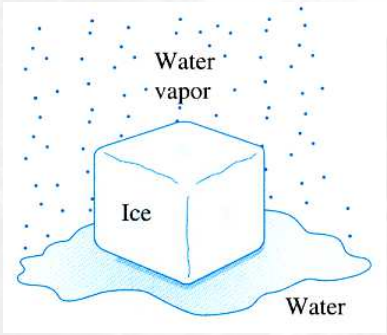


## Phase, 상 (**相**) ?

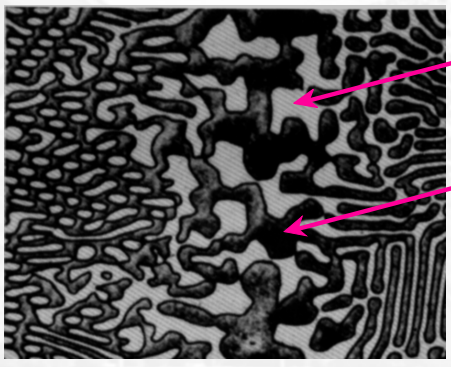


- ➢ a region of material that is chemically uniform, physically distinct, and (often) mechanically separable
- ➢ a chemically and structurally homogeneous region of material
- ➢ a physically and chemically distinct material region

1 component
3 phases



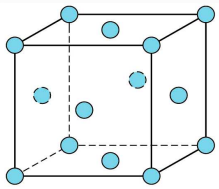

Aluminum-Copper Alloy



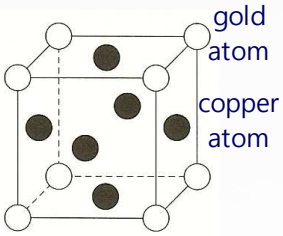
## Examples

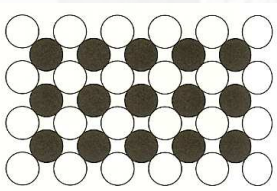


Crystal structure of Au & Cu



Crystal structure of $AuCu_3$



Portable XRF

Au, Cu

Au 30%, Cu 70%

Au, Cu

Au, $AuCu_3$

Cu, $AuCu_3$

Au, Cu, $AuCu_3$

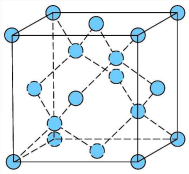
X-Ray Diffraction (XRD)



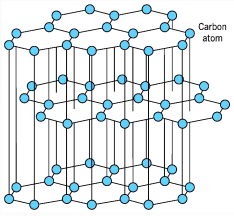
## Structure of carbon



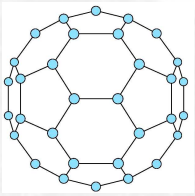
- Diamond (Si, Ge)



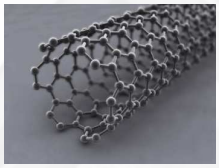
- Graphite (BN)



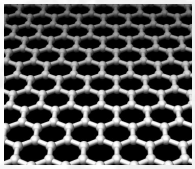

- Fullerene (buckyball)



- Carbon Nanotube



- Graphene

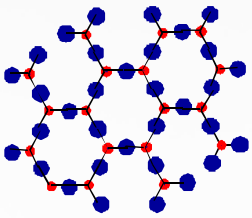


elemental analysis → carbon

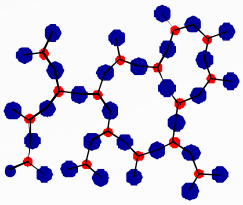
phase analysis → diamond, graphite, CNT, graphene

## Structure of $SiO_2$





crystalline $SiO_2$
quartz



noncrystalline $SiO_2$
fused silica

elemental analysis → Si & O

phase analysis → quartz, fused silica

concentricusllc.com/event/crystalmining/2019-10-12/

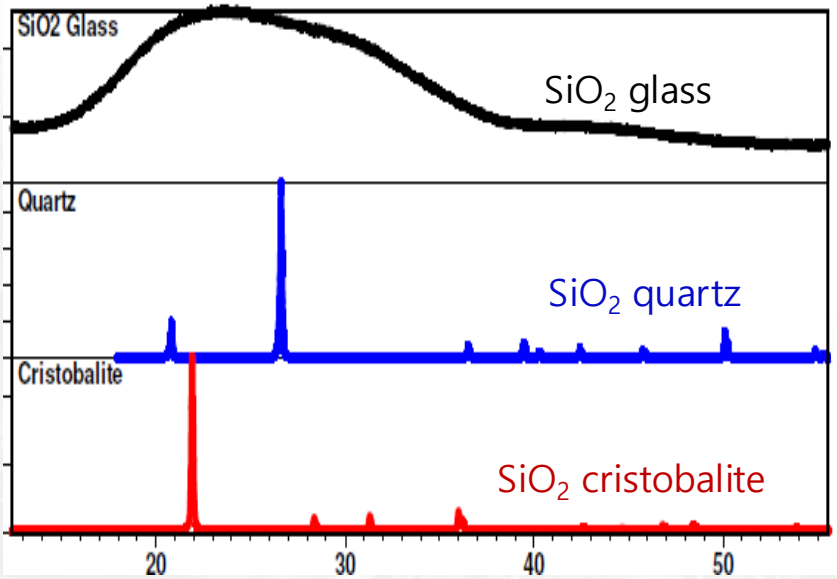
www.corning.com/kr/ko/products/advanced-optics/product-materials/semiconductor-laser-optic-components/high-purity-fused-silica.html

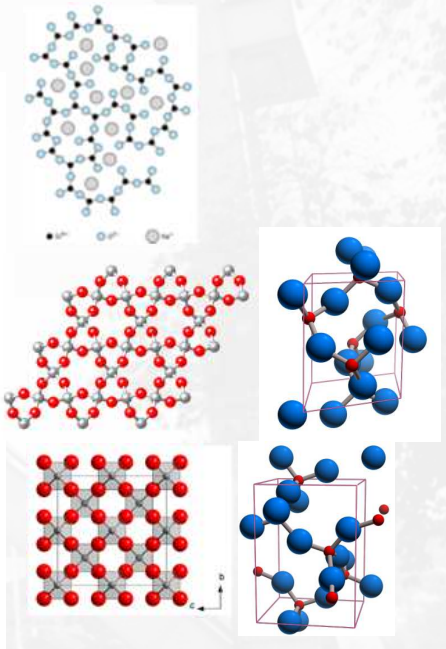


## XRD Pattern vs Crystal Structure



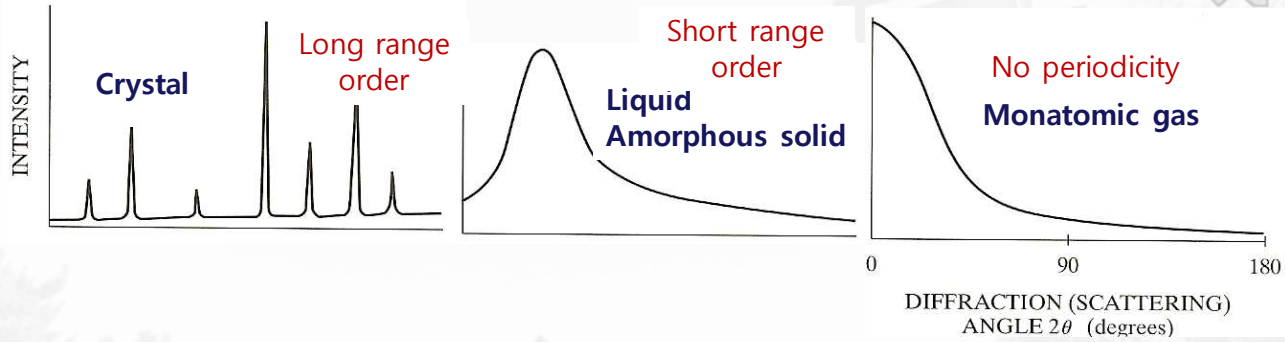
crystalline vs. non-crystalline (amorphous)



## Amorphous & partially crystalline samples



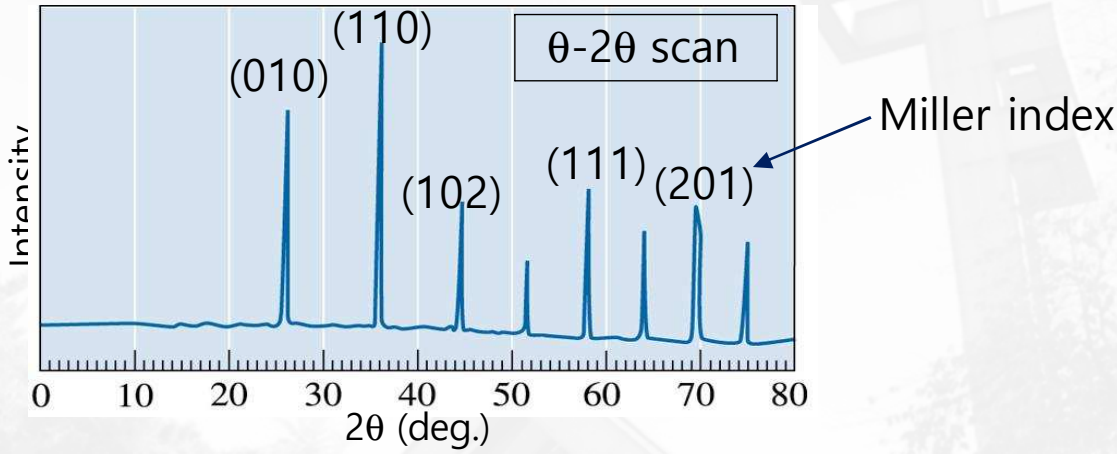


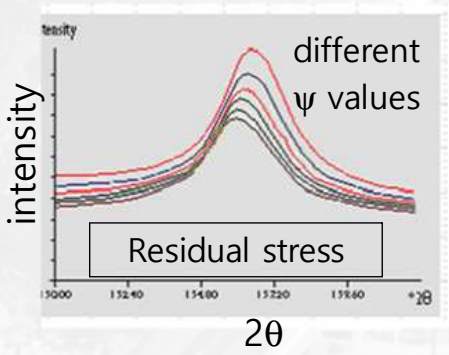

- A single atom scatters incident X-ray beam in **all** directions.
- Large # of atoms arranged in a perfectly periodic array in 3-D to form a crystal, scatter x-rays in **a few** directions.
- Crystal imperfection → diffraction @ non-Bragg angles → diffraction occurs in a narrow angular range with center @ $\theta_B$.

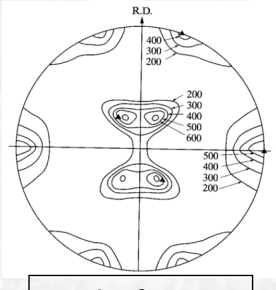


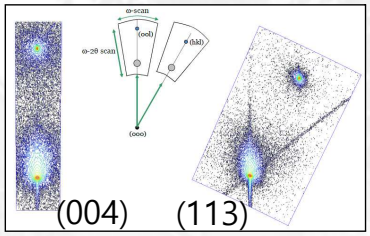
## XRD Patterns



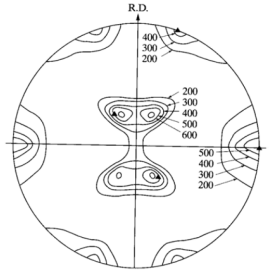


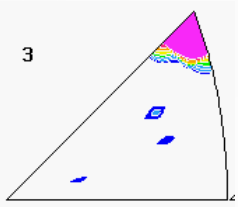



## XRD patterns > texture

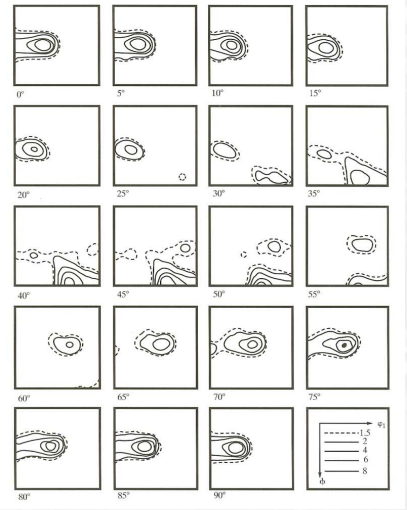


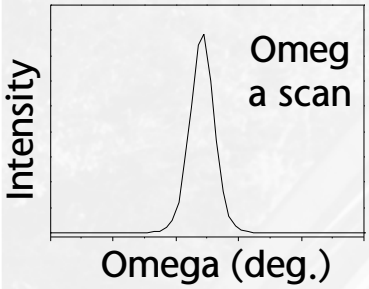

Pole figure

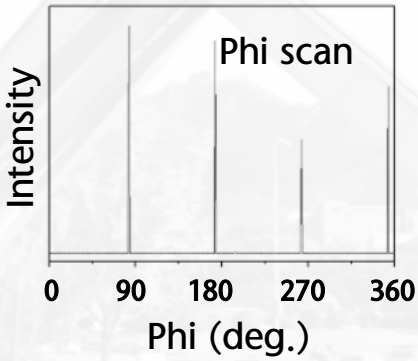



Inverse pole figure

Orientation distribution function (ODF)





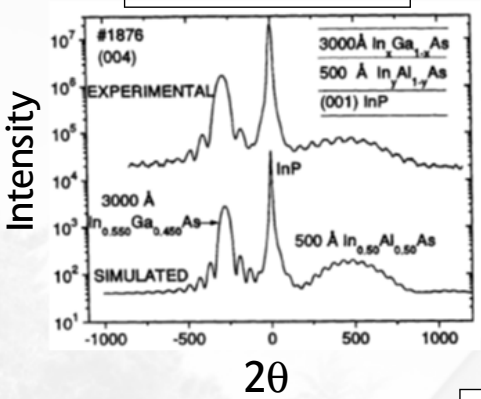



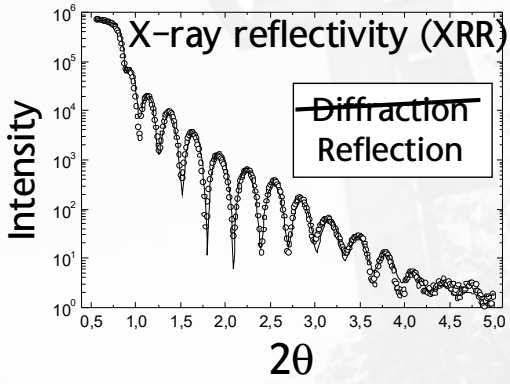



## XRD patterns > structure of film

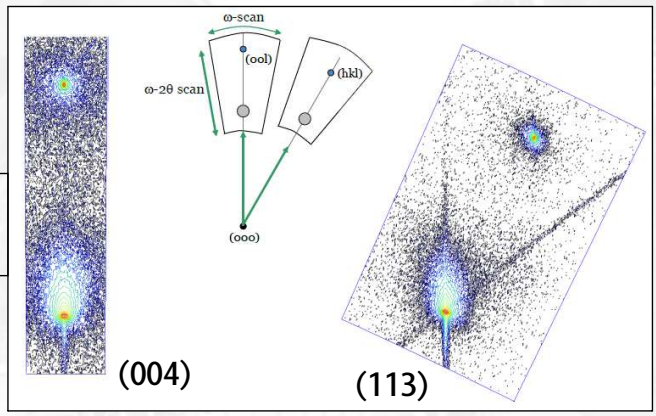


Rocking curve

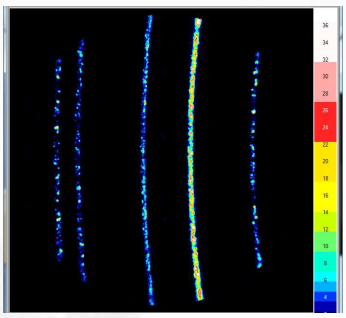


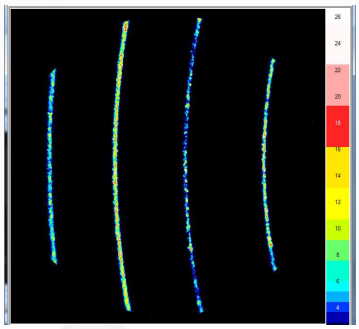

Reciprocal space mapping (RSM)



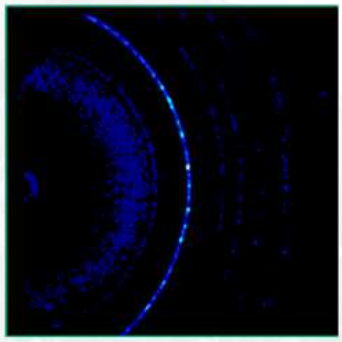
## XRD patterns > 2D detector



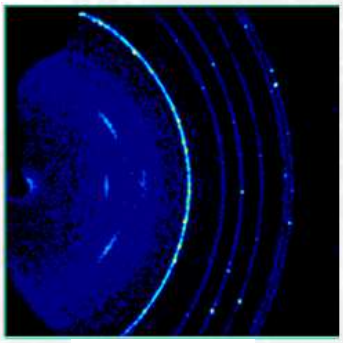
Corundum



$LaB_6$



unstretched



stretched

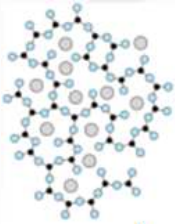




## Crystal, Unit Cell, Crystal System, Lattice Parameter

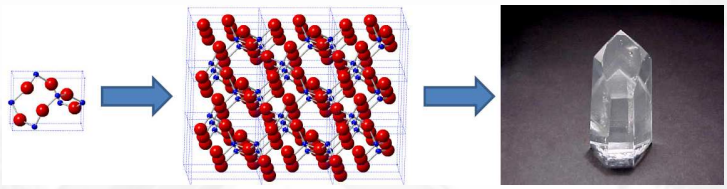
- Crystal ; long-range, 3-dimensional, orderly periodic arrangements of atoms

Crystalline solid

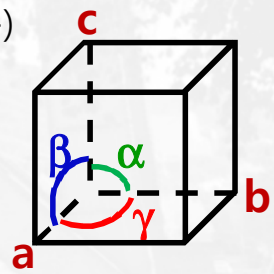


Non-crystalline solid

- Unit cell ; basic repeating unit that defines the crystal structure



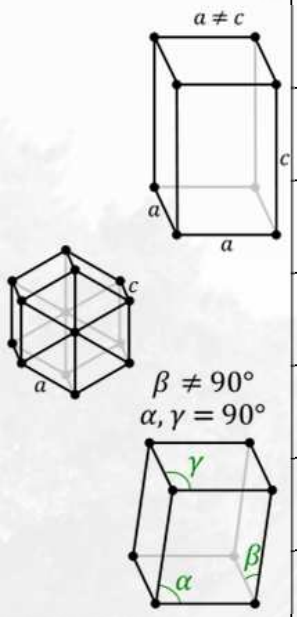
- **shape** of unit cell ← crystal system (cubic, tetragonal, ---)
- **size** of unit cell ← lattice parameter (a, b, c, α, β, γ)

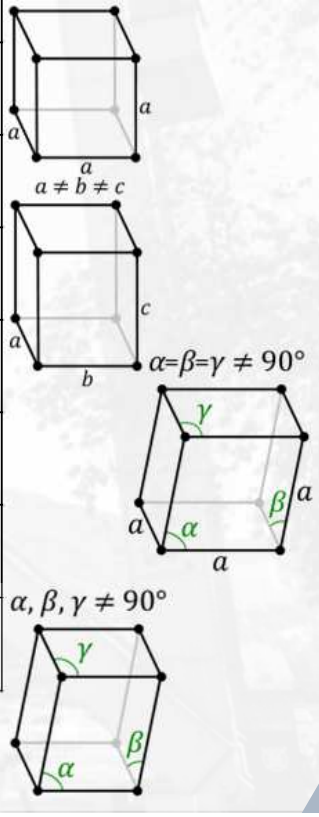


# **Shape** of Unit Cell ← 7 Crystal Systems



| Crystal System | Axis System |
|---|---|
| Cubic | a=b=c, α=β=γ=90 |
| Tetragonal | a=b≠c, α=β=γ=90 |
| Orthorhombic | a≠b≠c, α=β=γ=90 |
| Hexagonal | a=b≠c, α=β=90, γ=120 |
| Rhombohedral | a=b=c, α=β=γ≠90 |
| Monoclinic | a≠b≠c, α=γ=90, β≠90 |
| Triclinic | a≠b≠c, α≠β≠γ≠90 |






# Crystal Structure of "cubic $ZrO_2$"



- **Space Group Fm$\bar{3}$m (225)**
  → **cubic**
- **Lattice Parameter a=5.11Å**

| Atom | Wyckoff Site | x | y | z | $B_{iso}$ | occupancy |
|---|---|---|---|---|---|---|
| Zr | 4a | 0 | 0 | 0 | 1.14 | 1 |
| O | 8c | 0.25 | 0.25 | 0.25 | 2.4 | 1 |

International Tables for Crystallography,
Volume A: Space-group symmetry

$Fm\bar{3}m$ $O_h^5$ $m\bar{3}m$
No. 225 $F4/m\bar{3}2/m$ Patterson symmetry

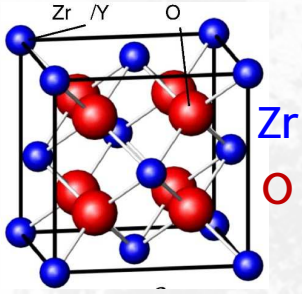
**Positions**

| Multiplicity, Wyckoff letter, Site symmetry | | | Coordinates (0,0,0)+ | (0,½,½)+ | (½,0,½)+ | (½,½,0)+ |
|---|---|---|---|---|---|---|
| 192 | l | 1 | (1) x,y,z | (2) x̄,ȳ,z | (3) x̄,y,z̄ | (4) x,ȳ,z̄ |
| 48 | h | m .m 2 | 0,y,y | 0,ȳ,y | 0,y,ȳ | 0,ȳ,ȳ | y,0,y | y,0,ȳ |
| | | | ȳ,0,y | ȳ,0,ȳ | y,y,0 | ȳ,y,0 | y,ȳ,0 | ȳ,ȳ,0 |
| 48 | g | 2 .m m | x,¼,¼ | x̄,¼,¼ | ¼,x,¼ | ¼,x̄,¼ | ¼,¼,x | ¼,¼,x̄ |
| | | | ¼,x,¼ | ¼,x̄,¼ | x,¼,¼ | x̄,¼,¼ | ¼,x,¼ | ¼,x̄,¼ |
| 32 | f | .3m | x,x,x | x̄,x,x | x,x,x̄ | x,x̄,x̄ | | |
| | | | x,x,x̄ | x̄,x̄,x̄ | x̄,x,x | x̄,x,x | | |
| 24 | e | 4m .m | x,0,0 | x̄,0,0 | 0,x,0 | 0,x̄,0 | 0,0,x | 0,0,x̄ |
| 24 | d | m .m m | 0,¼,¼ | 0,¼,¼ | ¼,0,¼ | ¼,0,¼ | ¼,¼,0 | ¼,¼,0 |
| 8 | c | $\bar{4}3m$ | ¼,¼,¼ | ¼,¼,¼ | | | | |
| 4 | b | $m\bar{3}m$ | ½,½,½ | | | | | |
| 4 | a | $m\bar{3}m$ | 0,0,0 | | | | | |

**Temperature factor**
$B_{iso}$ $U_{iso}$ $B_{ij}$ $U_{ij}$ $\beta_{ij}$

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

$$B = 8\pi^2 U^2$$




- Site occupancy = 1; every equivalent position of that site is occupied by that atom
- Site occupancy < 1; some of the sites are vacant
  - Site occupancy = 0.5; half of that site is occupied by the atom
- two atoms occupying the same site will each have a fractional site occupancy

## Fake diamond



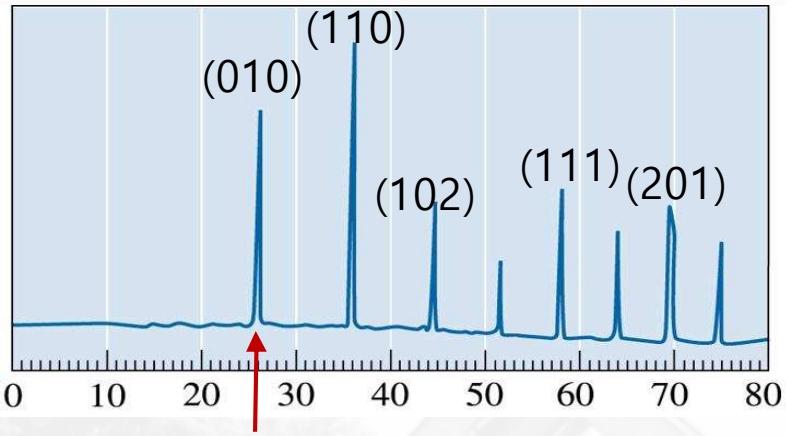
- Cubic zirconia ($ZrO_2$) - 8.5 on Mohs scale
- Moissanite (SiC) - 9.5 on Mohs scale, one of the best substitutes for diamond
- White sapphires ($Al_2O_3$) - 9 on Mohs scale
- Rutile ($TiO_2$) – 6 on Mohs scale
- White spinels - 8 on Mohs scale
- YAG (Y-Al garnet), GGG (Gd-Ga garnet) - 8 on Mohs scale
- Glass


Handheld XRF
X-ray fluorescence



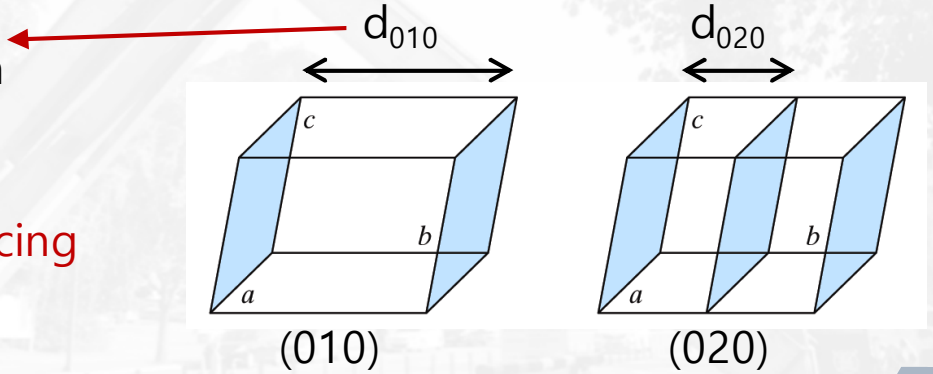
## XRD Pattern vs Miller Index






➢indexing

Peak position




**$d_{hkl}$**
Interplanar spacing
(면간 거리)

# Interplanar Spacing (면간 거리) ($d_{hkl}$)

$$\frac{1}{d_{hkl}^2}$$

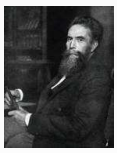
| | 결정축계 | |
|---|---|---|
| Cubic | 입 방 | $\frac{1}{a^2}(h^2+k^2+l^2)$ |
| tetragonal | 정 방 | $\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}$ |
| orthorhombic | 사 방 | $\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}$ |
| hexagonal | 육 방 | $\frac{4}{3a^2}(h^2+hk+k^2)+\frac{l^2}{c^2}$ |
| rhombohedral | 능 면 | $\frac{1}{a^2}\frac{(h^2+k^2+l^2)\sin^2\alpha+2(hk+kl+lh)(\cos^2\alpha-\cos\alpha)}{1+2\cos^2\alpha-3\cos^2\alpha}$ |
| monoclinic | 단 사 | $\frac{h^2}{a^2}+\frac{k^2}{b^2}-\frac{2kh\cos\gamma}{ab}\Big/\sin^2\gamma+\frac{l^2}{c^2}$ (first setting) |
| | | $\frac{h^2}{a^2}+\frac{l^2}{c^2}-\frac{2hl\cos\beta}{ac}\Big/\sin^2\beta+\frac{k^2}{b^2}$ (second setting) |
| triclinic | 삼 사 | $\frac{h^2}{a^2}\sin^2\alpha+\frac{k^2}{b^2}\sin^2\beta+\frac{l^2}{c^2}\sin^2\gamma+\frac{2hk}{ab}(\cos\alpha\cos\beta-\cos\gamma)+\frac{2kl}{bc}(\cos\beta\cos\gamma-\cos\alpha)+\frac{2lh}{ca}(\cos\gamma\cos\alpha-\cos\beta)\Big/1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma$ |





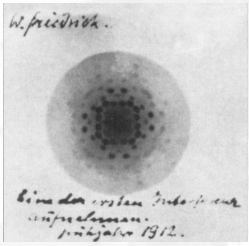
# X-ray

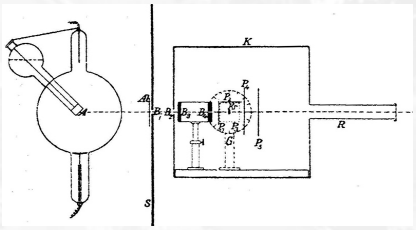
- W.C. Röntgen
  - ✓ 1895: Discovery of X-ray
  - ✓ 1901: First Nobel prize for Physics

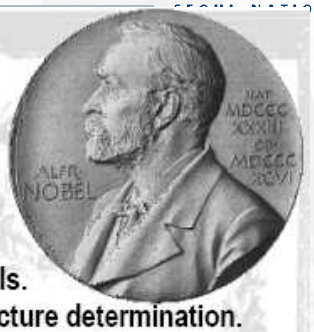
- M.T.F. von Laue
  - ✓ 1912: X-ray diffraction, with Friedrich and Knipping
  - ✓ Laue equation, Laue reflections
  - ✓ 1914: Nobel prize for Physics
- C.G. Darwin
  - ✓ 1912: Dynamical scattering theory
  - ✓ Darwin width
- W.H. and W.L. Bragg
  - ✓ 1914: X-ray diffraction from powder samples
  - ✓ Bragg's equation, Bragg reflections
  - ✓ 1915: Nobel prize for Physics
- P.P. Ewald
  - ✓ 1916: Theoretical description of X-ray diffraction
  - ✓ Ewald construction, reciprocal space

- XRD pattern of a single crystal ZnS
- University of Munich
- Confirmation of wave character of x-ray





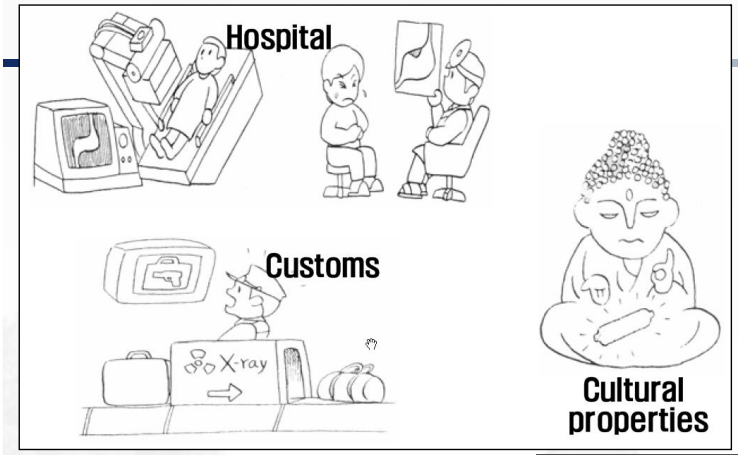
# Nobel Prizes for Research with X-Rays



1901 W. C. Röntgen in Physics for the discovery of x-rays.
1914 M. von Laue in Physics for x-ray diffraction from crystals.
1915 W. H. Bragg and W. L. Bragg in Physics for crystal structure determination.
1917 C. G. Barkla in Physics for characteristic radiation of elements.
1924 K. M. G. Siegbahn in Physics for x-ray spectroscopy.
1927 A. H. Compton in Physics for scattering of x-rays by electrons.
1936 P. Debye in Chemistry for diffraction of x-rays and electrons in gases.
1962 M. Perutz and J. Kendrew in Chemistry for the structure of hemoglobin.
1962 J. Watson, M. Wilkins, and F. Crick in Medicine for the structure of DNA.
1979 A. McLeod Cormack and G. Newbold Hounsfield in Medicine for computed axial tomography.
1981 K. M. Siegbahn in Physics for high resolution electron spectroscopy.
1985 H. Hauptman and J. Karle in Chemistry for direct methods to determine x-ray structures.
1988 J. Deisenhofer, R. Huber, and H. Michel in Chemistry for the structures of proteins that are crucial to photosynthesis.







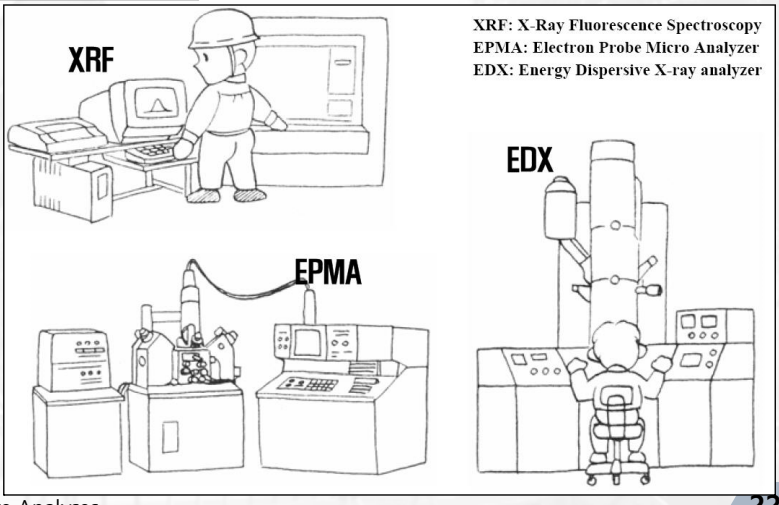

## X-ray Transmission

XRF;
X-ray fluorescence spectroscopy

EPMA;
electron probe micro analyzer

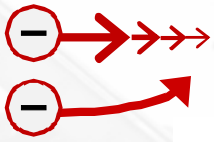
EDX;
energy dispersive X-ray analyzer

## X-ray Fluorescence

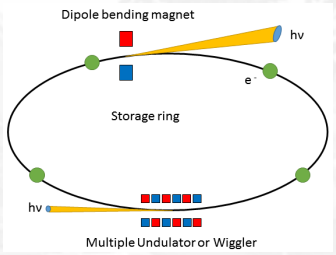


# X-ray

- Electromagnetic wave; wavelength 0.3Å ~3 Å
  - ✓ Invisible in air
- Wavelength ~ atomic distance → Diffraction
- Transmission → medical, nondestructive evaluation (NDE)
- Detection ; photographic, fluorescent, ionizing
- Generation
  - ✓ X-rays are produced when <u>any electrically charged particle</u> of <u>sufficient kinetic energy rapidly decelerates.</u>
    - change of speed of matter
    - change of direction of movement



- Sealed X-ray tube; Rotating anode tube; Synchrotron




www.researchgate.net/figure/Schematic-representation-of-the-synchrotron-radiation-source-The-electron-storage-ring_fig13_307606559

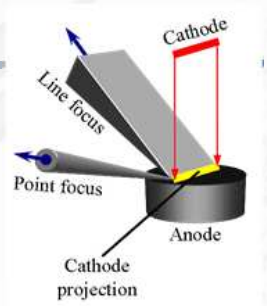
jayxray.com/x-rays/c-arm-buyers-guide/c-arm-talk/rotating-vs-stationary-anode-on-c-arm/

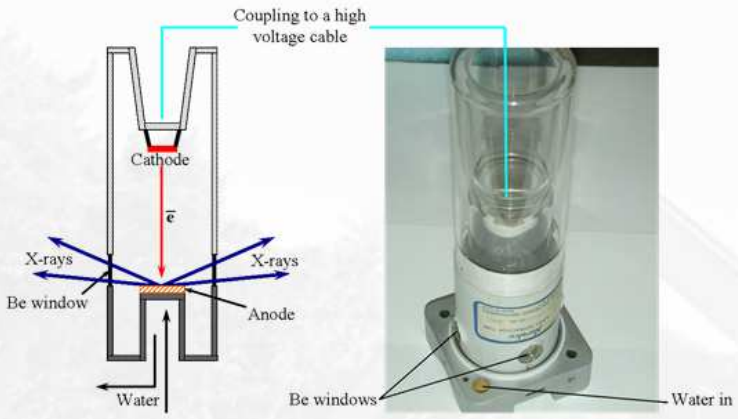
pd.chem.ucl.ac.uk/pdnn/inst1/xtube.htm

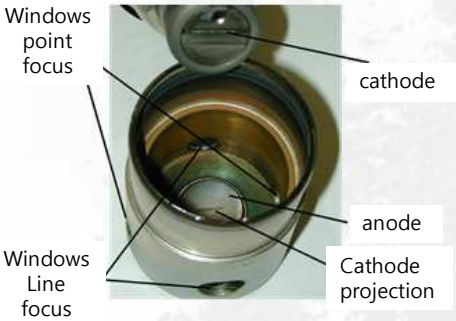


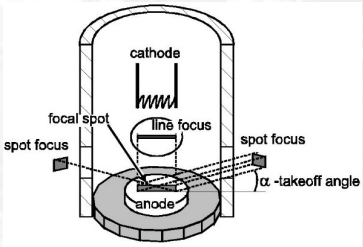
# Sealed X-ray tube

- Bombardment of a target by electrons
- Anode (Cu, Mo, W, Ag ..), Cathode (W, LaB6)
- $10^{-3}$ ~ $10^{-4}$ Torr chamber, high voltage (10 ~ 50kV)




Overall efficiency very low ← heat

Most of the kinetic energy striking the target is converted into heat.
→ < 1% is transformed into X-ray.

## Generation of X-ray



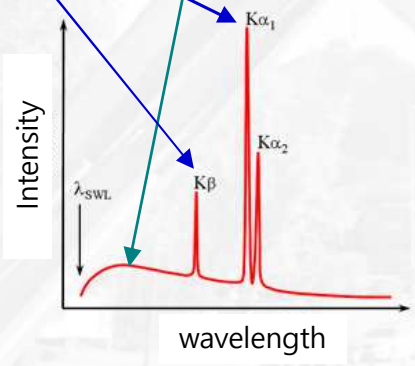
Loss of energy of the electrons caused by

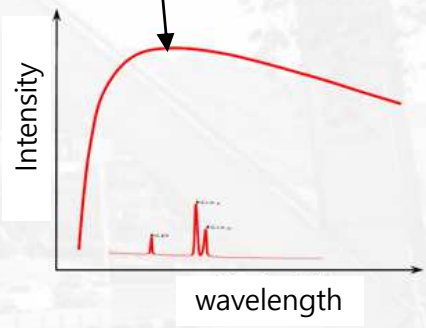
- atomic transitions → Characteristic radiation → emission of spectrum lines
- deceleration → Continuous radiation / White radiation / Bremsstrahlung
- direction change → Synchrotron radiation

Sealed X-ray tube

Rotating anode tube

Synchrotron

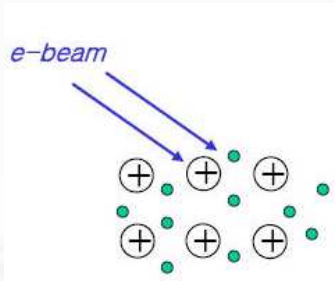


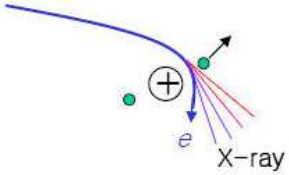



## Generation of X-ray

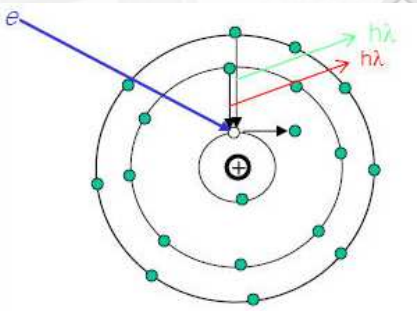




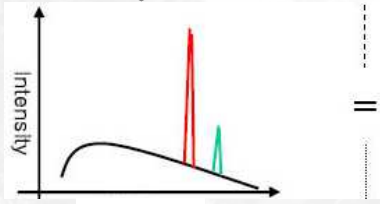

Energetic e-beam Bombardment on solid




Bremsstrahlung

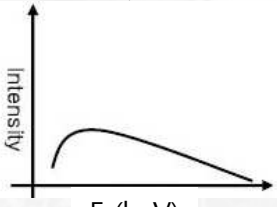



Transition of electrons in ion



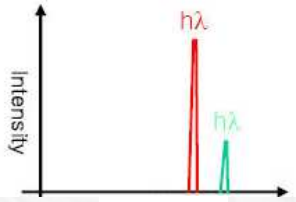

Spectrum from X-ray tube

=




Continuous X-ray spectrum

+



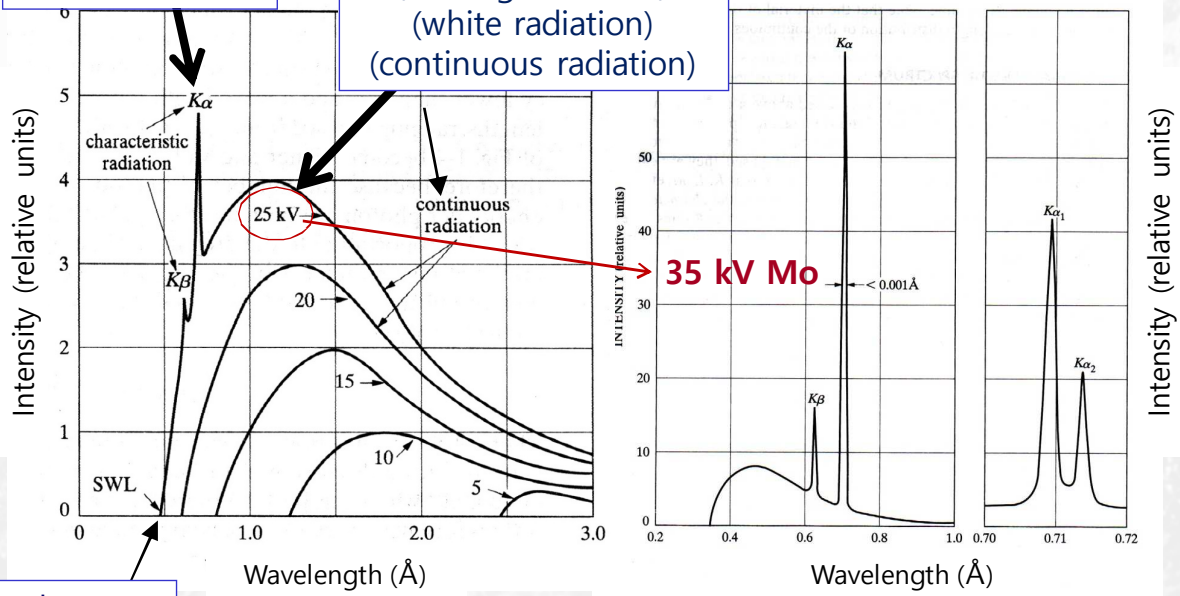

Characteristic X-ray lines

# X-ray spectrum of molybdenum



Characteristic radiation

Bremsstrahlung (braking radiation) (white radiation) (continuous radiation)



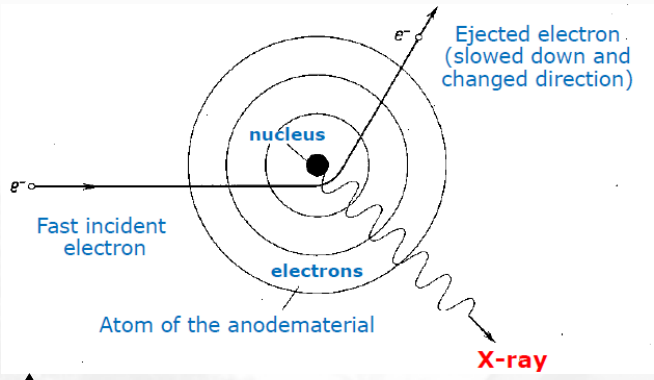

short wavelength limit

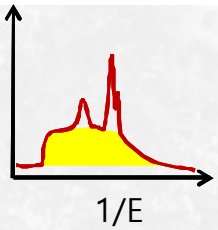


# Generation of X-ray

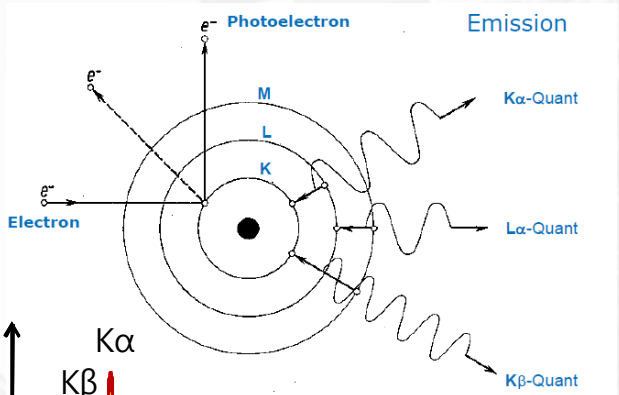


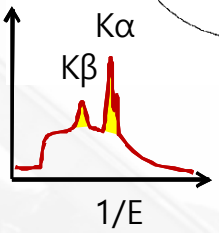
"Bremsstrahlung" Radiation




Characteristic Radiation

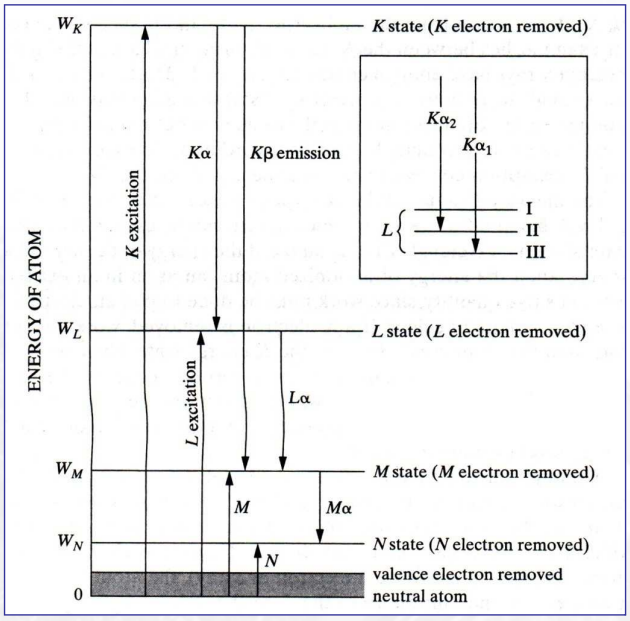



Cross Sections of Excitation

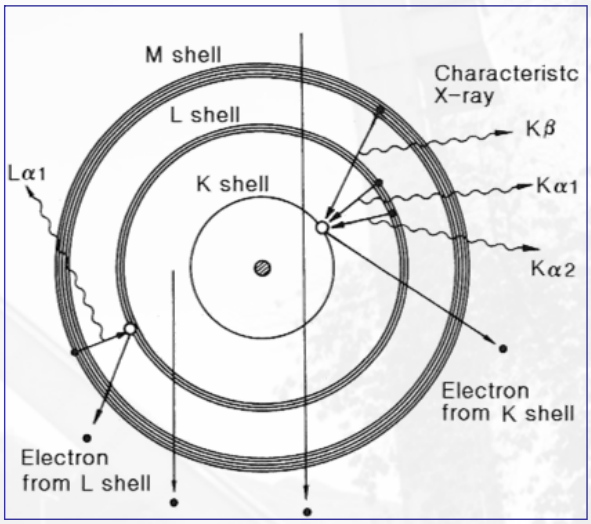
$K_{\alpha 1} : K_{\alpha 2} : K_{\beta} = 10 : 5 : 2$

# Atomic energy level




Cullity page 16

$K_\alpha=(2K_{\alpha1}+K_{\alpha2})/3$
β-filter, monochromator




Intensity ratios
$K_{\alpha1} : K_{\alpha2} : K_\beta = 10 : 5 : 2$

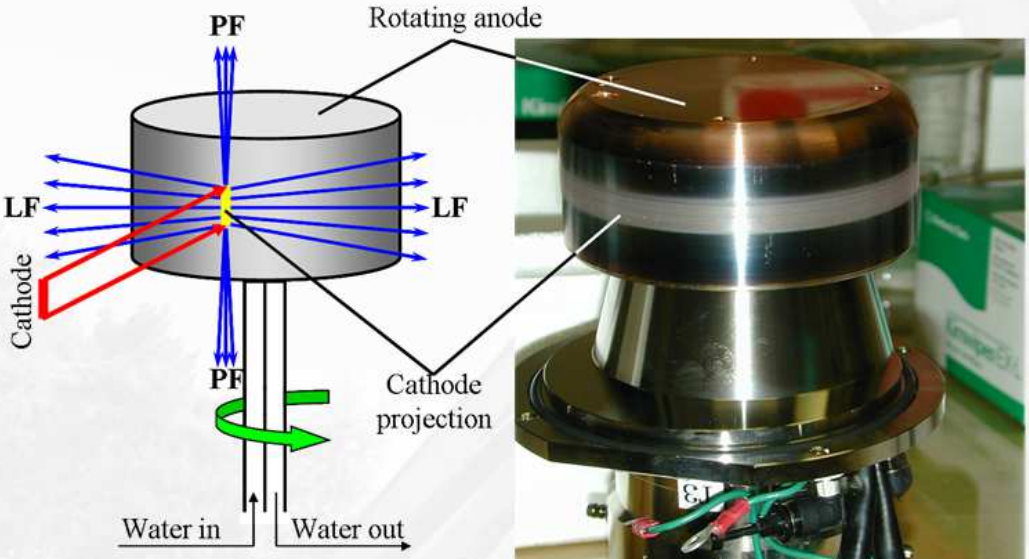


# X-ray from sealed tube/rotating anode



| Anode | $Kα_1$ (Å) | |
|---|---|---|
| Cu | 1.54060 | - Best for inorganics<br>- Fe and Co fluorescence |
| Cr | 2.28970 | - High Resolution for large d-spacing<br>- High attenuation in air |
| Fe | 1.93604 | - Used for ferrous alloys to reduce Fe fluorescence.<br>- Causes Cr fluorescence. |
| Co | 1.78897 | - Used for ferrous alloys to reduce Fe fluorescence. |
| Mo | 0.70930 | - Short wavelength used for small unit cells |

# Rotating anode X-ray source





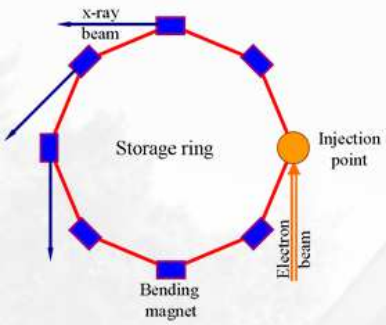

3,000 ~ 10,000 rpm

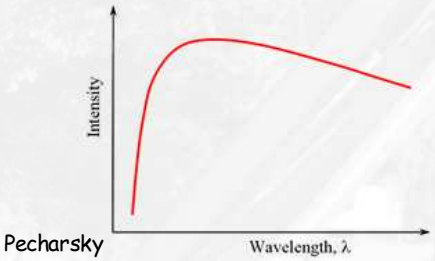


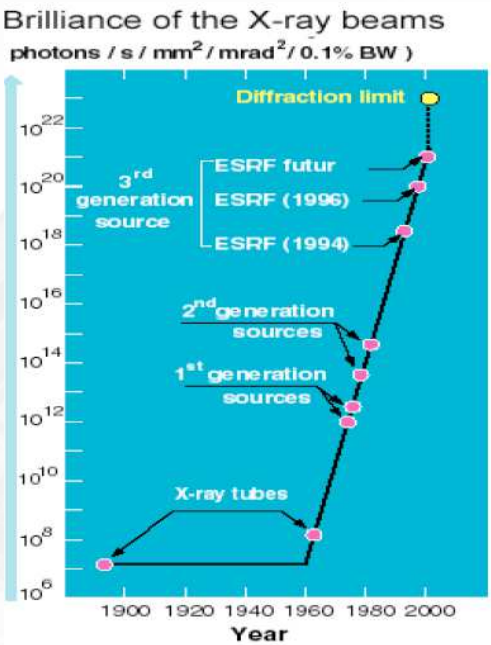


# Synchrotron X-ray

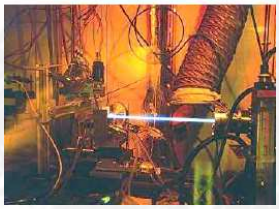
- Most powerful X-ray radiation source
- High brilliance X-ray beam
- Distribution of beam intensity as a function of wavelength

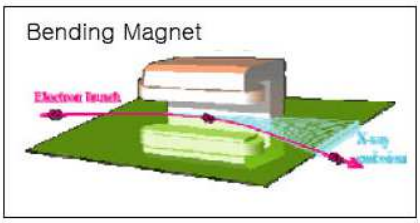


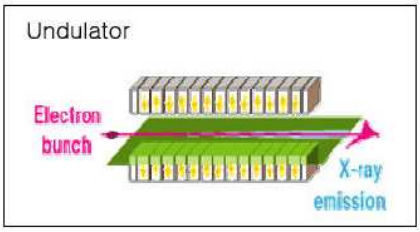




*Intensity !!!*






Synchrotron Radiation.
- Very High Dense Source.
- Good Coherent Property.
- Continuous Spectrum.
- Huge Apparatus.

## Brightness & Fluxes for Neutron & X-Ray Sources

| | Brightness $(s^{-1}m^{-2}ster^{-1})$ | dE/E (%) | Divergence $(mrad^2)$ | Flux $(s^{-1}m^{-2})$ |
|---|---|---|---|---|
| Neutrons | $10^{15}$ | 2 | $10\times10$ | $10^{11}$ |
| Rotating Anode | $10^{20}$ | 0.02 | $0.5\times10$ | $5\times10^{14}$ |
| Bending Magnet | $10^{27}$ | 0.1 | $0.1\times5$ | $5\times10^{20}$ |
| Undulator (APS) | $10^{33}$ | 10 | $0.01\times0.1$ | $10^{24}$ |





## Neutron diffraction

- Produced in nuclear reactors. White spectrum
- **Scattered by nuclei (electron clouds in X-ray).**
- Scattering factor remains constant over the whole range of Bragg angles.
- **Scattering factors not proportional to atomic number**
- Scattering factors are different for different isotopes of the same element.
- Neutrons have **spins** → interact with unpaired e′ spins (magnetic moments), can be used to determine ordered **magnetic structures.**

## Electron diffraction

- High vacuum is needed.
- e's strongly interact with materials. → dynamical theory of diffraction
- Cost of equipment

# Properties of Neutron

**Mass** **No Charge** **Spin 1/2**

| | |
|---|---|
| No charge | → Deep penetration |
| Wavelength Å ~ nm (Thermal & Cold Neutron) | → Atomic & Nanometer scale |
| Energy ~ meV | → Same magnitude as basic excitations in solids |
| Spin =1/2 | → Magnetic structure & dynamics |
| Interacts with nuclei | → Contrast variation ($b_H$ = -3.74fm, $b_D$ = 6.67fm) |

**HANARO at KAERI in Daejeon**

High-flux Advanced Neutron Application ReactOr
30 MW Multi-purpose Research reactor since 1995
Neutron Scattering, NAA, RI production, Irradiation Test, NTD


RX : Reactor Building RIPF : Radio-Isotope Production Facility
CNL : Cold Neutron Laboratory IMEF : Irradiated Material Examination Facility

**HANARO Reactor Hall**




# Neutron vs. X-ray

**Why Neutron?**

**X-rays**
Scattered from electrons
➢Scattering proportional to Z

| H | C | N | O | Al | Si | P | Ti | D |
|---|---|---|---|---|---|---|---|---|
| 1 | 6 | 7 | 8 | 13 | 14 | 15 | 22 | 1 |

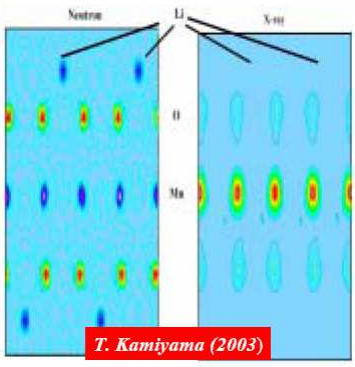
**Neutrons**
Scattered by nuclei
➢Scattering not proportional to Z

| H | C | N | O | Al | Si | P | Ti | D |
|---|---|---|---|---|---|---|---|---|
| 1 | 6 | 7 | 8 | 13 | 14 | 15 | 22 | 1 |
| -37.4 | 66.5 | 93.6 | 58.0 | 34.5 | 41.5 | 51.3 | -34.4 | 66.7 |

x10$^{-14}$

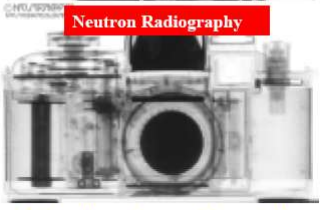
Presentation of Shin Ae Kim, KAERI

**Li-ion battery**




**X-ray Radiography**

**Neutron Radiography**



http://neutra.web.psi.ch

## X-ray, neutron, & electron



| | X-ray (conv/sync) | Neutron | Electron |
|---|---|---|---|
| nature | wave | particle | particle |
| medium | atmosphere | atmosphere | high vacuum |
| **Scattering by** | **e' density** | **nuclei, magnetic spins of e's** | **electrostatic potential** |
| Range of λ (Å) | 0.5~2.5 (0.1~10) | ~1 | 0.01~0.05 |
| l selection | fixed/variable | variable | variable |
| **Lattice image** | **reciprocal** | | **direct, reciprocal** |
| Direct structure image | no | | yes |
| Applicable theory of diffraction | kinematical | | dynamical |



## Safety (XRD)

- Electric shock
- Radiation hazard
  - ✓ Burns
  - ✓ Radiation sickness
  - ✓ Genetic mutation
- Be window

## Beryllium - MSDS



- Appearance: silvery solid or grey foil
  Melting point: 1278 C Boiling point: 2970 C
- Very toxic by inhalation - risk of serious damage to health. May act as a human carcinogen for which there is no safe exposure level. May act as a sensitizer.
- Toxicity data IVN-RAT LD50 0.5 mg kg-1
- Risk phrases R26 R27 R37 R39.

IVN – intravenous
LD50 – lethal dose 50% kill

R26 – very toxic by inhalation
R27 – very toxic in contact with skin
R37 irritating to respiratory system
R39 – danger of very serious irreversible effects

- No special health risks with Be in solid form
- Skin Contact with Beryllium
  - ✓ No effect on contact or temporary embedding.
  - ✓ Solvents will not generate beryllium dust, but some acids will. Don't etch beryllium.
  - ✓ Wear clean gloves to protect the skin and to protect the beryllium.

# Collimation Monochromatization Diffractometer



## Collimation & Monochromatization



- Conventional X-ray (sealed tube, rotating anode tube) has
  - ✓ Polychromatic nature → monochromatization
  - ✓ Angular divergence → collimation

1. White radiation → high background
2. Three intense characteristic lines ($K_{\alpha 1}$, $K_{\alpha 2}$, $K_{\beta}$) → three Bragg peaks from each (hkl)
3. Angular divergence → broad & asymmetric Bragg peaks

- **Incident X-ray beam needs to be conditioned** to improve the quality of diffraction pattern.
- How to reduce both the angular & wavelength dispersion?
- How to reduce both with minimal loss of intensity of incident & diffracted beams?

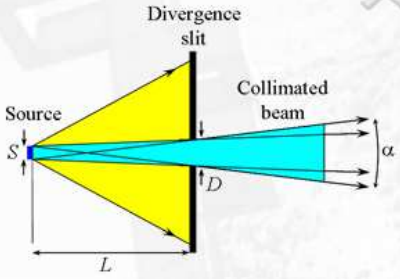
# Collimation slits

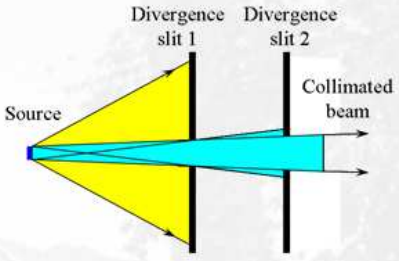


## Divergence slit



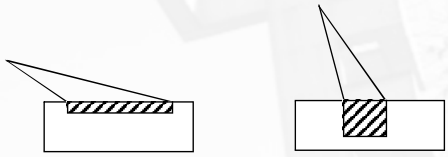
- The slits block X-rays that have large divergence.
- The size of the divergence slit influences peak intensity and peak shapes.
- Narrow divergence slits:
  - ✓ reduce the intensity of the X-ray beam.
  - ✓ reduce the length of the X-ray beam hitting the sample.
  - ✓ produce sharper peaks.
    - The instrumental resolution is improved so that closely spaced peaks can be resolved.



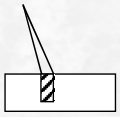
## Divergence slit

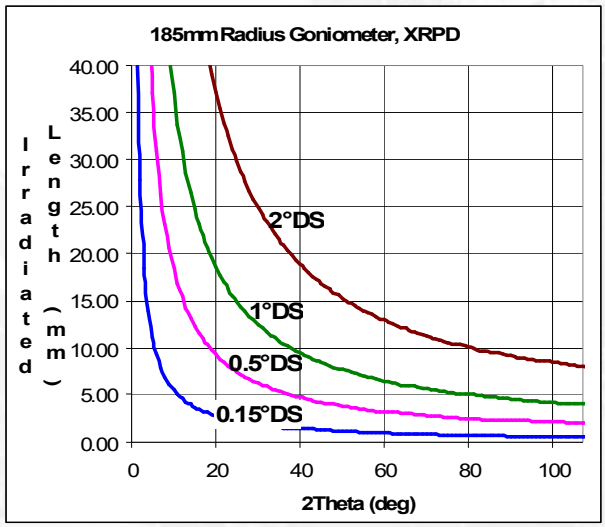
- The length of the incident beam is determined by the divergence slit, goniometer radius, and incident angle.



- This should be considered when choosing a divergence slit size:
  - ✓ if the divergence slit is too large, beam can be significantly longer than your sample at low angles.

  - ✓ if the slit is too small, you may not get enough intensity from your sample at higher angles.

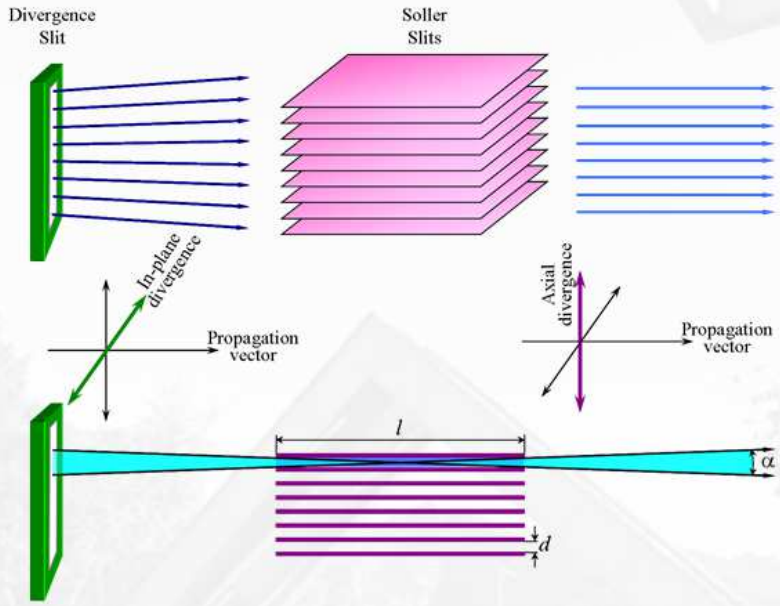








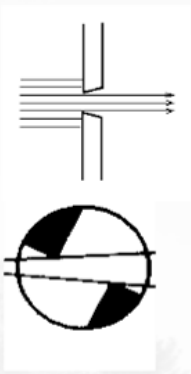

## Divergence slit & Soller slit




- Soller slit - reduce angular divergence of the incident X-ray beam in the direction // to goniometer axis (reduce axial divergence).

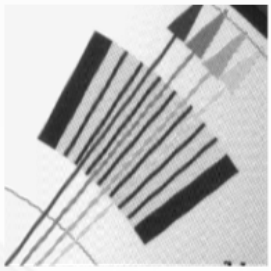
## Slit assemblies and soller slits

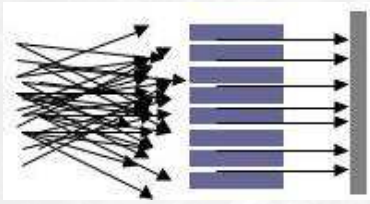




The normal slit consists of two blades, limiting the beam width.

For automatic changing of the slit width, turnable edges are used.

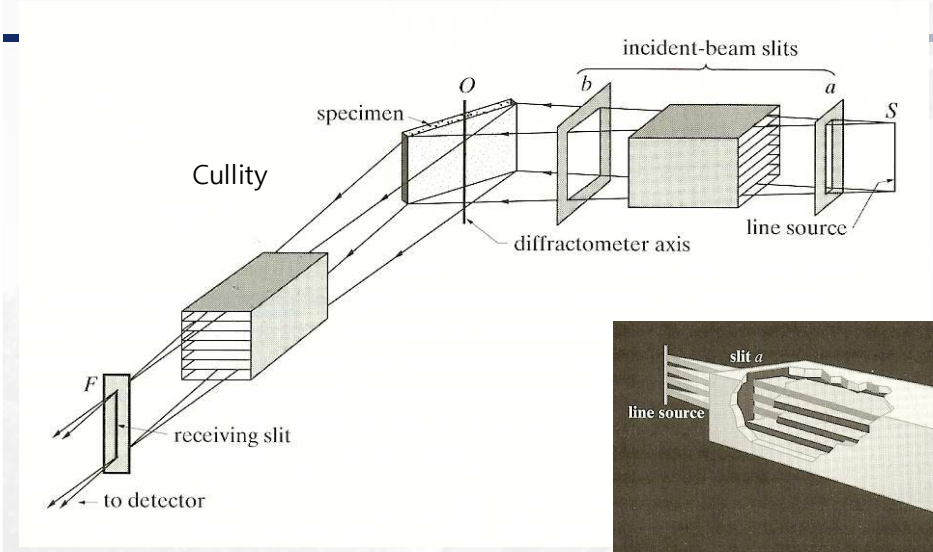


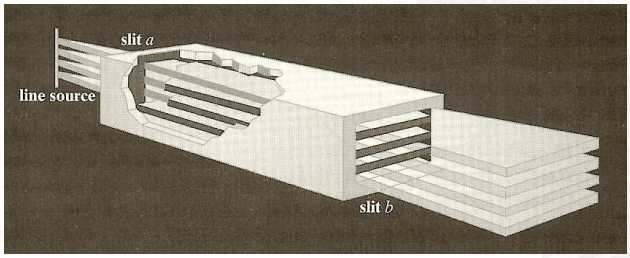
Parallel Plate Collimator & Soller Slits block divergent X-rays, but do not restrict beam size like a divergent slit.

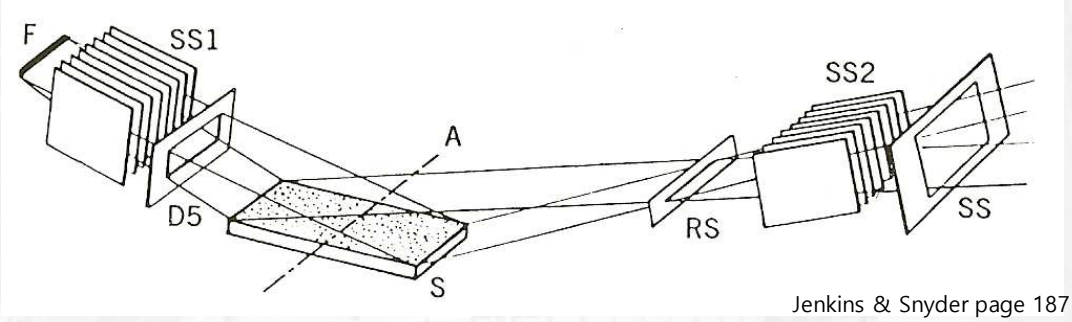


## Soller slit



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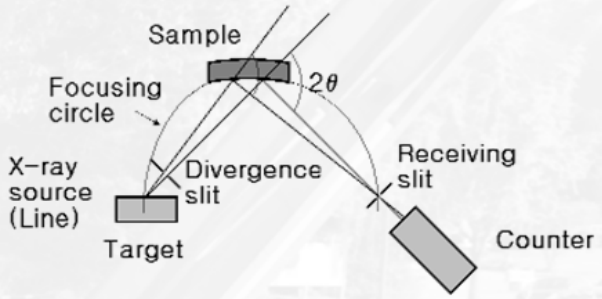
## Slit



- In case the line intensities are to be compared over the whole range of 2θ, the same divergence must be used and specimen must be larger than the beam at all angles.
- Variable divergence slit → irradiated area constant at all 2θ angles
- Fixed divergence slit → irradiated volume constant at all 2θ angles
- Receiving slit defines the width of beam admitted to the detector. Increase of receiving slit → increase of maximum intensity, loss of resolution

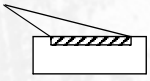




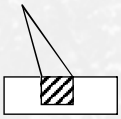

## Constant irradiated volume



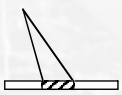
- In a polycrystalline sample of 'infinite' thickness, the change in the irradiated area as the incident angle varies is compensated for by the change in the penetration depth.



- These two factors result in a constant irradiated volume.
  - ✓ as area ↓, depth ↑; and vice versa

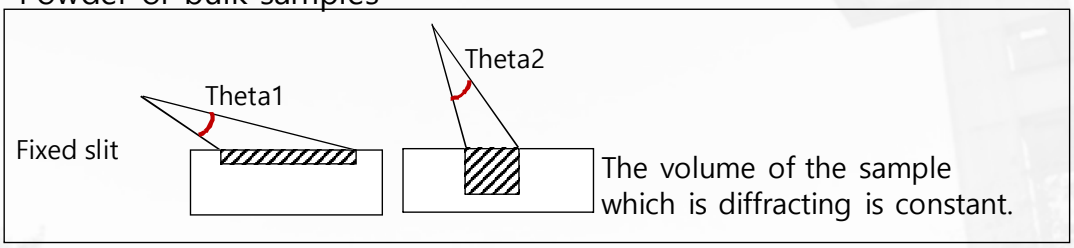


- This assumption is important for many aspects of XRPD.
  - ✓ Matching intensities to those in the PDF reference database
  - ✓ Crystal structure refinements
  - ✓ Quantitative phase analysis
- This assumption is not necessarily valid for thin films or small quantities of sample on a ZBH.

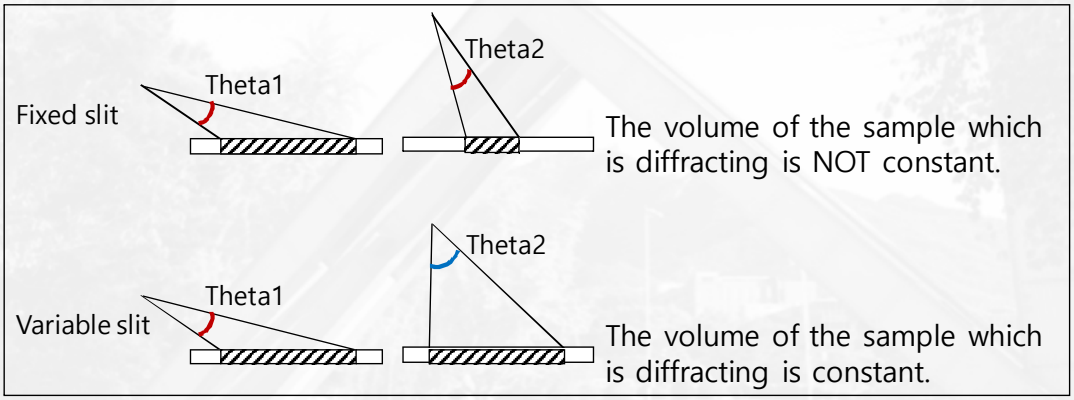


## Variable slit vs. Fixed slit

Powder or bulk samples




Thin samples








# Monochromators

remove unwanted wavelengths

## Monochromatic radiation



- Problems caused by polychromatic nature of diffracted beam & variability of angular dispersion
- XRD pattern from multiple wavelength, or that from unknown wavelength → difficulty in interpreting the pattern
- Why monochromatic beam is wanted? – we want to obtain experimental pattern from a single wavelength.
- Monochromatization by reducing the intensity of white radiation & by eliminating undesirable characteristic wavelengths from X-ray spectrum
  - ✓ β filter
  - ✓ Diffracted beam monochromator
  - ✓ Primary beam monochromator
  - ✓ Pulse height selection using proportional counter
  - ✓ Use of solid state detector (high resolution energy resolving detector)



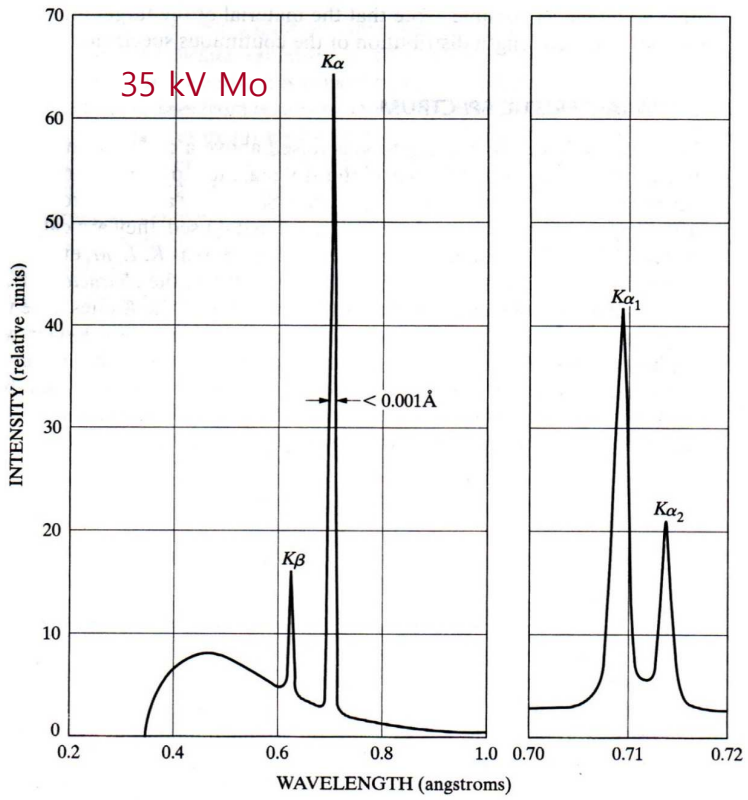
## X-ray spectrum of molybdenum



2p → 1s

α1, α2 doublet
β1, β3 doublet

3p → 1s

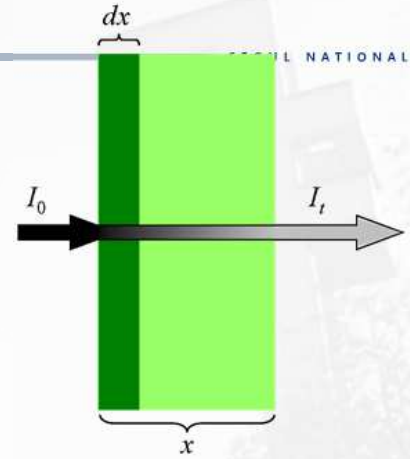


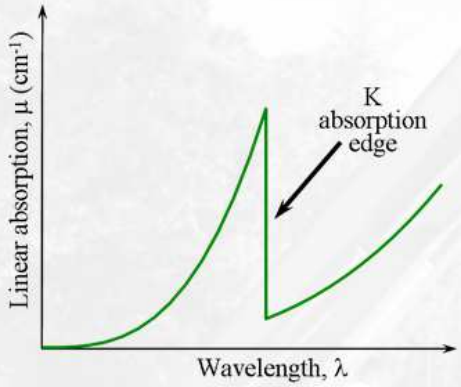
## Absorption of X-rays

$$I_x = I_0 e^{-(\mu/\rho)\rho x}$$

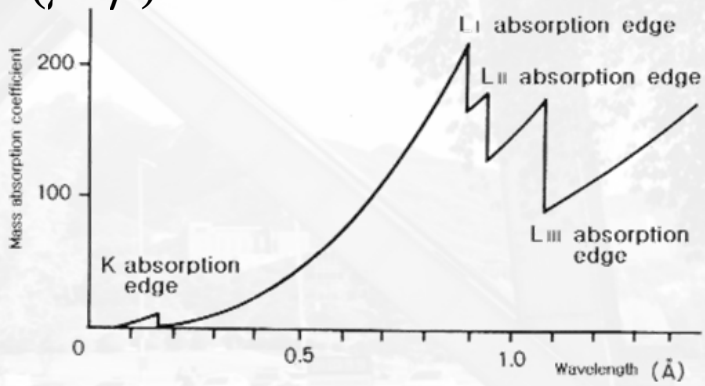
μ linear absorption coefficient

μ/ρ mass absorption coefficient



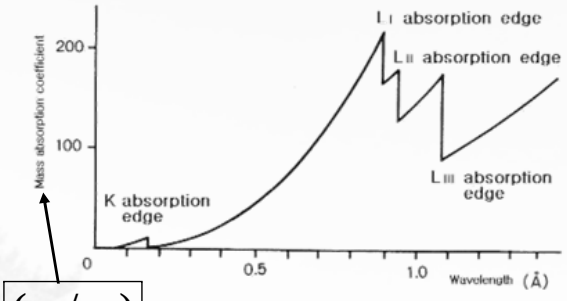




$(\mu/\rho)$



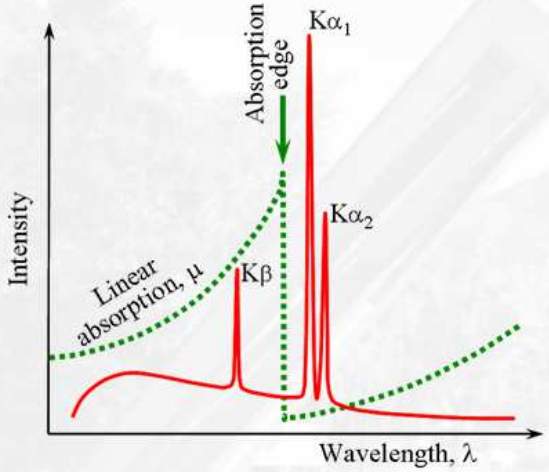


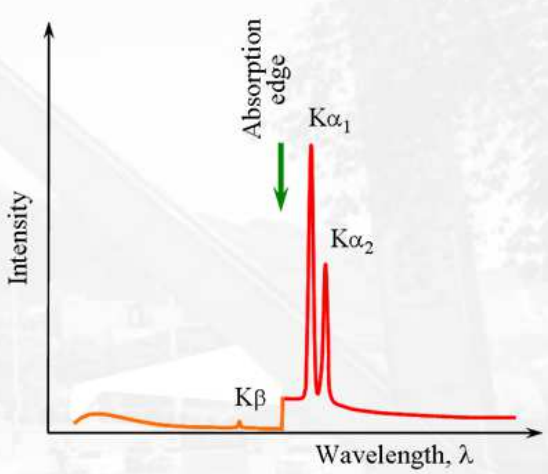

## β-filter




$(\mu/\rho)$

$$I_x = I_0 e^{-(\mu/\rho)\rho x}$$



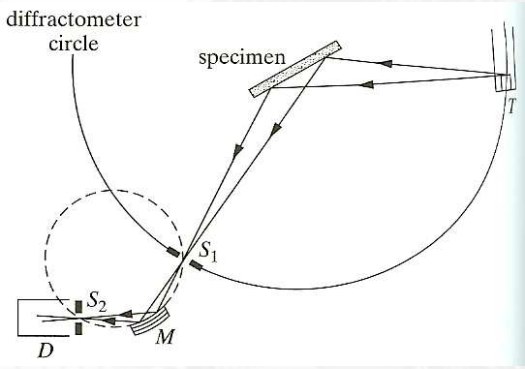




Cullity page 18

## Monochromators



- Ways to reduce BKG
  - ✓ Pulse-height analyser
  - ✓ Diffracted beam monochromator → suppress BKG radiation originating at the specimen (flourescent radiation, incoherent scattered radiation).
  - ✓ Balanced filter
- Monochromator can be placed in diffracted beam in diffractometer (not in the area detector).
- Incident beam monochromator → Lp factor has to be changed (has to include contribution from the diffraction at the monochromator).
- LiF, graphite, Si, Ge, $SiO_2$ (quartz), etc

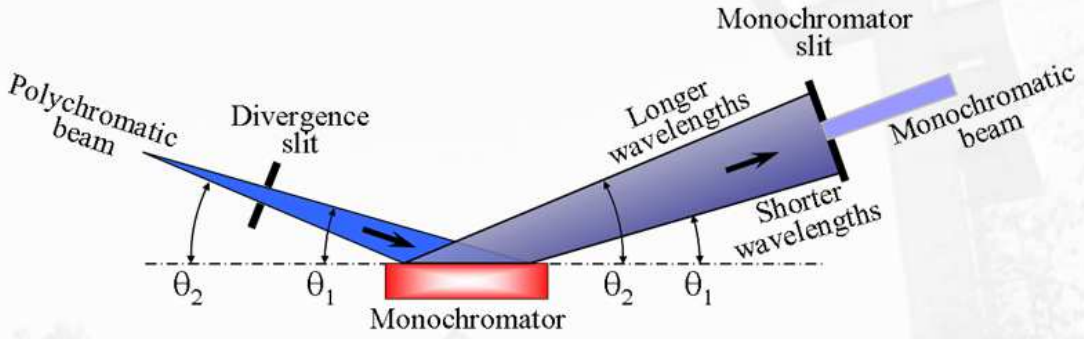


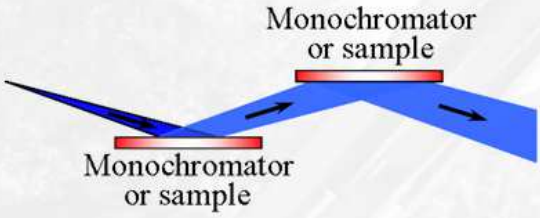

Cullity



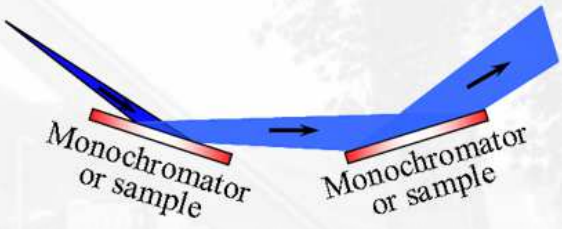
## Single crystal monochromator






Parallel arrangement



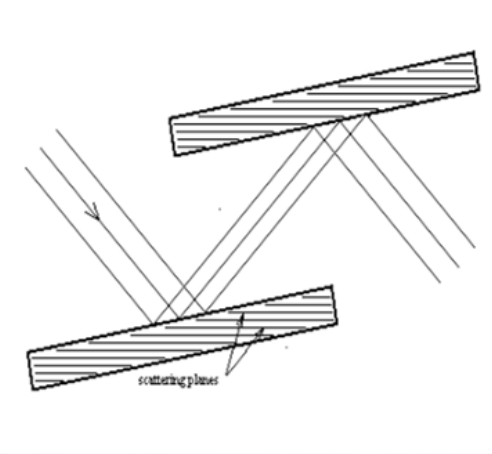

Angular arrangement

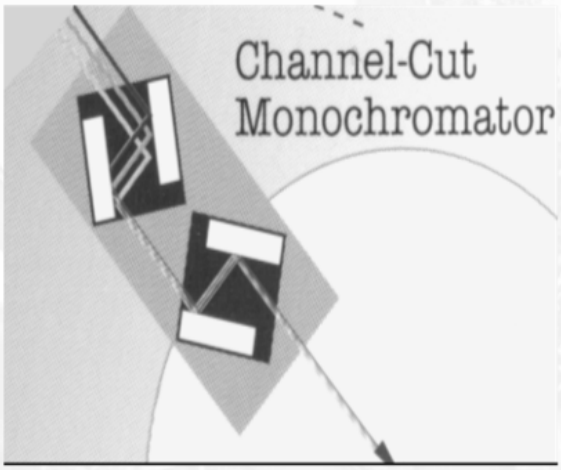
Pecharsky

## Multi bounce single crystal monochromators



An arrangement of two or four plane crystals provides a beam with very low wavelength dispersion and divergence. Using special channel cut crystals, a high brilliance source is yielded.

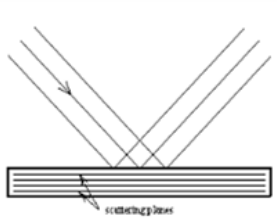


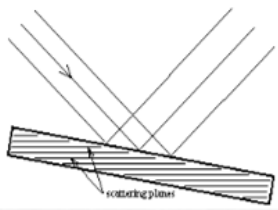



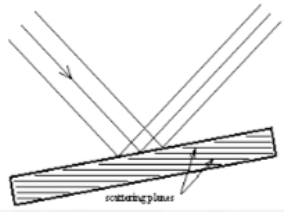



## Plane unbent crystal monochromators

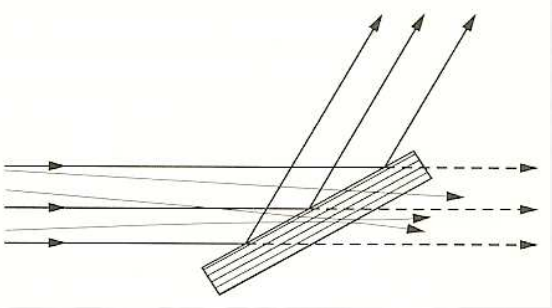




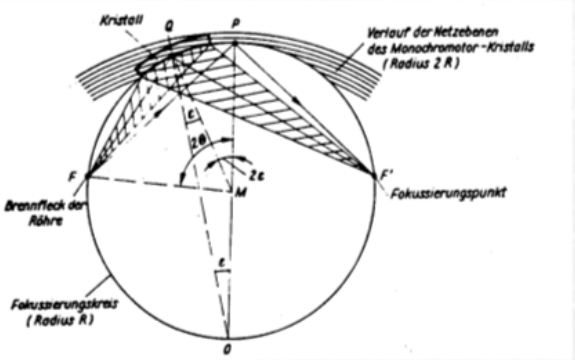



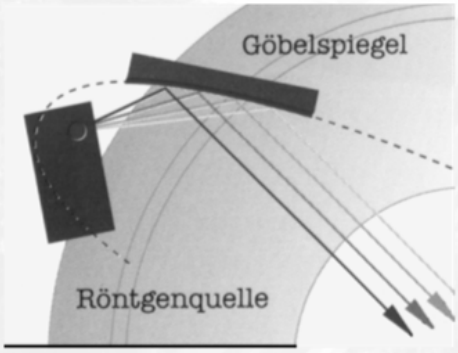

- A single crystal may reflect the primary beam, according to Bragg's law, if well aligned.
- It will reject radiation from the wrong direction or the wrong wavelength. → intensity low
- A perfect single crystal will show high resolution in angles or wavelength.
- A poly-domain crystal will show low resolution.
- The better the resolution, the more carefully it must be aligned.



## Bent crystal primary monochromators

A monochromator of type Johannson is special cut and bent single crystal. It enables the focal spot or the divergent primary beam to be focused to a point again.




The **Göbel Mirror** is bent like a parabola. The divergent beam emitted by the X-ray tube is converted into a parallel one illuminating the sample. Mounted in the diffracted beam, the beam off the mirror is reflected into the receiving slit.

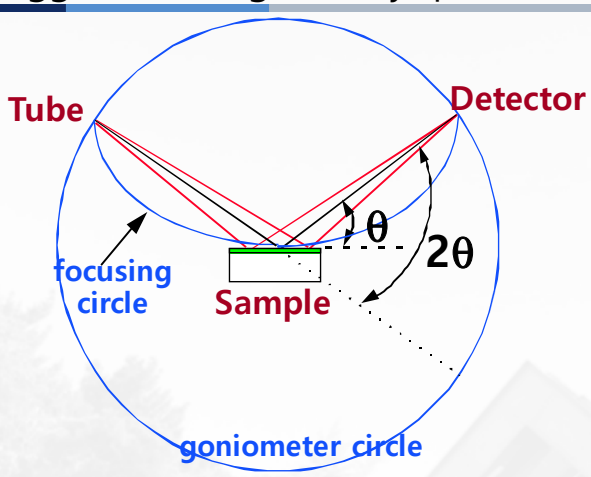


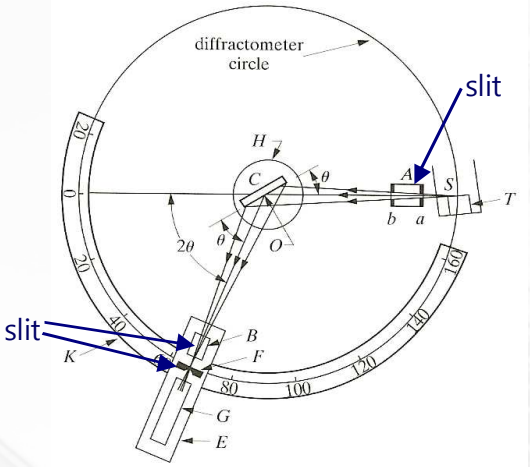


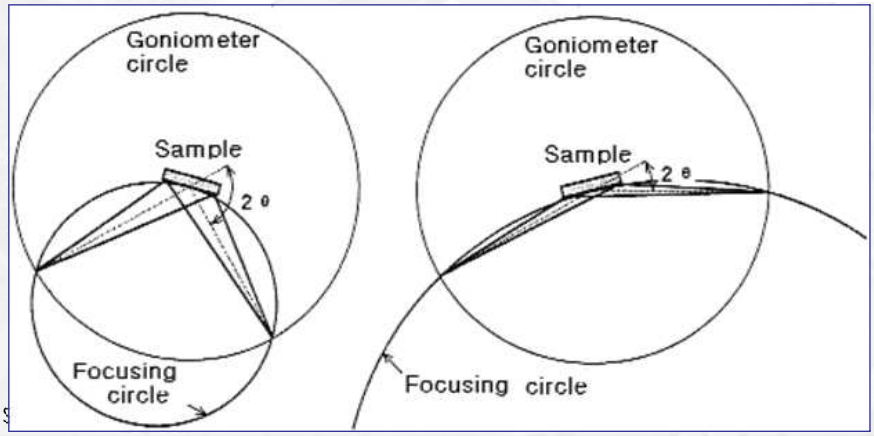
# X-ray Diffractometer

## Bragg-Brentano geometry (parafocusing geometry)





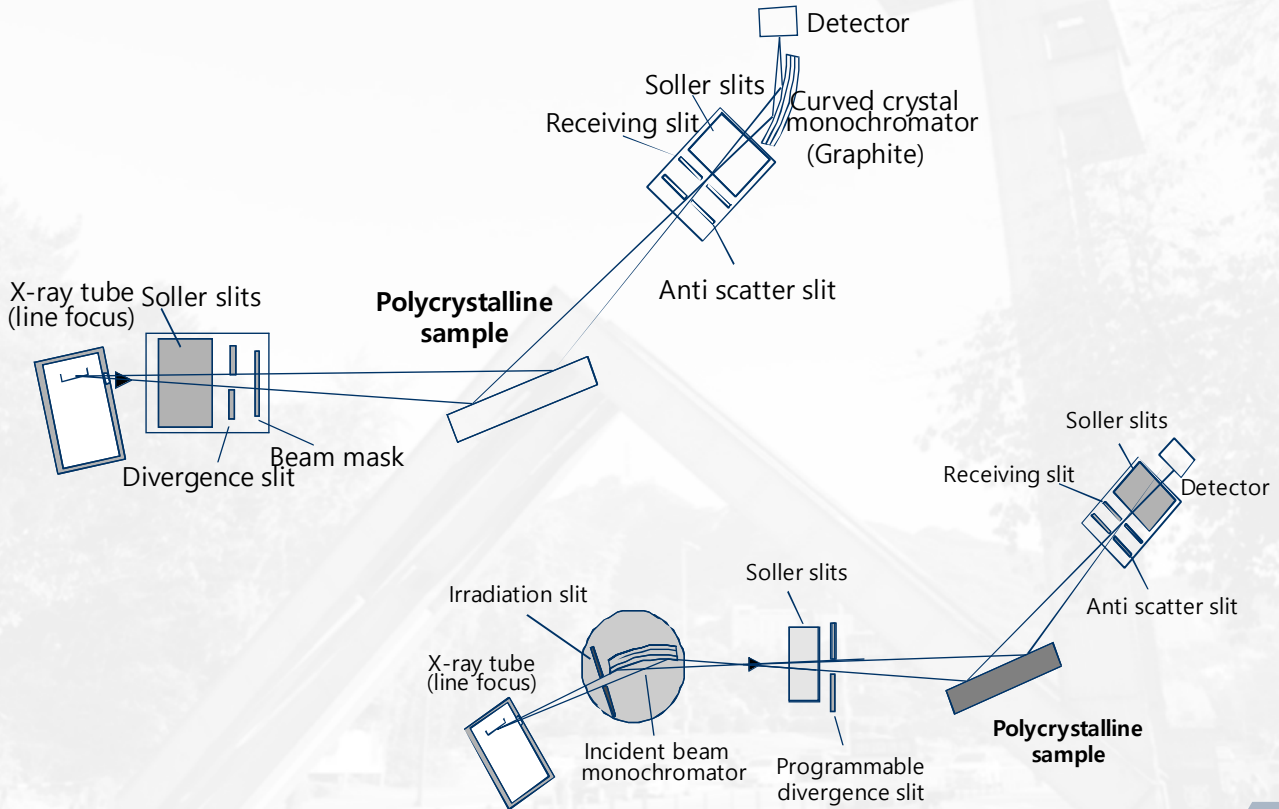






## X-ray diffractometer > Bragg-Brentano

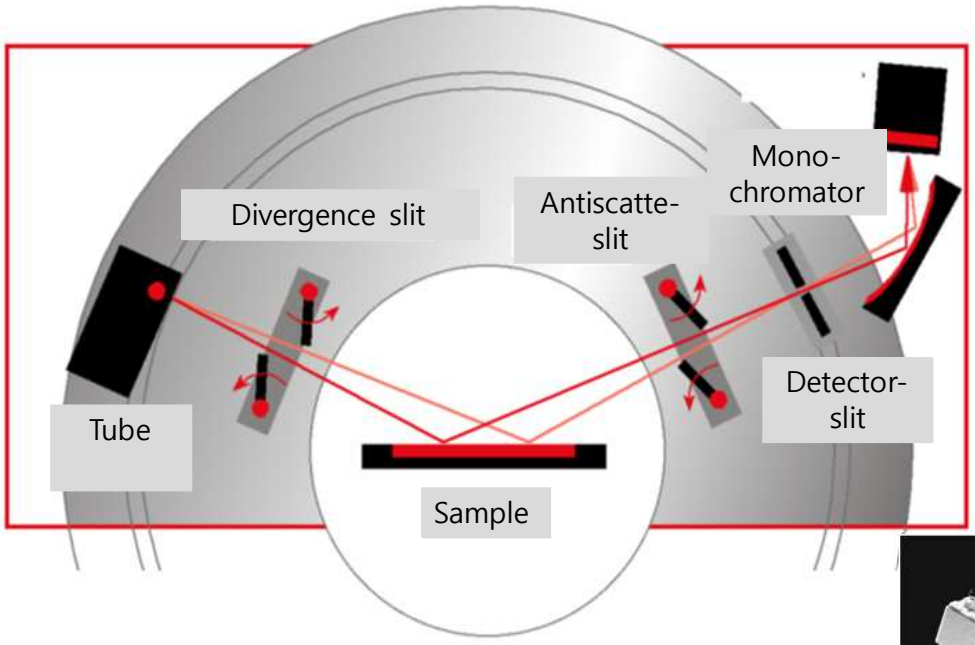


- monochromator or filter - suppress Kβ radiation, decrease BKG



# The Bragg-Brentano Geometry



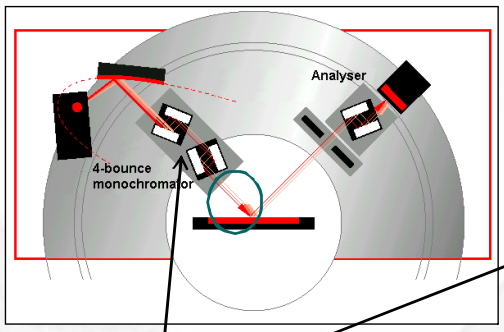


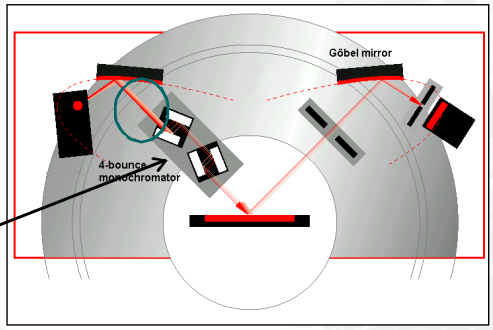




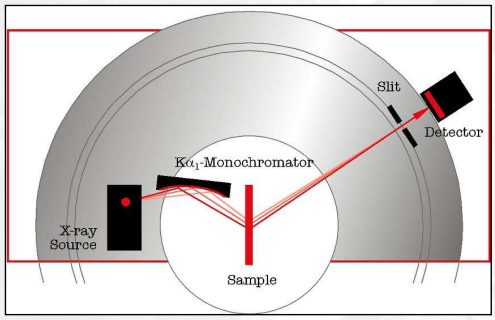
# X-ray diffractometer

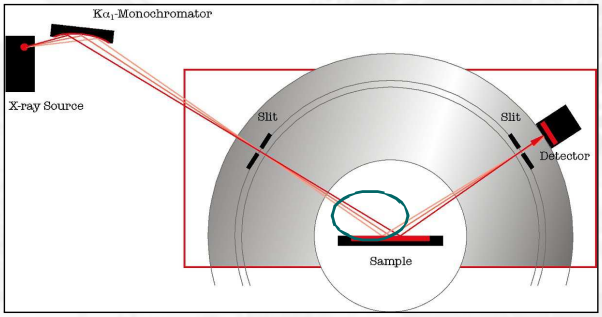




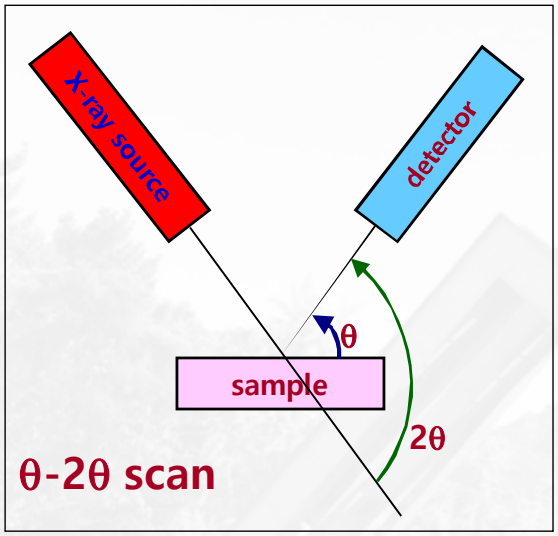



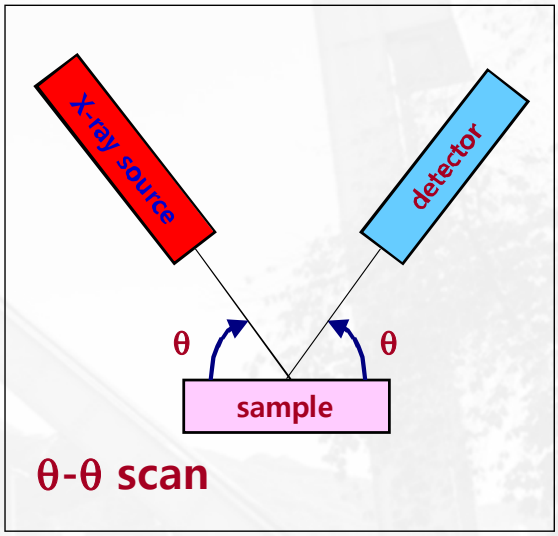

4-bounce monochromator



# θ-2θ scan vs. θ-θ scan

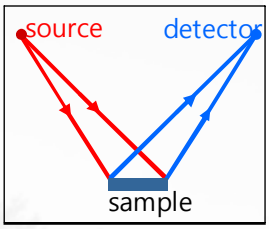


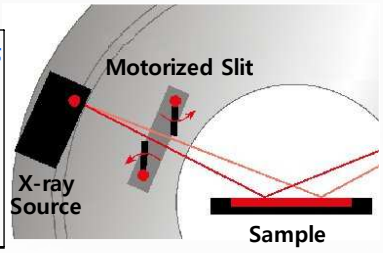



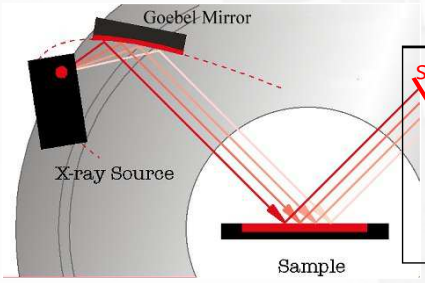


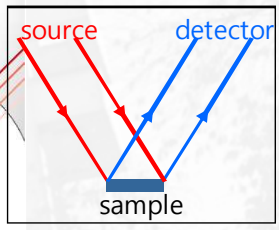



# Bragg-Brentano vs. Parallel Beam Geometry



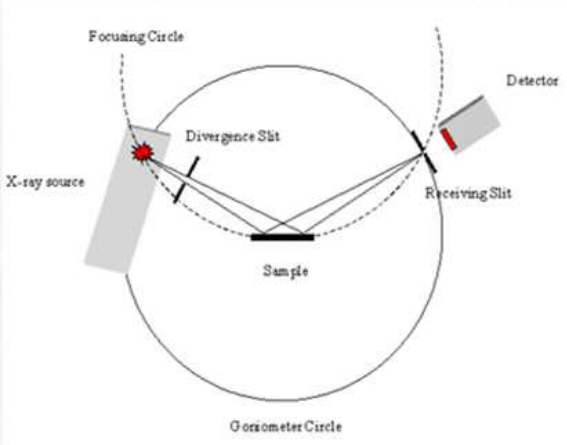



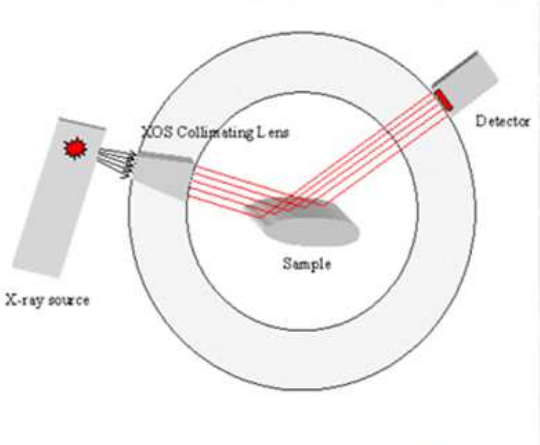




Bragg-Brentano Geometry
(para-focusing geometry)

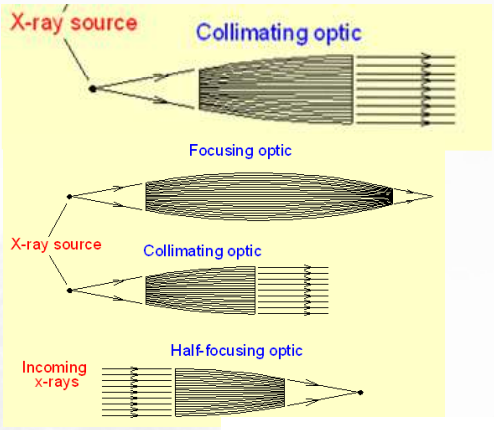
Parallel Beam Geometry
generated by Göbel Mirrors

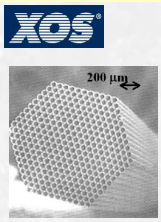


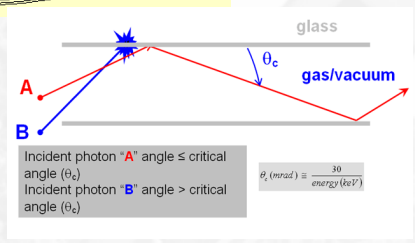



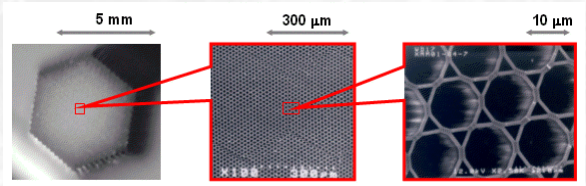
## Parallel beam optics → no sample displacement error

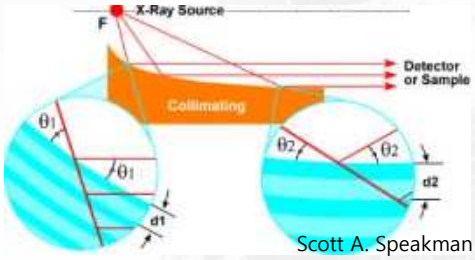




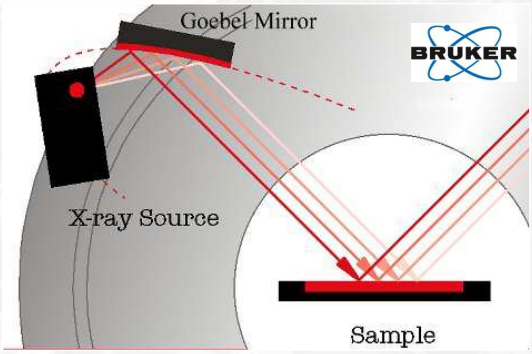




Scott A. Speakman






## Parallel beam geometry can be used for



- Analysis of samples with non-flat surfaces, e.g. corrosion on pipes
- Samples you would prefer not to grind to a powder, e.g. jewelry, archaeology or forensic samples

Sodalite Bracelet

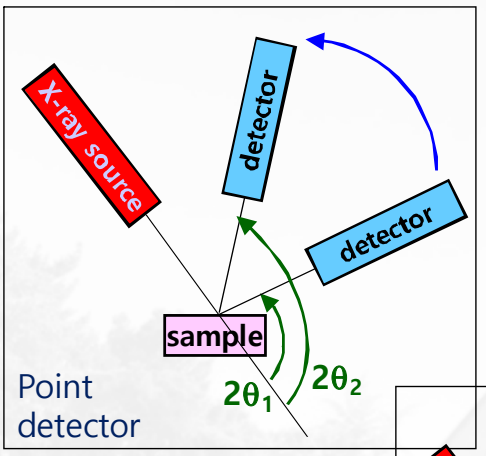
Vesuvianite Pebble

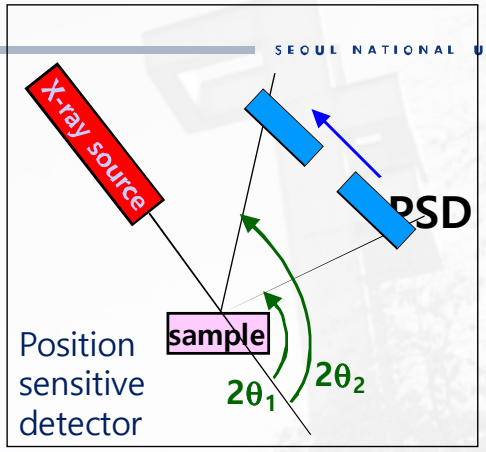
- Measure thermal expansion and contraction when using the heating/cooling stage.
- Grazing incidence diffraction (GID) of layers on substrates
- Reflectometry for thin film thickness and roughness

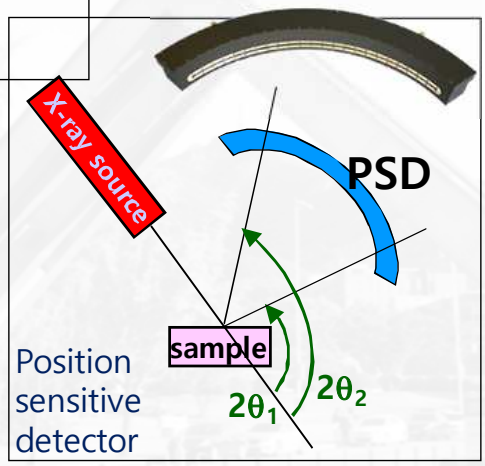
http://www.csec.ed.ac.uk/Instruments/D8_diffractometer/D8_parallel-beam.html

## Point, Line, & Area detector






area
detector

VANTEC 500

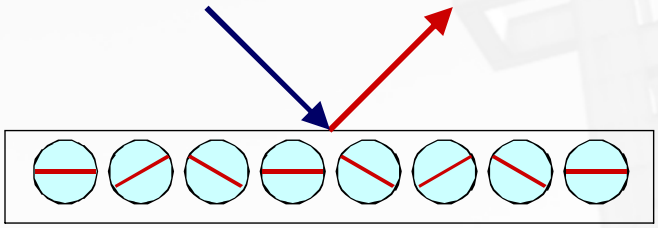
VANTEC 2000

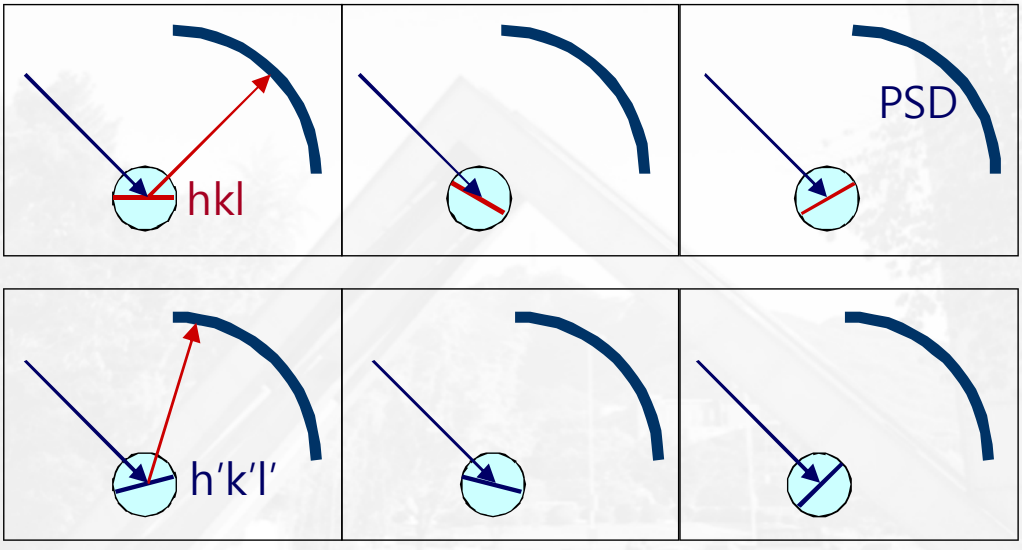
BRUKER



## Line detector, PSD

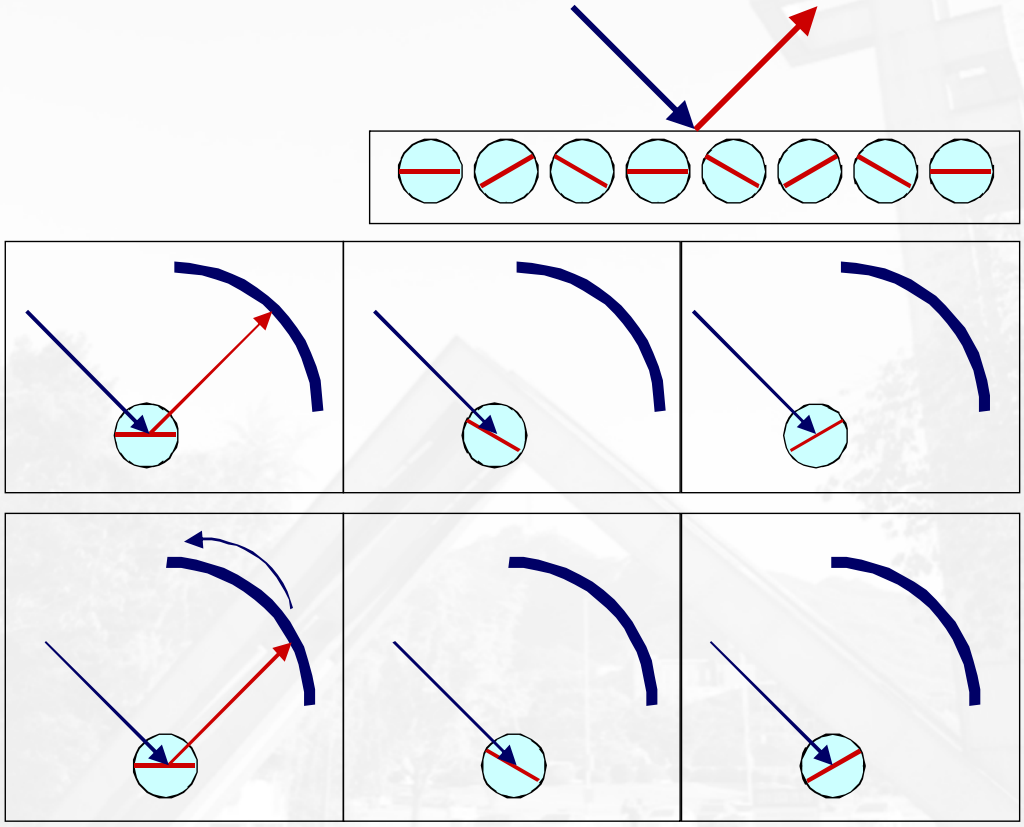






## Line detector, PSD

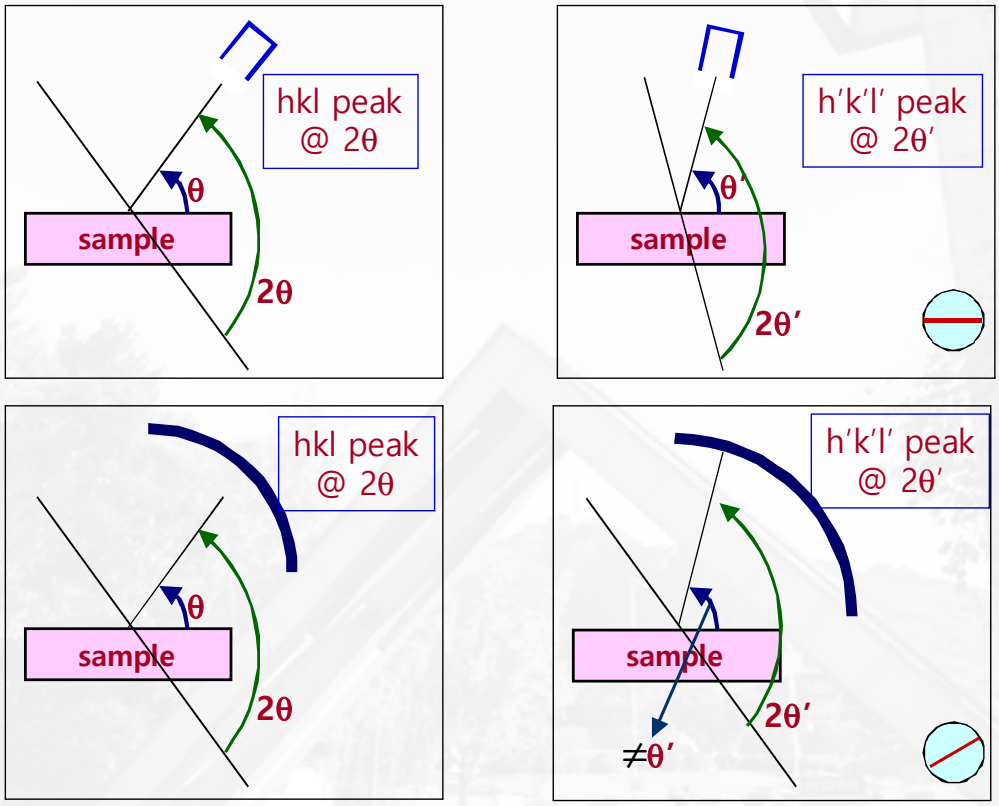






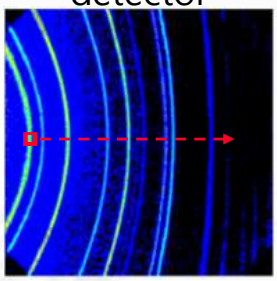
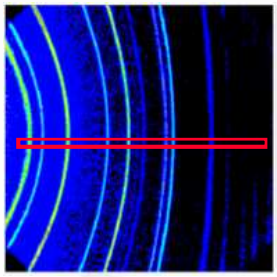
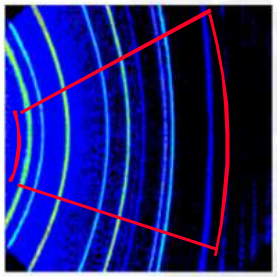
## Point detector vs. Line detector

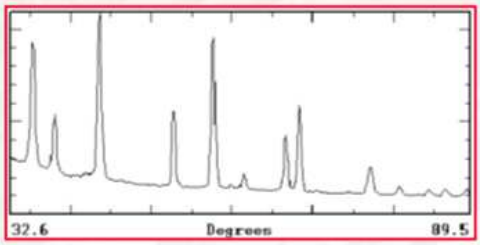




## Point, Line, and Area detector



| Scintillation detector | Line detector (PSD) | Area detector |
|---|---|---|
|  |  |  |
| ✓ small spot measured<br>✓ scan necessary<br>✓ long collection time | ✓ large 2θ range measured simultaneously<br>✓ medium collection time | ✓ large 2θ and chi range measured simultaneously<br>✓ measurement of oriented samples<br>✓ very short collection times |

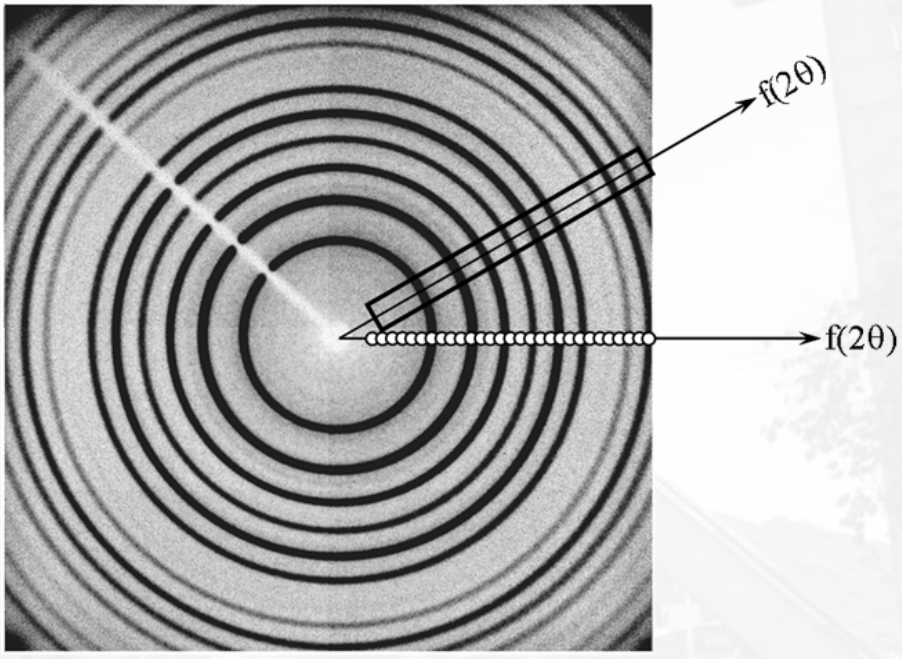



✓ intensity versus 2θ by integration of the data

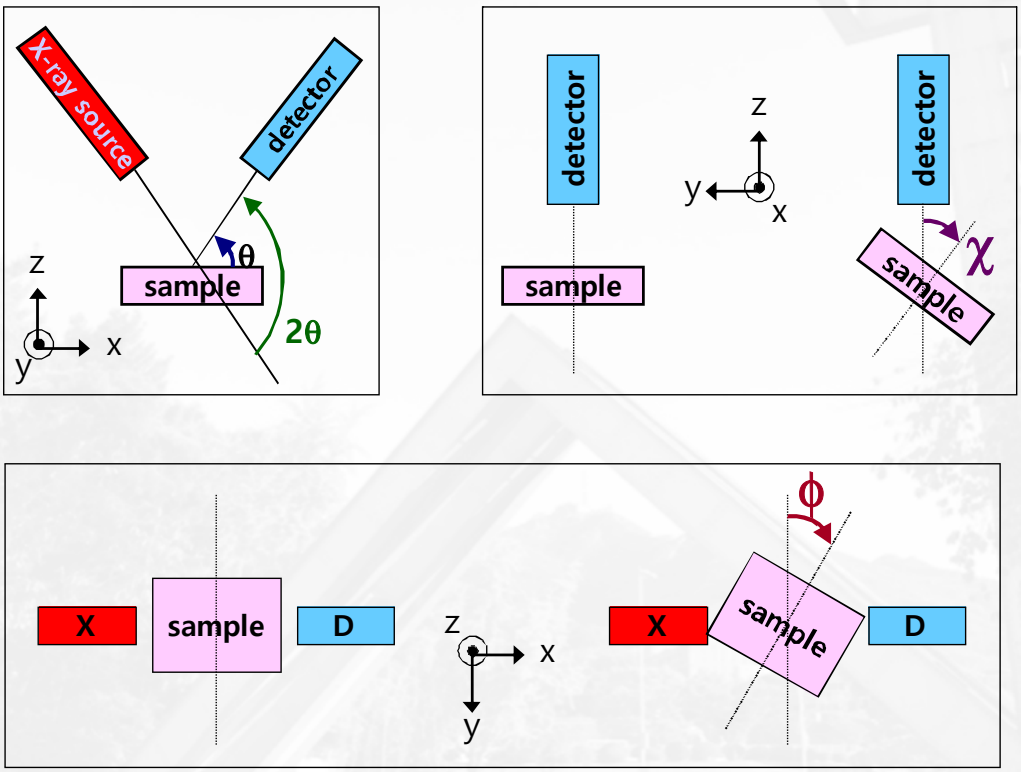


## Point, Line, and Area detector



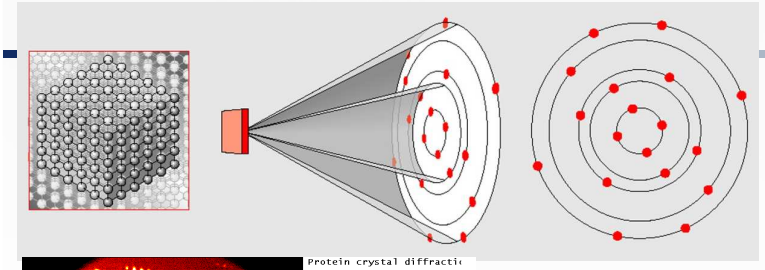


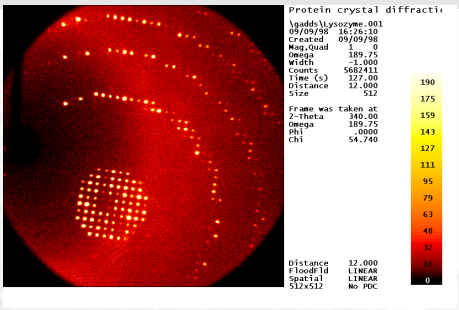
# Angles - θ(ω), 2θ, ϕ, χ





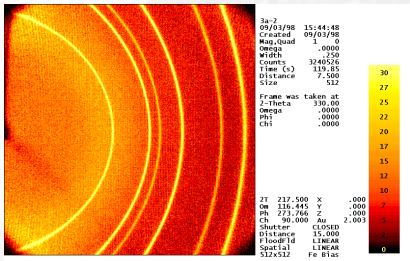


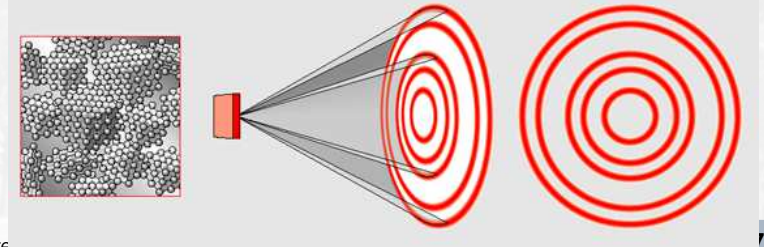





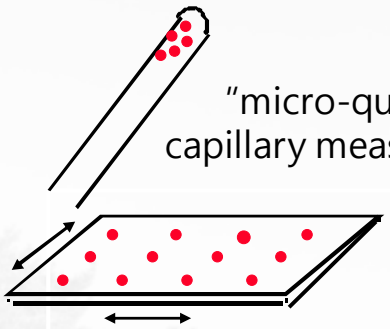
Single Crystal Diffraction

Powder Diffraction





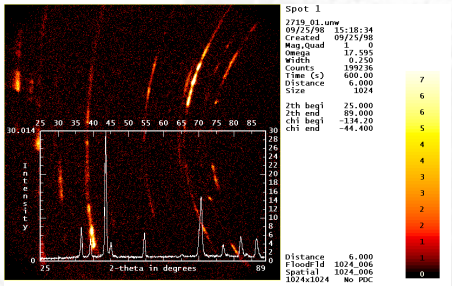
# Microdiffraction



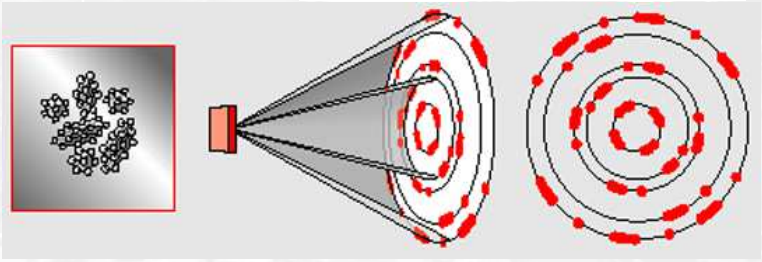
"micro-quantity"
capillary measurements

"micro-area"
X-ray microprobe

- qualitative phase analysis
- micro-texture
- quick point-and-shoot operation




Inspection of a gold pad



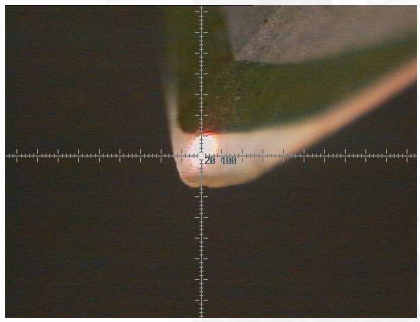


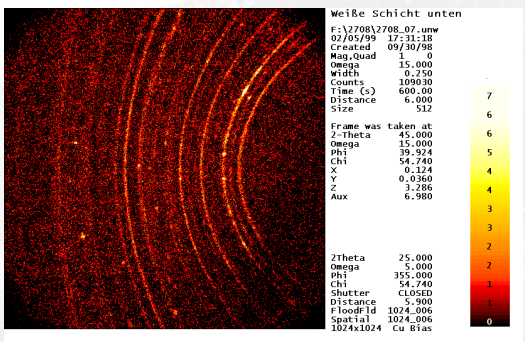


# Forensic Application

## Fatal Bicycle Accident Collection of Evidence

traces of car paint
found on the bicycle






Dr. W. Kugler
Landeskriminalamt
Baden-Württemberg
Stuttgart, Germany

# Detector



## Detectors



- X-ray detector = transducer + pulse formation circuit
- Transducer – convert the energies of X-ray photons to electric currents.
- Pulse formation circuit – convert current into voltage pulses that are counted/integrated by counting equipment.
- Transducer = detector or counter
- Gas proportional counter, scintillation counter, Si(Li) detector, intrinsic germanium detector → all use the ability of X-rays to ionize matter.

## Detectors



- point detectors
  - ✓ observe one point of space at a time.
    - slow, but compatible with most/all optics.
  - ✓ scintillation and gas proportional detectors count all photons, within an energy window, that hit them.
  - ✓ Si(Li) detectors can electronically analyze or filter wavelengths.

- position sensitive detectors
  - ✓ linear PSDs observe all photons scattered along a line from 2 to 120° long.
  - ✓ 2D area detectors observe all photons scattered along a conic section.
  - ✓ gas proportional (gas on wire; microgap anodes)
    - limited resolution, issues with dead-time and saturation
  - ✓ CCD
    - limited in size, expensive
  - ✓ solid state real-time multiple semiconductor strips
    - high speed with high resolution, robust



## Characteristics of detector



- Quantum efficiency
  - ✓ How efficiently it collects x-ray photons and then converts them into a measurable signal.
- Linearity
  - ✓ Linear when there is a linear dependence between the photon flux and the rate of signals generated by the detector per second.
  - ✓ Dead time
- Proportionality
  - ✓ How the size of the generated voltage pulse is related to the energy of the x-ray photon.
- Resolution
  - ✓ Ability to resolve x-ray photons of different energy and wavelength

**Table 5.3. Properties of Common X-ray Detectors**

| | Scintillation | | | Xe Sealed Gas | | | Si(Li) | | |
|---|---|---|---|---|---|---|---|---|---|
| Property | Cr | Cu | Mo | Cr | Cu | Mo | Cr | Cu | Mo |
| Quantum efficiency (%) | 60 | 98 | 100 | 90 | 90 | 75 | 90 | 95 | 80 |
| Linearity—loss at 40,000 c/s | Less than 1% | | | Up to 5% | | | Up to 50% | | |
| Proportionality | Very stable | | | Pulse shift at high c/s | | | Pileup, etc., at moderate c/s | | |
| Resolution (%) | 55 | 45 | 31 | 17 | 14 | 10 | 3 | 2 | 1 |

Jenkins & Snyder



## Photographic film



- Silver halide → metallic silver, when exposed to x-ray photons
- Once developed (darkened), further incoming X-rays can change nothing.
  → loss of information (dead time in electronic counters)
- Film darkening is proportional to the intensity of exposing X-rays over LINEAR RANGE of the film.
- When measuring intense sources
  - ✓ (1) Have to reduce X-ray intensity with filters or reduce incident beam flux.
  - ✓ (2) extend linear range of the film.
- Low proportionality range, limited spatial & energy resolution

## Detector



- All use the ability of X-rays to ionize matter.
  - ✓ Matter = gas → Proportional, Geiger
  - ✓ Matter = solid → Scintillation, Semiconductor

- Proportional
- Geiger
- Scintillation
- Semiconductor

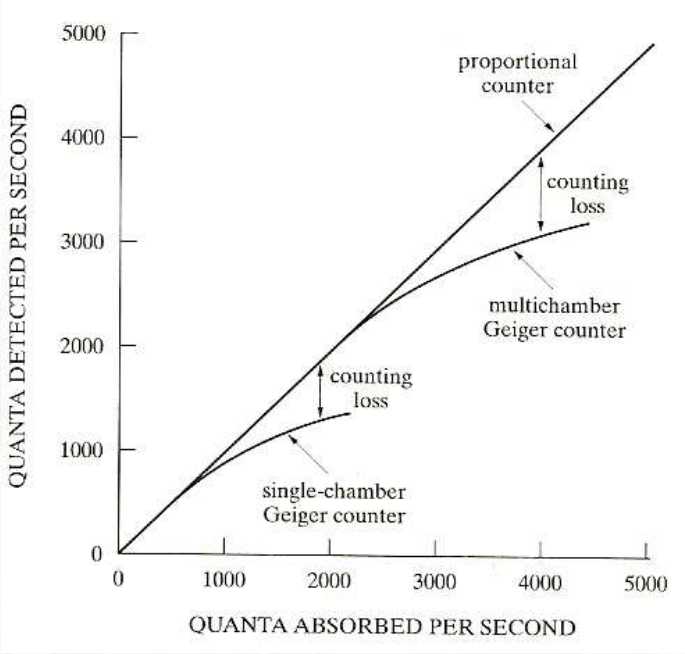


## Counting loss



- When time interval between pulses is very small, adjacent pulses may not be counted as separate pulses. → counting loss begins

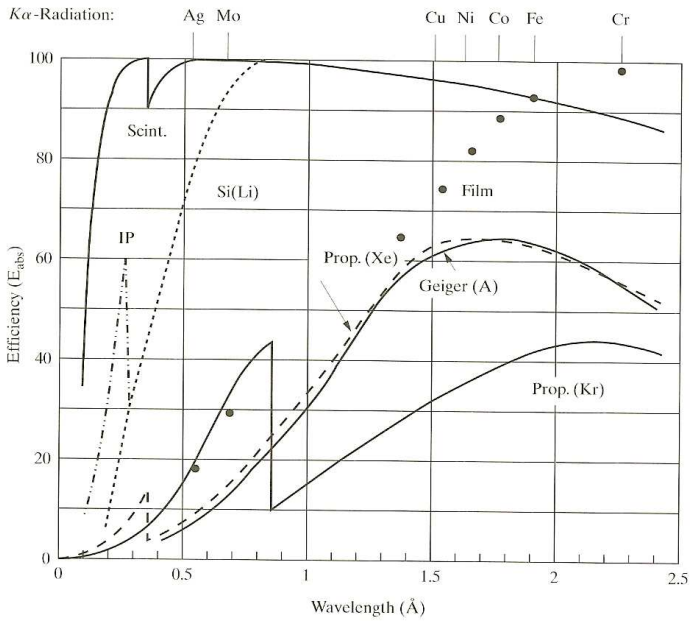
- Resolving time ($t_s$)– minimum time between two resolvable pulses



## Counting efficiency



- Efficiency of detector in collecting radiation incident upon it
- Most detectors designed for XRD are optimized for the measurement of Cu Kα radiation. Loss of efficiency can result when different λ is used.

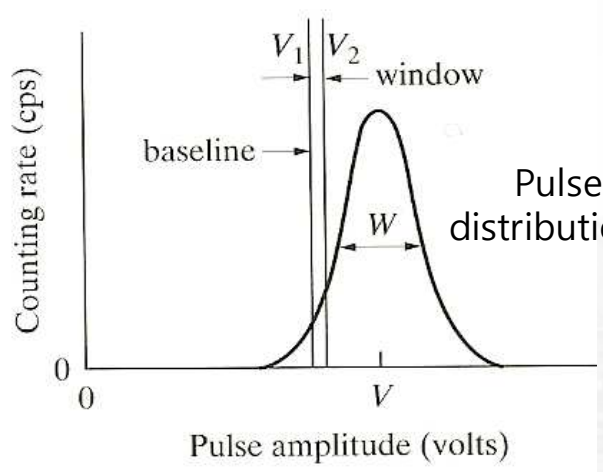





## Resolution



- A measure of detector's ability to resolve two X-ray photons of different energy
- Size of voltage pulses produced by detectors are proportional to the energy of the x-ray quantum absorbed.
- Resolution R = W/V

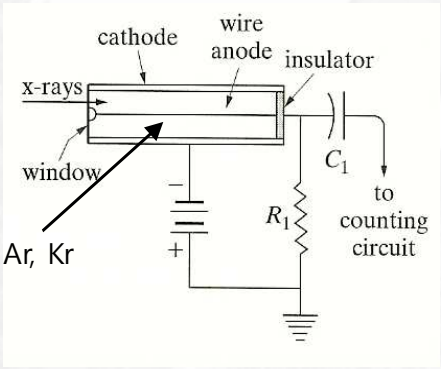


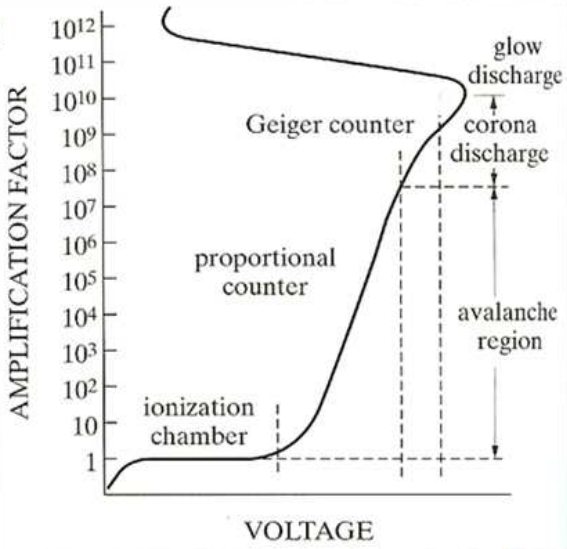

Pulse-size distribution curve

## Proportional counters



- Size of pulse ∝ energy of X-ray quantum absorbed → X-ray quanta of different energies can be distinguished.
- Gas is ionized by incoming X-ray.
- e′ → anode, positive ion → cathode (cylindrical metal shell)
- Multiple ionization → gas amplification



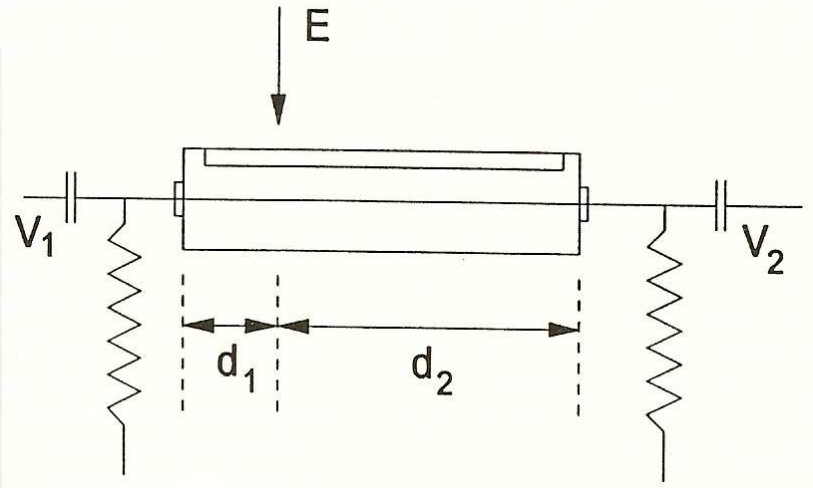

Cullity



## Position sensitive proportional counter



- Increased speed of data acquisition
- Measure "rise time" (rate at which a pulse develops) at each end of the wire. → detect position can be located.
- Angular resolution not very high

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## Geiger counter

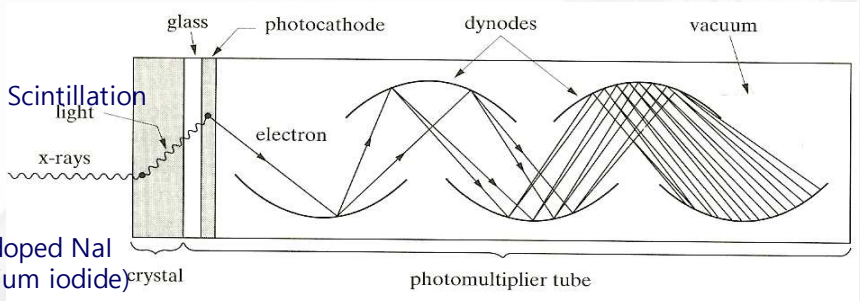
- Very high voltage in a proportional counter → Geiger counter
- Gas amplification factor much larger than proportional counter
- All pulses have the same size, regardless of the energy of X-ray quanta.
- Cannot count at high rates without losses. → seldom used in diffractometry.

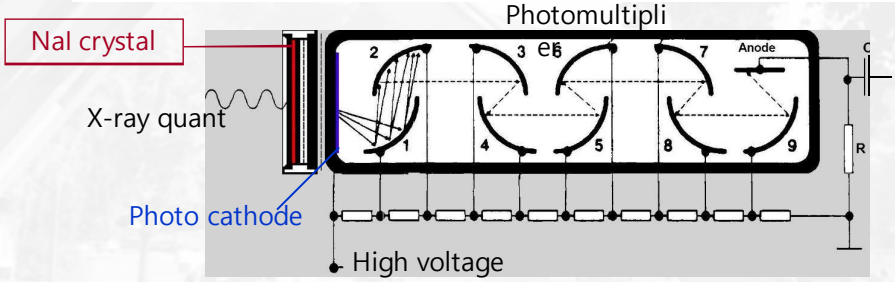




## Scintillation detector

- X-ray can cause certain substances to fluoresce visible light.
- Amount of light ∝ emitted X-ray intensity
- Pulses produced ∝ energy of X-ray quanta
- Difficult to discriminate between X-ray quanta of different energies. → energy resolution not great

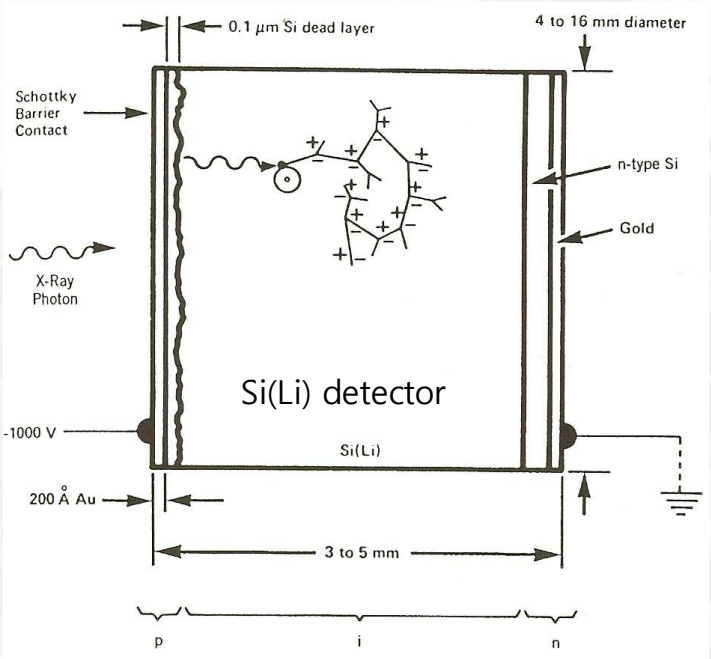


## Semiconductor detector



- Best energy resolution
  - ✓ Produces pulses proportional to the absorbed X-ray energy with better energy resolution than any other detector.
- Si(Li), Ge(Li), HPGe
- Need LN2 cooling

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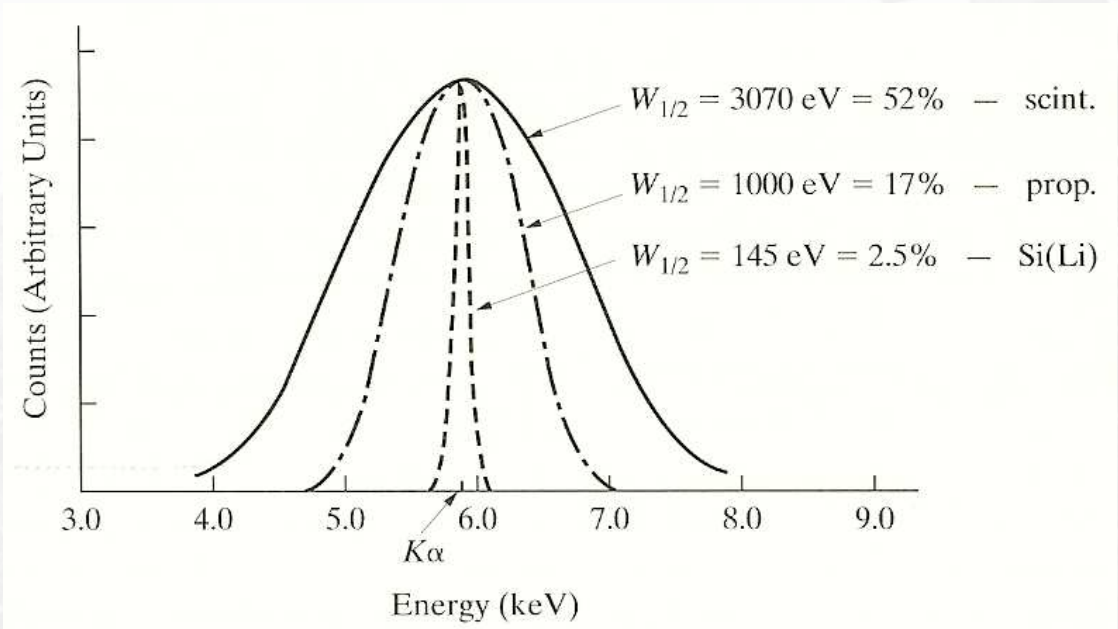
## Pulse-height distribution curves



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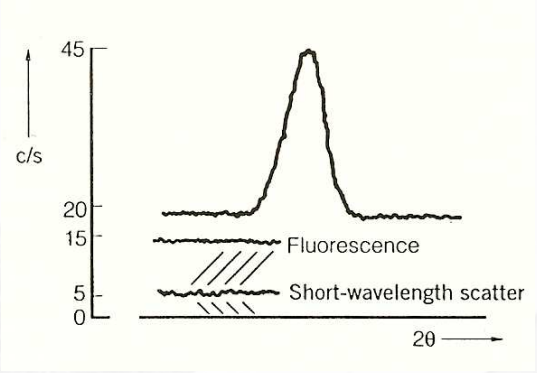
## Pulse height selection (PHS)



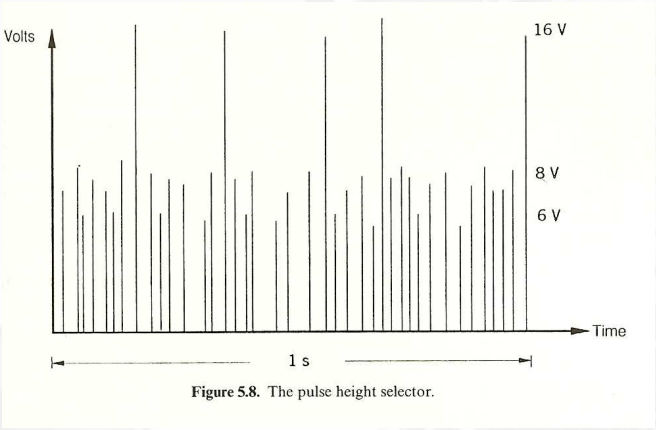
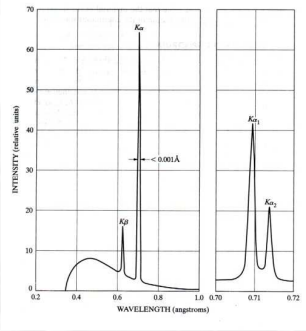




**Figure 5.8.** The pulse height selector.

- Different energy → different size of voltage pulse → can be electronically discriminated. --- PHS, pulse height analyzer (PHA)
- Can remove such effects as sample fluorescence & BKG that may arise from short wavelength X-rays from X-ray tube continuum that pass the β filter.

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## Pulse height selection (PHS)

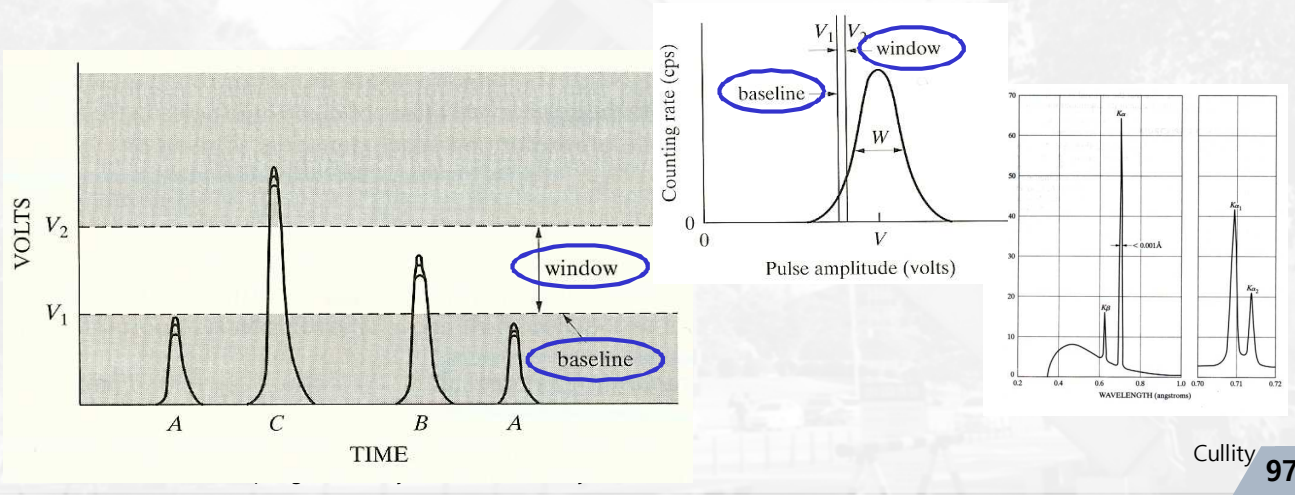
- Proportional, scintillation semiconductor detectors "proportional" ; they produce pulses having a size proportional to the energy of the incident X-rays.
- If pulses of different size can be distinguished, X-rays of different energies can be distinguished.

- Pulse-height discriminator
- Single-channel pulse-height analyzer
- Multi-channel pulse-height analyzer (MCA)

## Pulse height analysis



- Pulse-height discriminator
  - ✓ Reject any pulses smaller than $V_1$.
- Single-channel pulse-height analyzer
  - ✓ Only pulses having sizes between $V_1$ & $V_2$ can pass
  - ✓ Can reduce BKG of diffraction pattern by excluding short l white radiation.
- Multi-channel pulse-height analyzer (MCA)
  - ✓ Can separate pulses from a detector that is re.ceiving incident radiation of many wavelengths, by sorting pulses according to their size.






## Pulse height analysis



- Pulse-height discriminator
- Single-channel pulse-height analyzer
  - ✓ Entire energy range is scanned serially in time by moving channel.
- Multi-channel pulse-height analyzer (MCA)
  - ✓ A large number of fixed channels cover the entire range
  - ✓ All channels simultaneously receive the count-rate information appropriate to each channel.