DIFFRATION

BY

MR. S. V. MALGAONKAR M.Sc. (Assist. Prof.)

DEPARTMENT OF PHYSICS
VIVEKANAND COLLEGE, KOLHAPUR (Autonomous)

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outlines

Diffraction

X-ray and X-ray diffraction

Neutron and neutron diffraction

Instrumental features

DIFFRACTION

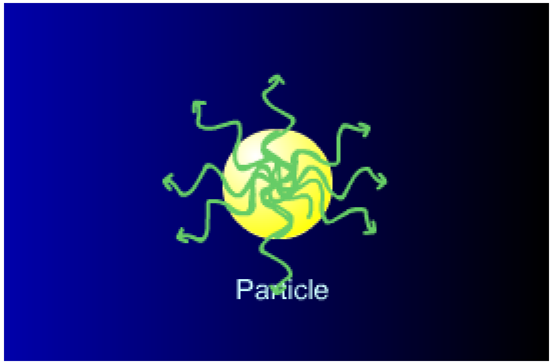
- Diffraction is a wave phenomenon in which bending and spreading of waves occur at an obstruction.

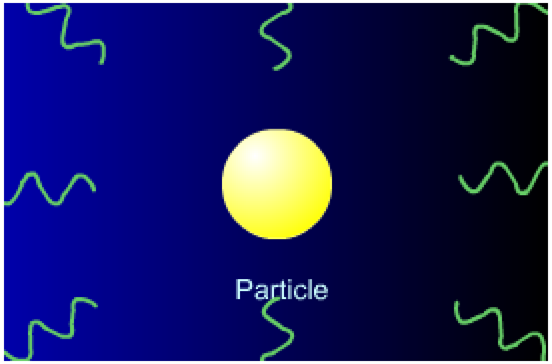
- Diffraction occurs with electromagnetic waves, such as light and radio waves, and also in neutron, sound waves and water waves.

- Diffraction is explained by interference pattern of waves

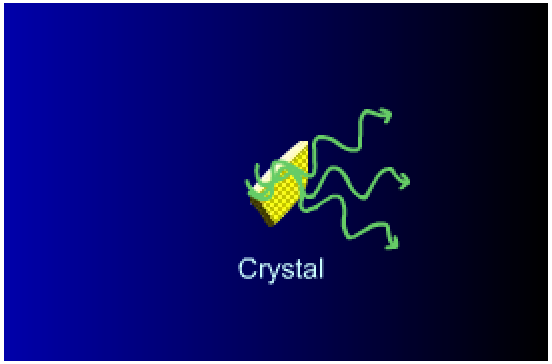
Diffraction from a particle and solid

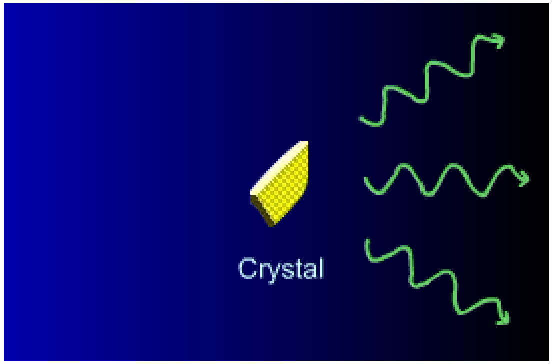
Single particle: Incident beam scattered uniformly in all direction



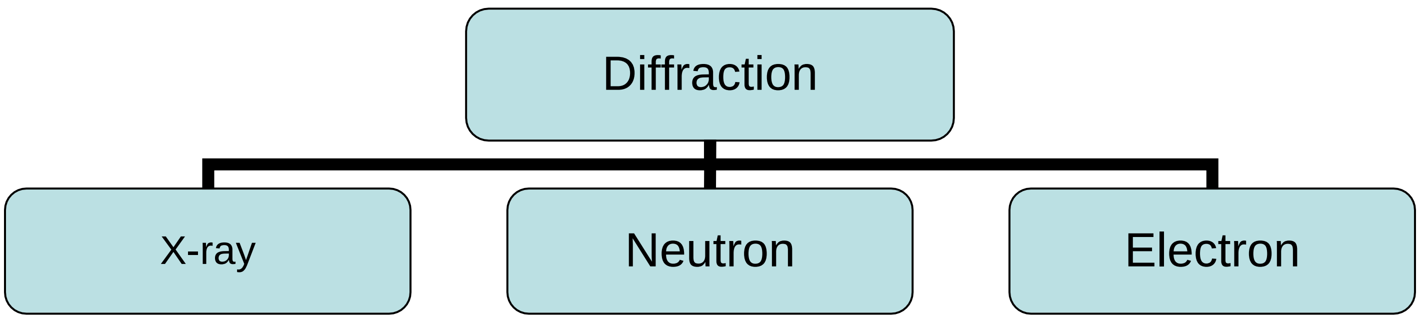


Solid material: Scattered beams interfere depending on phase(path) differences giving diffraction pattern



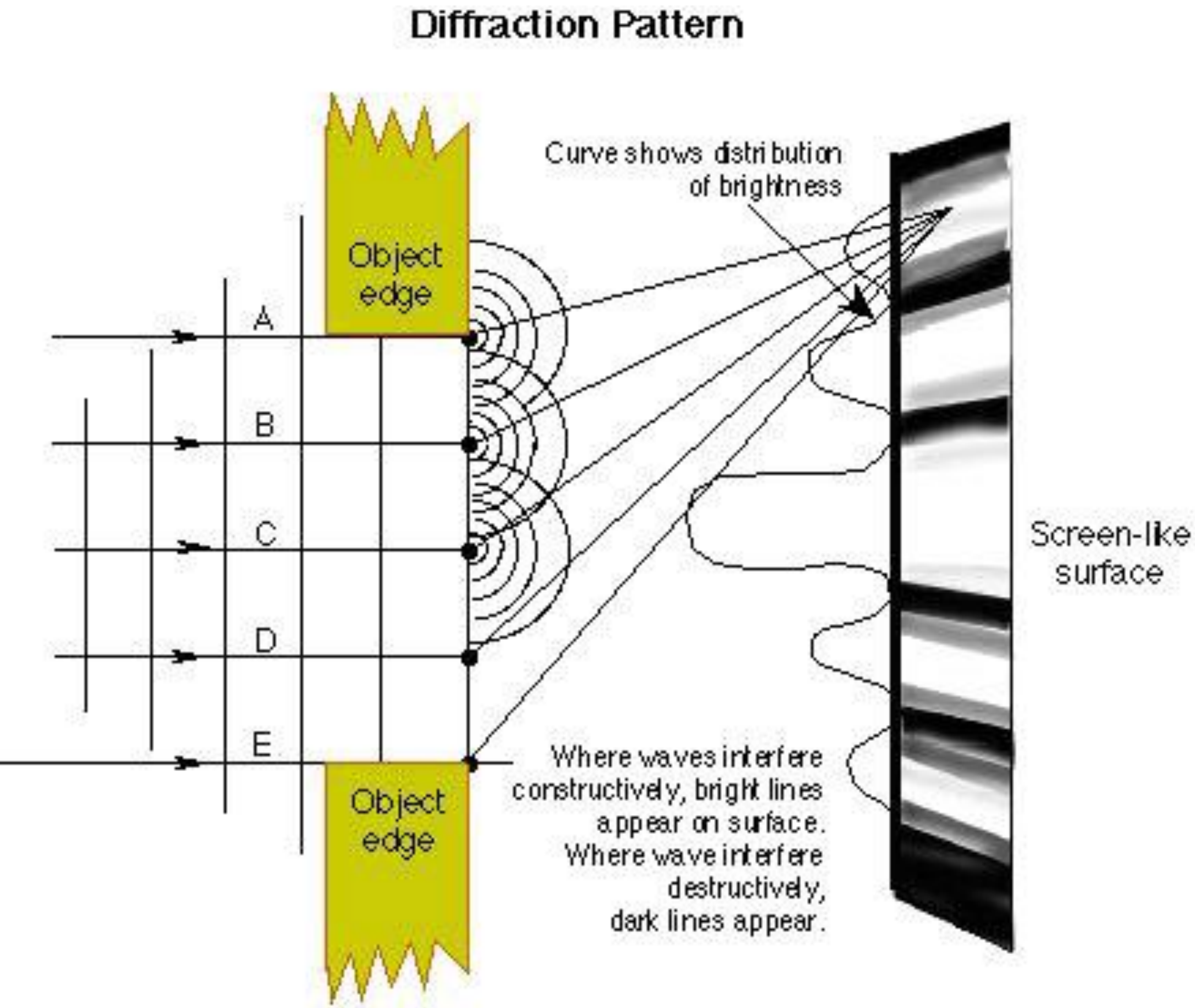


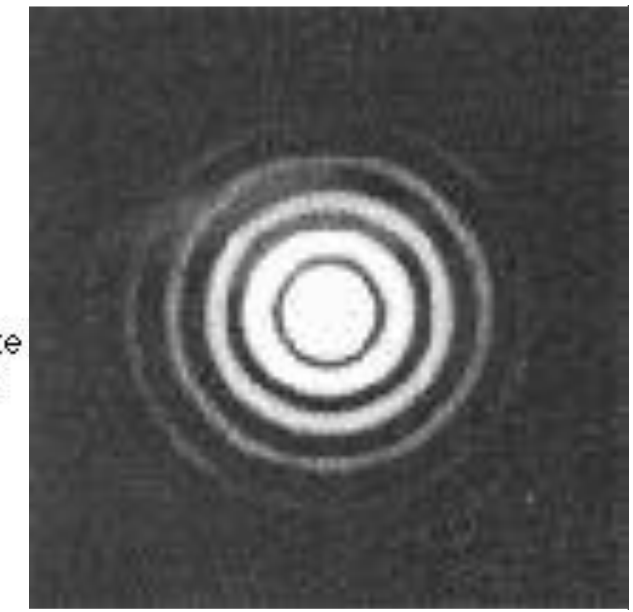
Diffraction of Waves by Crystals



The general princibles will be the same for each type of waves.

LIGHT INTERFERENCE

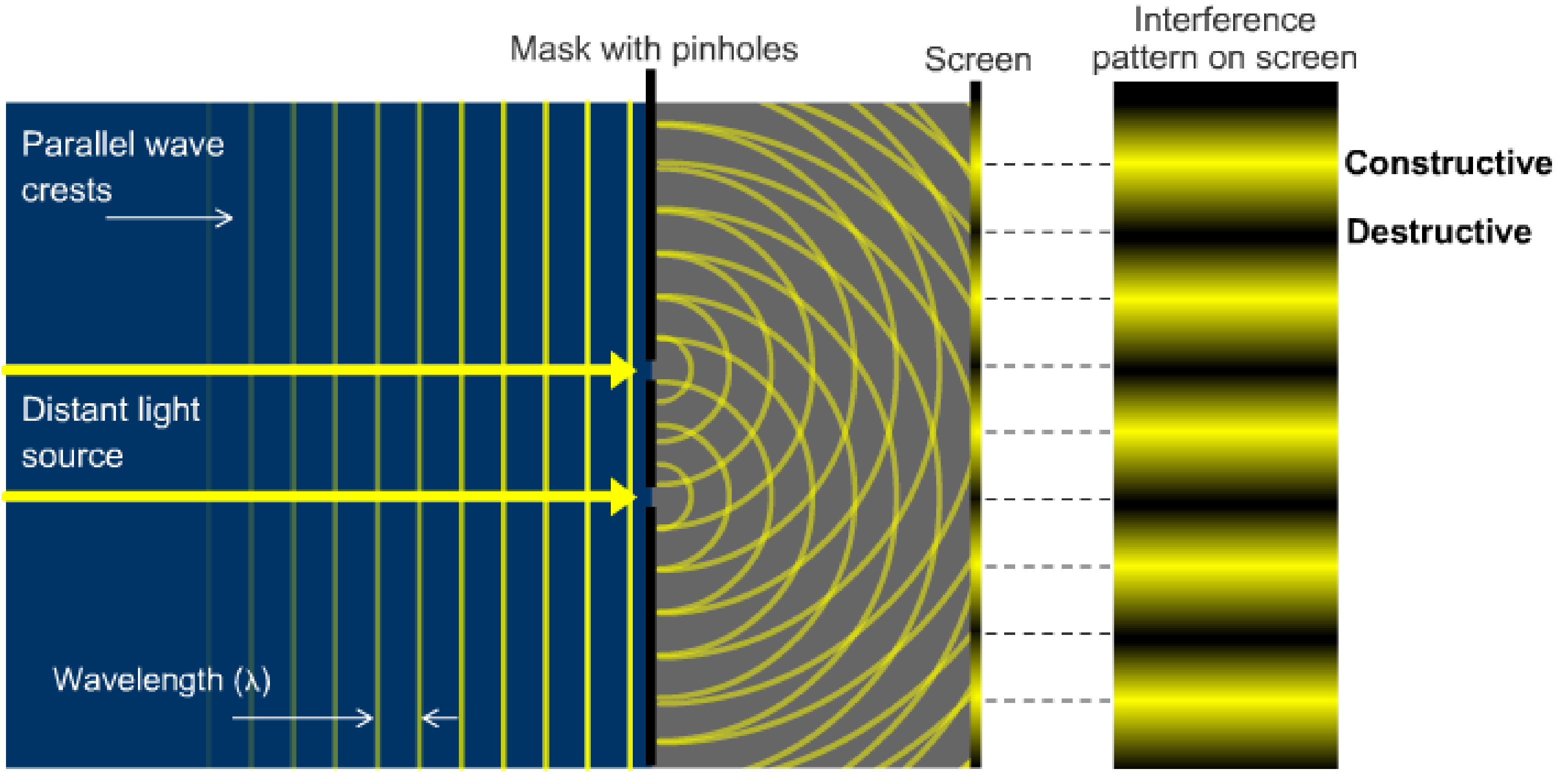


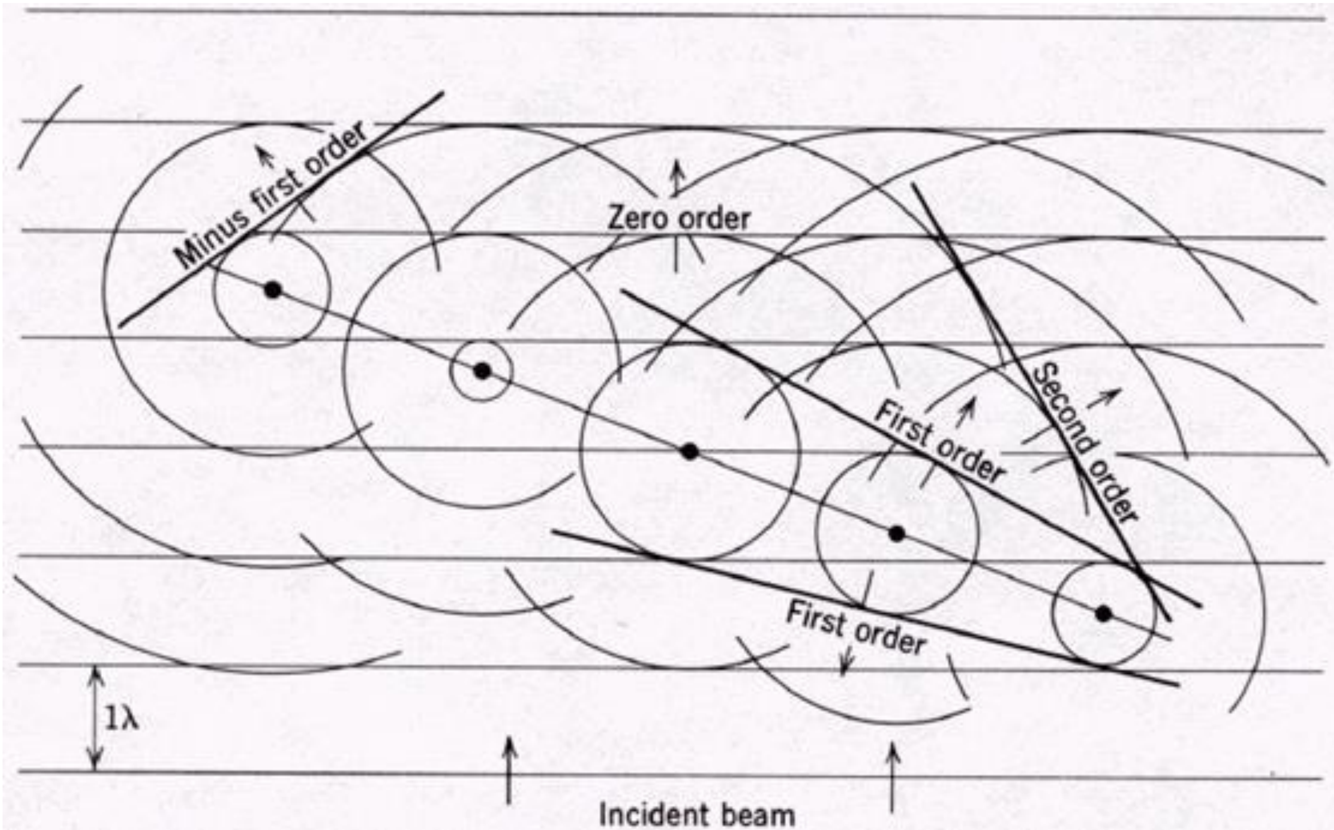


Constructive & Destructive Waves

- **Constructive interference is the result of synchronized light waves that add together to** increase **the light intensity.**
- **Destructive İnterference . results when two out-of-phase light waves cancel each other out, resulting in darkness.**

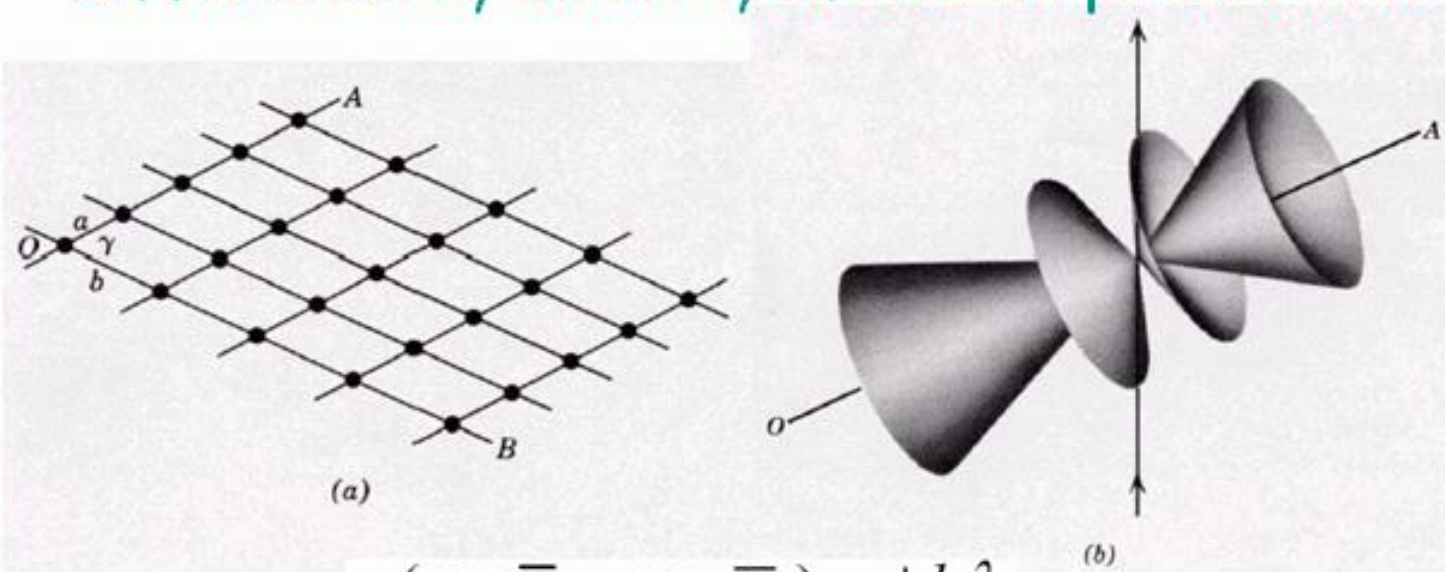
Light Interference





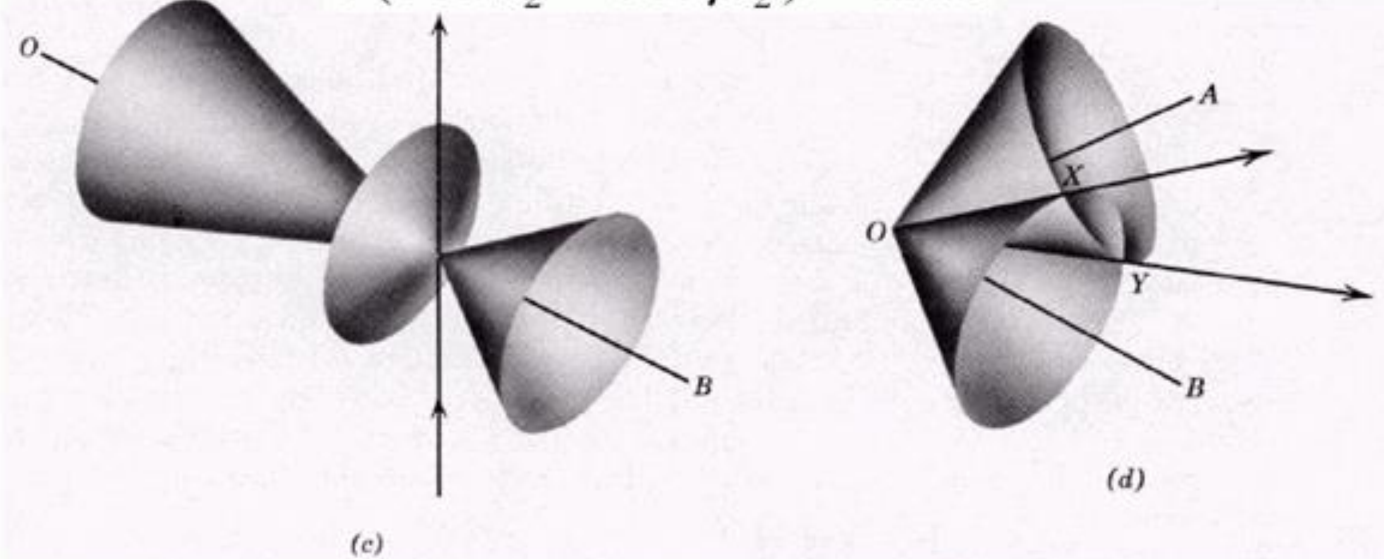
Minus first order
Zero order
Second order
First order
First order
1λ
Incident beam

Diffraction by an array of atoms: plane lattice

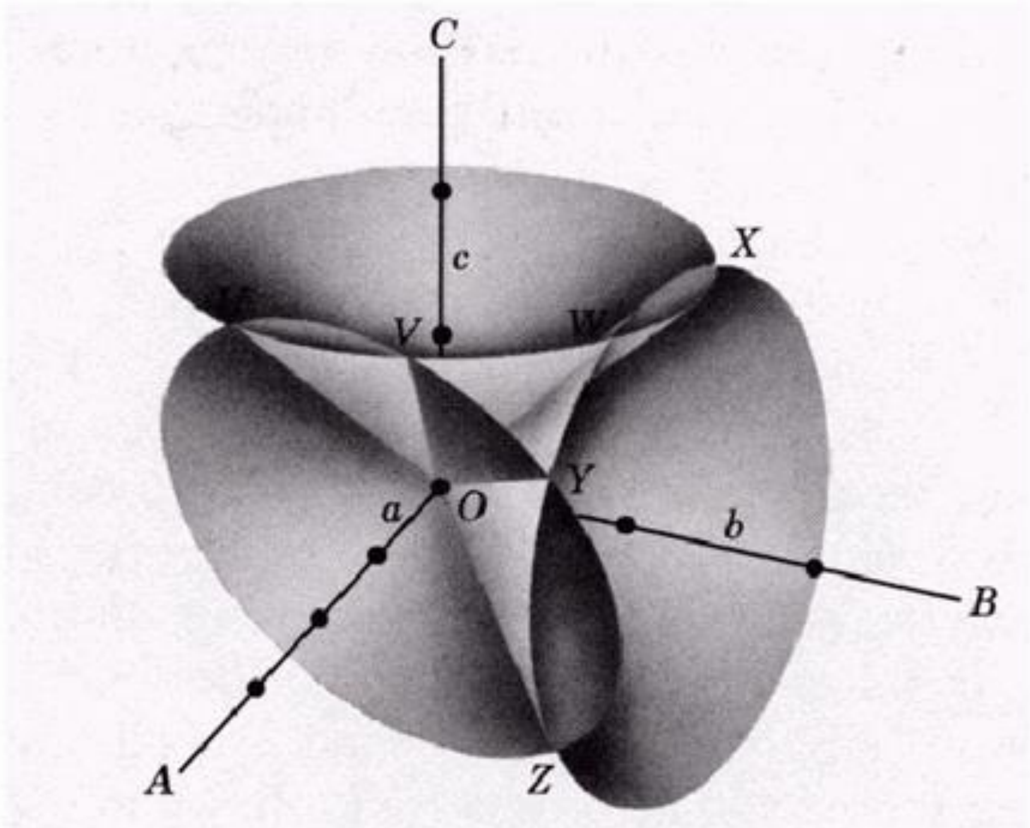


$$a(\cos \bar{\nu}_1 - \cos \bar{\mu}_1) = \pm h\lambda$$

$$b(\cos \bar{\nu}_2 - \cos \bar{\mu}_2) = \pm k\lambda$$



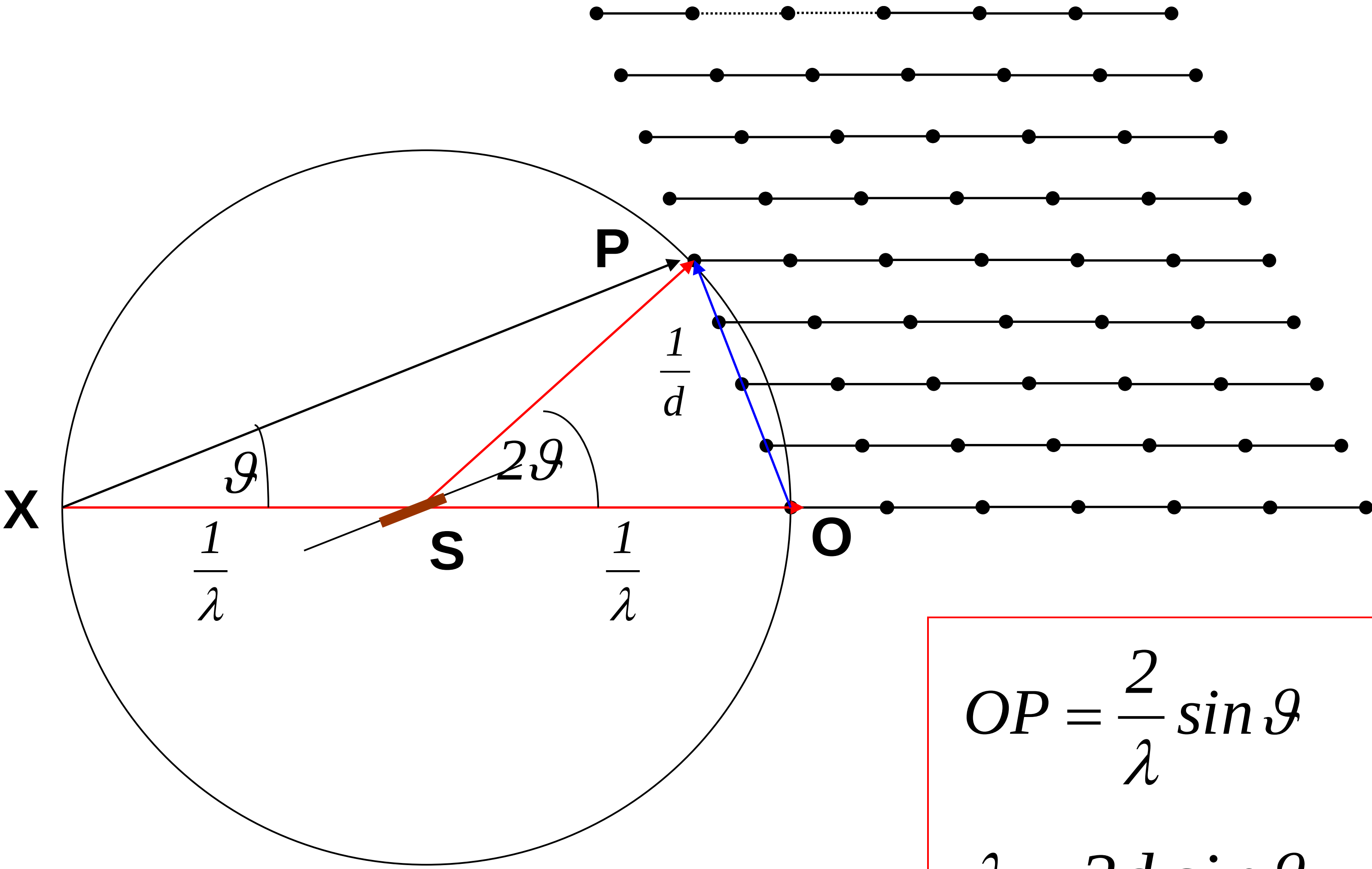
Diffraction by a 3-D array of atoms



$$a(\cos\overline{\nu}_1 - \cos\overline{\mu}_1) = \pm h\lambda$$

$$b(\cos\overline{\nu}_2 - \cos\overline{\mu}_2) = \pm k\lambda$$

$$c(\cos\overline{\nu}_3 - \cos\overline{\mu}_3) = \pm l\lambda$$



$$OP = \frac{2}{\lambda} \sin\vartheta$$

$$\lambda = 2d \sin\vartheta$$

Diffraction of Waves by Crystals

- ***The structure of a crystal*** can be determined by studying the ***diffraction pattern of a*** beam of radiation incident on the crystal.
- Beam diffraction takes place ***only in certain specific directions***, much as light is diffracted by a grating.
- By measuring the ***directions of the diffraction*** and the ***corresponding intensities***, one obtains information concerning the ***crystal structure*** responsible for diffraction.

Various XRD experimental setups

X-ray diffraction experimental set up requires an X-ray source, the sample under investigation and a detector to pick up the diffracted X-rays.

Variables:

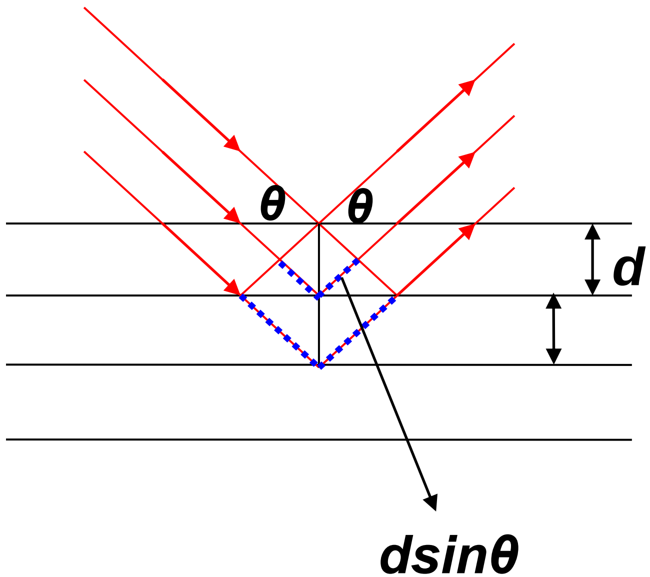
a. Radiation : Monochromatic or Polychromatic
b. Sample : Single crystal or polycrystalline
c. Detector : Radiation counter or photographic film

Wavelength	Sample	Detector	Method
Monochromatic	Powder	Counter	Diffractometer
		Film	Debye-Scherrer, Guiner
	Single crystal	Film	Rotation
			Weissenberg
			Precession
		Counter	Automatic diffractometer
Variable	Solid piece	Film	Laue

Bragg's Law

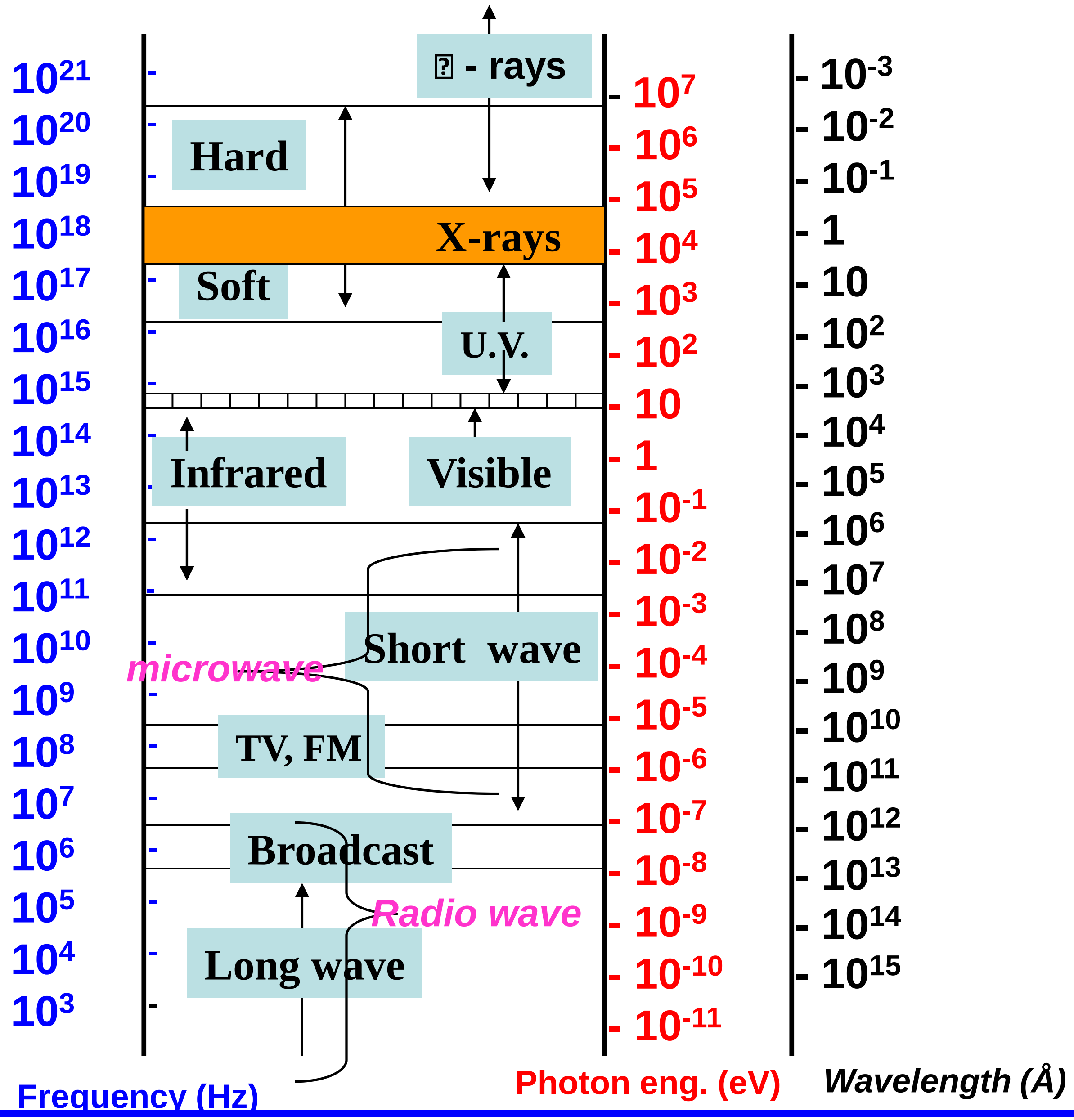
$$n\lambda = 2d\,sin\theta$$

Where
λ = wavelength of x-rays
θ = glancing angle (called as Bragg angle)
d = inter-planar separations
n = order of diffraction



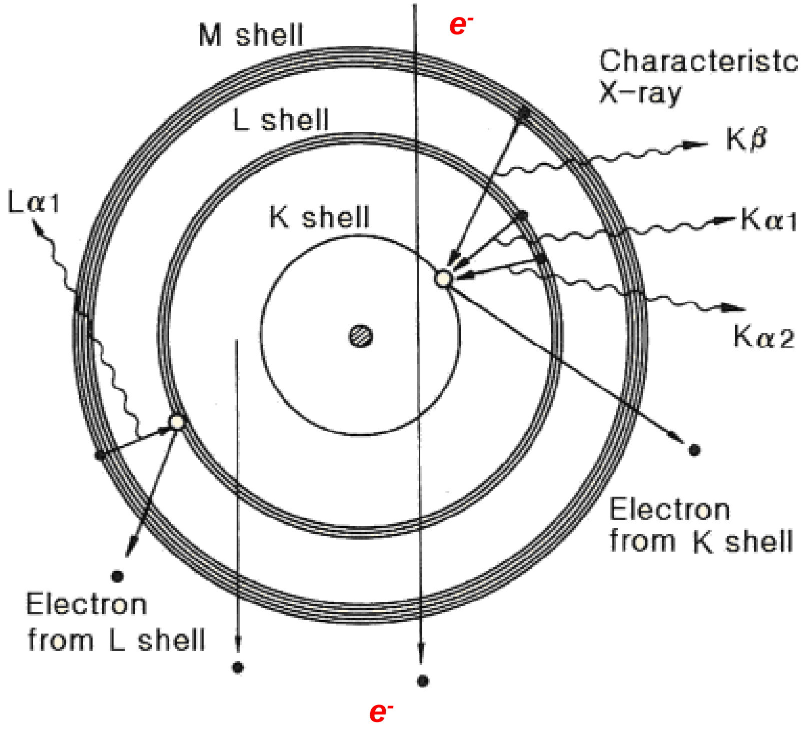
The Electromagnetic Spectrum

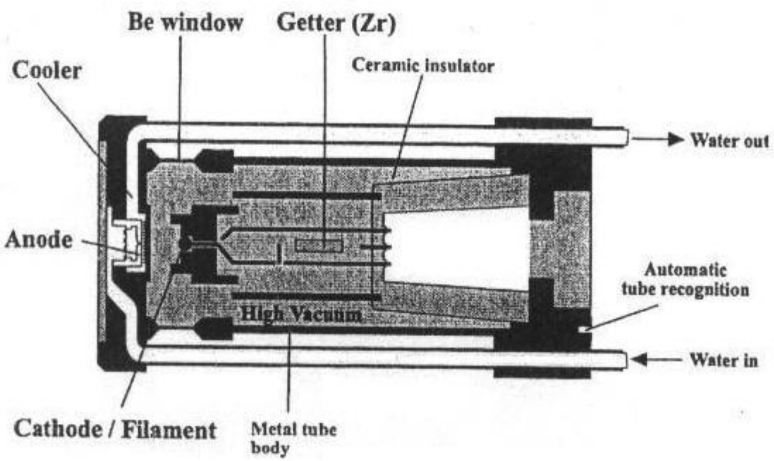
X-ray ?



Origin of X-ray production

X-rays are produced by impinging high energy electrons on a substrate (anode)





X-ray tube

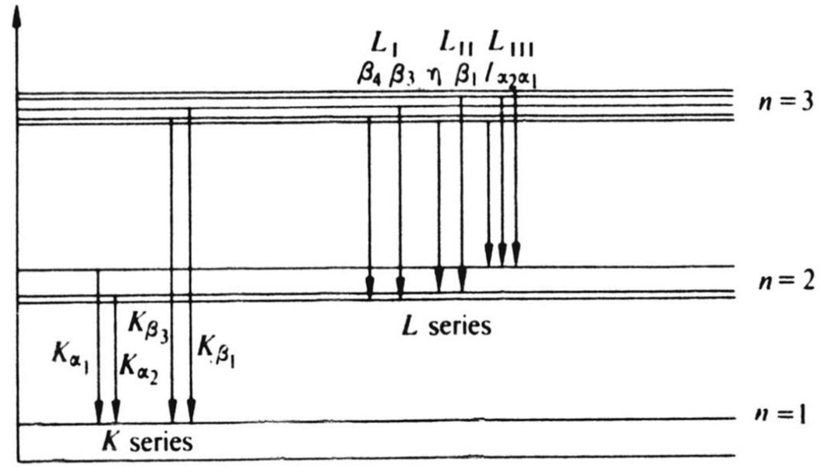
2P→1S: Kα
3P→1S : Kβ

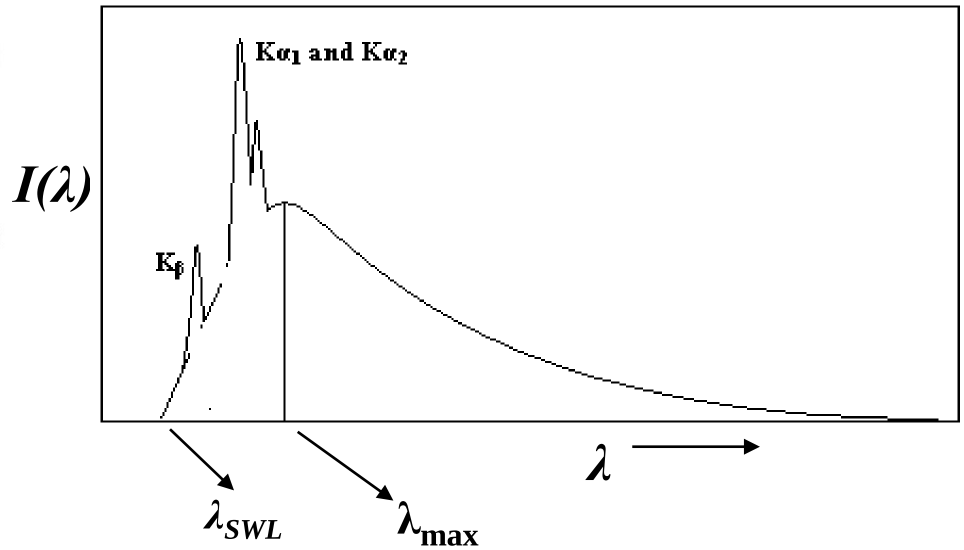
PROPERTIES OF X-RAYS

- Invisible electromagnetic rays
- Electrically neutral
- Wavelengths ≈ 0.04 – 1000 Å
- A white as well as characteristics radiation
- Velocity same as that of light
- Ionizing radiation
- They can cause fluorescence
- They cannot be focused by a lense
- They affect photographic plate producing a latent image which can be developed chemically
- They produce chemical and biological changes
- Intensity of x-rays fall-off as inverse square of distance
- X-ray emerge from the tube in straight lines
- They produce secondary radiation

The X-ray spectrum is composed of two components

A continuum and Characteristic radiation





Selection rules

$\Delta n \geq 1$

$\Delta l \geq 1$

$\Delta j \geq 0$

$2P_{3/2} \rightarrow 1S_{1/2}$: $K\alpha_1$

$2P_{1/2} \rightarrow 1S_{1/2}$: $K\alpha_2$

$\lambda_{SWL} = hc/qV$

λ_{SWL} (Å) = 12.4/V (in kilovolts)

$I_{conti.} = K\,i\,Z\,V^2$; $I_{char.} = K\,i\,(V-V')^{1.5}$

$$I(\lambda)d\lambda = K\,i\,Z\left(\frac{\lambda}{\lambda_{SWL}} - 1\right)\frac{1}{\lambda^2}d\lambda$$

X-ray tubes: Operating conditions

Anode material (Z)	Filter (Z-1)	Wave-length (nm)	Energy (keV)	(Excitation voltage)$_{Critical}$	Optimum kV
Cu	Ni	0.1542	8.04	8.98	30-45
Co	Fe	0.1791	6.92	7.87	25-40
Fe	Mn	0.1937	6.40	7.11	20-35
Cr	V	0.2291	5.40	5.99	20-30
Mo	Nb	0.0710	17.77	20.00	60

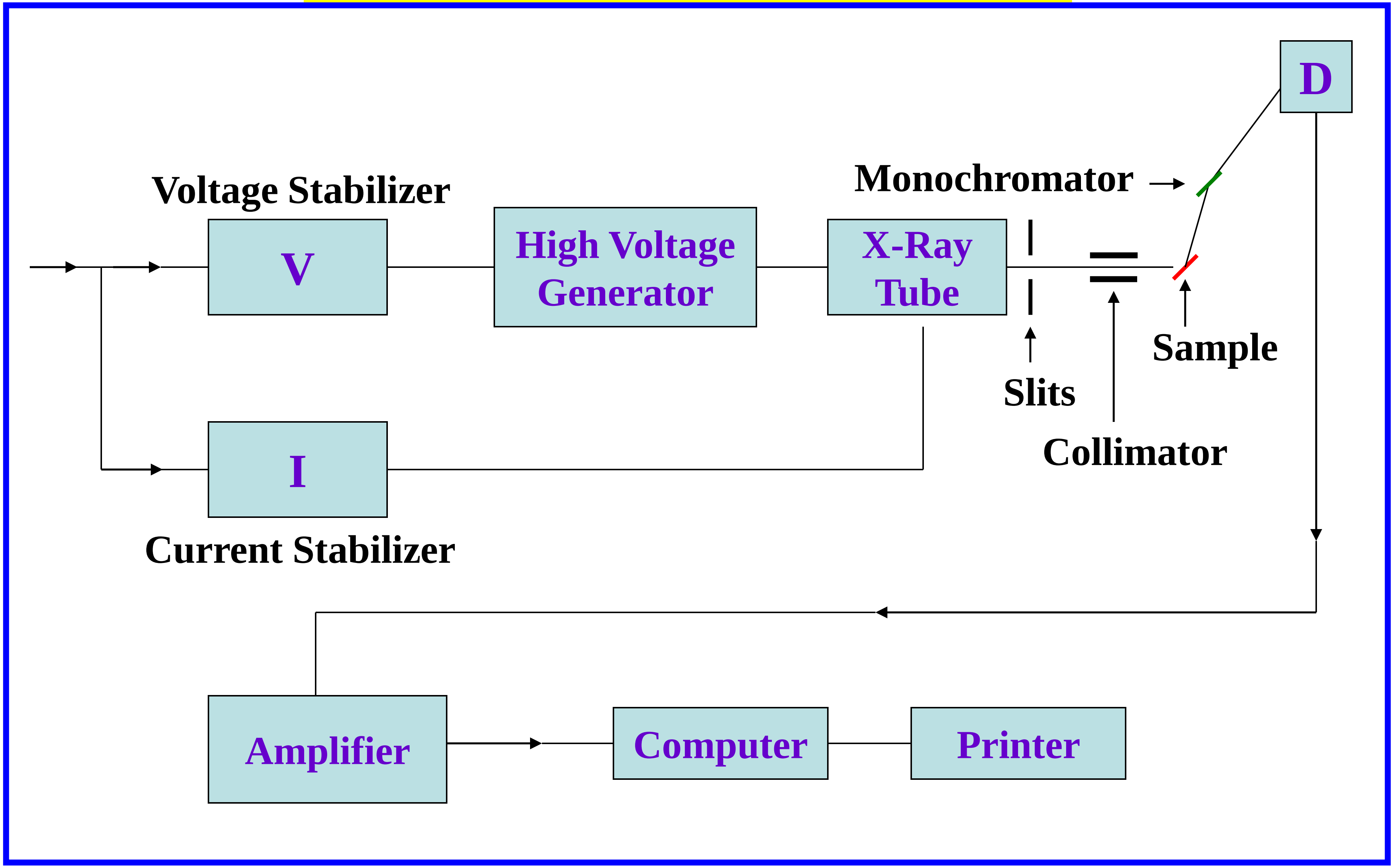
X-ray tubes: Focus selection

Type	Acronym	Dimension (mm x mm)	Remark
Fine Focus	FF	0.4 x 8	Improved texture applications
Normal Focus	NF	1.0 x 10	Older type cameras
Broad Focus	BF	2.0 x 12	Higher intensity, Poor resolution
Long Fine Focus	LFF	0.4 x 12	Standard Focus Type

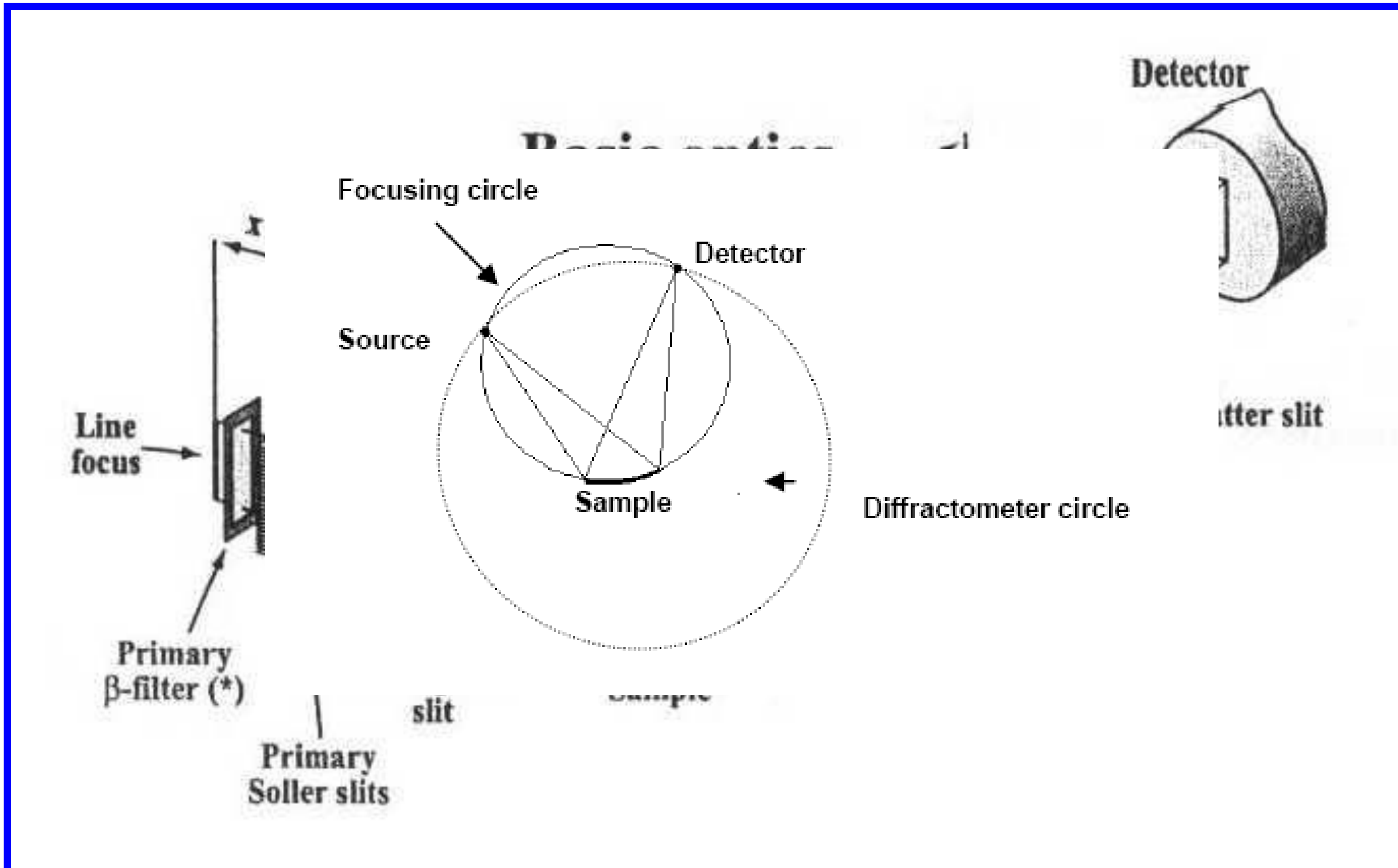
X-ray tube: Selection

Anode material	Wave-length (nm)	Applications
Cu	0.1542	Standard tube
Co	0.1791	Ferro-materials
Fe	0.1937	Matrix effects of Fe & Cr
Cr	0.2291	Large unit cells (clays, organics, Zeolites
Mo	0.0710	Single crystal work
Ag	0.0561	For highly absorbing materials
W	0.020	Laue camera (continuum is needed)

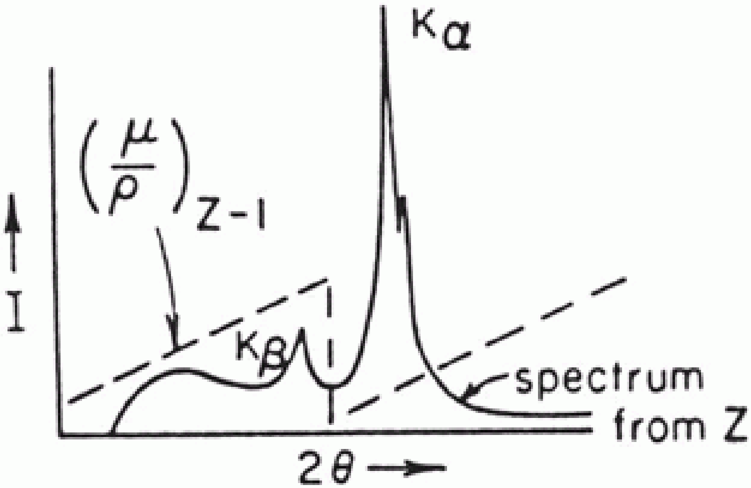
Block Diagram Of XRD unit



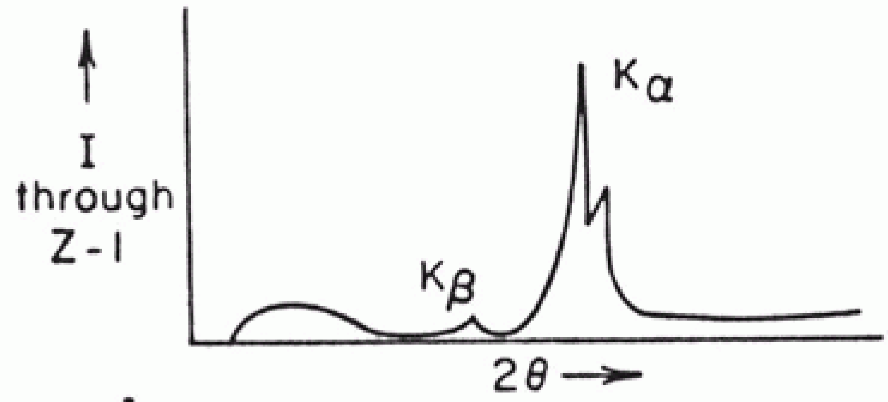
Classical Powder Diffractometer



Filters



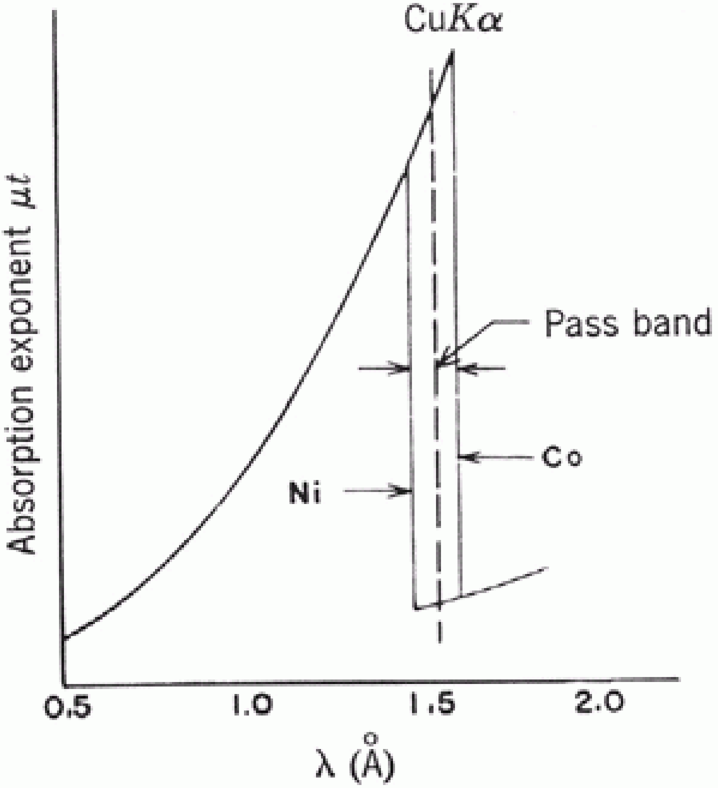
a



b

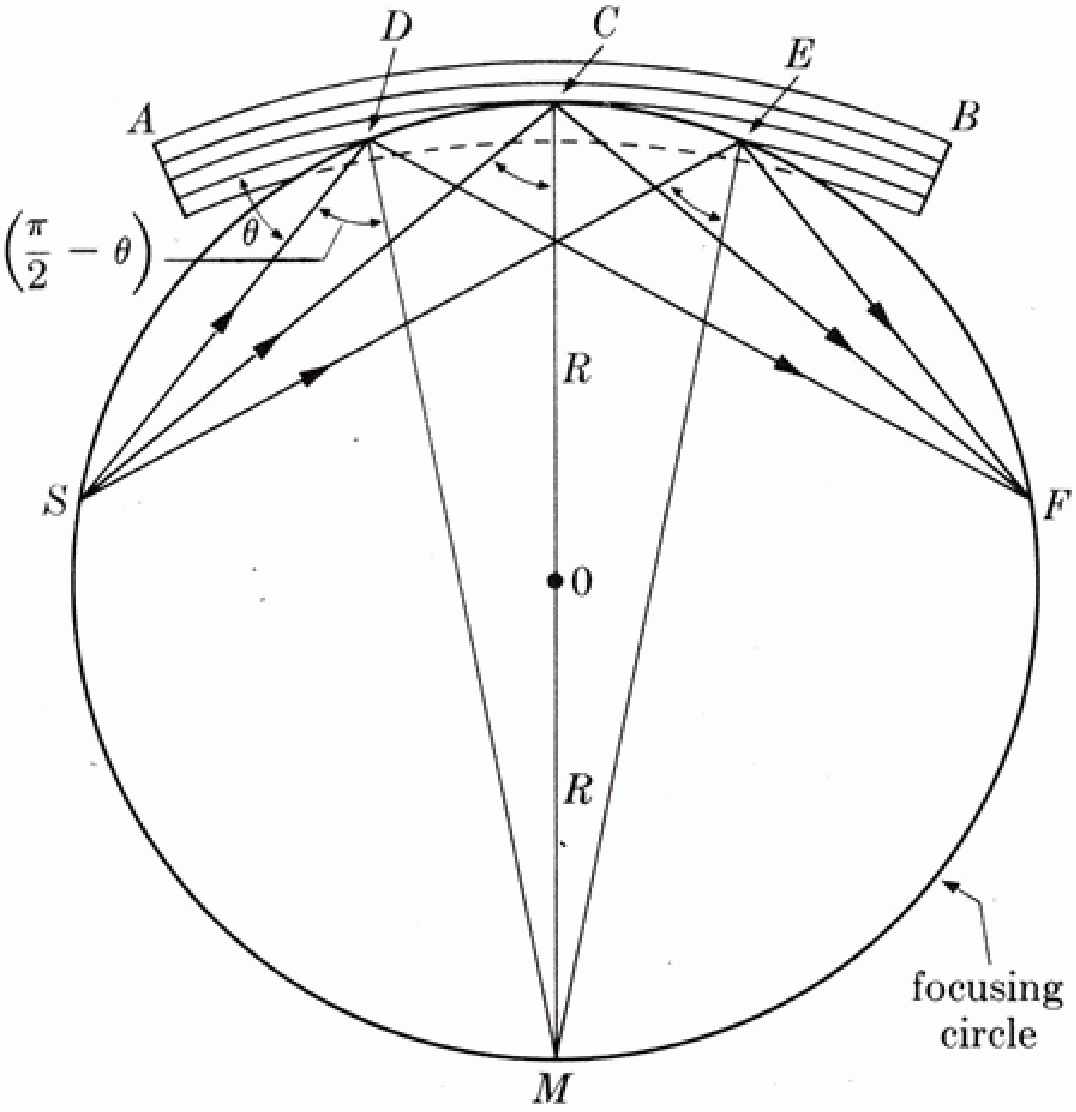
Target	Filter	Incident beam $\frac{I(K\alpha)}{I(K\beta)}$	Filter thickness for $\frac{I(K\alpha)}{I(K\beta)} = \frac{500}{1}$ in trans. beam		$\frac{I(K\alpha)\text{ trans.}}{I(K\alpha)\text{ incident}}$
			mg/cm^2	in.	
Mo	Zr	5.4	70	0.0043	0.30
Cu	Ni	7.5	18	0.0008	0.42
Co	Fe	9.4	13	0.0006	0.47
Fe	Mn	9.0	12	0.0006	0.47
Cr	V	8.5	9	0.0006	0.48

Balanced filters



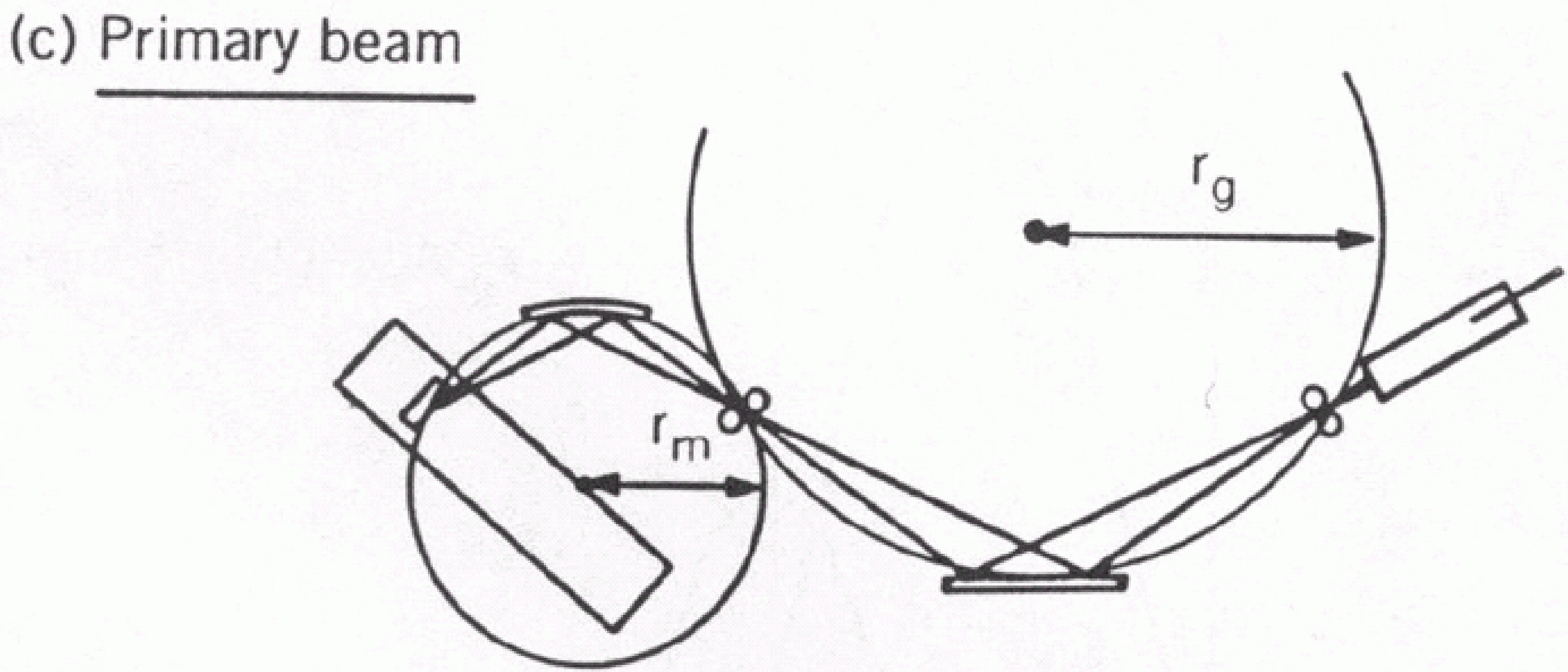
Target Element	Filter Pair (A)	Filter Pair (B)	(A) Thickness Millimeters	(A) Thickness Mils[b]	(A) Thickness Grams/cm²	(B) Thickness Millimeters	(B) Thickness Mils[b]	(B) Thickness Grams/cm²
Ag	Pd	Mo	0.0275	1.08	0.033	0.039	1.53	0.040
Mo	Zr	Sr	0.0392	1.54	0.026	0.104	4.09	0.027
Mo	Zr	Y	0.0392	1.54	0.026	0.063	2.49	0.028
Cu	Ni	Co	0.0100	0.38	0.0089	0.0108	0.42	0.0095
Ni	Co	Fe	0.0094	0.37	0.0083	0.0113	0.45	0.0089
Co	Fe	Mn	0.0098	0.38	0.0077	0.0111	0.44	0.0083
Fe	Mn	Cr	0.0095	0.37	0.0071	0.0107	0.42	0.0077
Cr	V	Ti	0.0097	0.38	0.0059	0.0146	0.58	0.0066

Curved Crystal Focusing Monochromator



$$SC = R \frac{\lambda}{d}$$

Incident beam monochromator



Advantage of placing monochromator in incident beam:

1. eliminate $K\alpha_1$
2. improve resolution

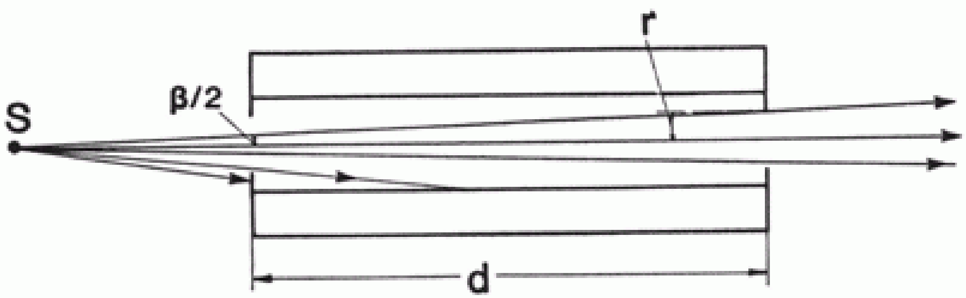
Advantage of placing monochromator in diffracted beam:

1. eliminate fluorescence
2. increase in intensity by removing divergence slit and $K\beta$
3. filter shields radioactive samples

Collimators

Beams from x ray tube are composed of a large portion of convergent and divergent rays.

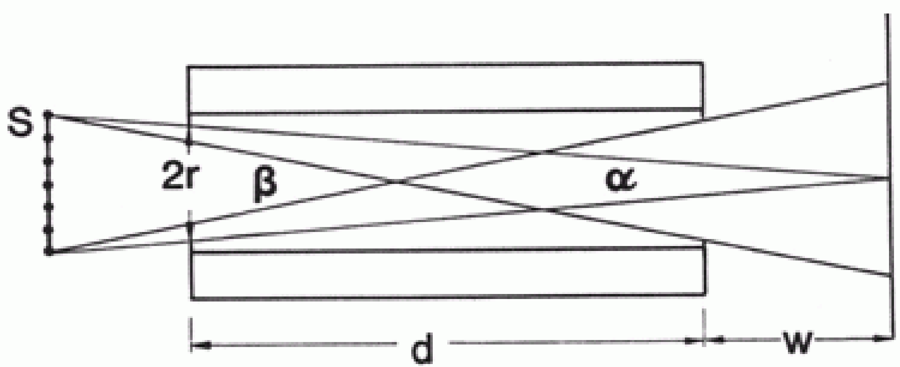
<u>Types of collimators</u>:
a) pinhole b) crossed slits c) Soller d) Gobel mirror e) polycapillary lens



Geometry of a pinhole collimator with a point source

Point source

$$\beta = \frac{2r}{d}$$

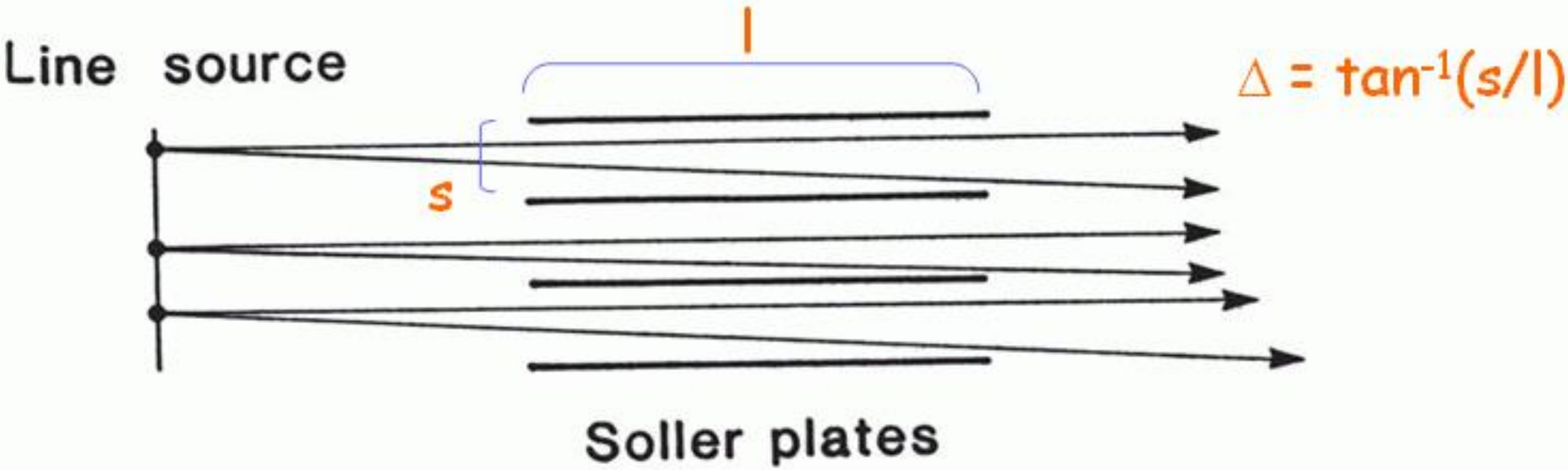


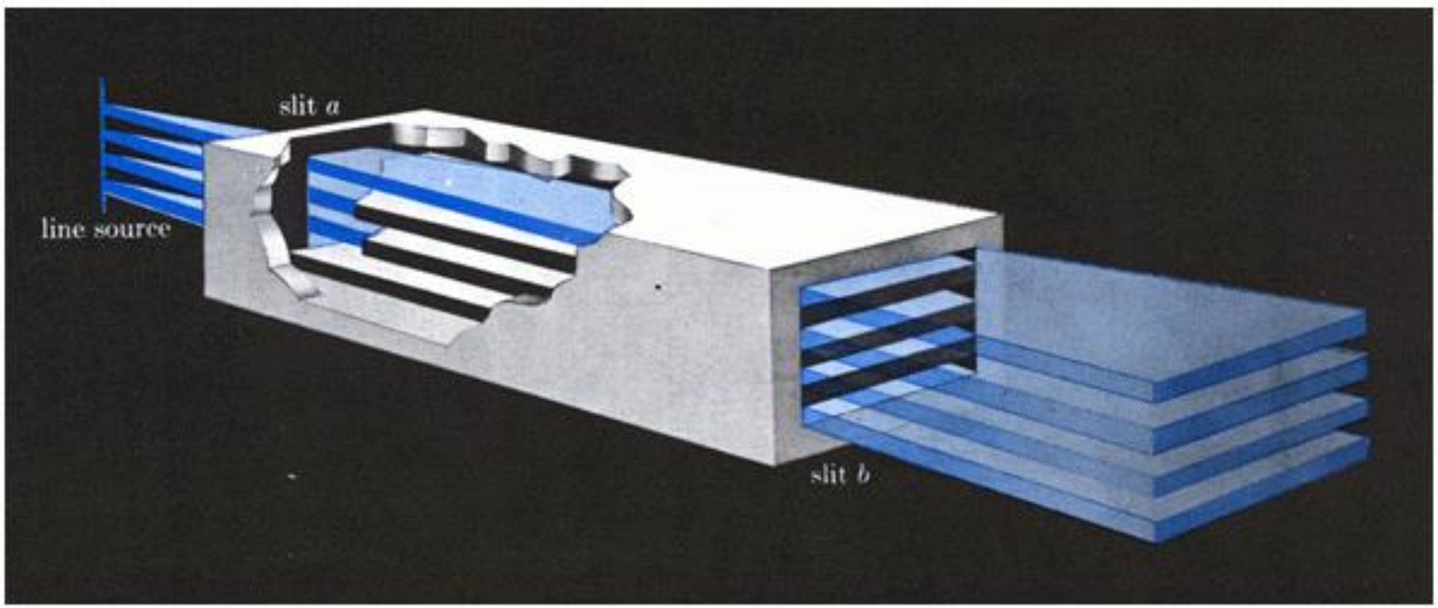
Line source

$$\beta = \frac{4r}{d}$$

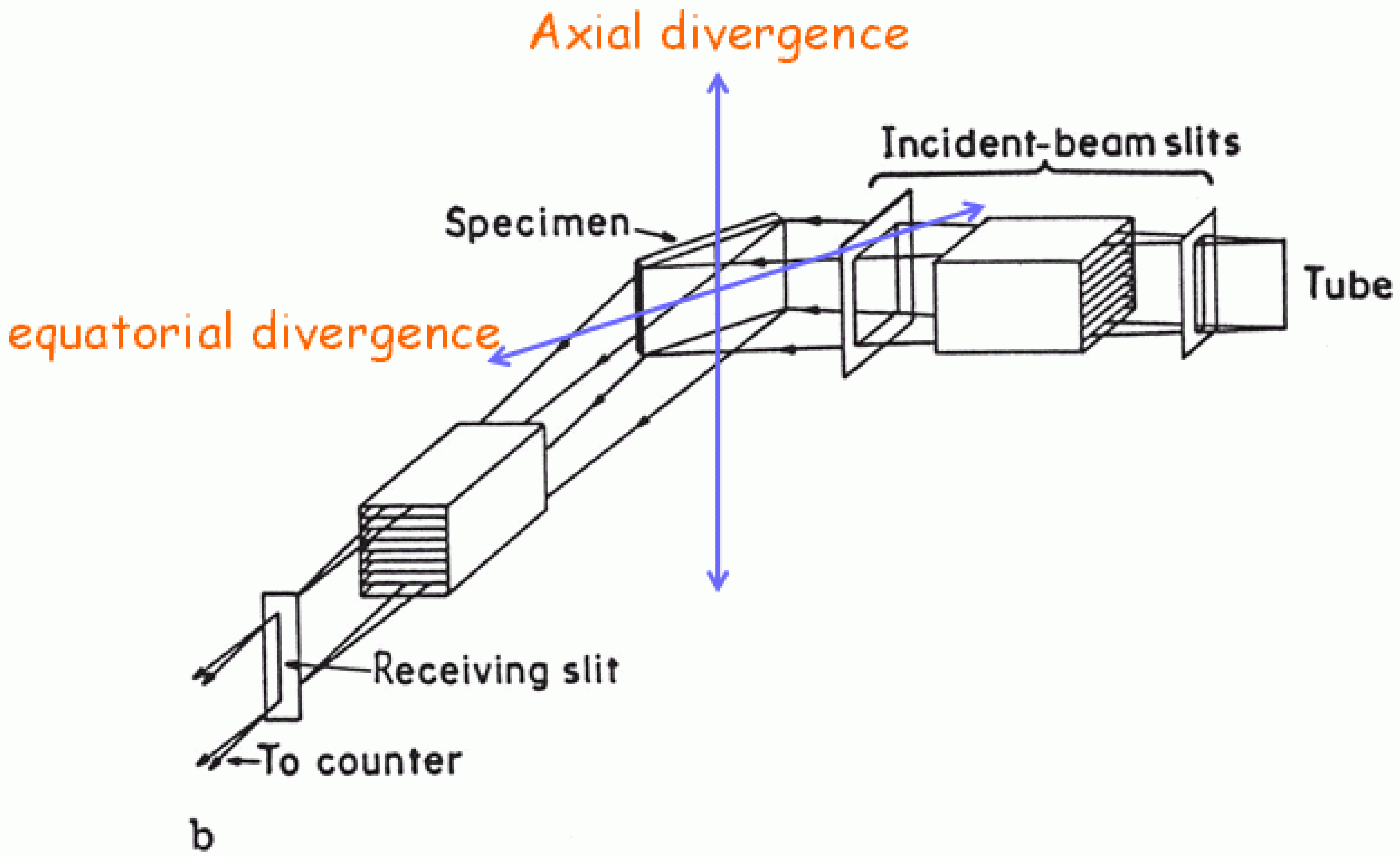
$$\alpha = \frac{2r}{d+w}$$

Sollers

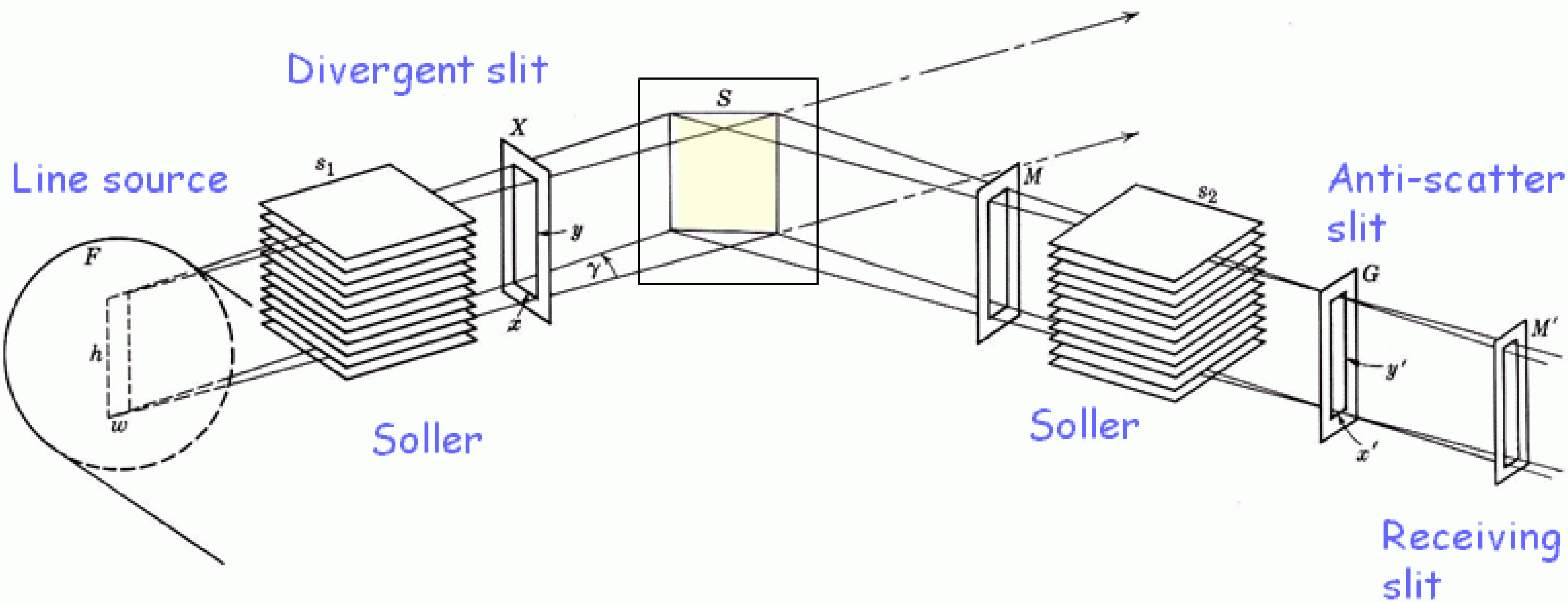

Line source
l
s
Δ = tan-1(s/l)
Soller plates


slit a
line source
slit b

Sollers


Axial divergence
Incident-beam slits
Specimen
Tube
equatorial divergence
Receiving slit
To counter
b

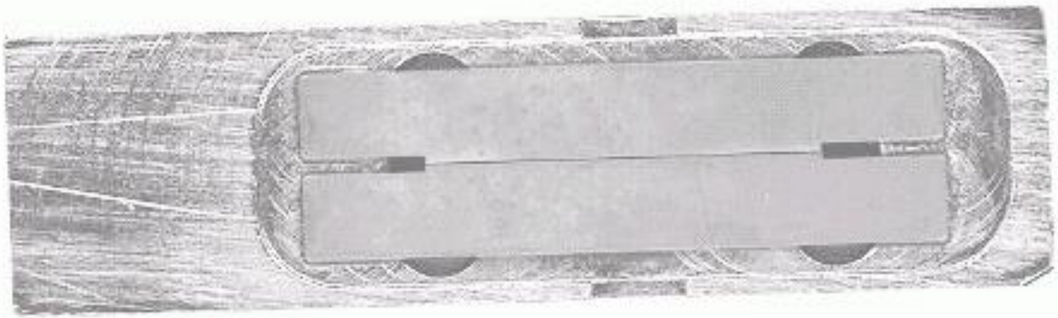
Slits

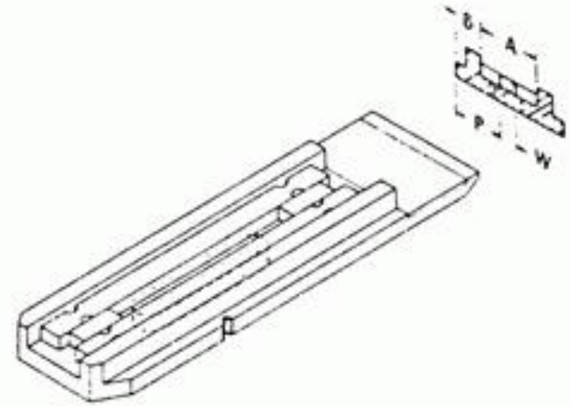


<u>Types of slits:</u>

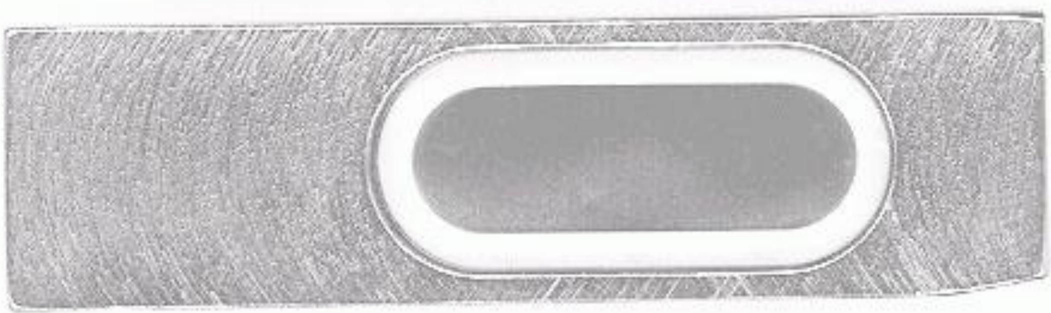
1. Fixed (divergent, anti-scatter, receiving)
2. Automatic (divergent, anti-scatter)

Slits (contd.)





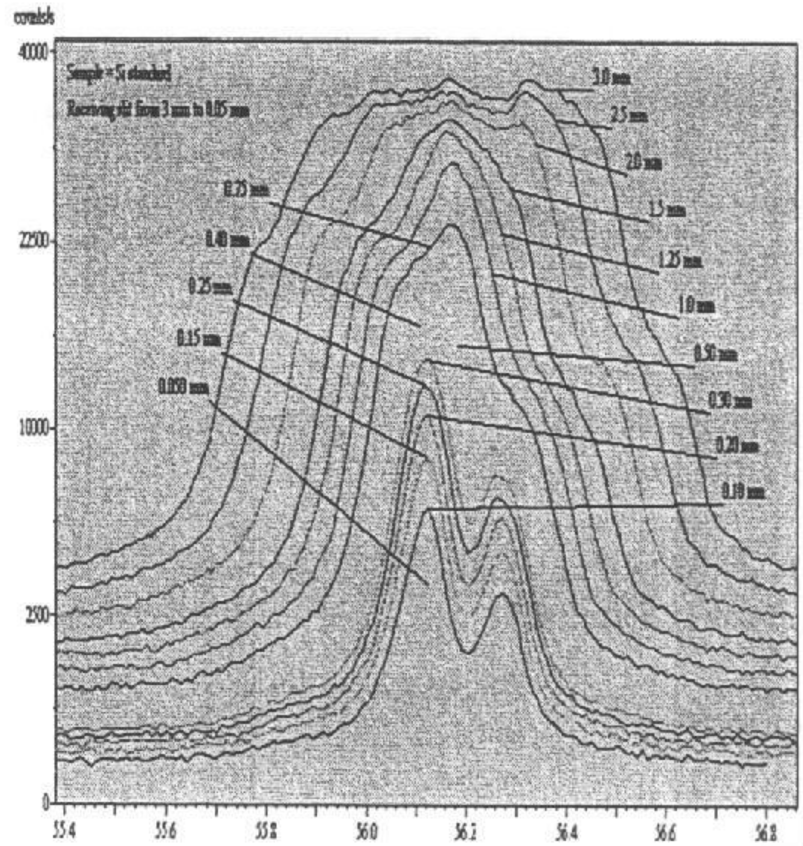
0.5 mm receiving slit



Ni K β filter

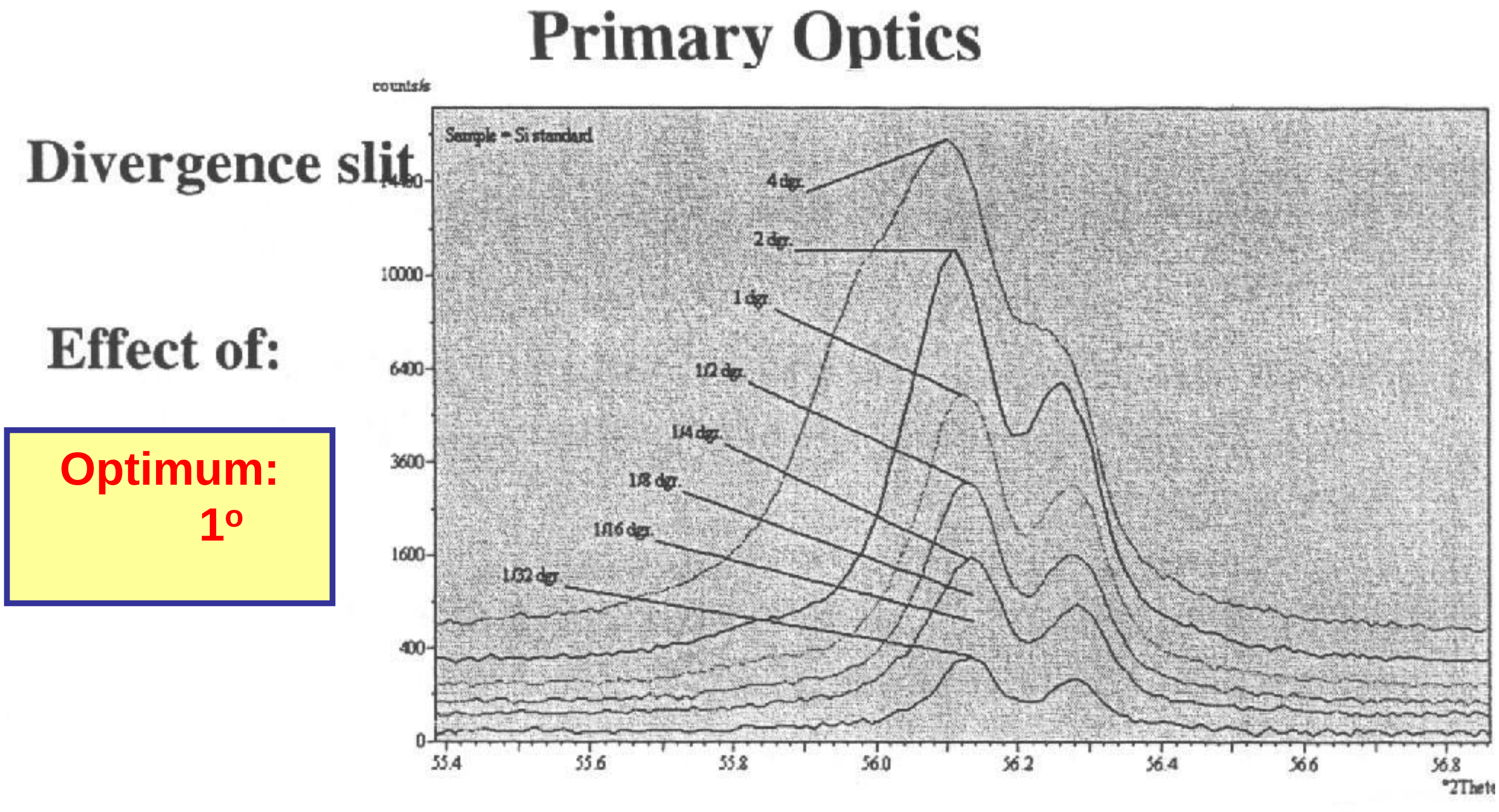
Effect of Receiving slit size

Effect of Receiving slit opening



Optimum: 0.2 mm

Effect of Divergence slit



Optimum: 1°

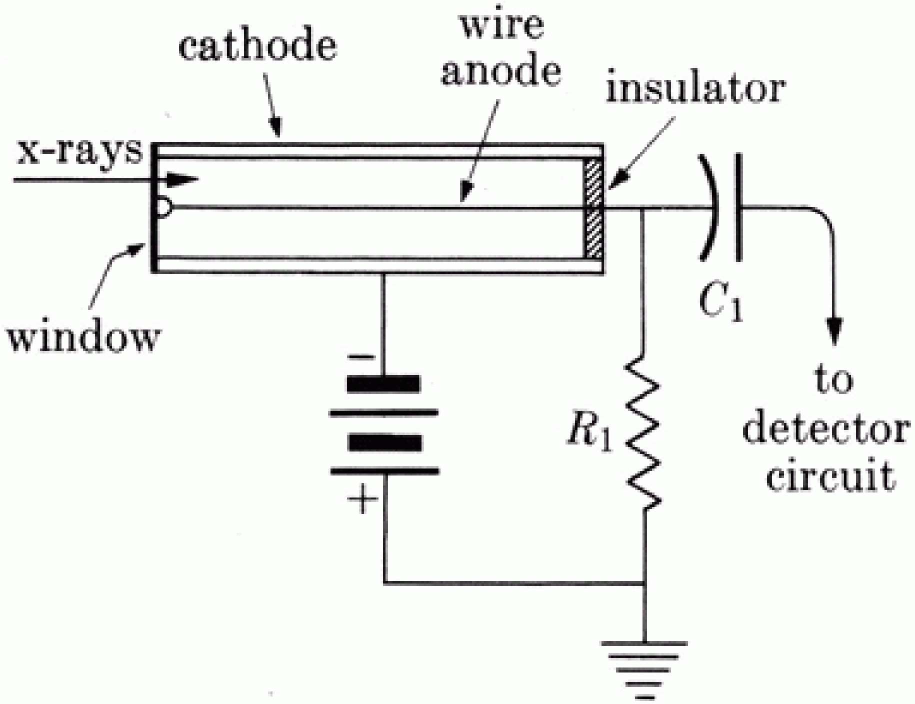
For layered materials : RS: ¼°, 1/8 °, 1/16 °, 1/32 °
DS: 0.1 mm or smaller

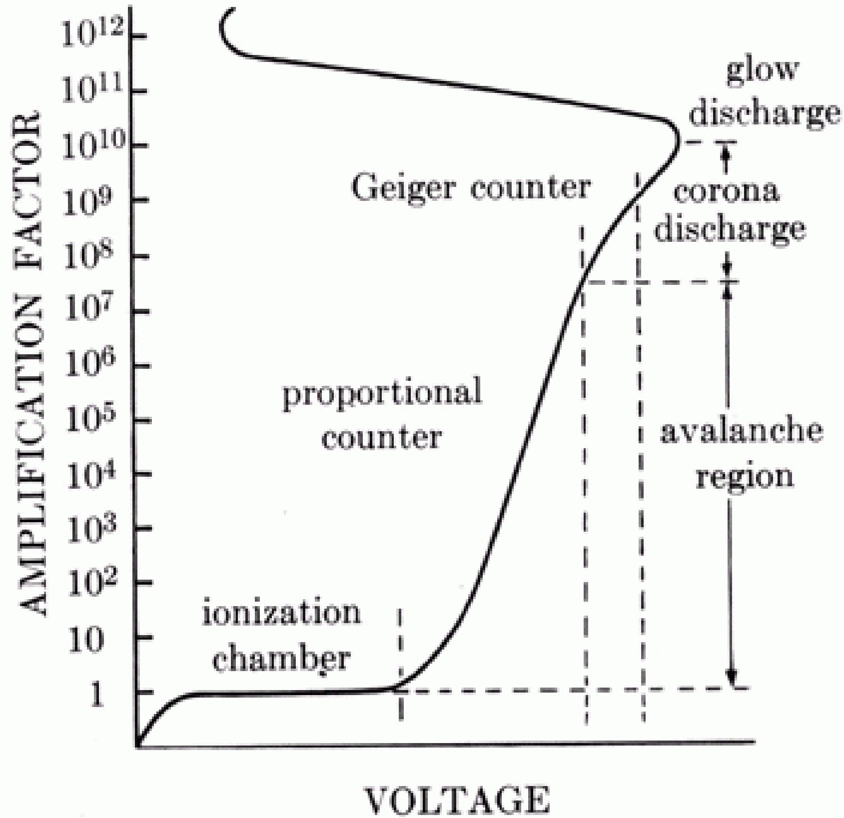
Detecting & recording diffracted intensity

Types of recording devices :

1. Photographic film (Debye-Scherrer Camera) 'Area'
2. Gieger-Muller counters 'Point'
3. Proportional counters 'Point'
4. Scintillation detectors 'Point'
5. Position sensitive detectors 'Line'
6. Phased array 'Line' (Pananalytical Xcelerator)
7. Si(Li) detectors 'Point'
8. 2D PSD 'Area'
9. CCD plate 'Area'
10. Image plates 'Area'

Proportional counter

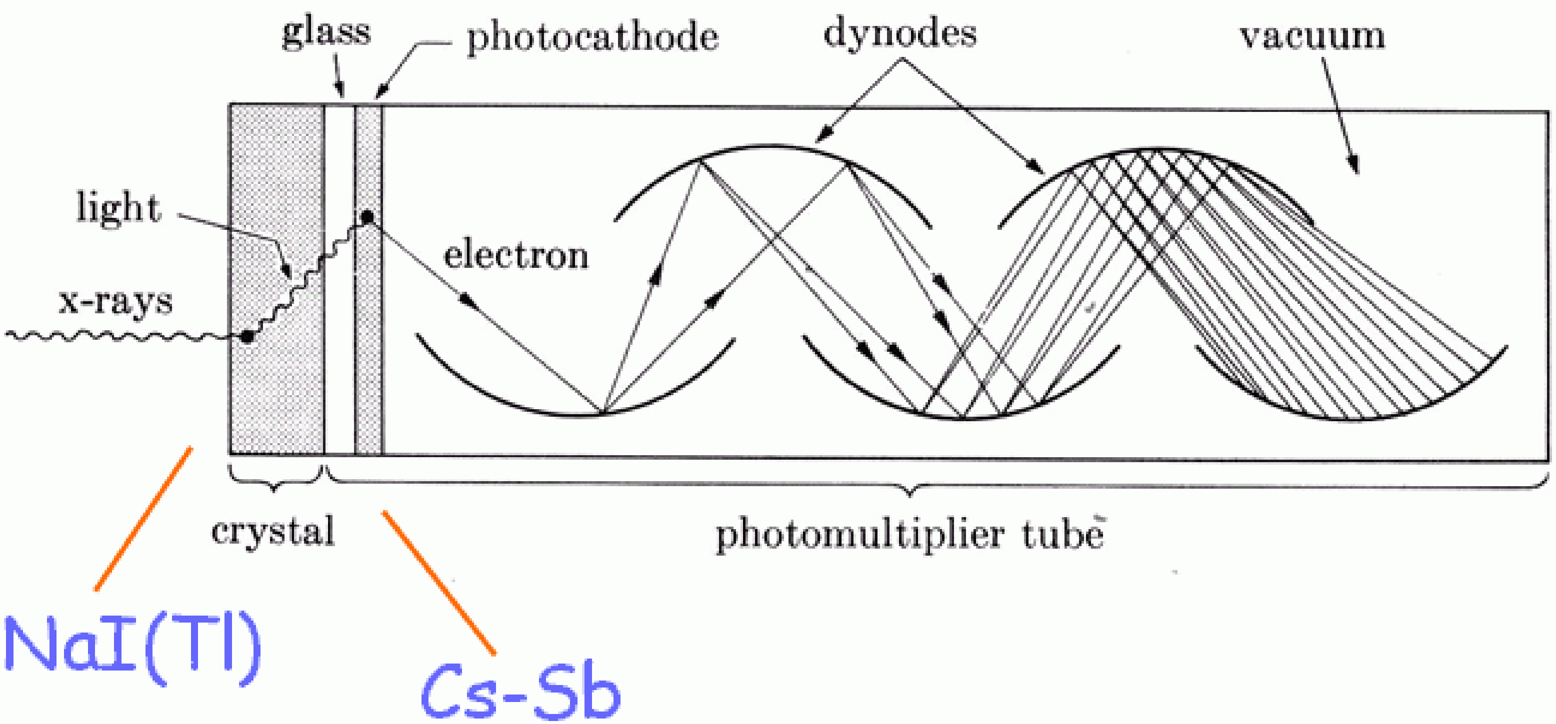




Krypton, argon xenon with quenching gas such as, chlorine, bromine, alcohol

- High counting rates (10^6 /sec)
- Good energy resolution

Scintillation detector



Gain/ dynode = 5

Multiplication factor for 10 dynodes = $5^{10} = 10^{7}$

- High counting rates (10^{5} /sec)
- Energy resolution poorer than proportional counters

Neutron Sources

Some isotopes undergo spontaneous fission with emission of neutrons (e.g. ^{252}Cf)

α- particles bombardment of on several low Z elements like Be, C, O (e.g. PuBe, AmBe, AmLi (rate ~ 1×10^{6} to 1×10^{8} neutrons per second)

γ- radiation with energy more than the neutron binding energy of a nucleus

$$^{2}H + \gamma \;\; 2.26\ \text{MeV} \rightarrow {}^{1}n + {}^{1}H$$

$$^{9}Be + \gamma \;\; 1.7\ \text{MeV} \rightarrow {}^{1}n + 2\,{}^{4}He$$

Nuclear reactor produces very large quantities of neutrons (fission of fissile materials, U, Pu)

Spallation source (high-flux source) Accelerated proton hits target metal (heavy Z metal like Bi, W, U, Pb etc.)

Reactor-based sources now produce 10^{15} n/(cm² s) while spallation sources generate greater than 10^{17} n/(cm² s

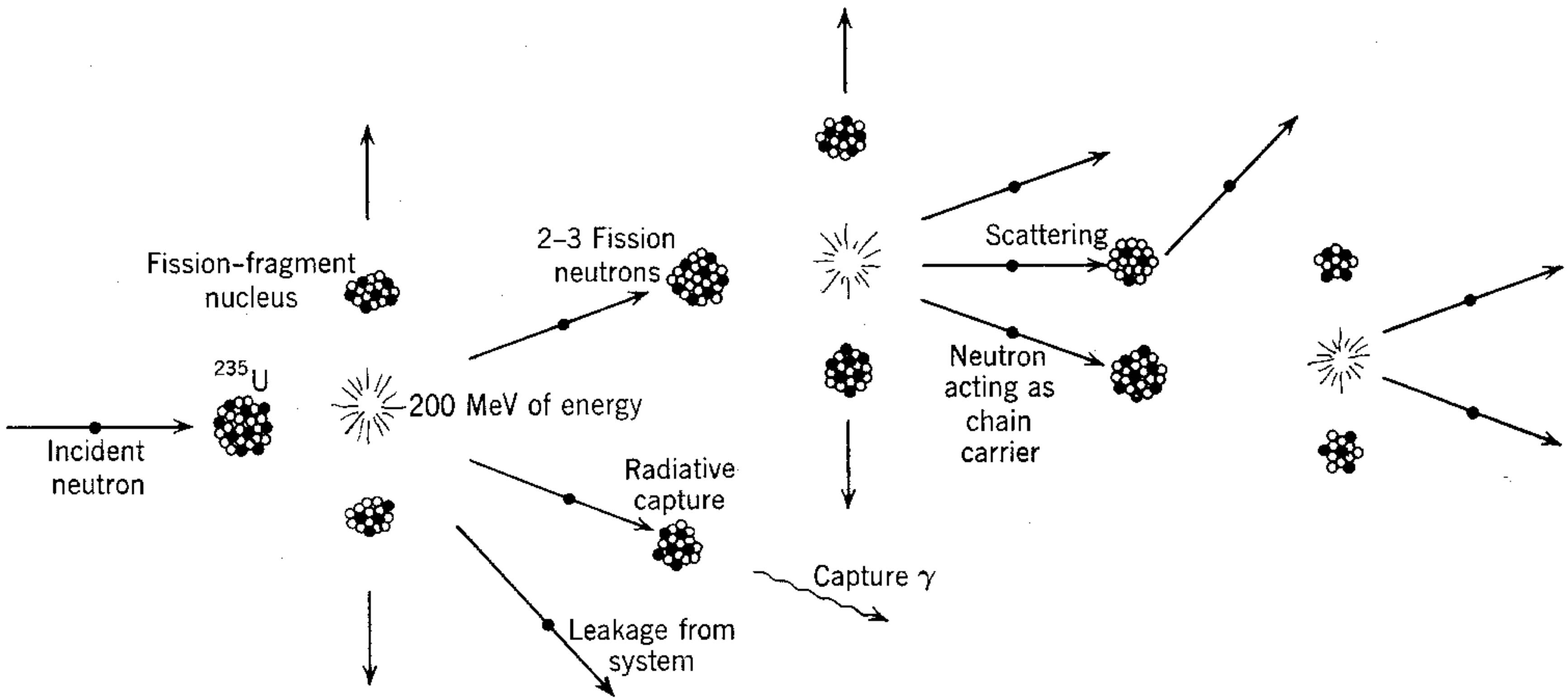


FIGURE 3-1. A simple schematic of a fission chain reaction.

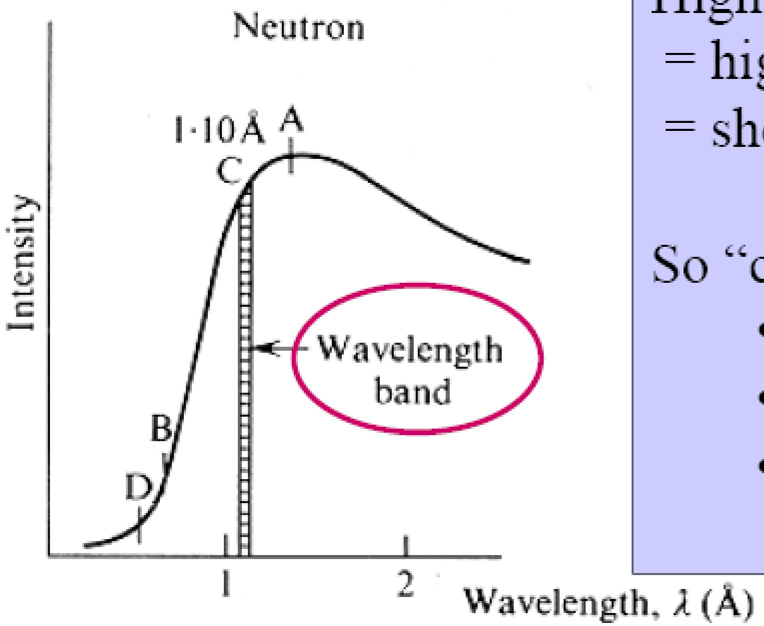
$$ {}^{1}_{0}n + {}^{235}_{92}U \rightarrow \left({}^{236}_{92}U\right)^{*} \rightarrow {}^{140}_{55}Cs + {}^{93}_{37}Rb + 3\left({}^{1}_{0}n\right) $$

Planck's constant → h

Neutron mass → m

Neutron velocity → v

Wavelength → $\lambda = h/mv$



Higher energy
= higher neutron velocity
= shorter neutron wavelength

So "cold neutrons" have

- low energy
- low velocity
- long wavelength

Neutron Diffraction - *G.E. Bacon*

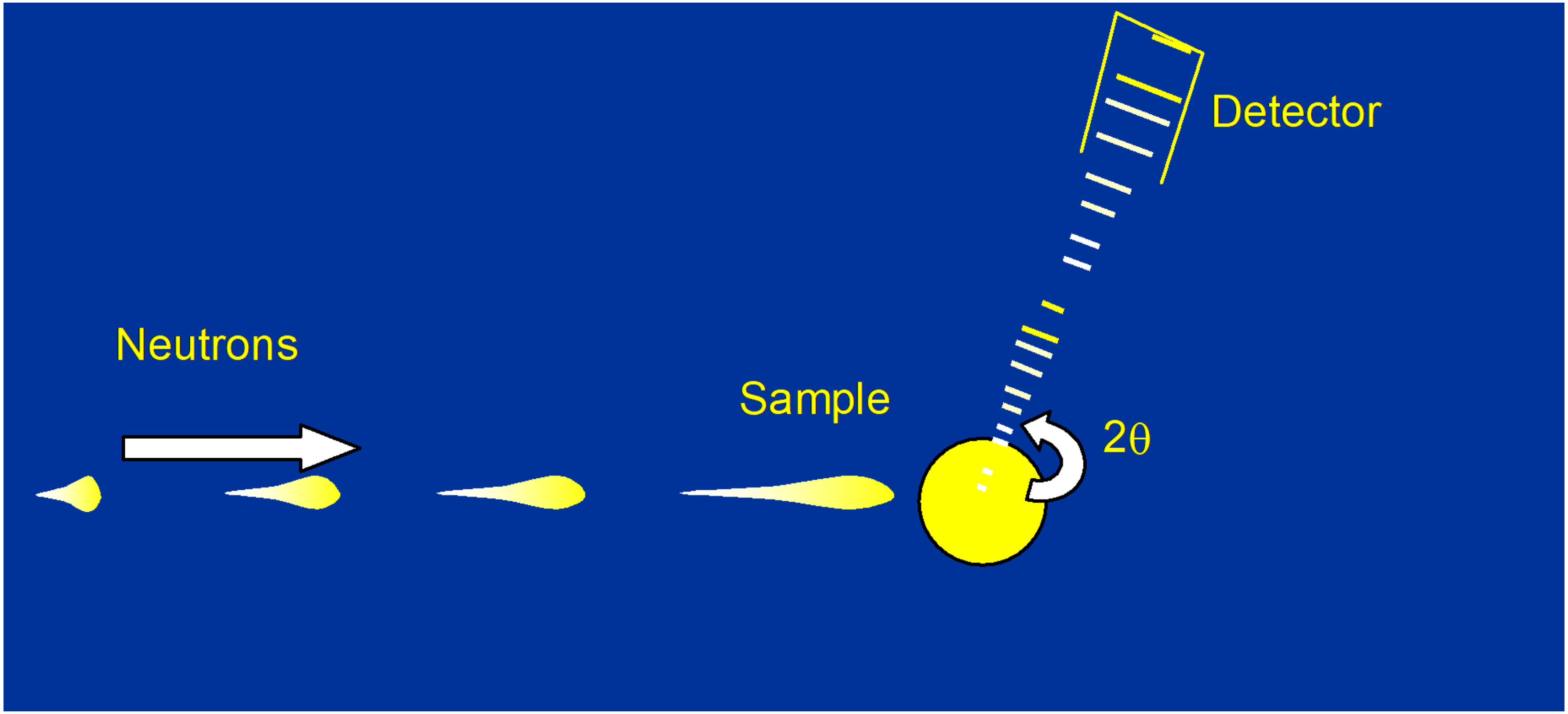
Spin = ½, Charge = 0, Magnetic moment = -1.913 μ_N (μ_N= 5.05 X 10-27 J/T)

de Broglie wavelengths of the neutrons with thermal energies between 10 and 100 meV are 2.86 – 0.905 Å

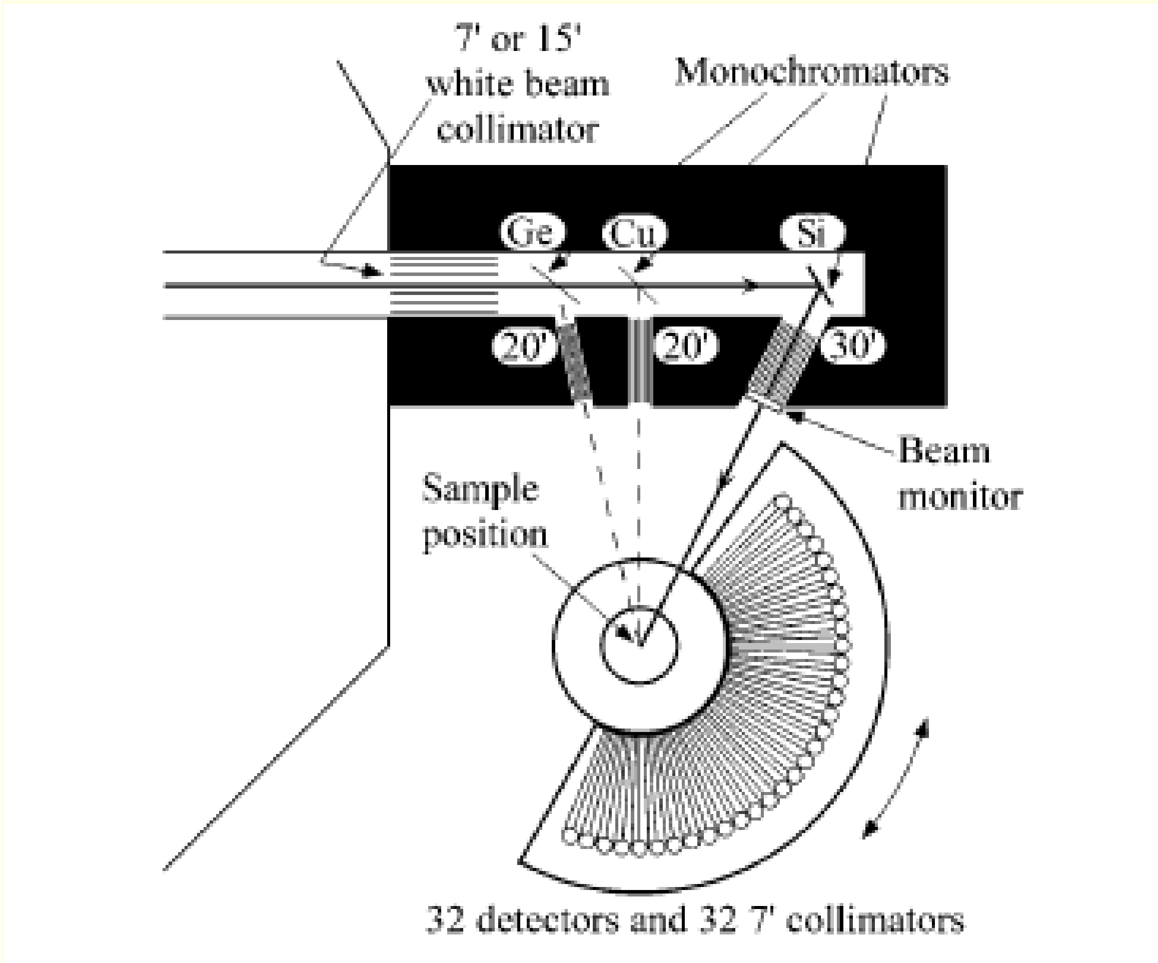
Zero electric charge of neutrons also helps them to penetrate high into matter and therefore, the study of bulk materials is possible.

Comaparble nuclear scattering length (~ 10^{-12} cm)

Prompt neutrons are born at energies between 0.1 MeV and 10 MeV. The average prompt neutron energy is about 2 MeV

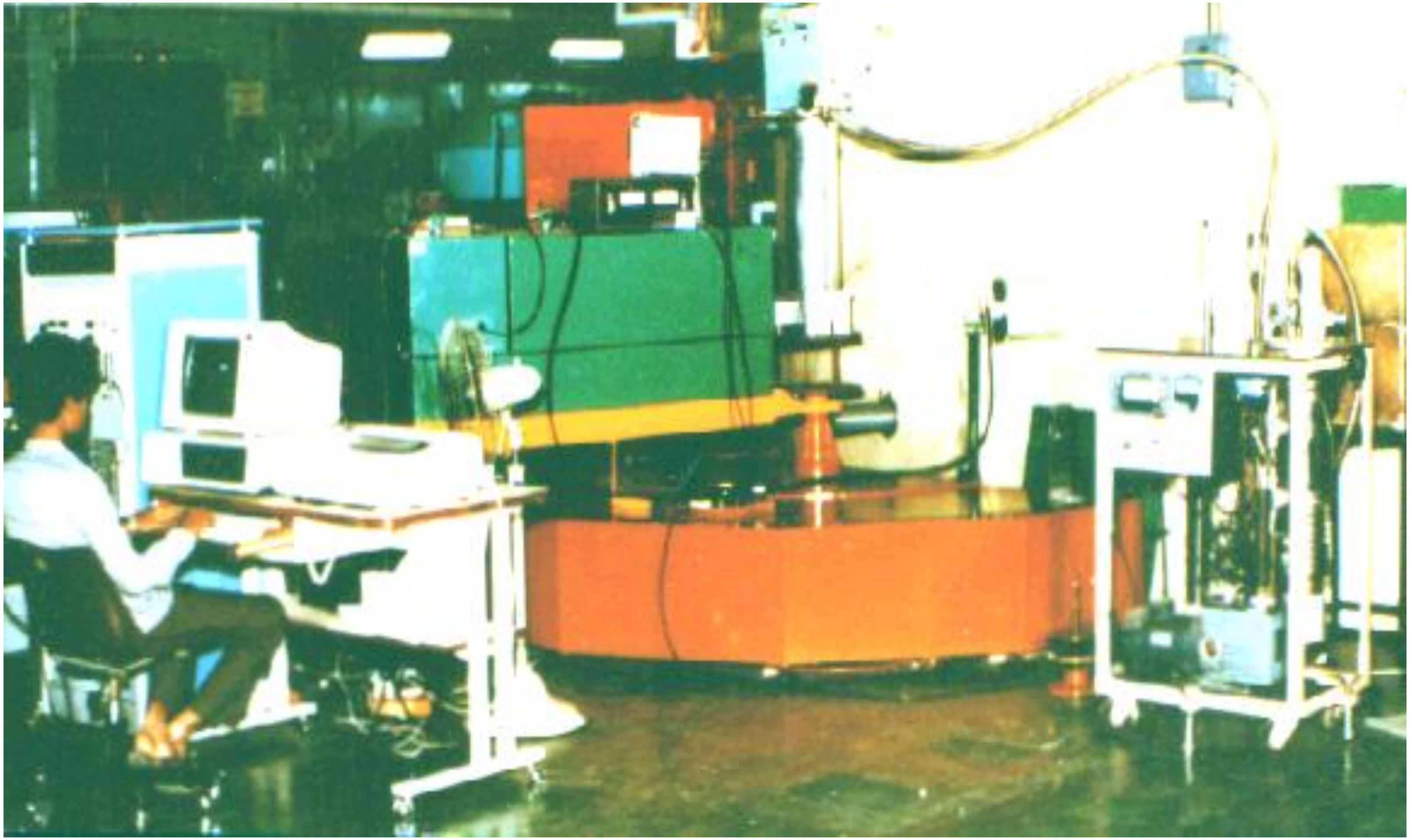


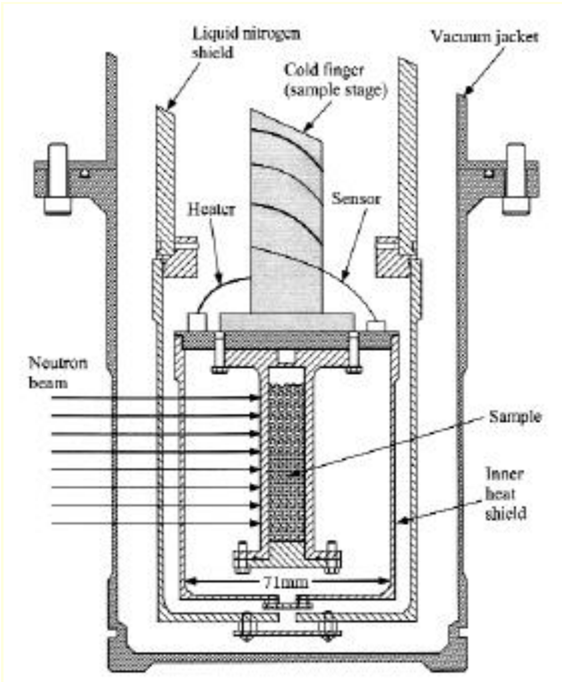
Detector
Neutrons
Sample
2θ



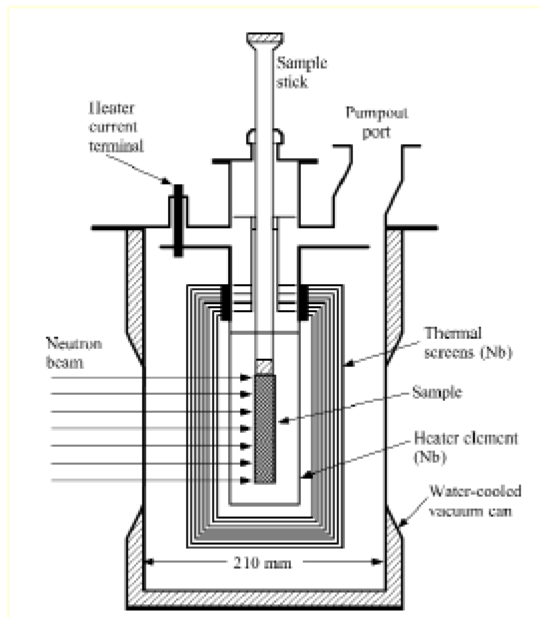
BT1 Spectrometer at the NIST Research Reactor

1-D Position Sensitive Detector based Neutron Powder Diffractometer at Dhruva Reactor

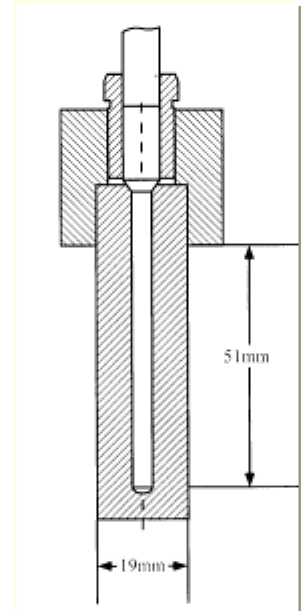




Low temperature setup



High temperature setup (furnace)



High pressure cell

Scattered intensity from an electron (I_e) at an angle (φ) and at distance r

$$I_e = I_o \frac{e^4}{r^2 m^2 c^4} (\frac{1+\cos^2\varphi}{2})$$

where I_o = incident intensity of x-ray beam
e and m are electron charge and mass
c = velocity of electromagnetic radiation in vacuum

Intensity scattered in all spherical direction

$$P_e = \frac{8\pi}{3} \frac{I_o e^4}{m^2 c^4}$$

Scattering power of an electron

$$f_e = \frac{p_e}{I_o} = \frac{8\pi}{3} \frac{e^4}{m^2 c^4}$$

fo/*fe* = Z*fe*/*fe* = Z.

$$f = f_0 e^{\frac{-B \sin^2 \vartheta}{\lambda^2}}$$

$$F_{hkl} = \sum_{j \to 1}^{j \to N} f_j e^{2\pi i (hx_j + ky_j + lz_j)}$$

$$I \propto F \times F^* \times Lp \times Abs$$

$$\rho(xyz) = \frac{1}{Vc} \sum_h \sum_k \sum_l F_{hkl} e^{2\pi i (hx + ky + lz)}$$

Resonant scattering

$$\sigma = 4\pi\left(\xi - \frac{\Gamma}{2kE_R}\right) = 4\pi b^2$$

Potential scattering

$$b = b - \Delta b$$

$$\left|F_{hkl}\right|_{Nuclear} = \sum b_j e^{2\pi i(hx_j+ky_j+lz_j)} e^{-\frac{B\sin^2\vartheta}{\lambda^2}}$$

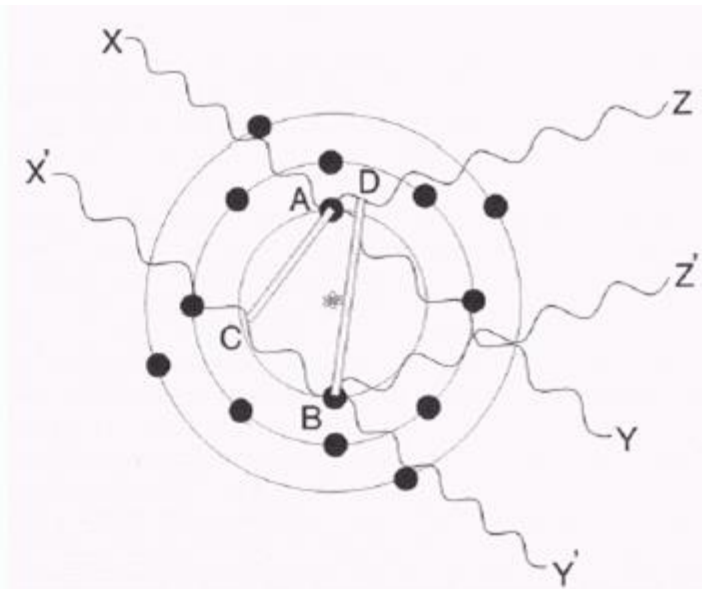
$$\left|F_{hkl}\right|_{Mag} = \sum p_j e^{2\pi i(hx_j+ky_j+lz_j)} e^{-\frac{B\sin^2\vartheta}{\lambda^2}}$$

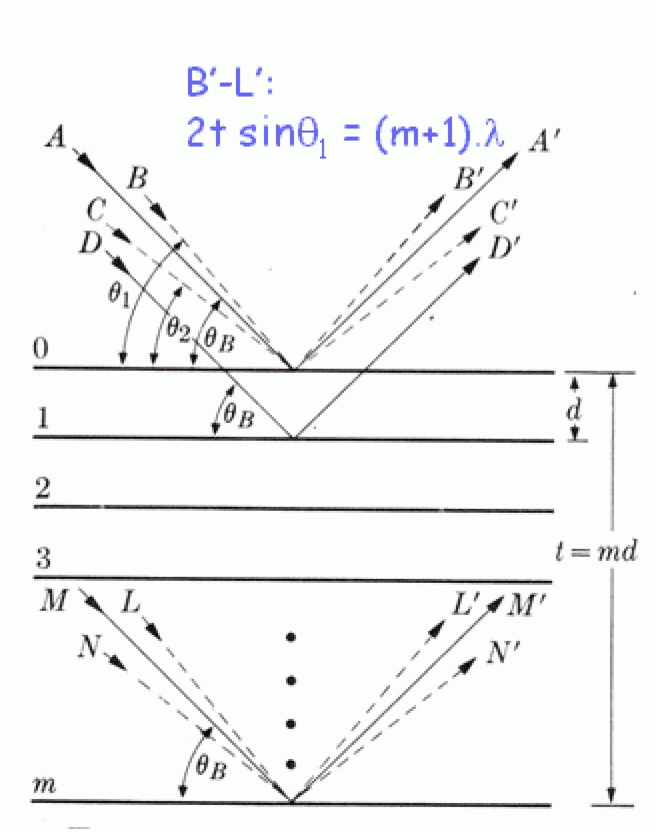
$$p = \frac{e^2\gamma S f_{x-ray}}{mc^2} = 0.53 S f_{x-ray}$$

$$\left|F_{total}\right|^2 = \left|FNuclear\right|^2 + q^2\left|F_{magnetic}\right|^2$$

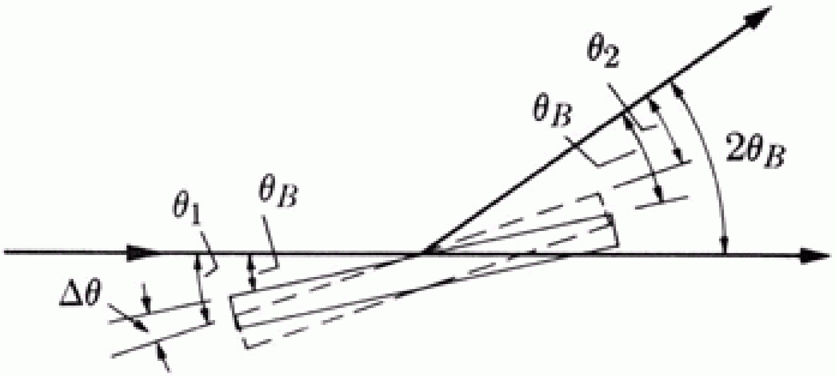
$$\left|F_{hkl}\right|^2 = (b_j^2 + q^2 p_j^2)\sum e^{2\pi i(hx_j+ky_j+lz_j)} e^{-\frac{B\sin^2\vartheta}{\lambda^2}}$$

$$q^2 = 1 - (\varepsilon \cdot k)^2 = \sin^2\alpha$$

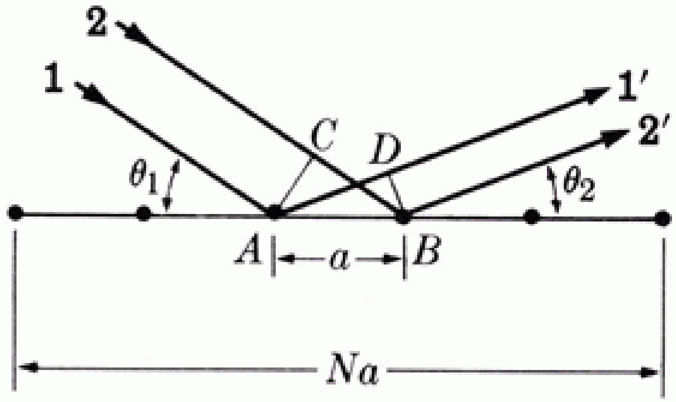

X
X'
Z
Z'
A
D
C
B
Y
Y'


B'-L':
2t sinθ1 = (m+1).λ
A
B
C
D
A'
B'
C'
D'
θ1
θ2
θB
0
1
2
3
m
d
t = md
M
L
N
L'
M'
N'

Lorentz Factor (contd.)



(a)



(b)

Diff in path length = AD-CB

$= 2.a.\Delta\theta.\ \sin\theta_B$

$\therefore \quad \Delta\theta = \lambda/(2.N.a.\ \sin\theta_B)$ i.e. $I_{max} \propto 1/\sin\theta_B$

As width (B) $\propto 1/\cos\theta_B$

Integrated intensity $\propto 1/\sin\theta_B.\ \cos\theta_B$

$\propto 1/\sin 2\theta_B$

APPLICATIONS OF XRD

- Nature of sample (Crystalline or amorphous)
- Phase identification
- Monitoring solid state reactions
- Phase transitions
- Unit cell determination
- Crystallite size
- Structure
- Defects
- Surface structure (GI-XRD, SAXS)
- Polycrystalline texture
- Phase relations/phase diagrams
- Solid solution formation
- Order disorder PTs
- Strain

Applications of High Temperature XRD

- **Phase transitions**
- **Order-disorder phenomenon**
- **Lattice thermal expansion, and NT Expansion**
- **Study of point defects (*in conjunction with dilatometry*)**
- **Construction of phase diagrams**
- **Terminal solubility of a guest ion into the host lattice**
- **Devitrification studies on glasses**
- ***In situ* monitoring of course of solid state reactions, phase evolution**
- **Kinetics of solid state reactions**
- ***In situ* monitoring of solid-gas reactions**
- **Agglomeration studies**
- **Variation of strain as a function of temperature**

	x-ray	neutron
Source	Fixed target/SR	Reactor/Spallation
Width	0.001 Å	0.05 Å
Wave length	12.4/V in KV (Å)	0.28/√(E in eV)
	1-10 Å	~ 0.03 eV
Scatterer	electron	Nucleus + electron
Scattering power	$f = \int 4\pi r^2 \rho(r) \frac{\sin kr}{kr} dr$	$b = \left(\xi - \frac{\Gamma}{2kE_R} \right)$
Θ dependency	depends	isotropic
Z dependency	Z	$1.5 \times 10\text{-}5\ A^{1/3}$

Property	X-ray diffraction	Neutron diffraction
Location of low Z elements	Not favourable	Favourable
Neighbouring elements	Difficult to distinguish	Easy to distinguish
Penetration	10-100 μm	Few cm
Sample size	Few mg	5-10 gm
Resolution	Good	Very good
Single crystal work	Easy to do	Not so easy
Monochromatization	Easy	Difficult
Isotopes	Cannot be differentiated	Can be differentiated
Magnetic structure	Cannot be obtained	Can be obtained
Study of lattice vibrations (dynamic)	Not possible	Possible
Preferred orientation	Problem	No effect
Intensity	Drops as angle increases	No correlation with angle

Thank you very much