X-rays

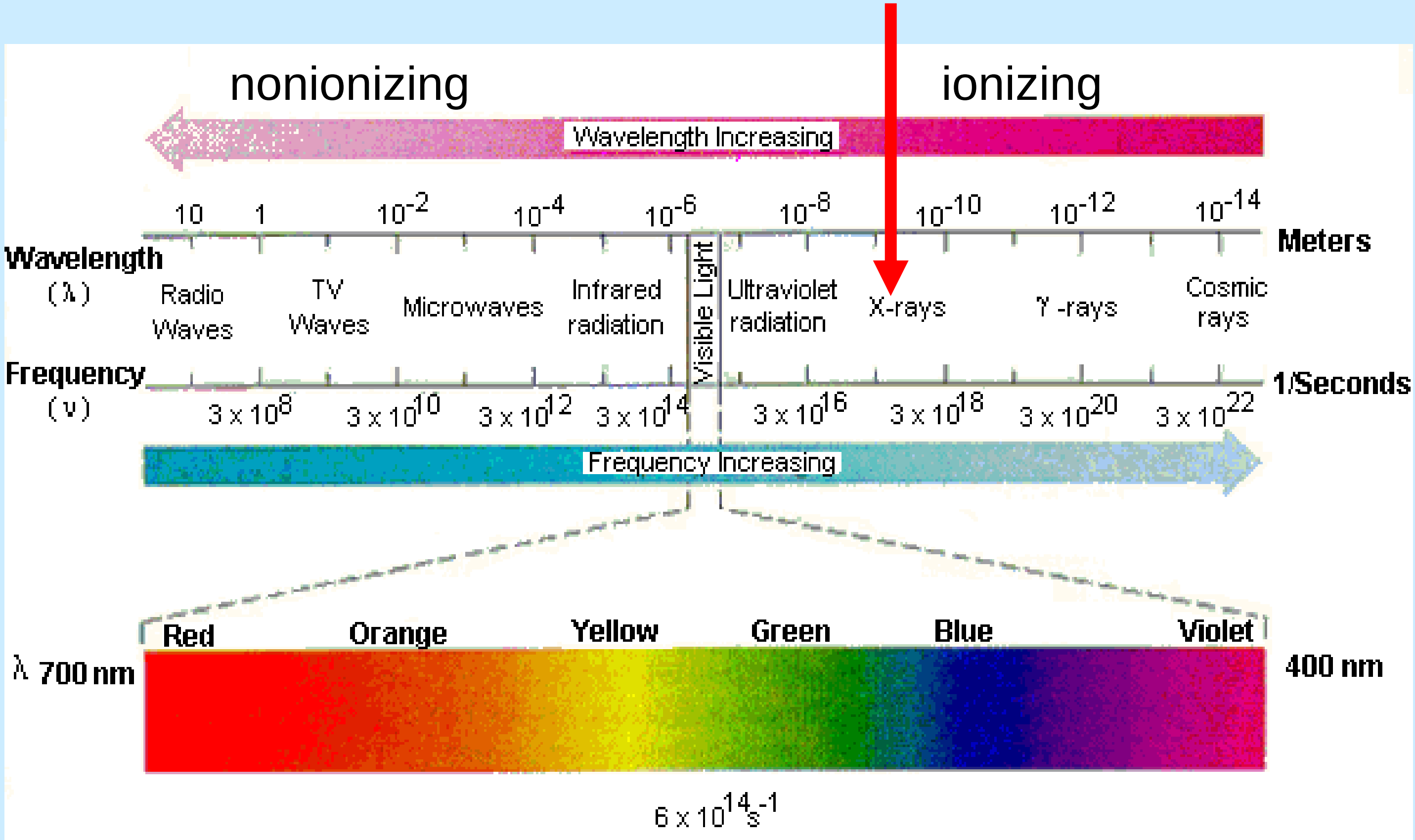
Discovered on
November 8, 1895

Wilhelm K. Roentgen
(1845-1923)
NP in Physics 1901
(The first Nobel Price in Physics)

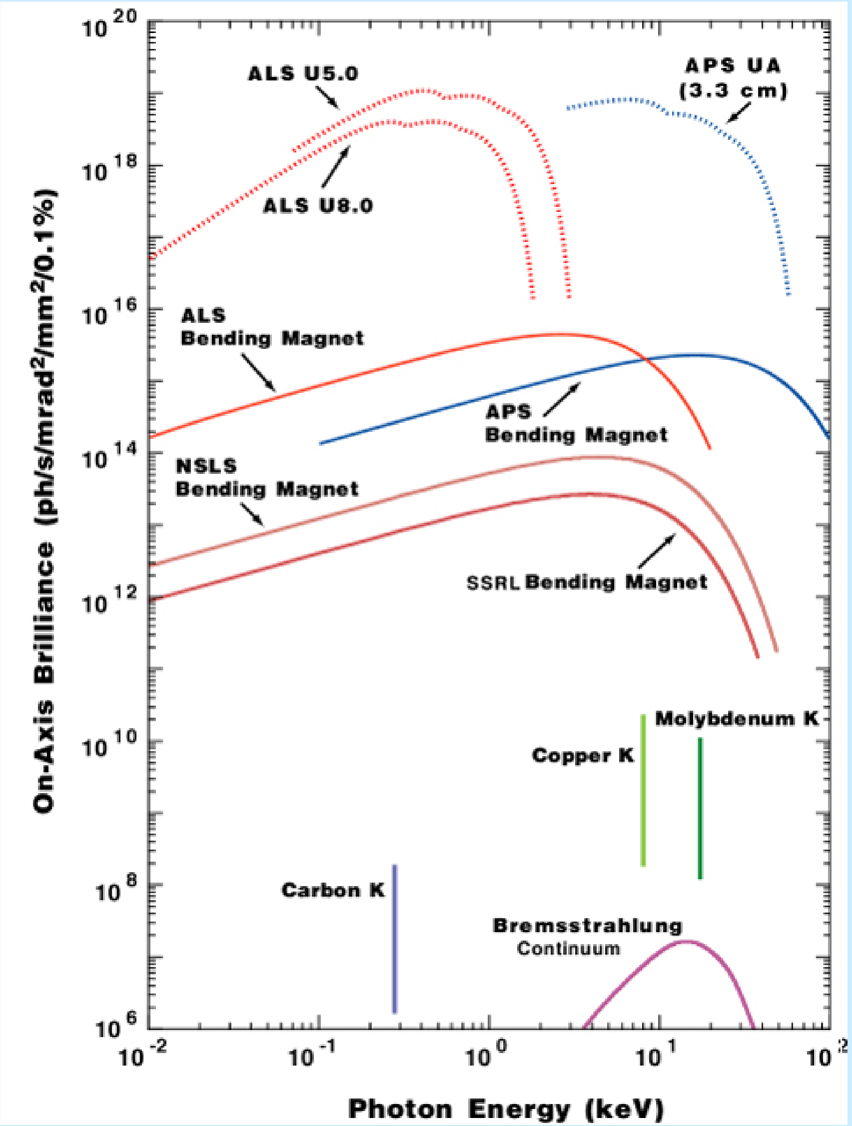
- X-ray Radiography - absorption is a function of Z and density
- X-ray Crystallography
- X-ray Spectrometry

X-rays

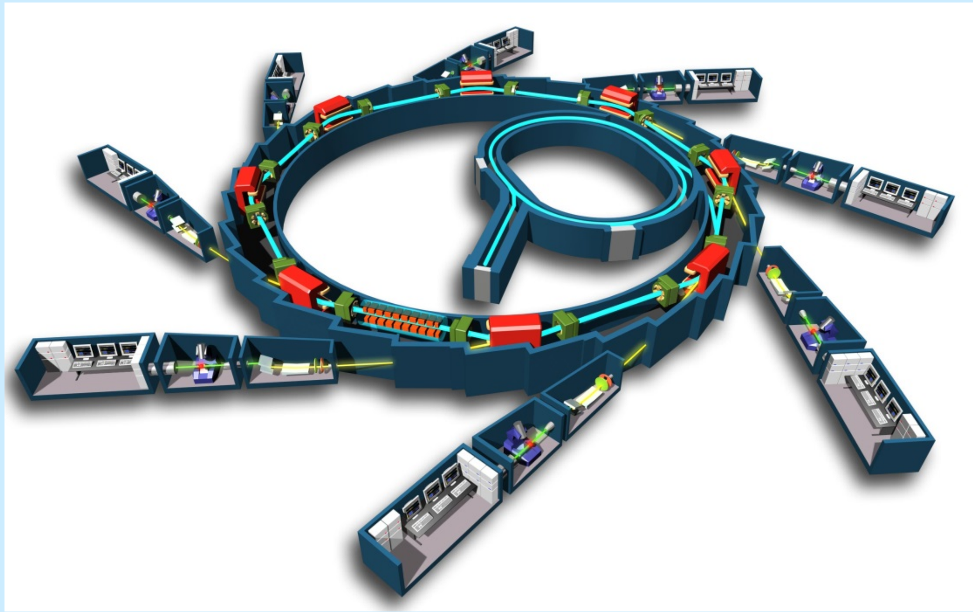
Between 0.1 and 10 Å (1 Å = 0.1 nm)



X-ray sources: Synchrotron Radiation

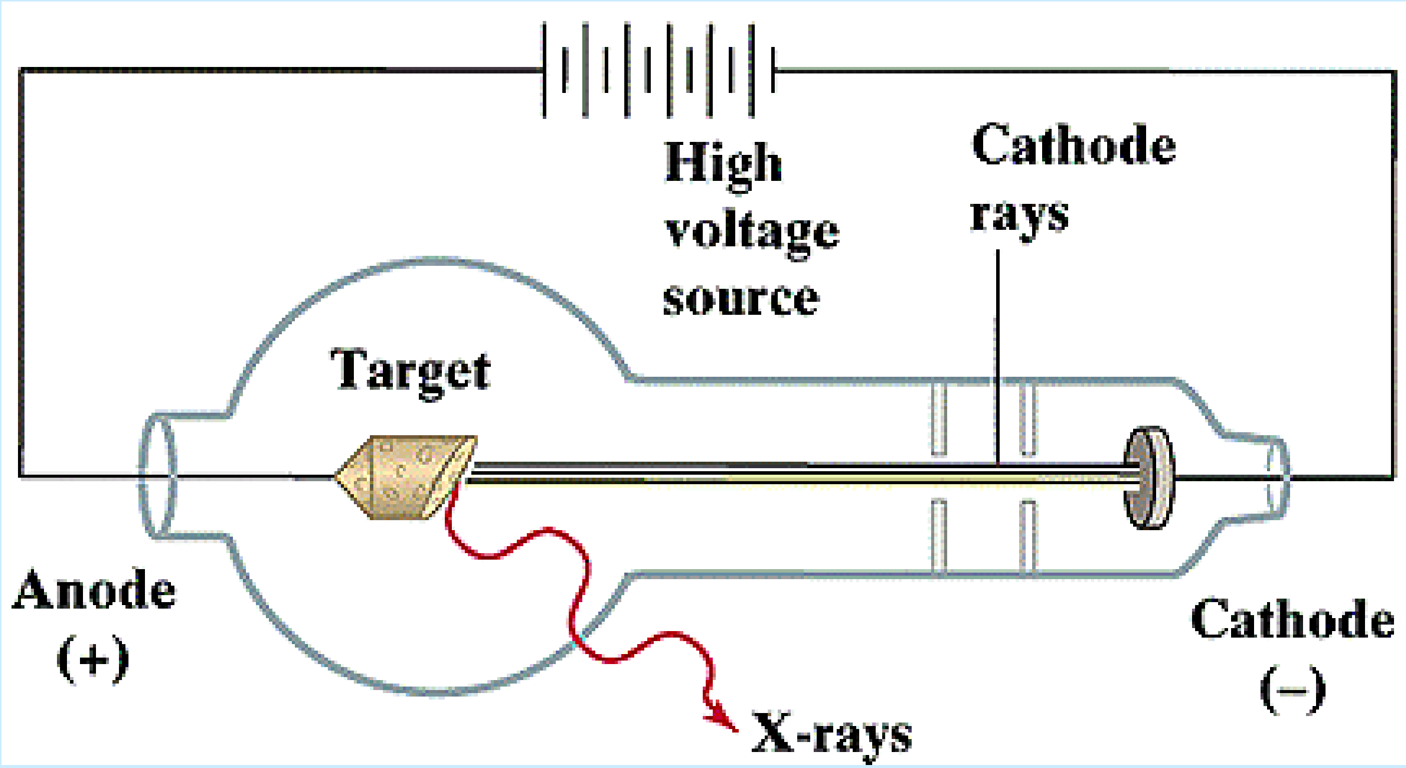


Brightest X-ray sources
Far more intense ($>10^6$) than X-ray tubes
Tunable energy
High collimation
Pulsed operation - rapid pulses – time-resolved experiments



Bremsstrahlung (“braking radiation”)

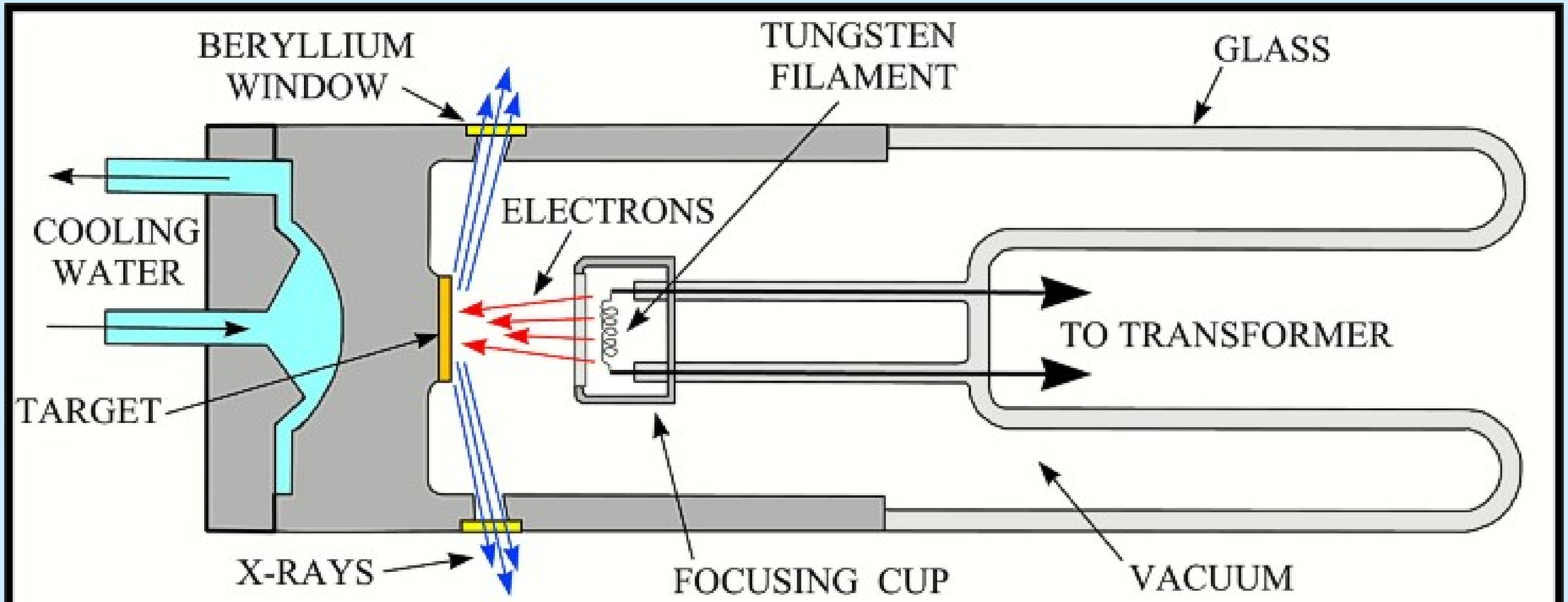
X-ray Tubes



Cu K_α E = 8.05 keV λ = 1.541 Å

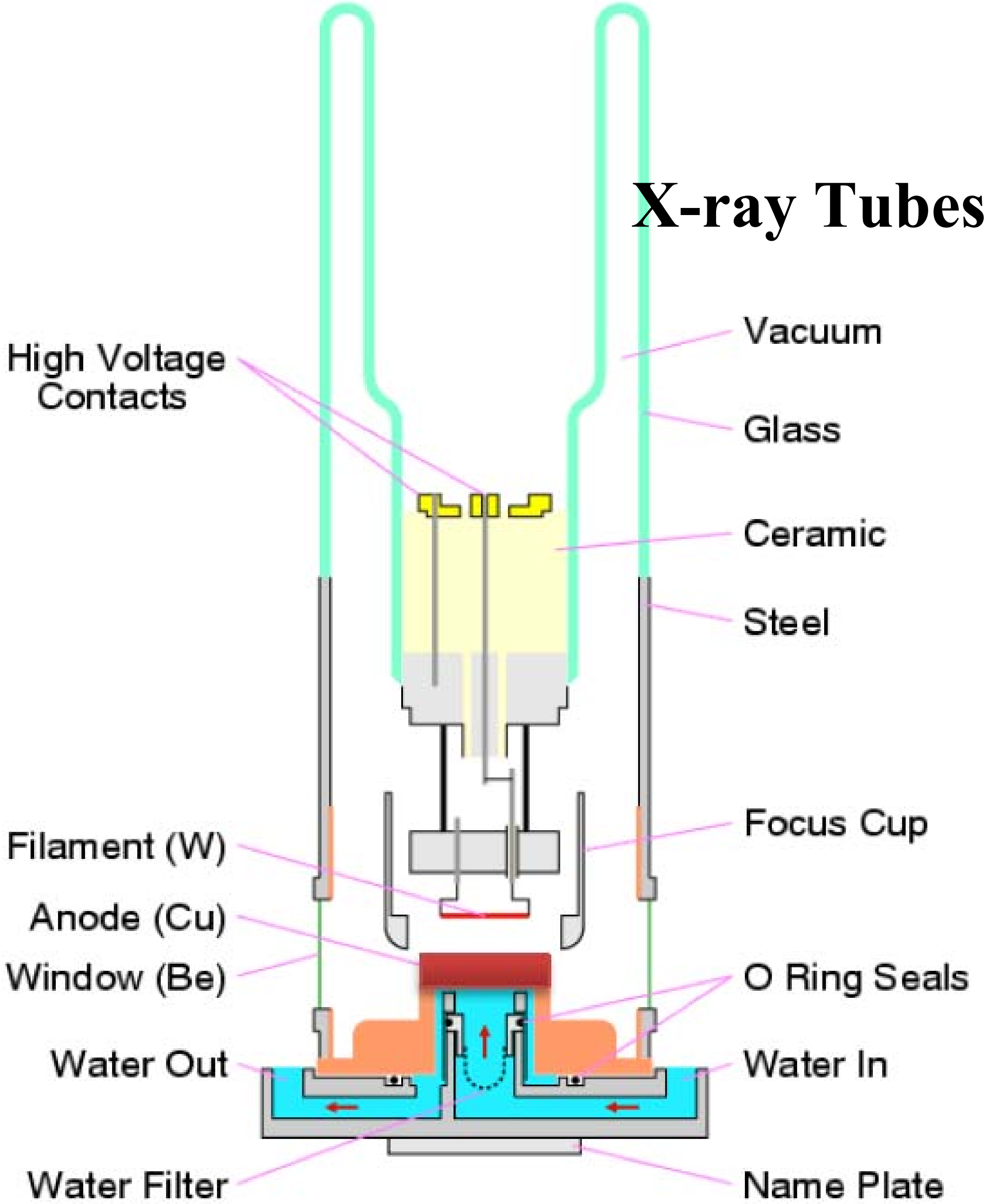
X-ray wavelength is comparable to atomic distances

X-ray Tubes



SCHEMATIC CROSS SECTION OF AN X-RAY TUBE

X-ray Tubes



Tungsten wire
1200 - 1800 °C
Filament current: 2 - 3 A

High Voltage 20 - 60 kV
Electronic current: 30 - 40 mA

Power 0.6 - 3 kW
(1% converted to X-ray,
99% to heat)

Typical operating values

Cu: 40 kV, 35 mA

Mo: 45 kV, 35 mA

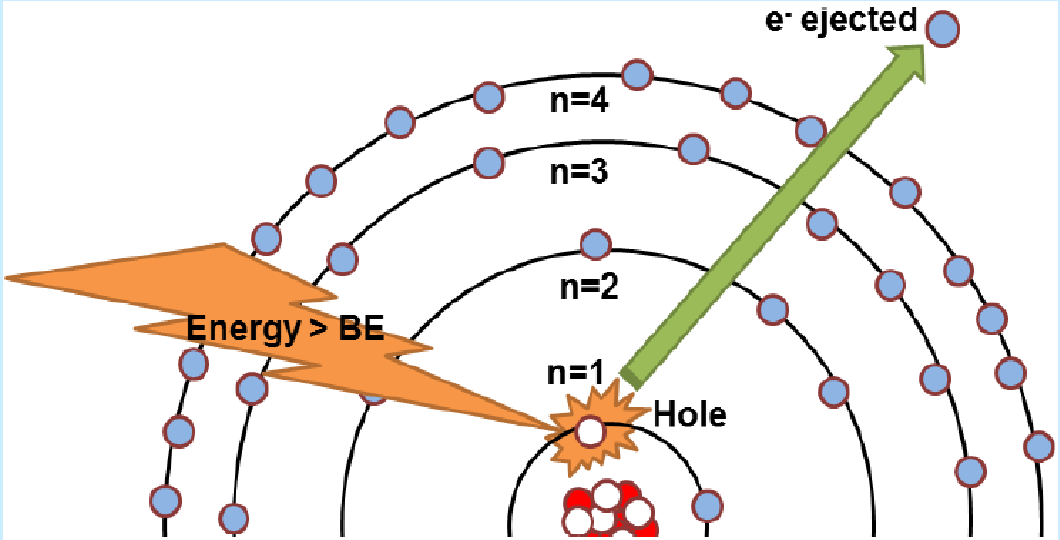
Interaction of Electrons with Matter

Emission of electromagnetic radiation:
- Characteristic radiation, discrete energies
- Bremsstrahlung, continuous energy distribution
- Luminiscence (UV or visible region)

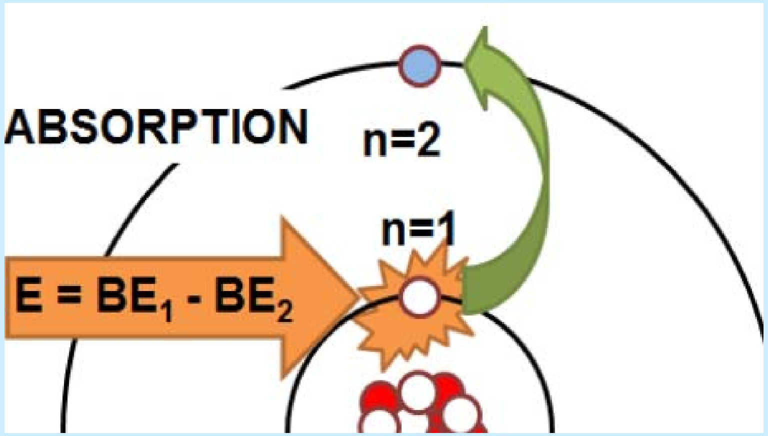
Electron emission:
- Backscattered electrons (BSE)
- Auger electrons
- Secondary electron emission (SE)

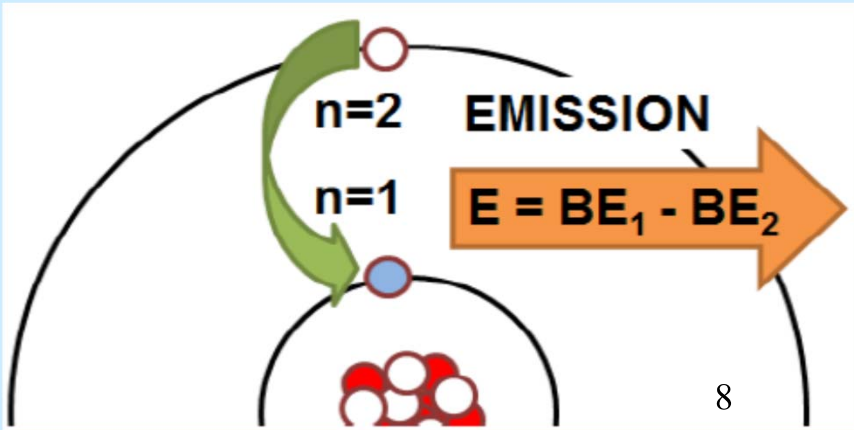
Effects in the Target:
- Electron Absorption (ABS)
- Heat

Interaction of Electrons with Matter



Binding Energy = energy needed to remove an electron from its energy level
BE increases (absolute value) for energy levels closer to the nucleus and in atoms with higher Z





Spectrum of an X-ray Tube

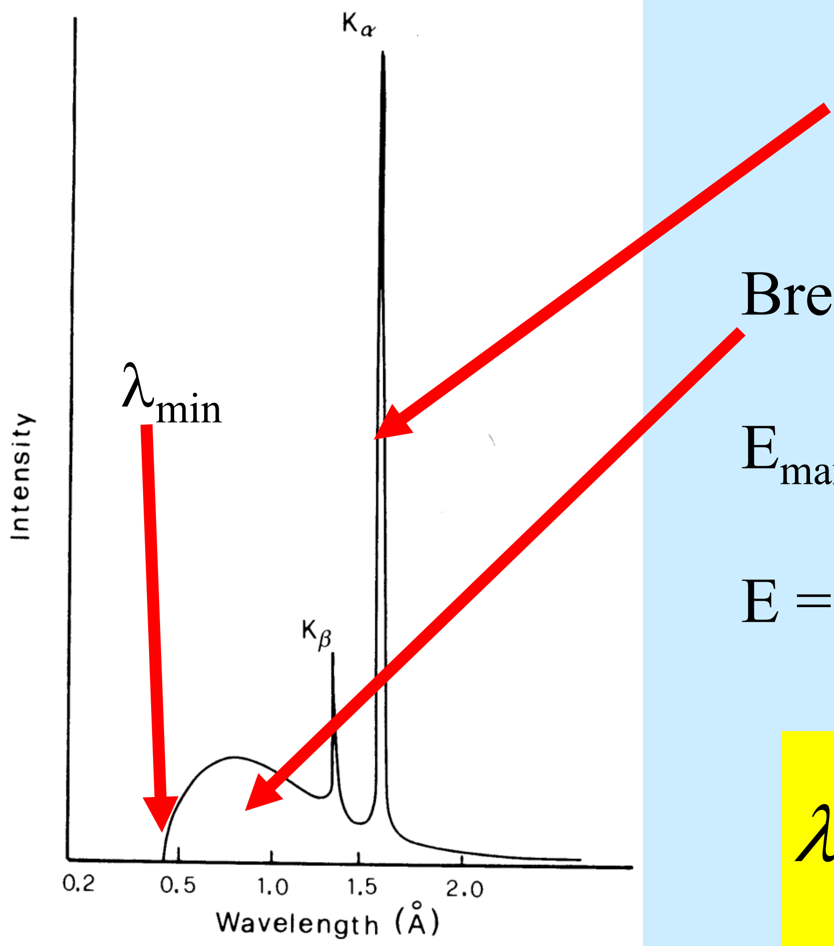


Fig. 4.2. Characteristic spectrum of copper superimposed on the white radiation spectrum. Notice the ratio of the relative intensities of the K_α and K_β lines.

Characteristic radiation

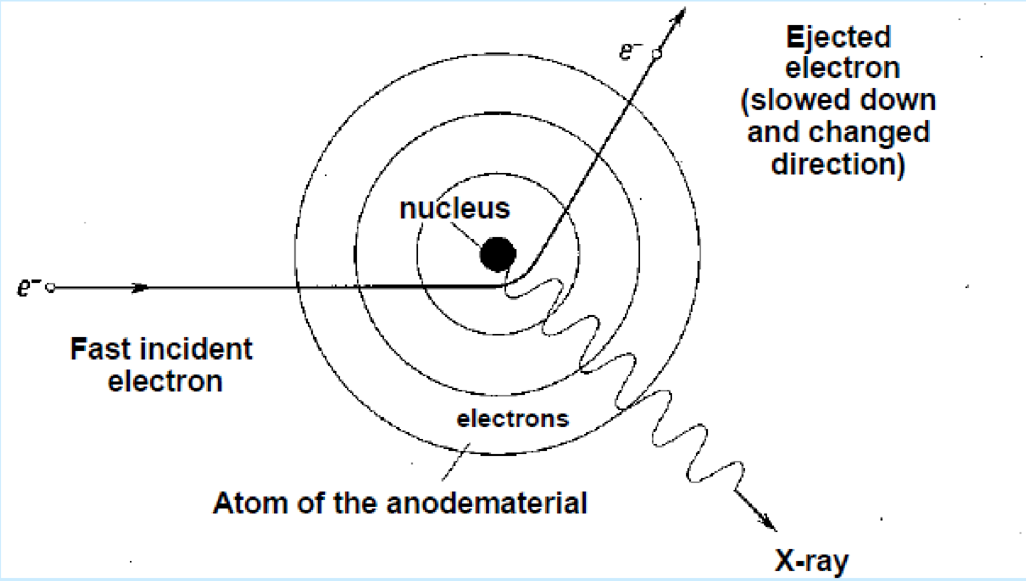
Bremstrahlung (white radiation)

$E_{max} = E_0 = e \times V_0$

$E = (h \times c) / \lambda$

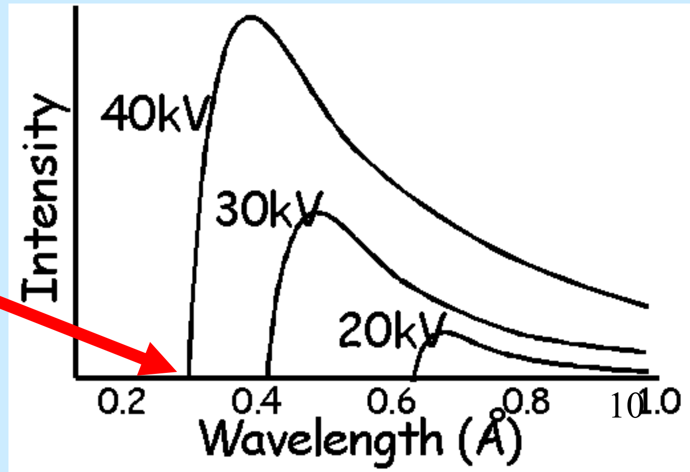
$$\lambda_{min}(\mathrm{nm}) = \frac{hc}{eV_0} = \frac{1.2398}{V_0(\mathrm{kV})}$$

Spectrum of an X-ray Tube

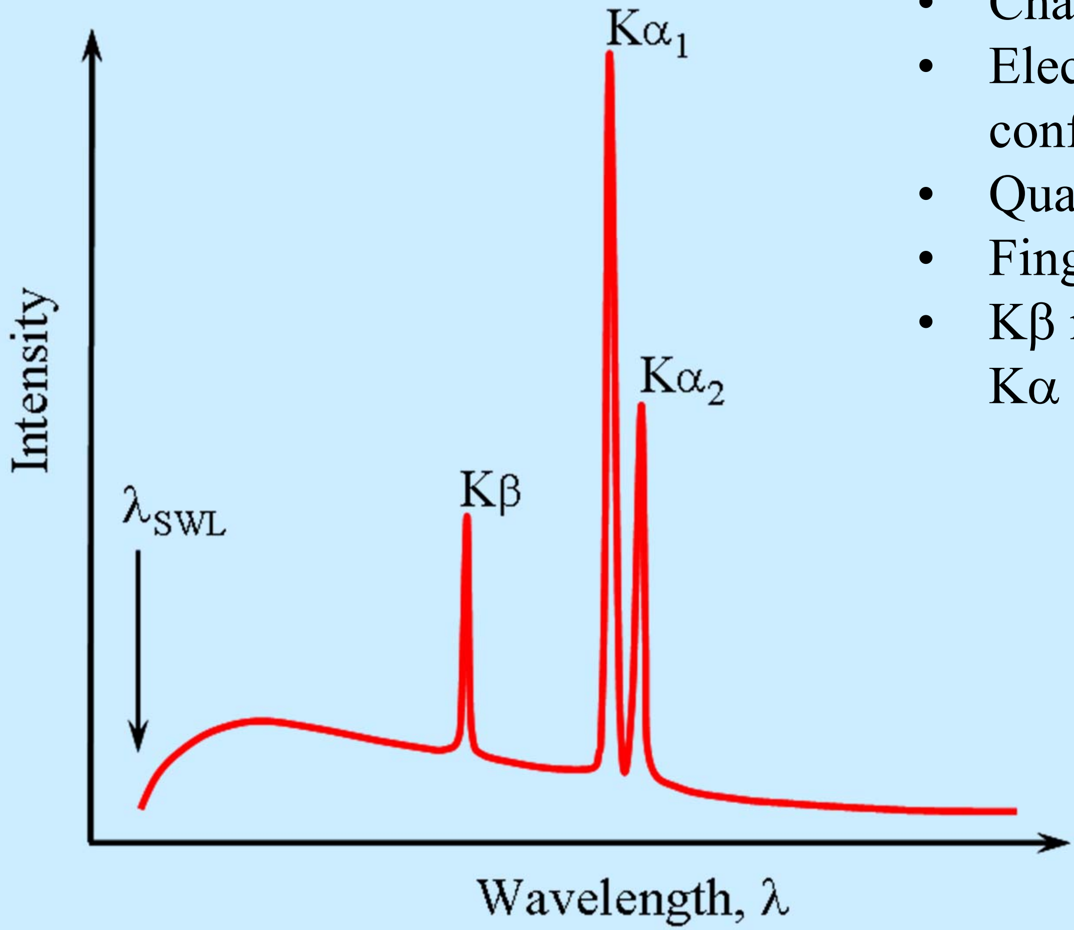


Bremstrahlung
(white radiation - continuous)
Electrons hit target surface,
loose energy, stop
no change of target electron
configuration
Removed by filtering

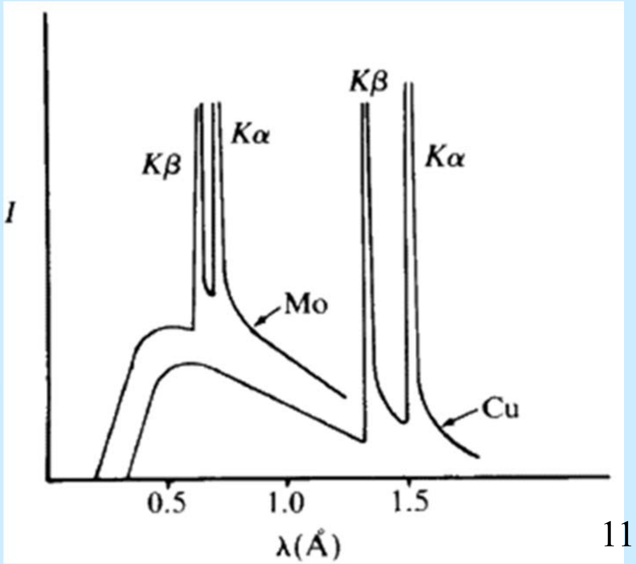
$$\lambda_{\min}(\text{nm}) = \frac{1.2398}{V_0(\text{kV})}$$



Spectrum of an X-ray Tube

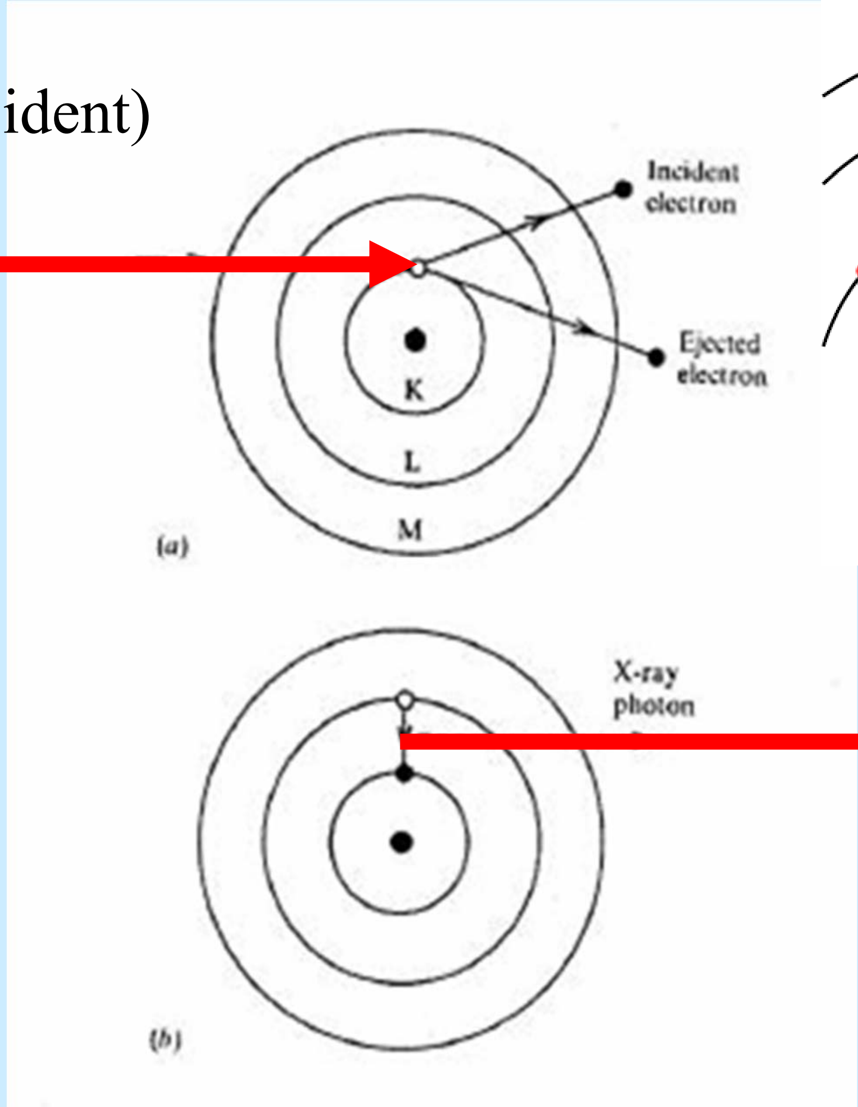


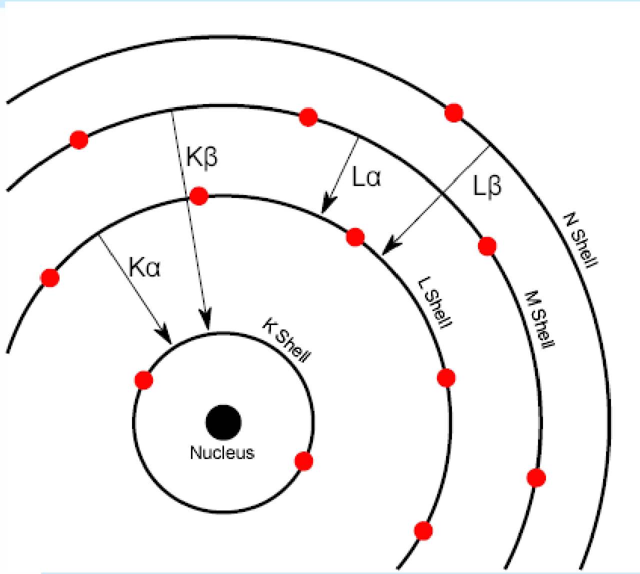
- Characteristic radiation
- Electrons interact with target electron configuration
- Quantized energy
- Fingerprint of target metal
- Kβ radiation has more energy than Kα radiation



Characteristic X-ray Radiation

Primary (incident) electron





X-ray (fluorescence) photon K_α

Wavelengths of Characteristic X-Radiation

Copper Anodes	Bearden (1967)	Holzer et al. (1997)		Cobalt Anodes	Bearden (1967)	Holzer et al. (1997)
Cu Kα1	1.54056Å	1.540598 Å		Co Kα1	1.788965Å	1.789010 Å
Cu Kα2	1.54439Å	1.544426 Å		Co Kα2	1.792850Å	1.792900 Å
Cu Kβ	1.39220Å	1.392250 Å		Co Kβ	1.62079Å	1.620830 Å
Molybdenum Anodes				Chromium Anodes		
Mo Kα1	0.709300Å	0.709319 Å		Cr Kα1	2.28970Å	2.289760 Å
Mo Kα2	0.713590Å	0.713609 Å		Cr Kα2	2.293606Å	2.293663 Å
Mo Kβ	0.632288Å	0.632305 Å		Cr Kβ	2.08487Å	2.084920 Å

- Often quoted values from Cullity (1956) and Bearden, *Rev. Mod. Phys.* **39** (1967) are incorrect.
  - Values from Bearden (1967) are reprinted in *International Tables for X-Ray Crystallography* and most XRD textbooks.
- Most recent values are from Hölzer et al. *Phys. Rev. A* **56** (1997)
- Has your XRD analysis software been updated?

Selection Rules

- n = 1, 2, 3…. principal quantum numbers,
  correspond to K, L, M... shells

- l = 0, 1, ..., n – 1 …orbital quantum numbers: s, p, d, f,...

- j =| l ± s|;   s = 1/2   spin-orbit coupling

- m_j = j, j – 1, j – 2, ..., – j

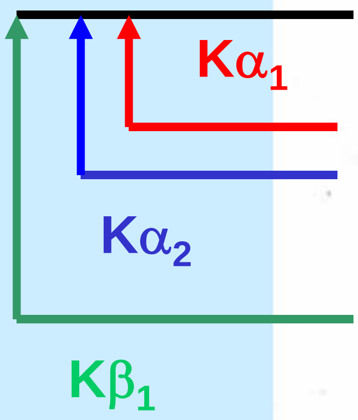
Transition only, when :

$$\Delta n \geq 1, \qquad \Delta l = \pm 1, \qquad \Delta j = 0 \text{ or } \pm 1$$

$$\Delta n \geq 1, \qquad \Delta l = \pm 1, \qquad \Delta j = 0 \text{ or } \pm 1$$

Selection Rules

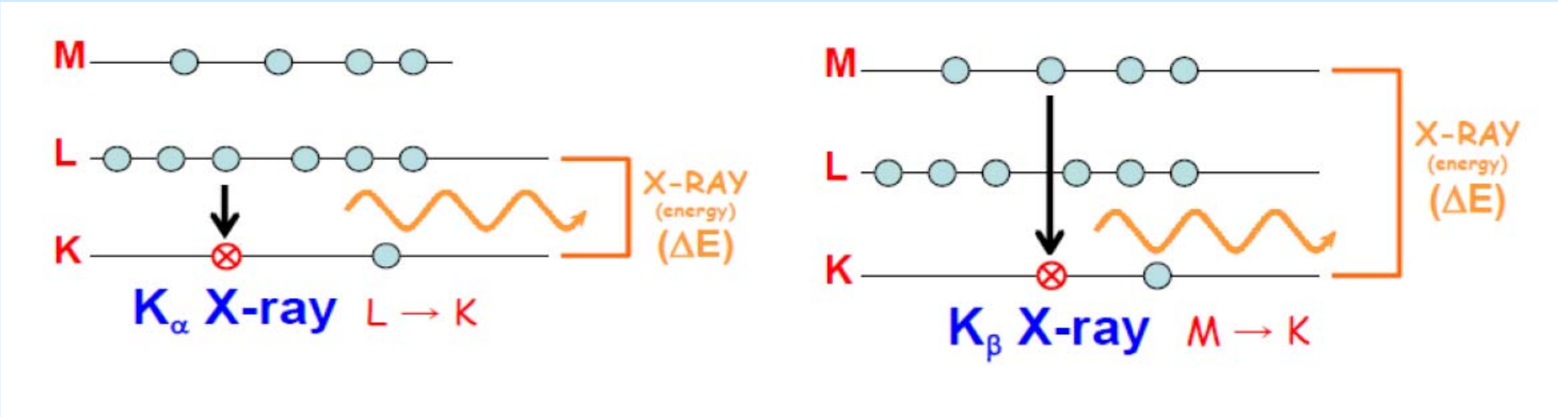
$M = 2J + 1$

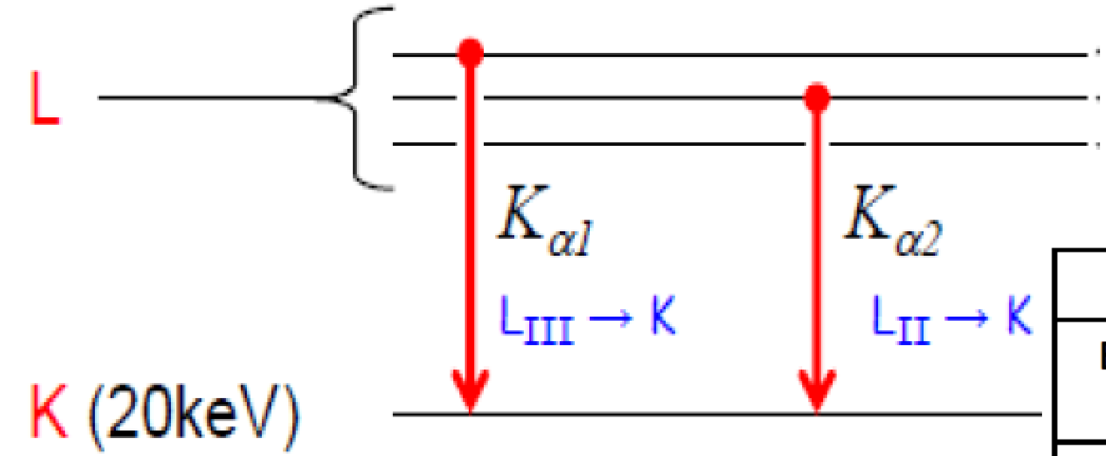


X-ray notation	Quantum numbers				Maximum electron population
	n	l	j	m_j	
K	1	0	$\frac{1}{2}$	$\pm\frac{1}{2}$	2
L_I	2	0	$\frac{1}{2}$	$\pm\frac{1}{2}$	2
L_{II}	2	1	$\frac{1}{2}$	$\pm\frac{1}{2}$	2
L_{III}	2	1	$\frac{3}{2}$	$\pm\frac{3}{2}, \pm\frac{1}{2}$	4
M_I	3	0	$\frac{1}{2}$	$\pm\frac{1}{2}$	2
M_{II}	3	1	$\frac{1}{2}$	$\pm\frac{1}{2}$	2
M_{III}	3	1	$\frac{3}{2}$	$\pm\frac{3}{2}, \pm\frac{1}{2}$	4
M_{IV}	3	2	$\frac{3}{2}$	$\pm\frac{3}{2}, \pm\frac{1}{2}$	4
M_V	3	2	$\frac{5}{2}$	$\pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2}$	6
N_I	4	0	$\frac{1}{2}$	$\pm\frac{1}{2}$	2
N_{II}	4	1	$\frac{1}{2}$	$\pm\frac{1}{2}$	2
N_{III}	4	1	$\frac{3}{2}$	$\pm\frac{3}{2}, \pm\frac{1}{2}$	4
N_{IV}	4	2	$\frac{3}{2}$	$\pm\frac{3}{2}, \pm\frac{1}{2}$	4
N_V	4	2	$\frac{5}{2}$	$\pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2}$	6
N_{VI}	4	3	$\frac{5}{2}$	$\pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2}$	6
N_{VII}	4	3	$\frac{7}{2}$	$\pm\frac{7}{2}, \pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2}$	8

2s → 1s ?

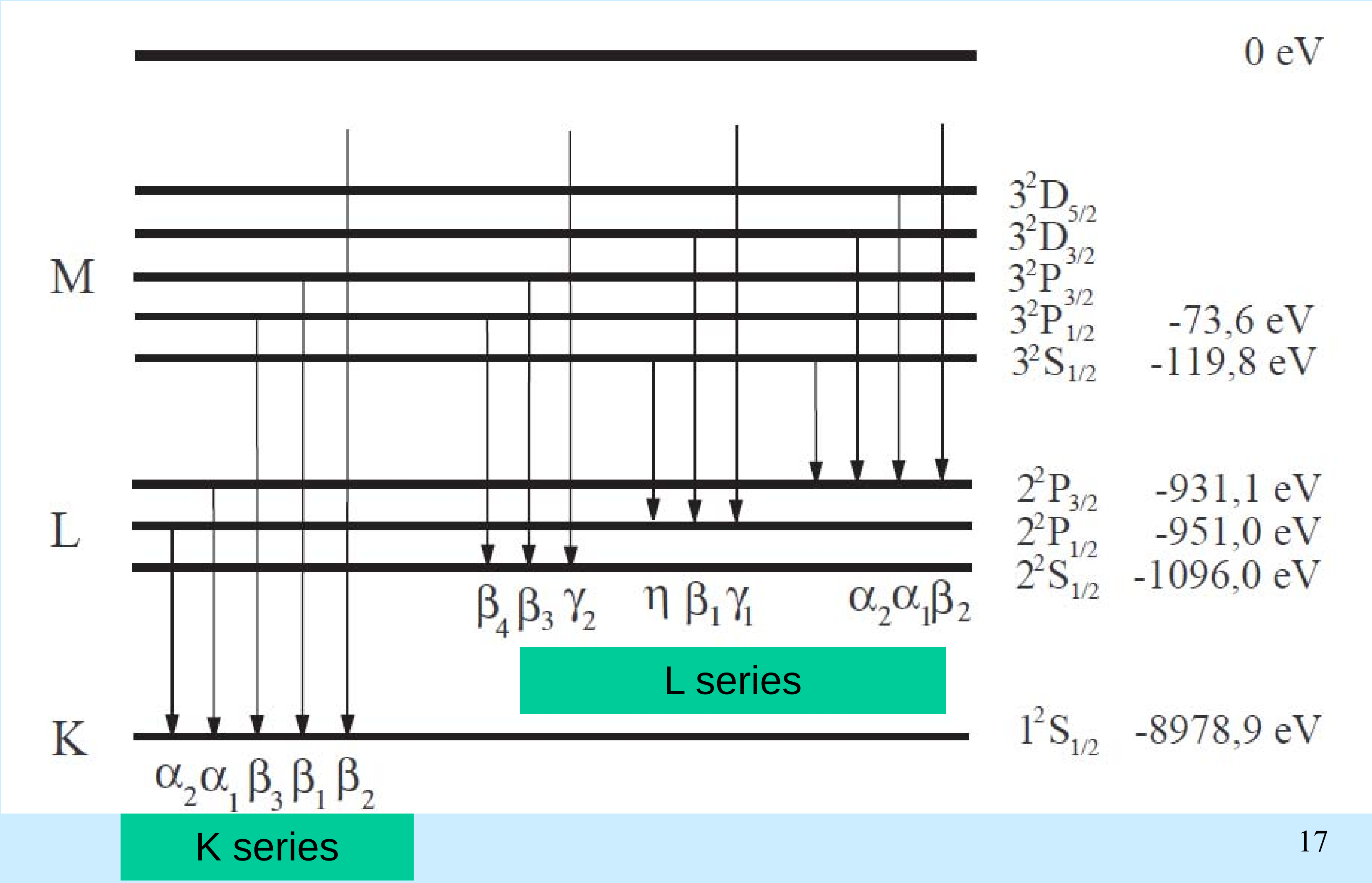
Characteristic X-ray Radiation



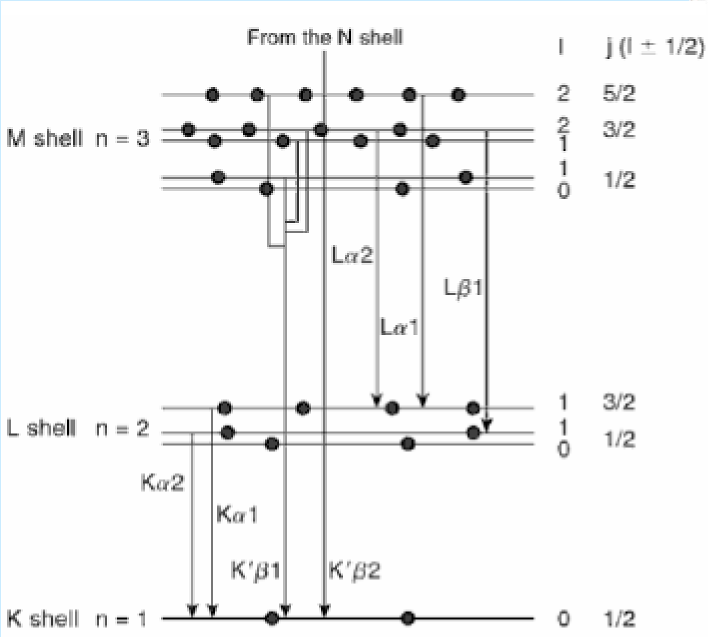


Cu	$K_{\alpha1}$	$K_{\alpha2}$	k_{β}
E [kev]	8.047	8.027	8.907
λ [Å]	1.5406	1.5444	1.3922
Intensity	100	50	15

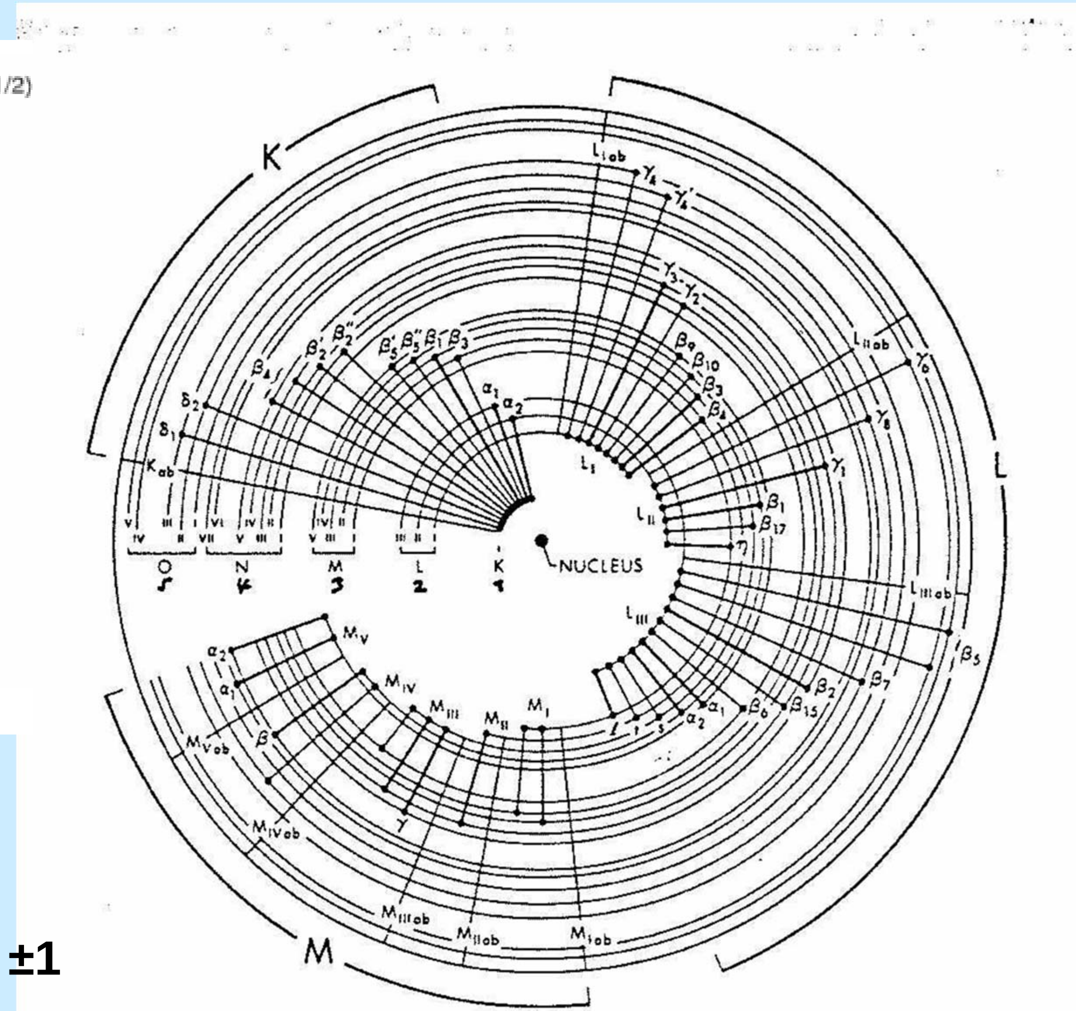
Copper (Z = 29) X-ray Lines



Allowed Transitions



Siegbahn notation



$\Delta n \geq 1$, $\Delta l = \pm 1$, $\Delta j = 0$ or ± 1

Characteristic Wavelengths as a Function of Z

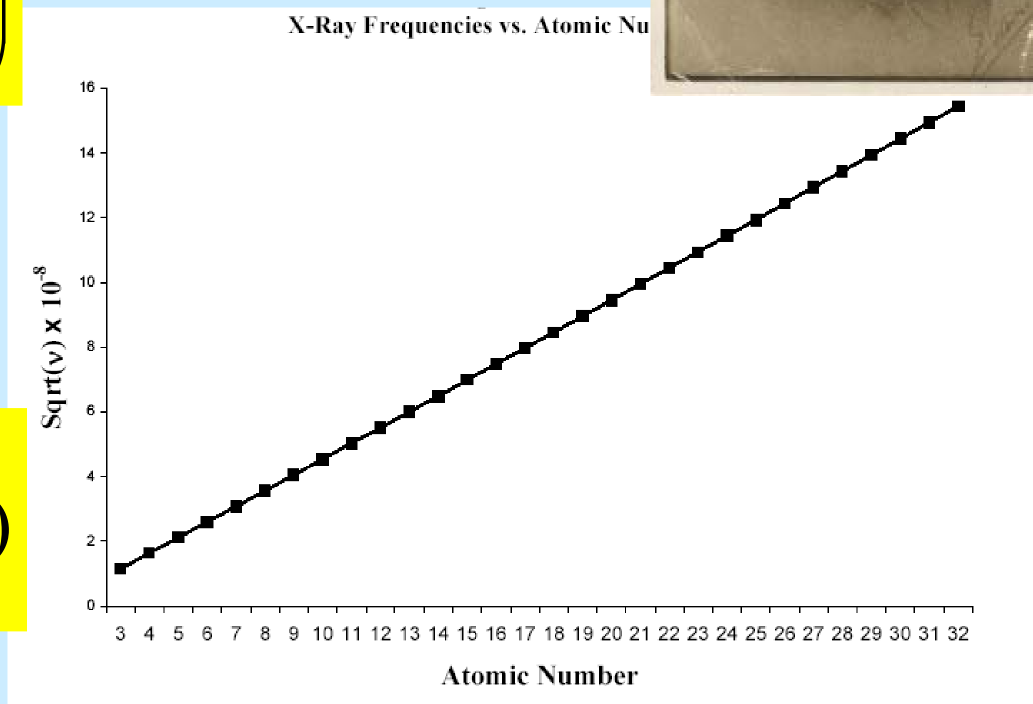
Element (Z)	$K_{\alpha 2}$	$K_{\alpha 1}$	K_{β}	K abs. edge
Cu (29)	1.54433	1.54051	1.39217 1.38102	1.380
Mo (42)	0.713543	0.70926	0.62099	0.61977
Ag (47)	0.563775	0.559363	0.49701 0.48701	0.4858
W (74)	0.213813	0.208992	0.17950	0.17837

Mosley's Law
(for multiple electron atoms)

$$\frac{1}{\lambda} = c(Z-\sigma)^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

- Z = atomic number
- σ = shielding constant
- n = quantum number

$$\sqrt{\nu(K_\alpha)} = \sqrt{\frac{3}{4}R(Z-1)}$$



Decreasing wavelength λ with increasing Z

Interaction of X-rays with Matter

X-ray interaction modality with matter depends on:
• the X-ray energy, E, of the incident beam
• the atomic number Z of the sample

Low energy X-ray (~10 keV) used in XRD interacts with matter by:

• **Absorption**: X-rays transfer energy to the sample (electronic transitions)
Photoelectric Effect (low E and high Z)

• **Scattering**: X-ray is deflected in all direction from is original path with or without energy loss

Rayleigh - Coherent Scattering (very low E)

Compton - Incoherent Scattering (middle E and low Z)

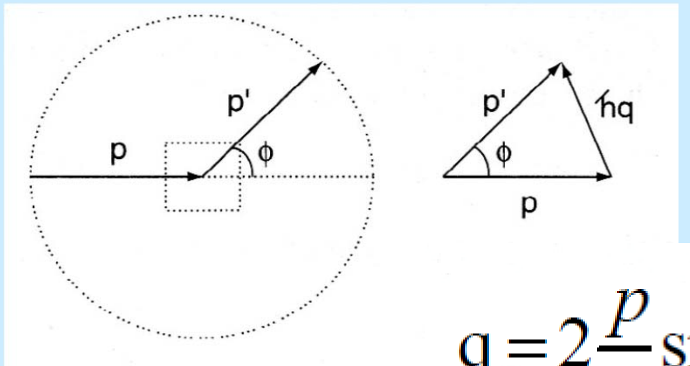
Scattering

Scattering is the process in which waves or particles are forced to deviate from a straight trajectory because of *scattering centers* in the propagation medium.

X-rays scatter by interaction with the electron density of a material.
Neutrons are scattered by nuclei and by any magnetic moments.
Electrons are scattered by electric/magnetic fields.

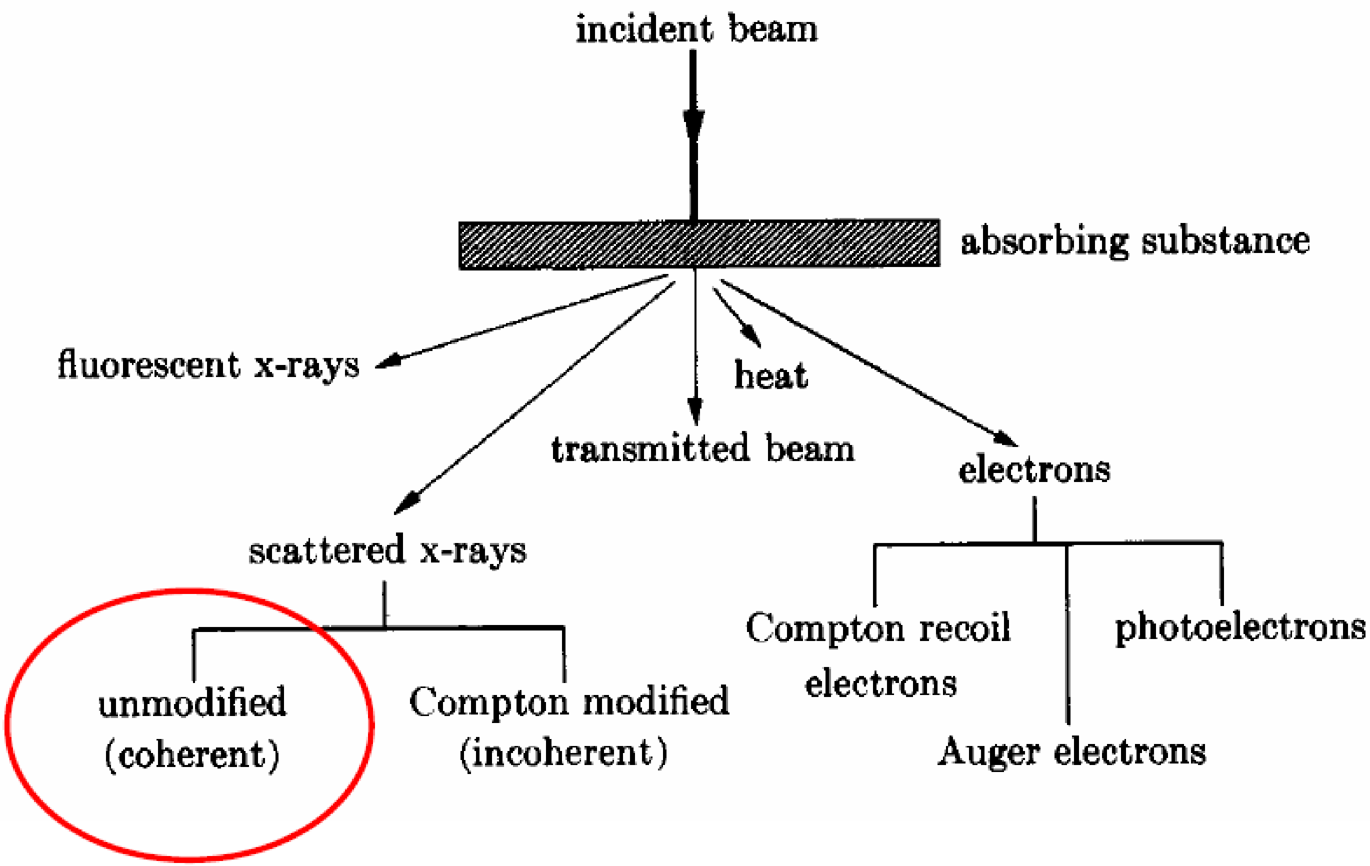
Elastic
Rayleigh ($\lambda >> d_{object}$)
Mie ($\lambda \approx d_{object}$)
Geometric ($\lambda << d_{object}$)
Thompson (X-rays)
Inelastic
Compton (photons + electrons)
Brillouin (photons + quasiparticles)
Raman (photons + molecular vib./rot.)

Momentum transfer:
$\mathbf{p'} - \mathbf{p} = (h/2\pi)\mathbf{q}$



$$q = 2\frac{p}{\hbar}\sin\frac{\phi}{2}$$

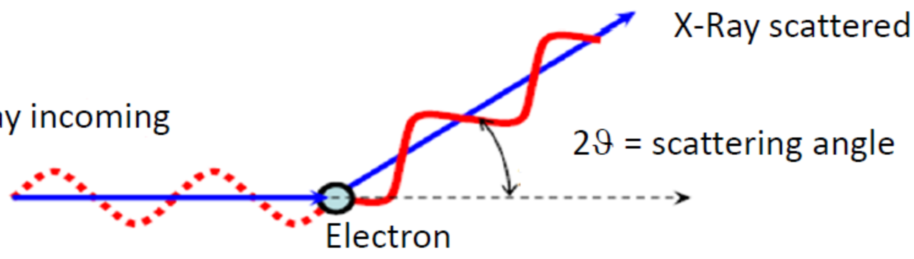
Interaction of X-rays with Matter

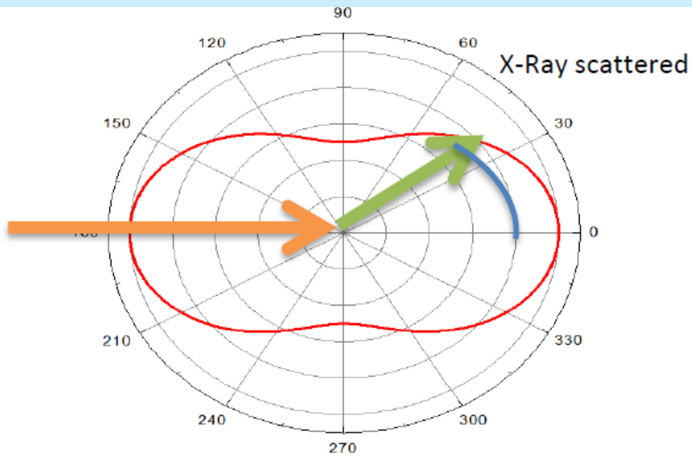


These are the diffracted X-rays

Rayleigh Scattering

Elastic scattering = charged particles (electrons) scatter electromagnetic radiation (x-rays), incident X-ray does not lose energy. The varying electric field of the X-ray induces oscillations of the electron which then acts as a source of electromagnetic radiation, an X-ray with the **same energy** is re-emitted, the x-rays are scattered in all directions.





$$I(2\theta) = I_0 \frac{e^4}{m^2c^4} \frac{1}{r^2} \frac{1+(\cos 2\vartheta)^2}{2}$$

Incoming X-ray Intensity

$I \propto {}^1/_{m^2}$ -> p^+ scatter much less than e^-:
X-Rays are scattered mainly by electrons

Polarization term: angular distribution of scattering intensity

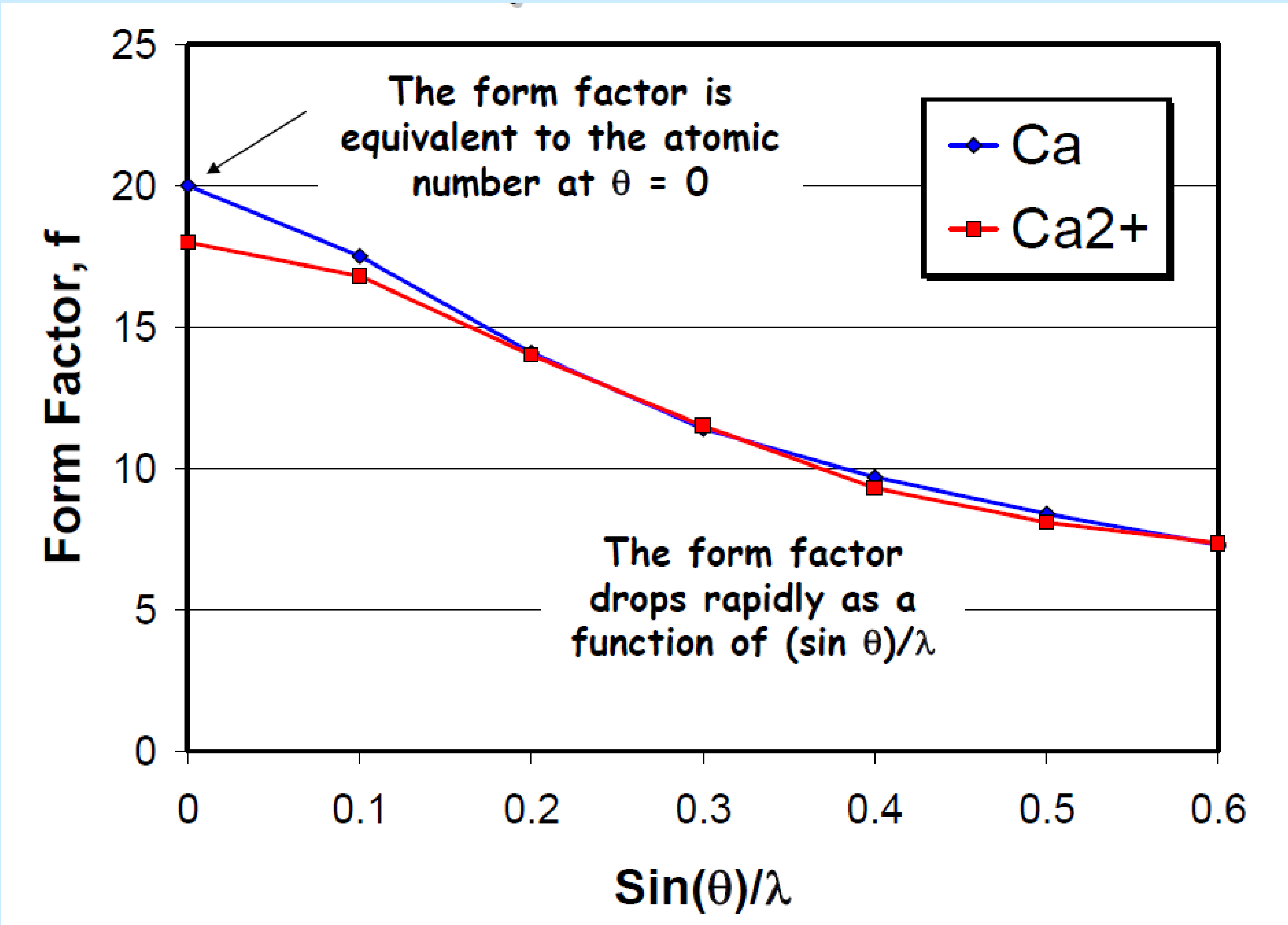
Scattering by an Atom

An atom = a collection of electrons
The electrons around an atom scatter X-ray radiation
Due to the coherence of the radiation - interference effects from different electrons within an atom.

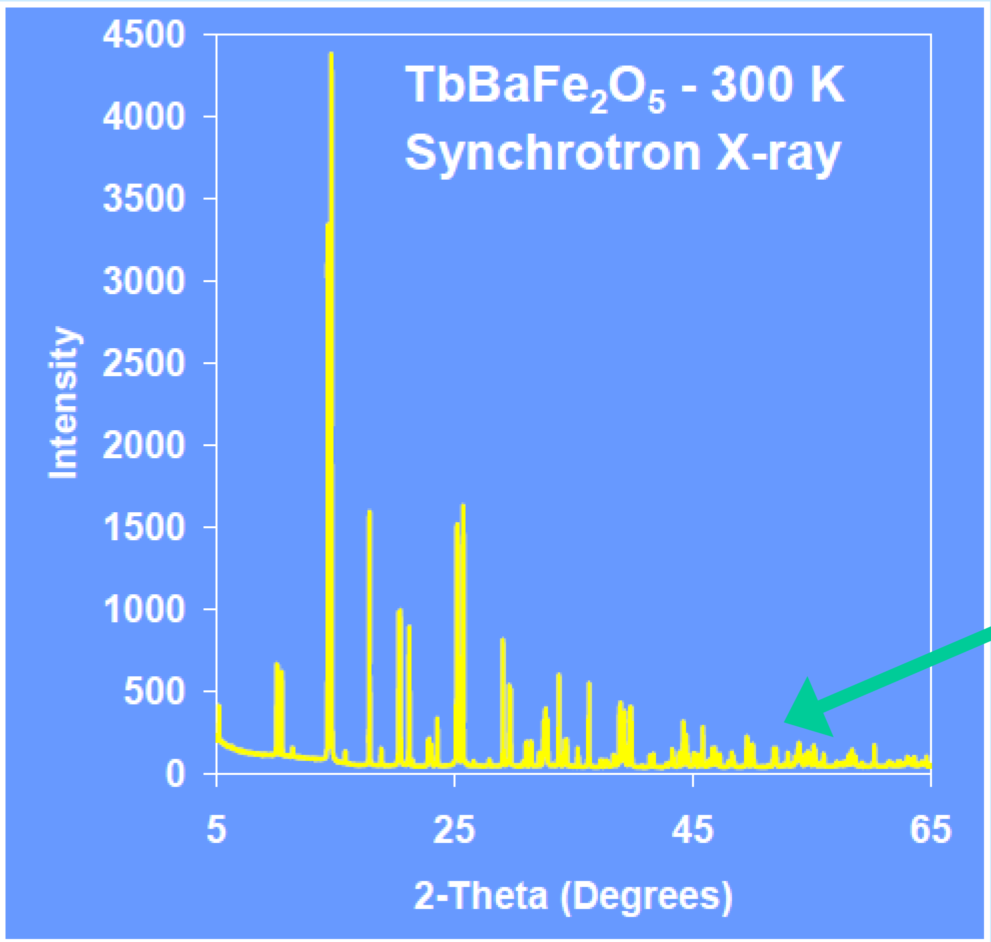
This leads to a strong anglular dependence of the scattering

The scattering power of an atom is expressed by its **form factor (f)**

Scattering by an Atom

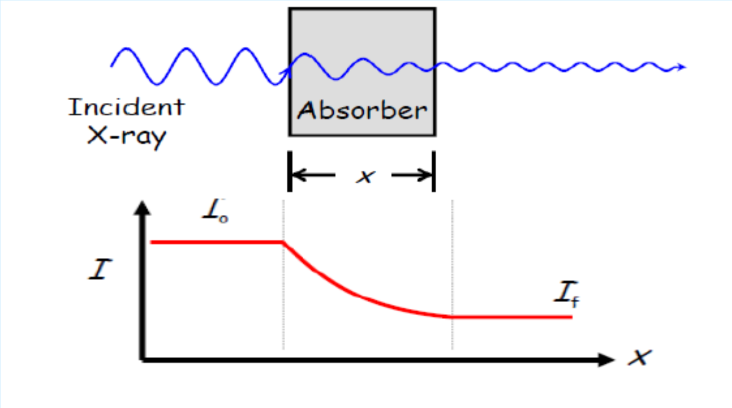


The Effect of Form Factors on Diffraction Patterns



The peak intensities drop off at high angles in an X-ray diffraction pattern because the form factor decreases

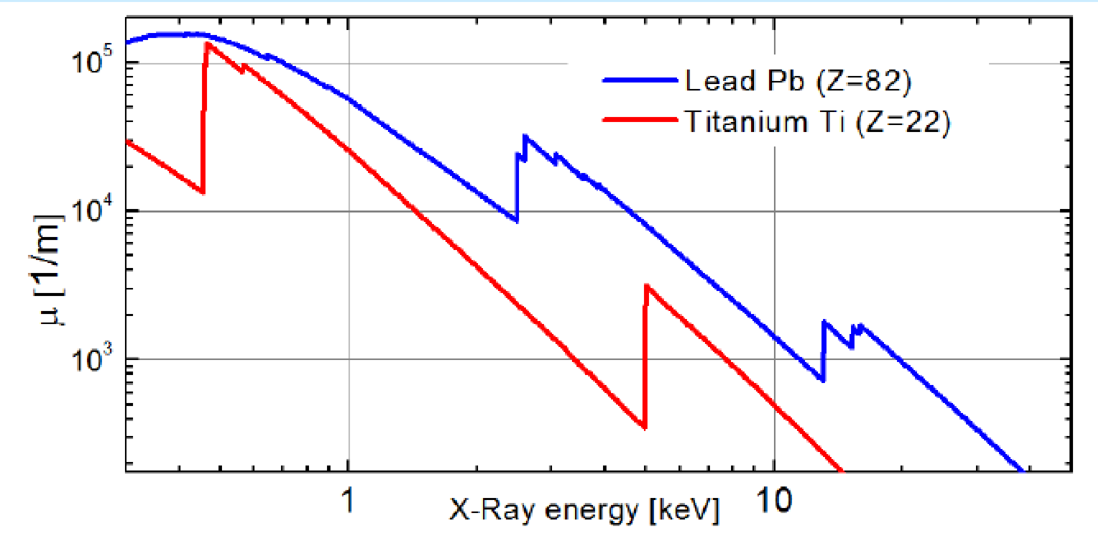
Absorption



X-ray intensity decreases exponentially on passing through matter (Beer's Law)

$$I(x) = I_0 e^{-\mu x}$$

I_0 = initial X-ray intensity [$m^{-1}s^{-1}$]
μ = X-ray absorption coefficient [m^{-1}]
x = penetration depth [m]



μ decreases with increasing X-ray E for a selected absorber Z:

$\mu \sim E^{-3}$

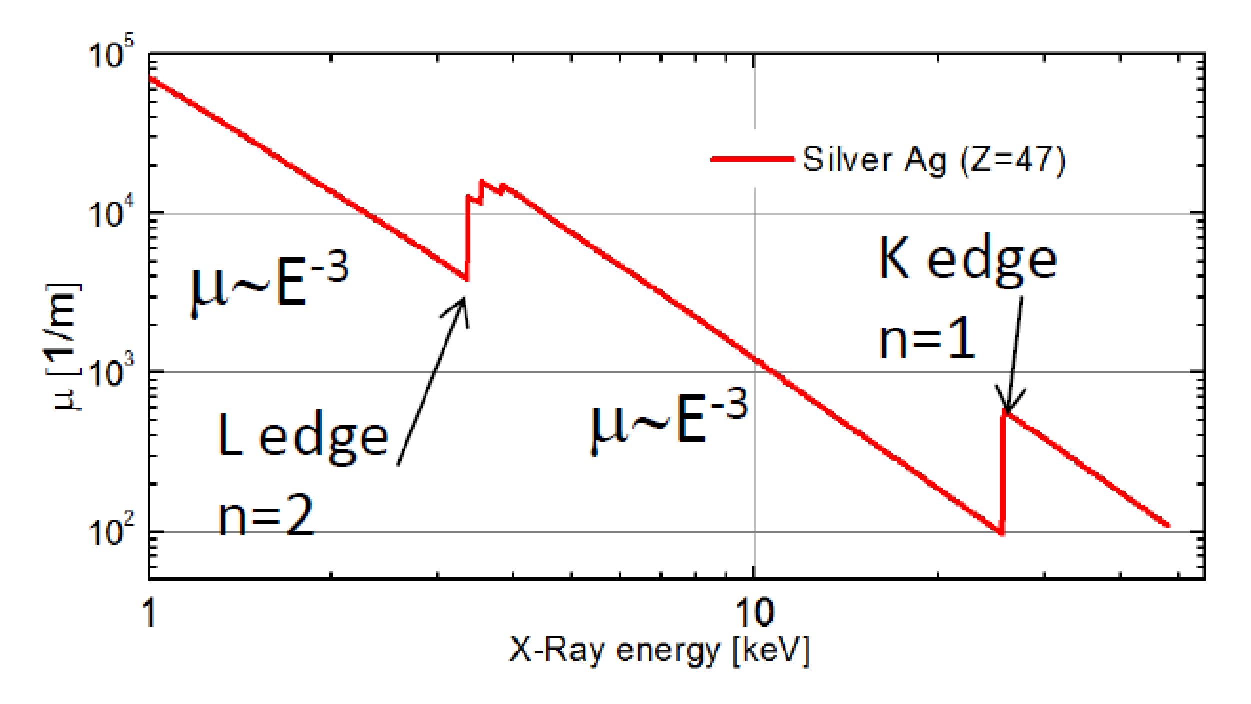
μ increases with increasing Z for a selected X-ray E:

$\mu \sim Z^3$

Photoelectric effect

X-ray is absorbed by material and a photoelectron is ejected. A core-hole is left in the atom.

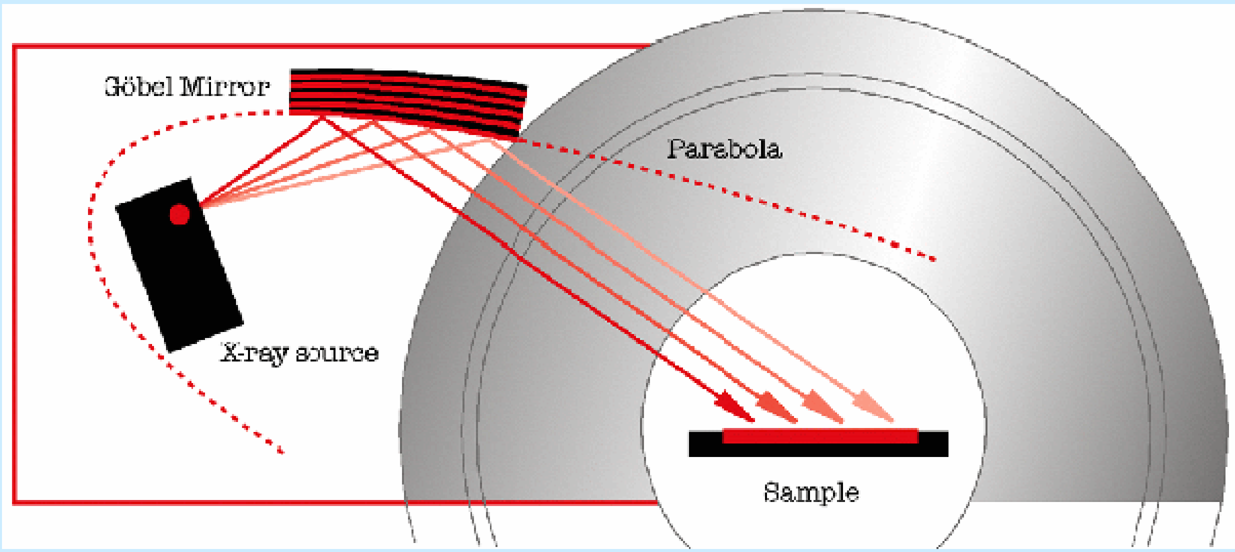
When X-ray energy is equal to the binding energy of an energetic level of the abosorber atom, μ increases suddenly (absorption edge).
K (n=1) L (n=2)….



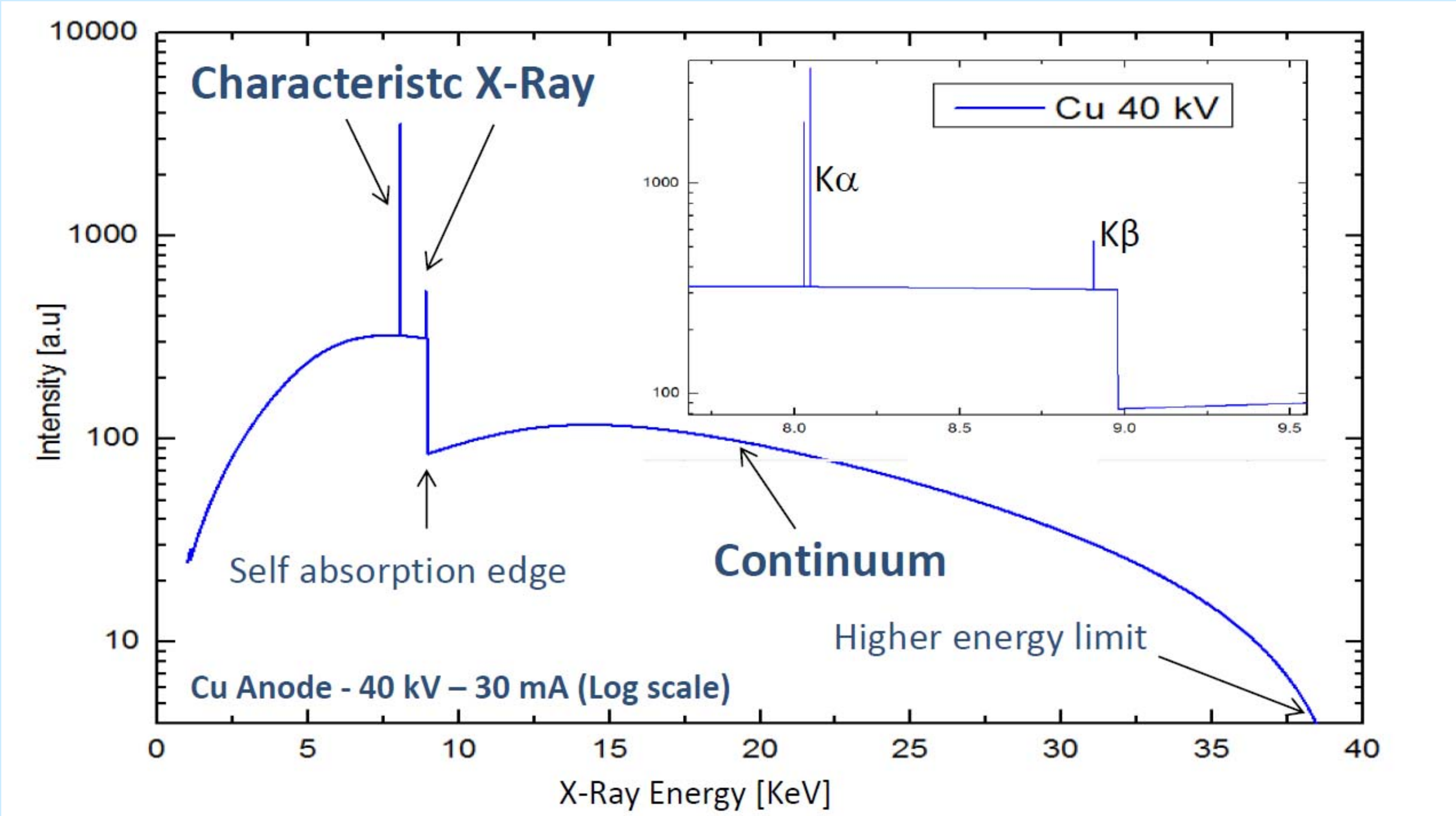
Monochromatisation of X-rays

• Filters - a foil of the next lightest element
Ni filter for Cu K_α
Zr filter for Mo K_α

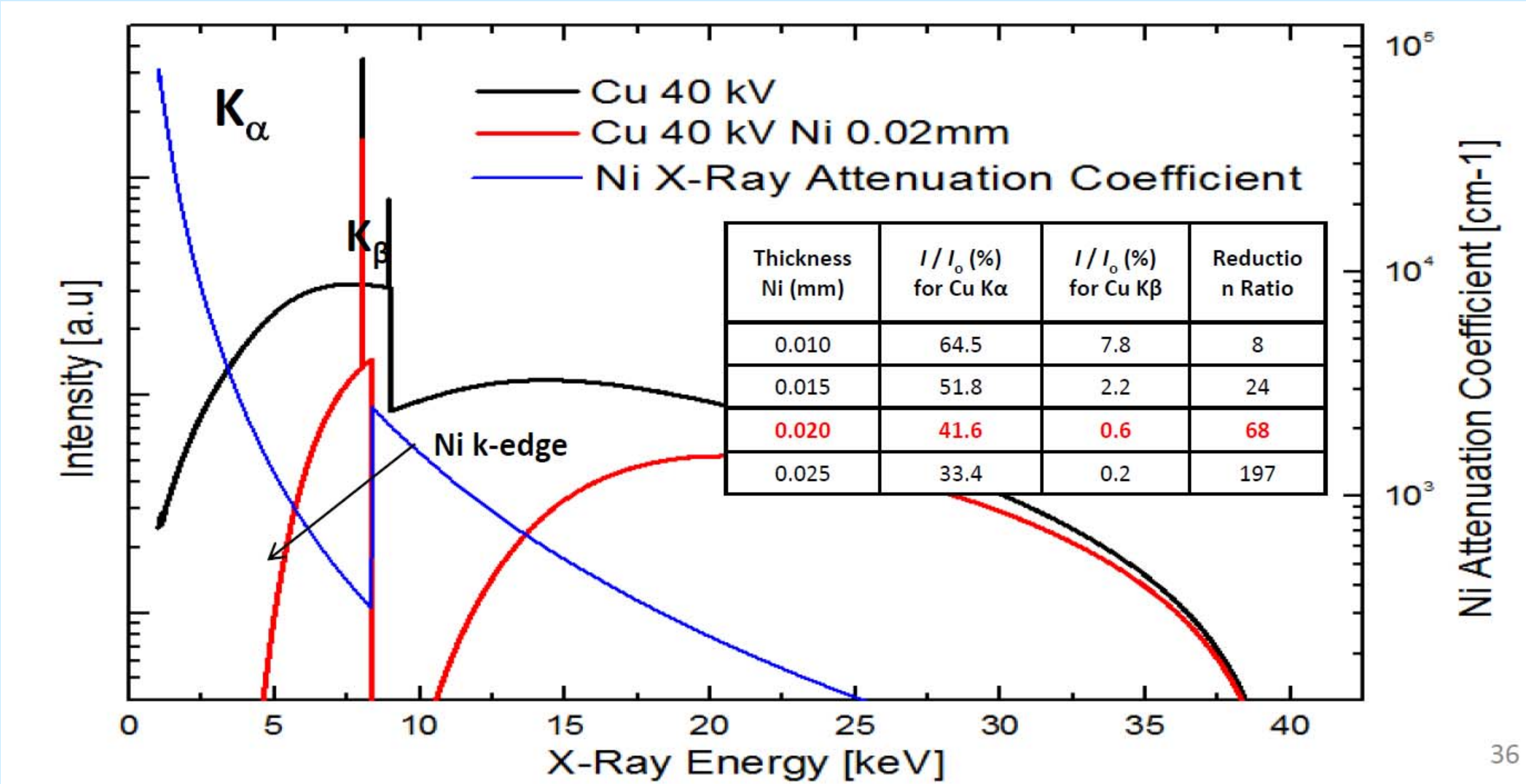
• Crystal Monochromators
diffraction from a curved crystal (or multilayer) to select X-rays of a specific wavelength



Characteristic Wavelengths



Kβ filtering



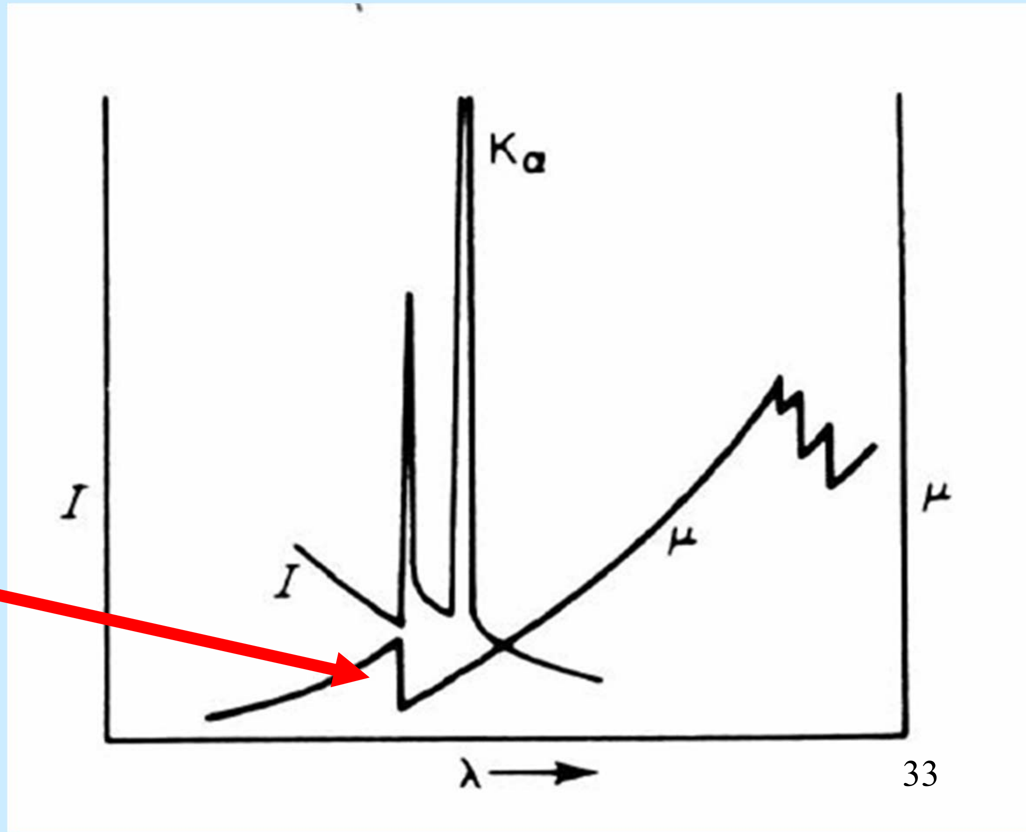
Thickness Ni (mm)	I / I_o (%) for Cu Kα	I / I_o (%) for Cu Kβ	Reductio n Ratio
0.010	64.5	7.8	8
0.015	51.8	2.2	24
0.020	41.6	0.6	68
0.025	33.4	0.2	197

X-ray Absorption

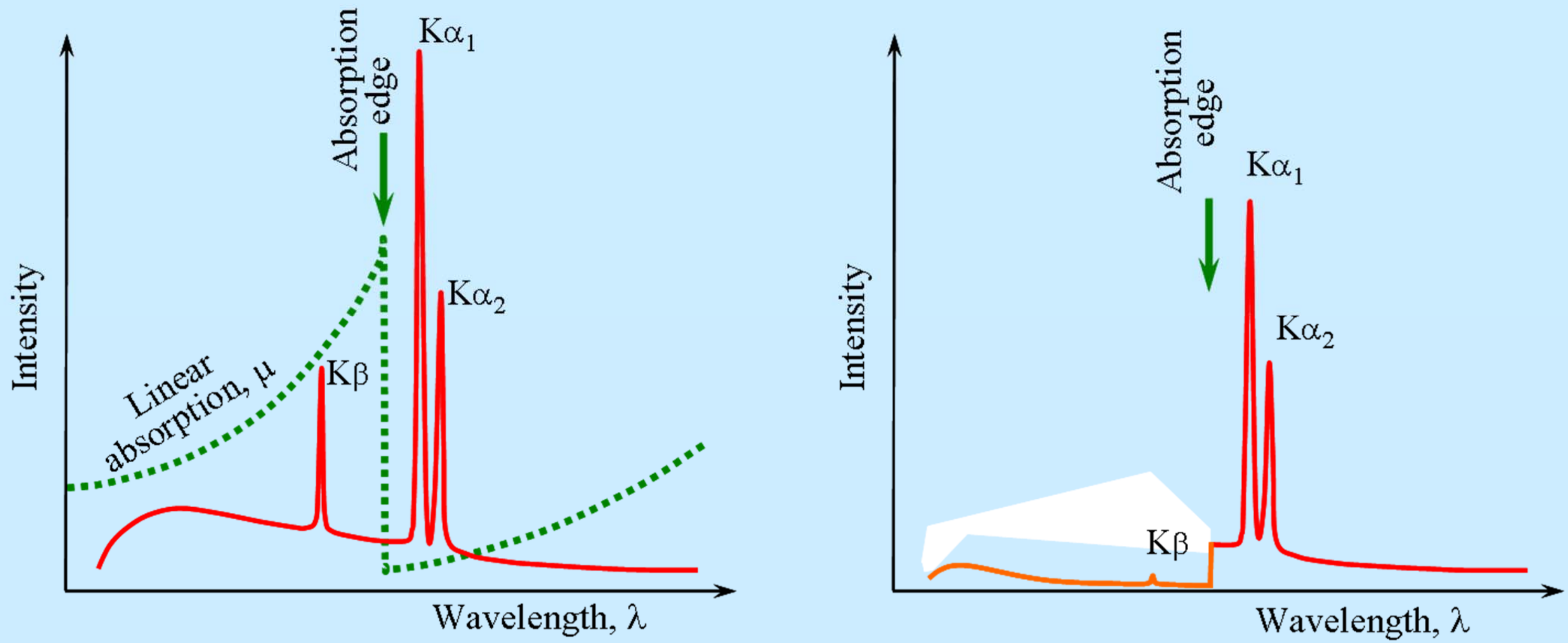
At the absorption edge, the incident X-ray quantum is energetic enough to knock an electron out of the orbital = **Photoelectric effect**

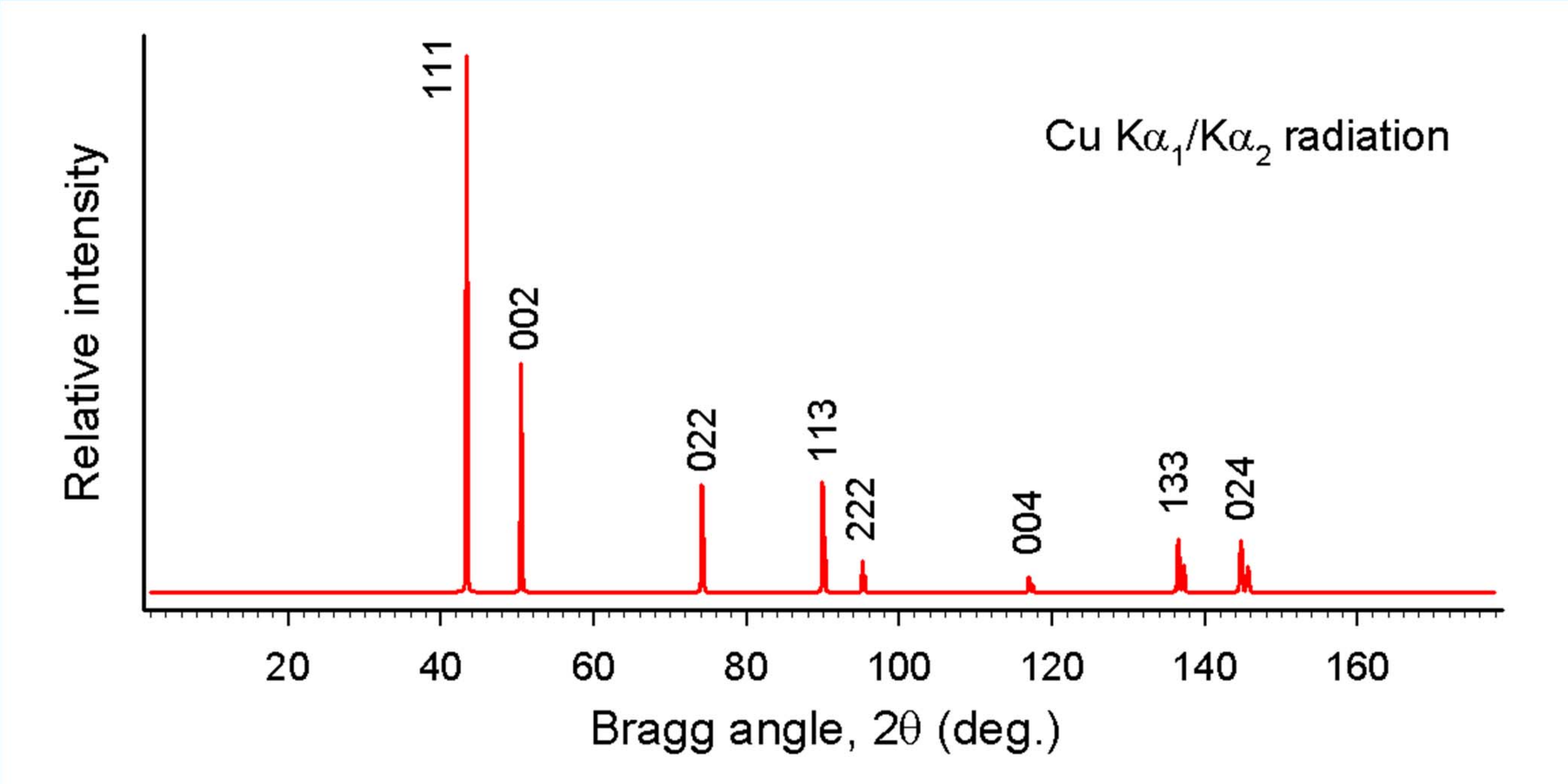
μ = absorption coefficient

Absorption edge

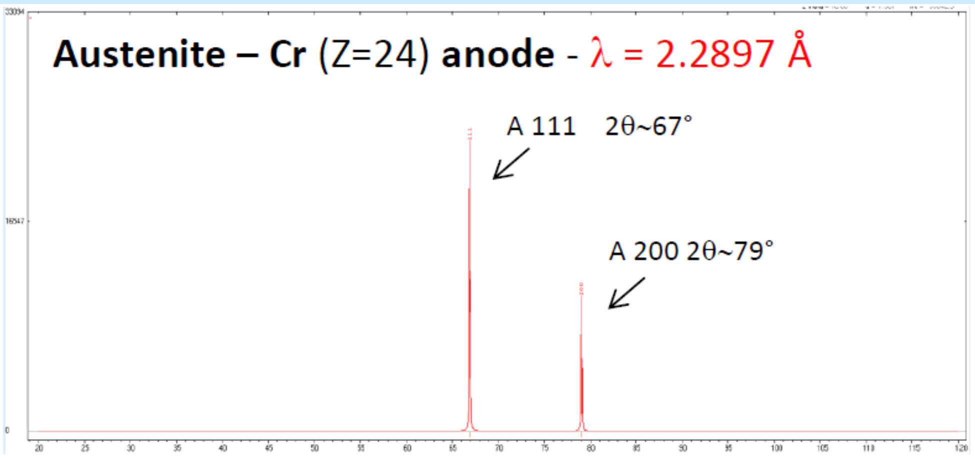


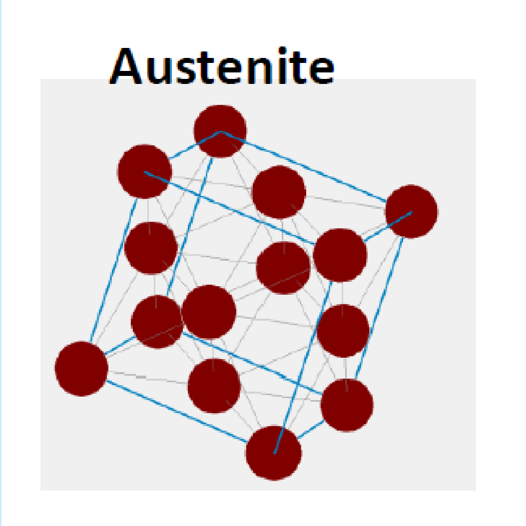
Action of the Ni filter

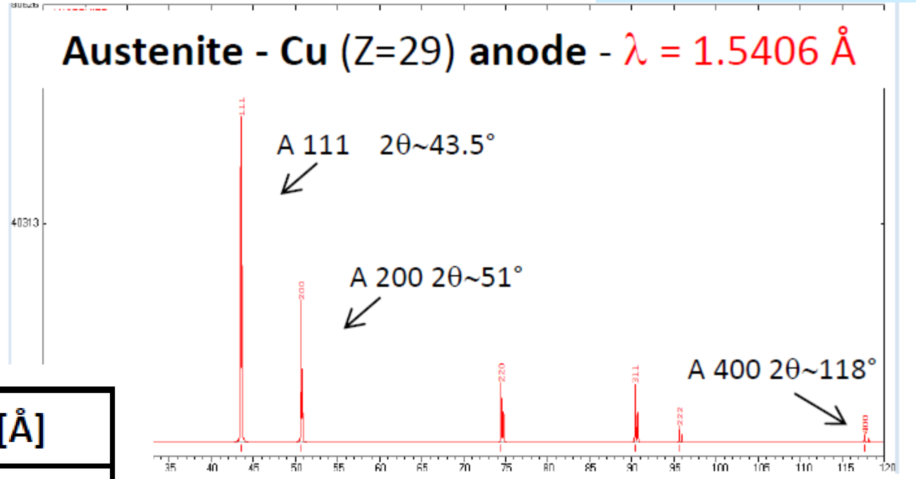




Relative intensity
111
002
022
113
222
004
133
024
Cu Kα1/Kα2 radiation
20
40
60
80
100
120
140
160
Bragg angle, 2θ (deg.)

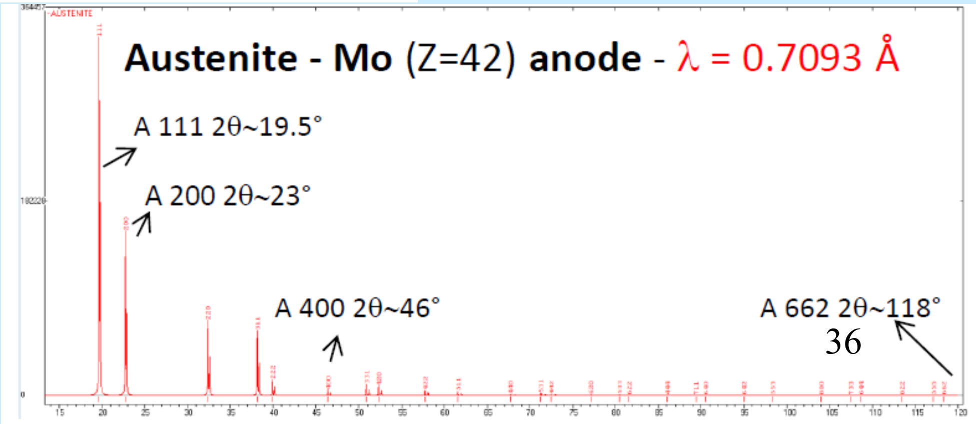






Peak	d [Å]
111	2.078
200	1.8
400	0.9
662	0.413

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



Fluorescence

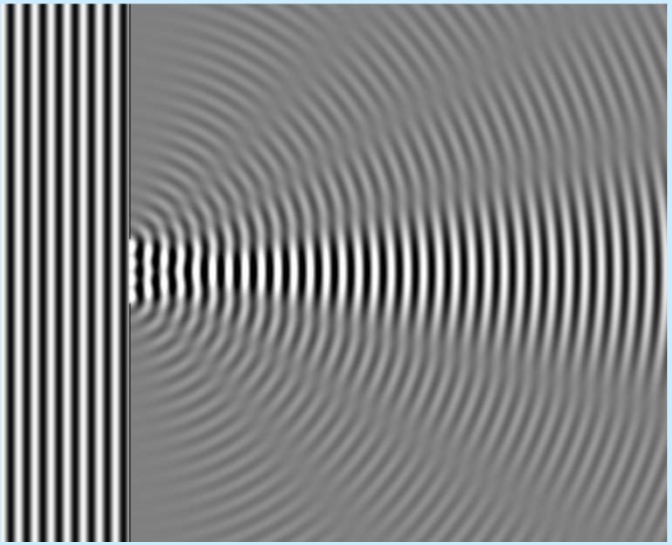
Cathode	Fluorescing elements
Mo	Y, Sr, Rb
Cu	Co, Fe, Mn
Co	Mn, Cr, V
Fe	Cr, V, Ti
Cr	Ti, Sc, Ca

Diffraction

Diffraction = apparent bending of waves around small objects and the spreading out of waves past small apertures.

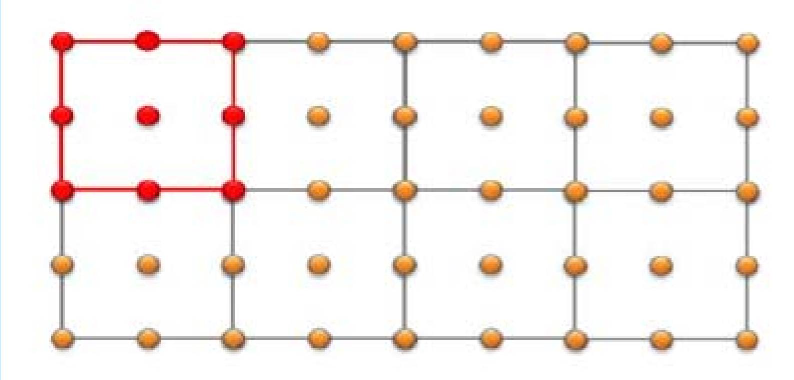
Diffraction = the scattering of a coherent wave by the atoms in a crystal. A diffraction pattern results from interference of the scattered waves.

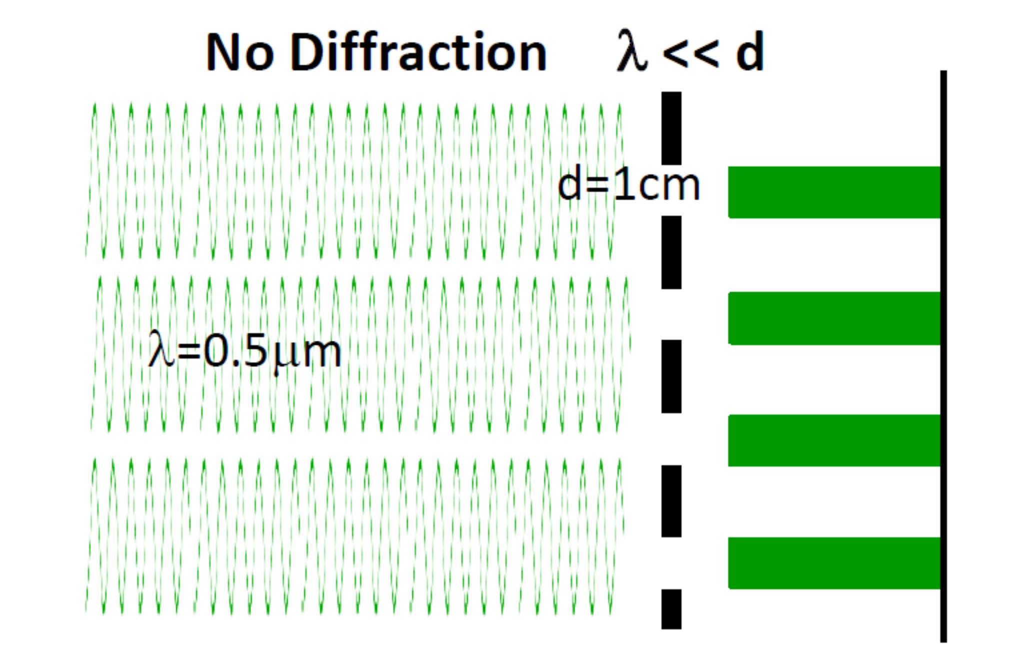
Refraction = the change in the direction of a wave due to a change in its speed.

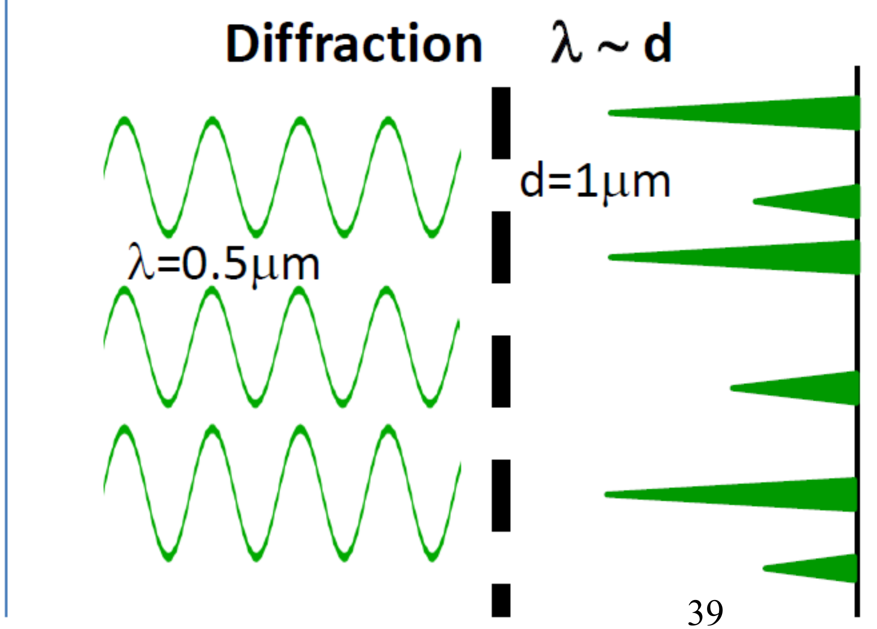


Diffraction

REQUIREMENTS for DIFFRACTION
- Waves
- Sample with periodic structure
- Sample size ~ Wavelenght

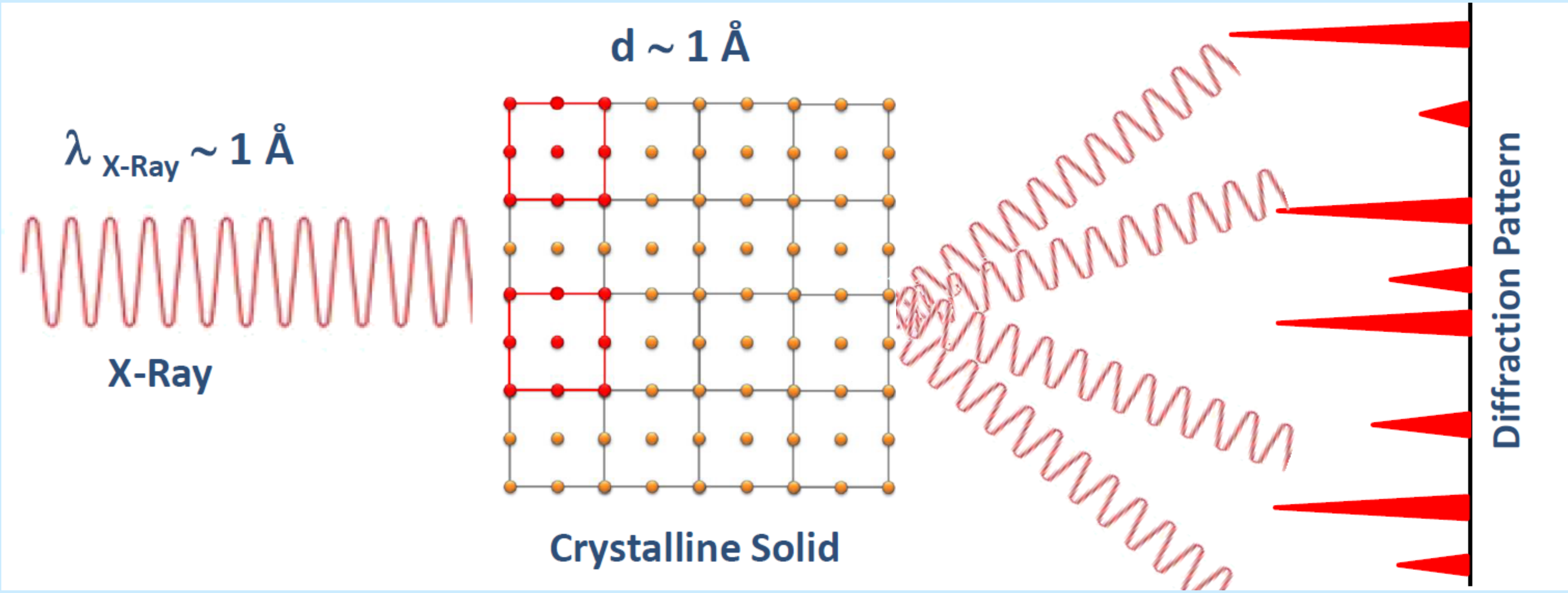




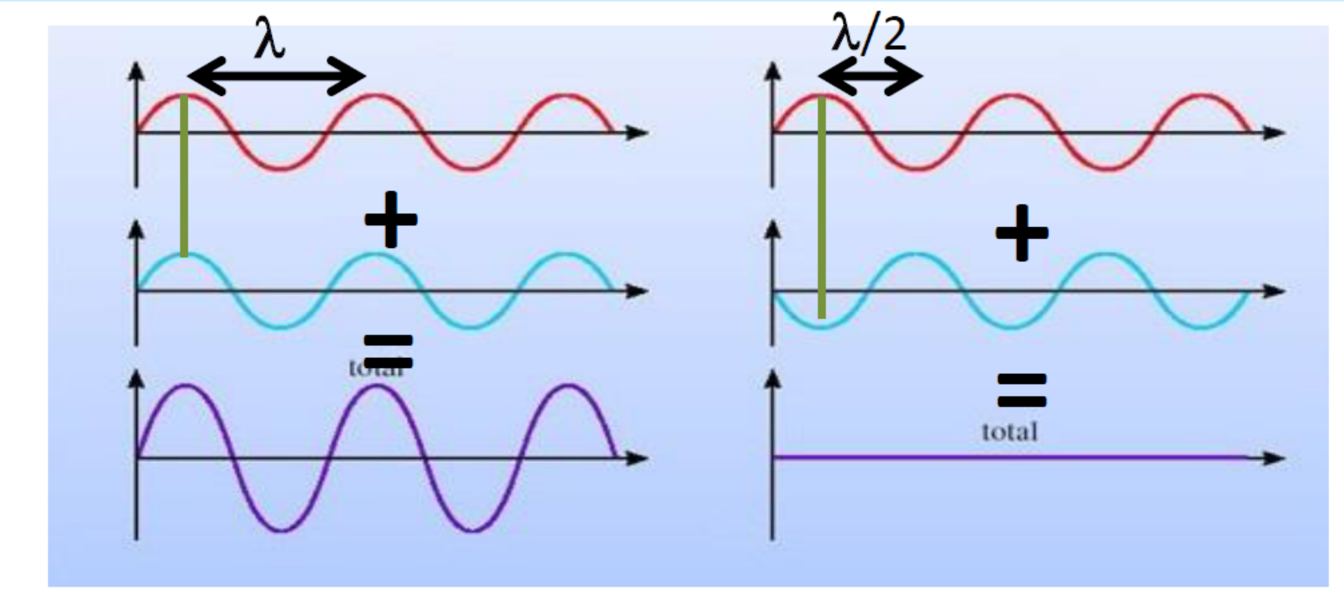


Diffraction

Diffraction occurs when X-Rays are scattered **(Rayleigh)** by a periodic array of atoms with long-range order, producing constructive interference at specific angles

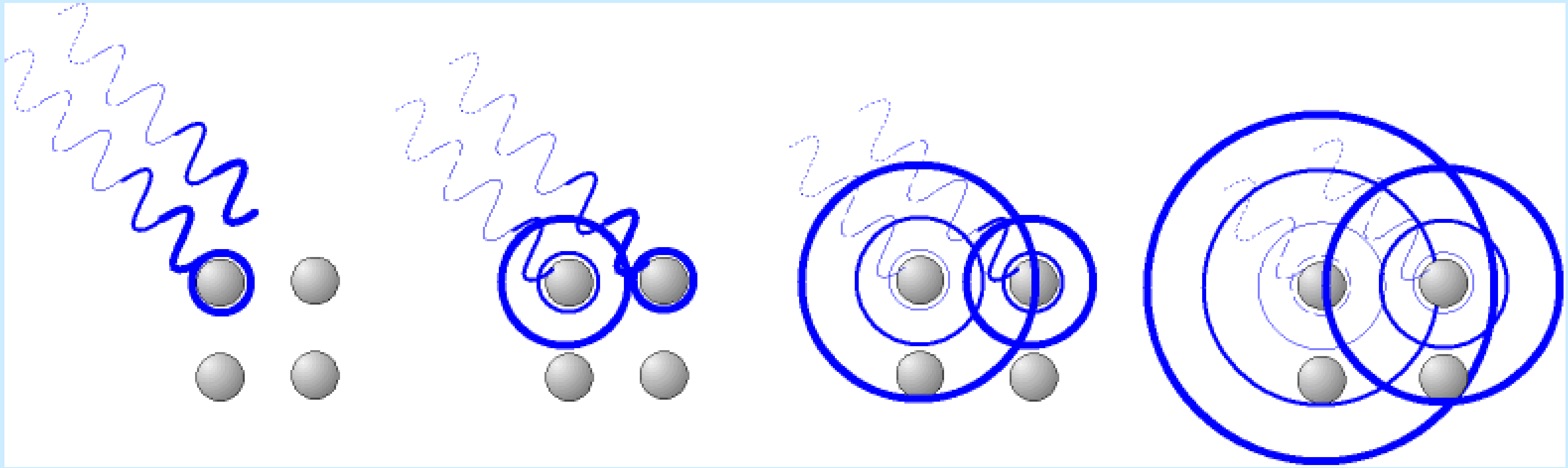


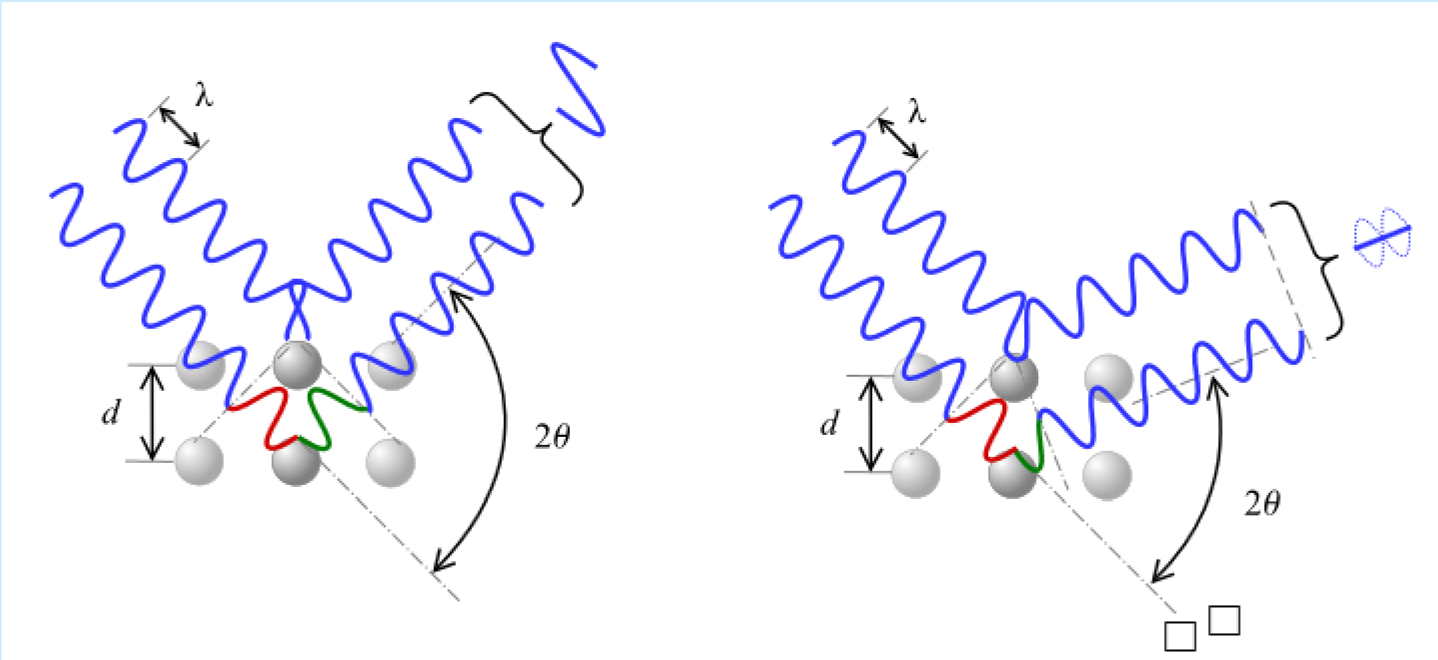
Interference



CONSTRUCTIVE INTERFERENCE
Summing 2 waves **in phase** (shifted by a integer **multiple of** λ) the resulting wave has **double intensity**

DESTRUCTIVE INTERFERENCE
Summing 2 waves **out of phase** (shifted by a integer **multiple of** λ**/2**) the resulting wave has **zero intensity**



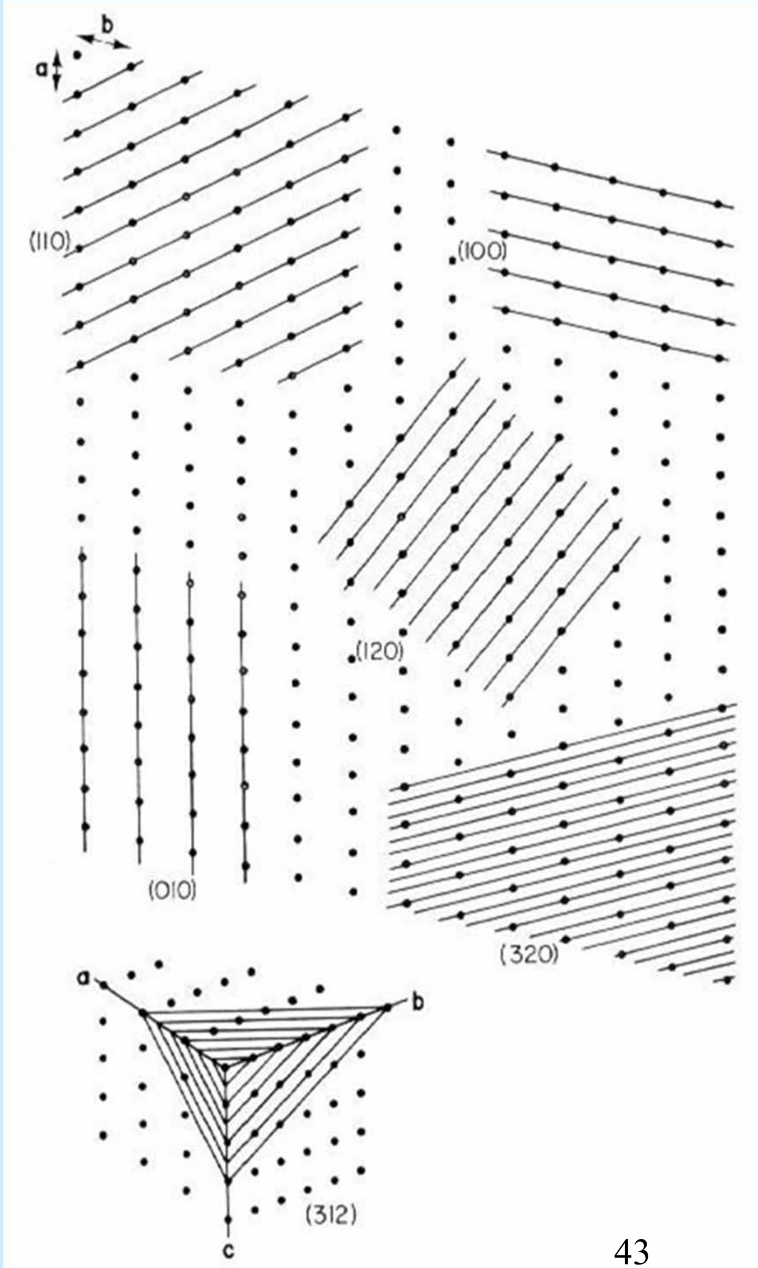

λ
d
2θ
λ
d
2θ

Crystal

Crystal = parallel planes of atoms separated by distance *d*

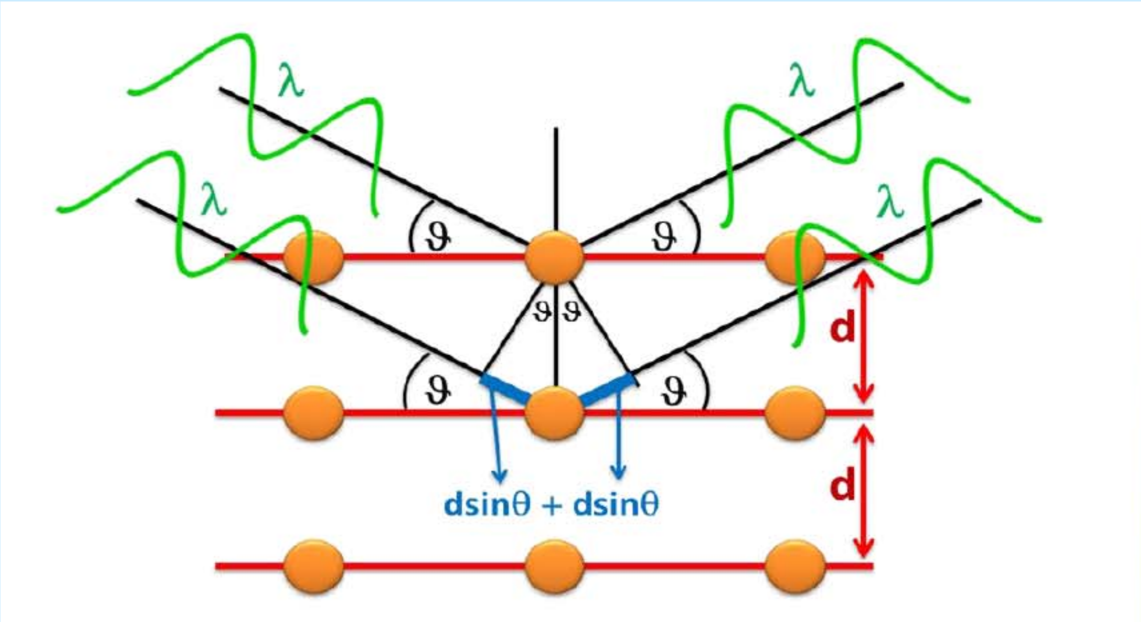
Assume specular reflection of X-rays from any given plane

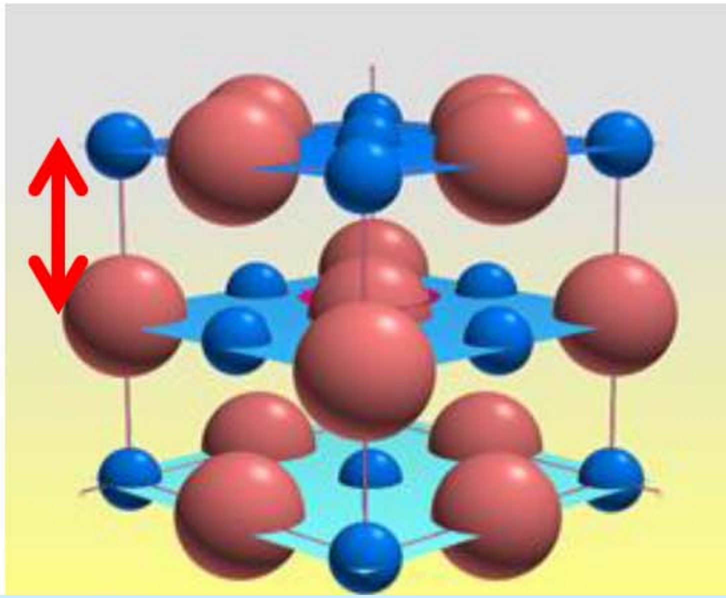
Peaks in the intensity of scattered radiation will occur when rays from successive planes interfere constructively



Bragg's Law

Diffraction is pictured as a reflection of incident X-Ray beam from atomic lattice planes = a simplicistic model that allows to calculate the distance between atomic planes

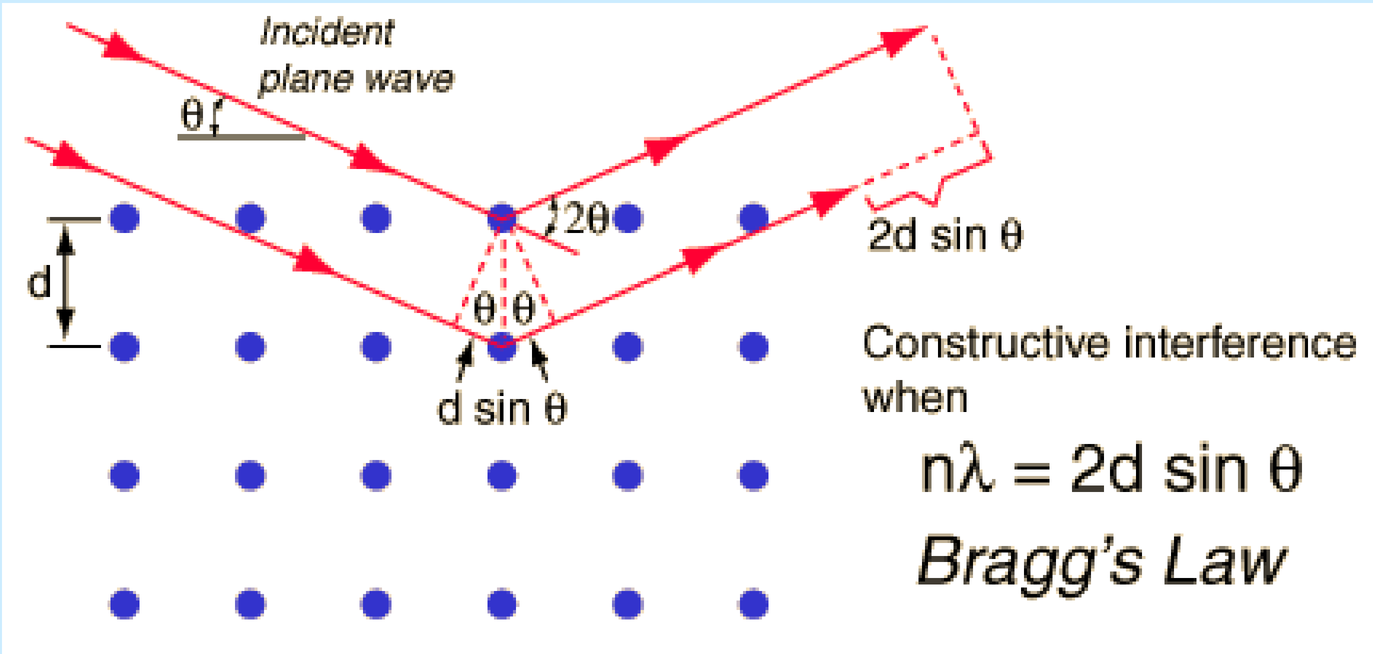




X-ray Powder Diffraction

William Bragg *(1912)*

$$n.\lambda = 2\ d \sin \Theta$$



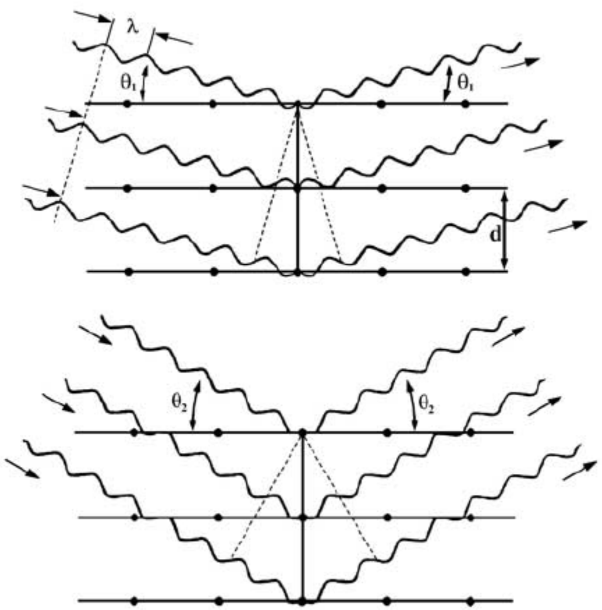
Diffraction Order

1st order:

$$\lambda = 2d \sin \theta_1$$

2nd order:

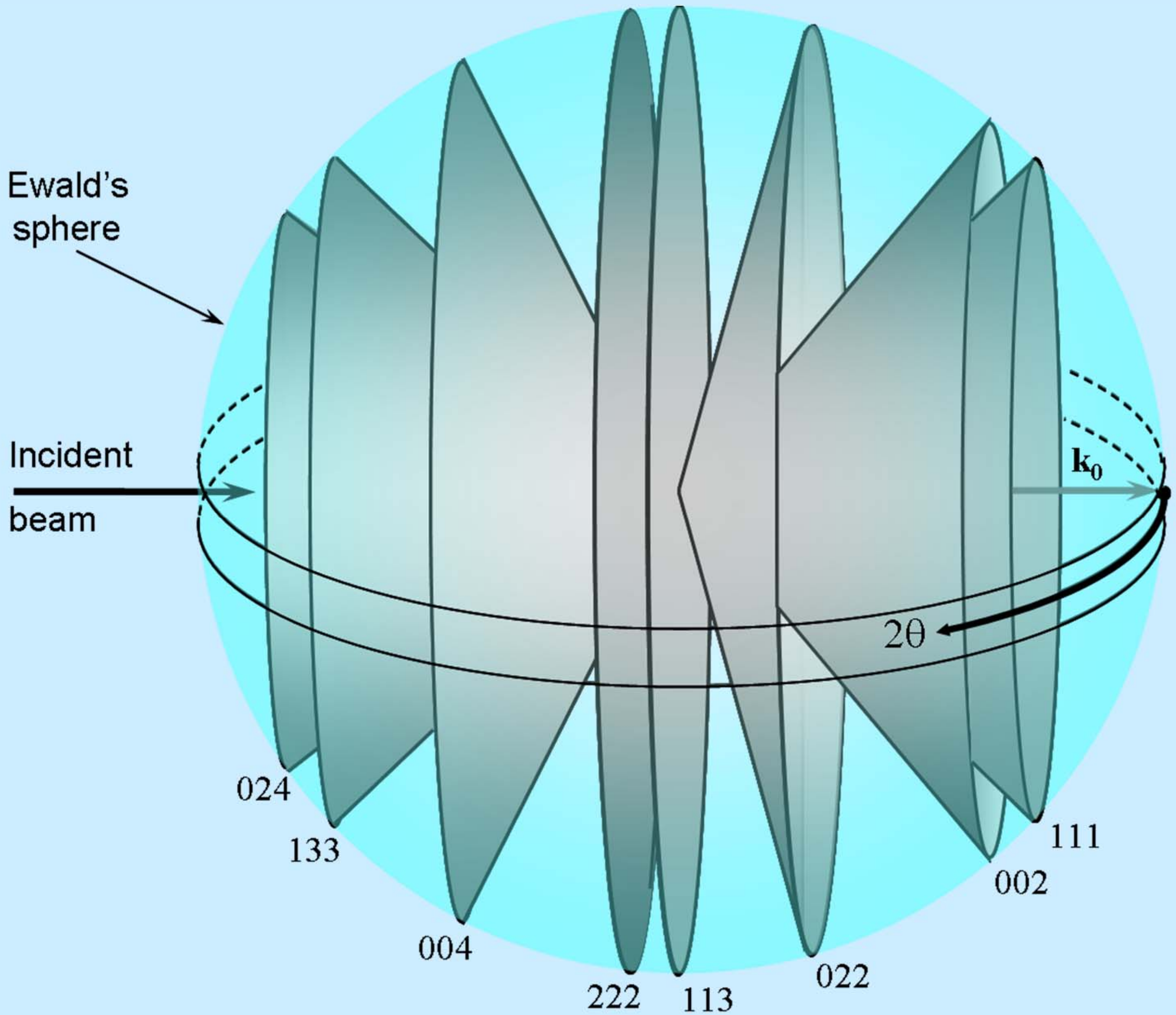
$$2\lambda = 2d \sin \theta_2$$



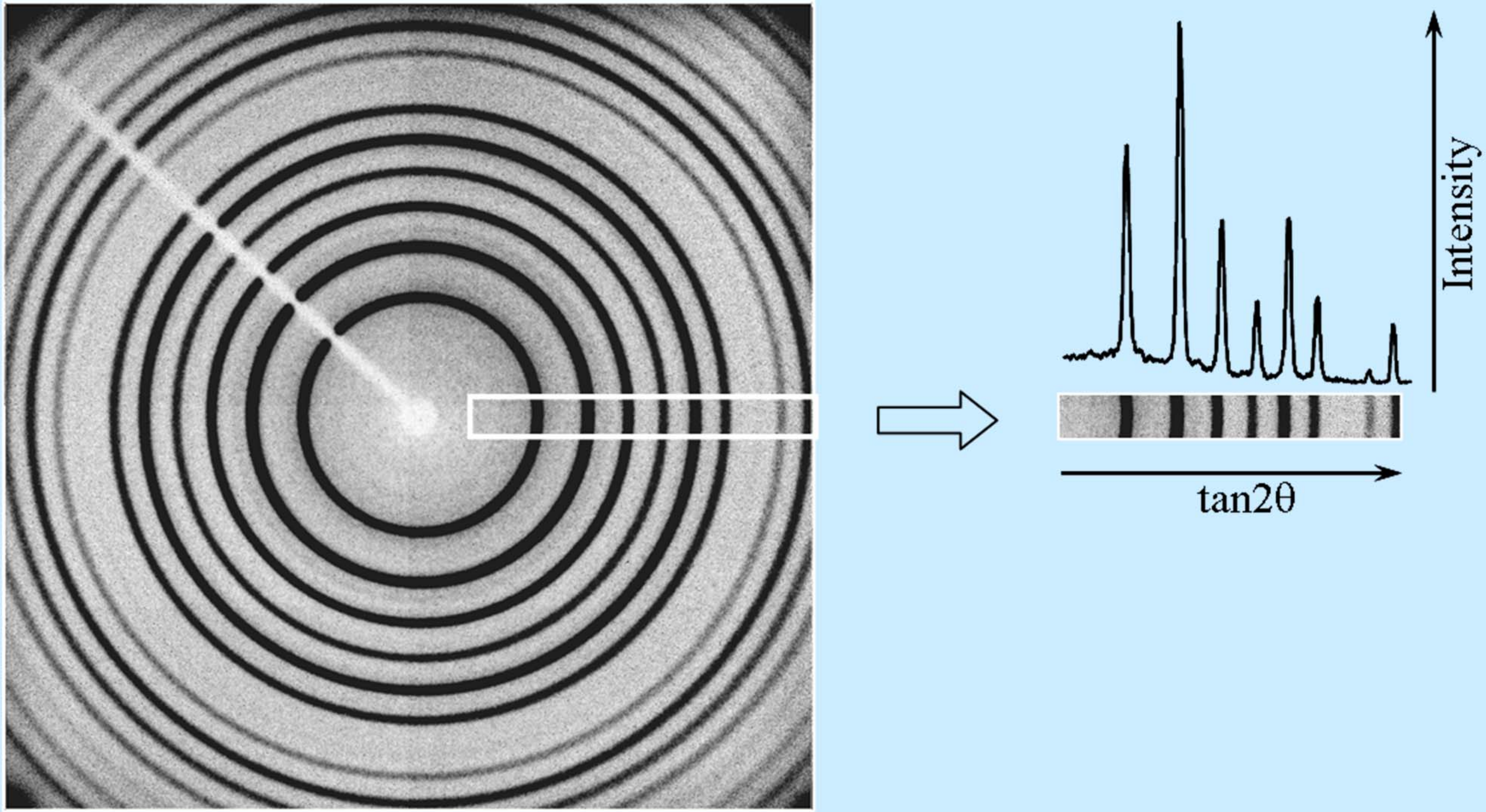
By convention, set the diffraction order = 1 for XRD
when n = 2, just halve the d-spacing to make n = 1
e.g. the 2nd order reflection of d_{100} occurs at same θ as 1st order reflection of d_{200}

$$2\lambda = 2d \sin \theta_2 \quad \Rightarrow \quad \lambda = 2(d/2) \sin \theta_2$$

X-ray Powder Diffraction

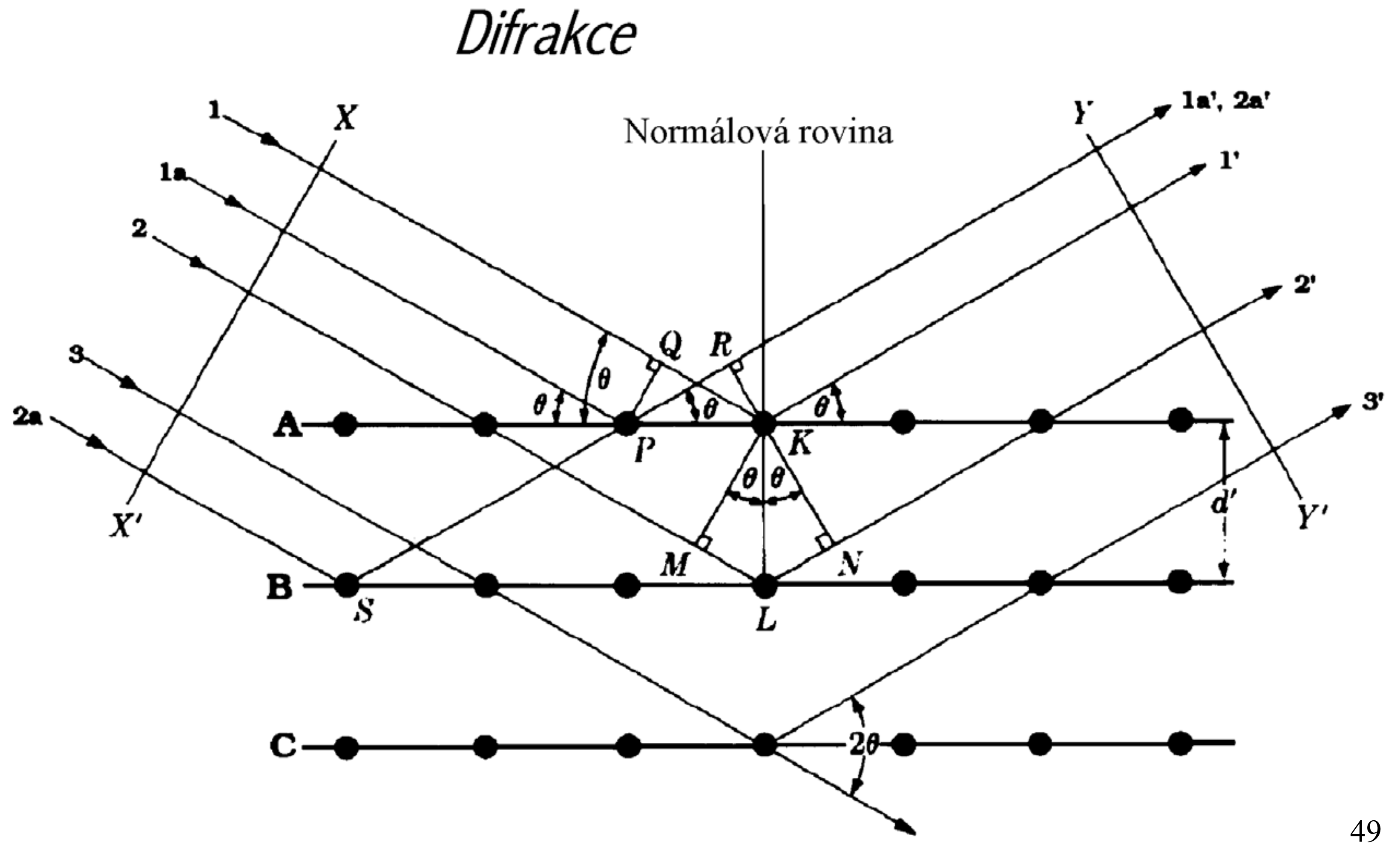


X-ray Powder Diffraction



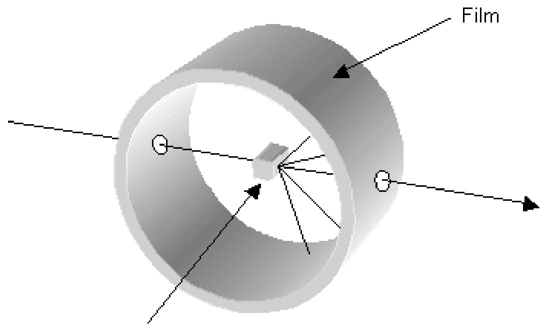
Laue method ⟶ Single crystals

Debye-Scherrer, diffractometers ⟶ polycrystalline

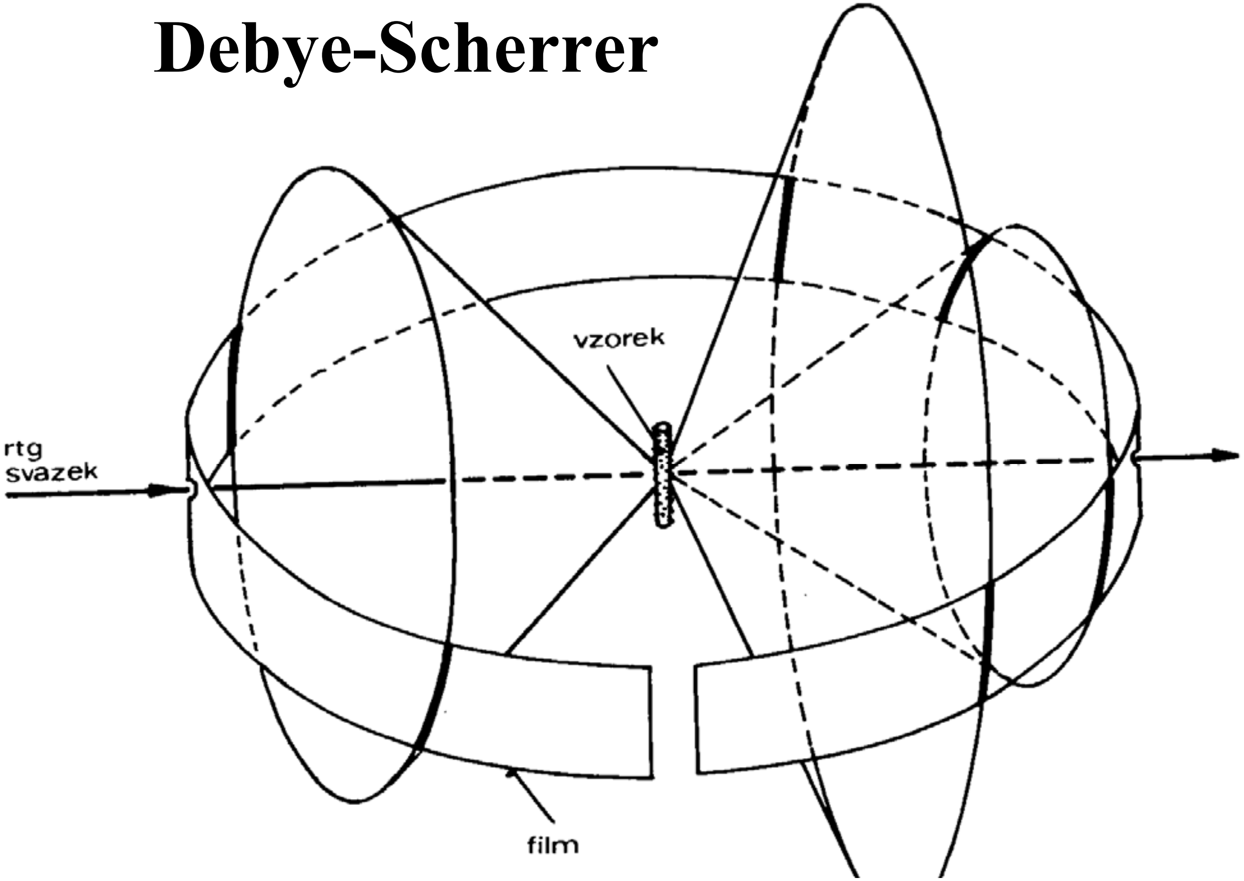


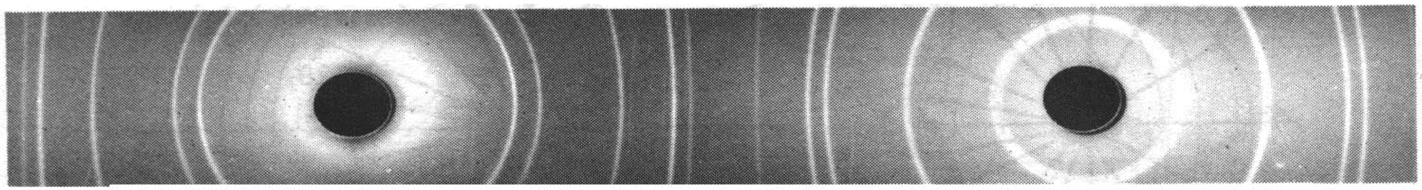
Different Geometries of Powder Diffractometers

- Debye-Scherrer
- Bragg-Brentano
- Guinier



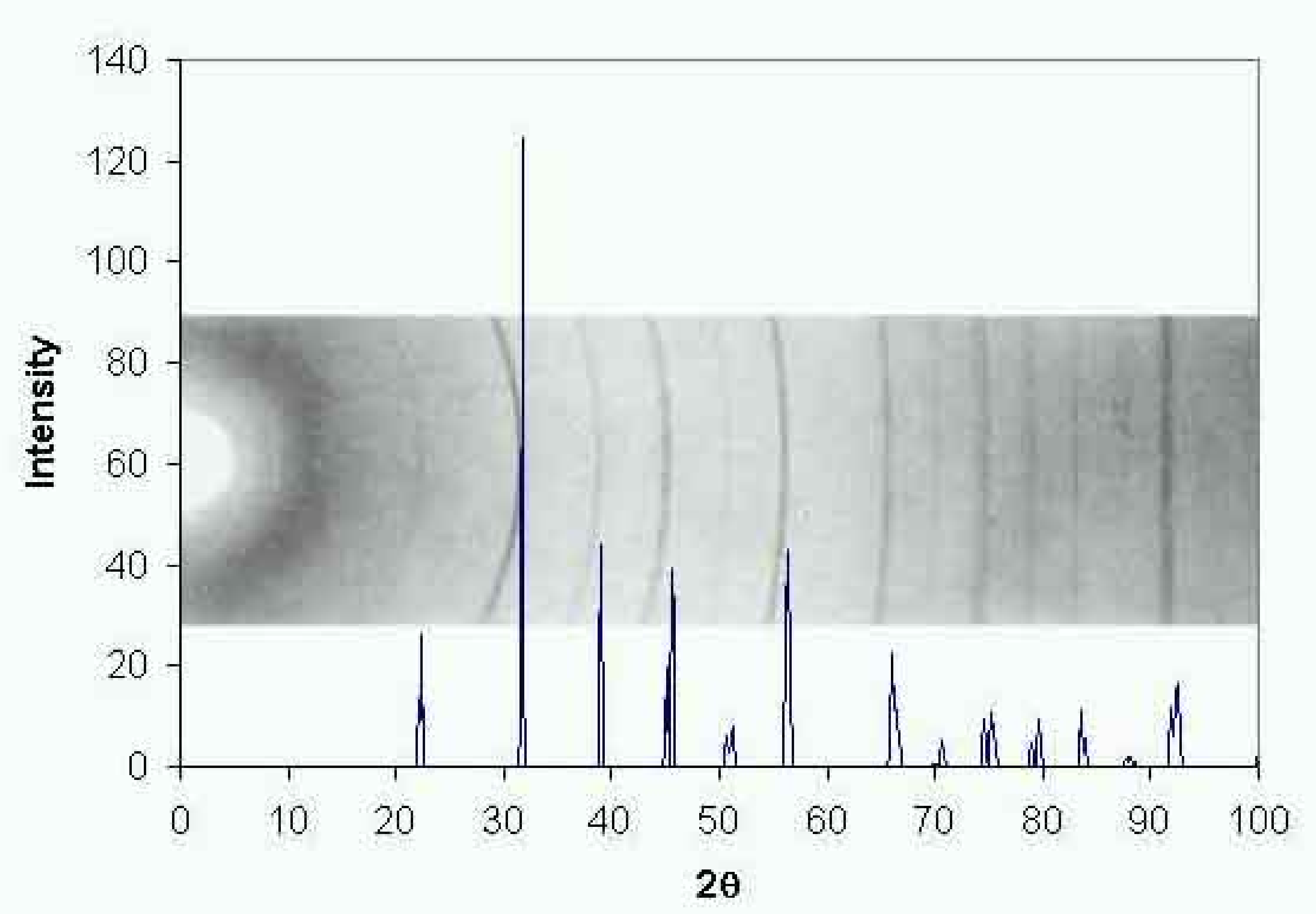
Debye-Scherrer



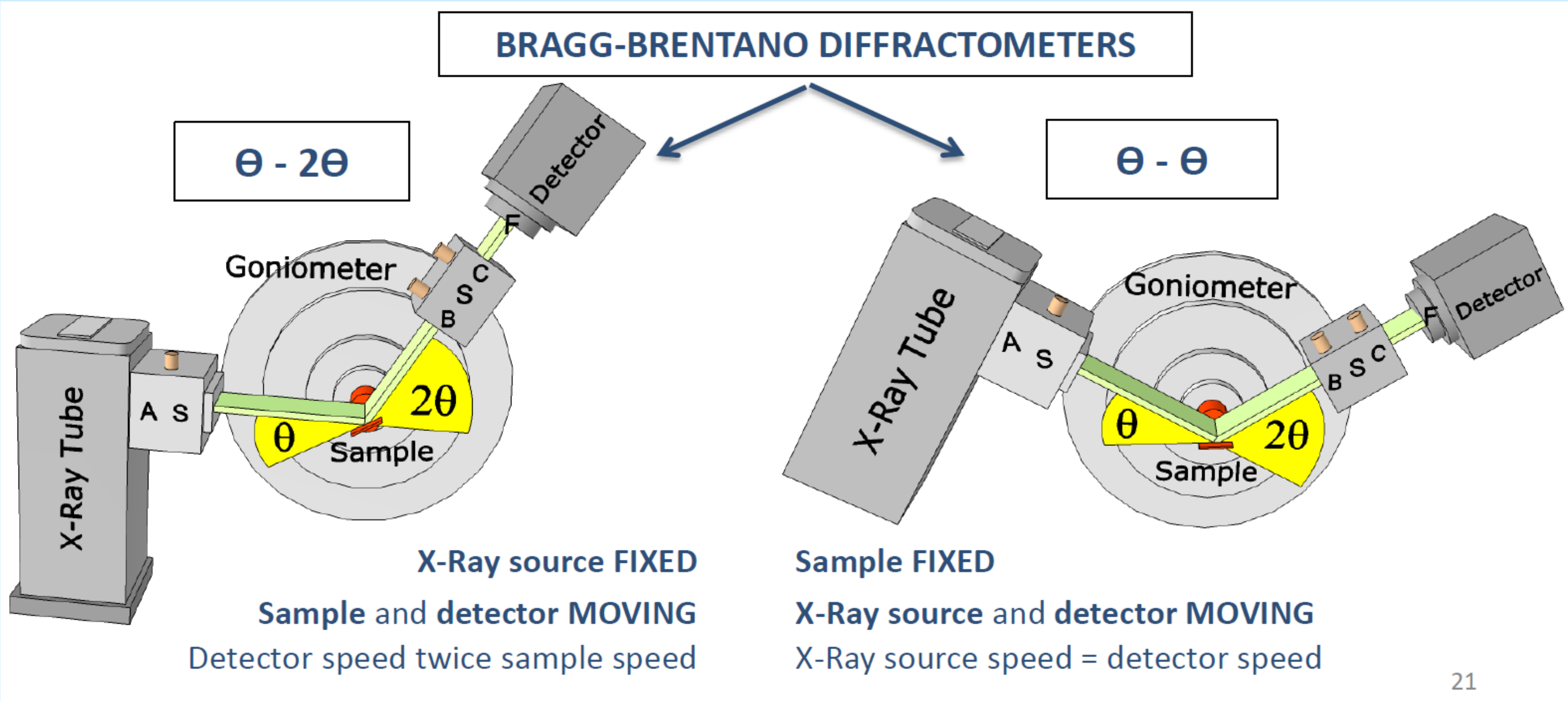


Debyegram práškového stříbra ($\lambda = 1{,}54 \cdot 10^{-10}$ m)

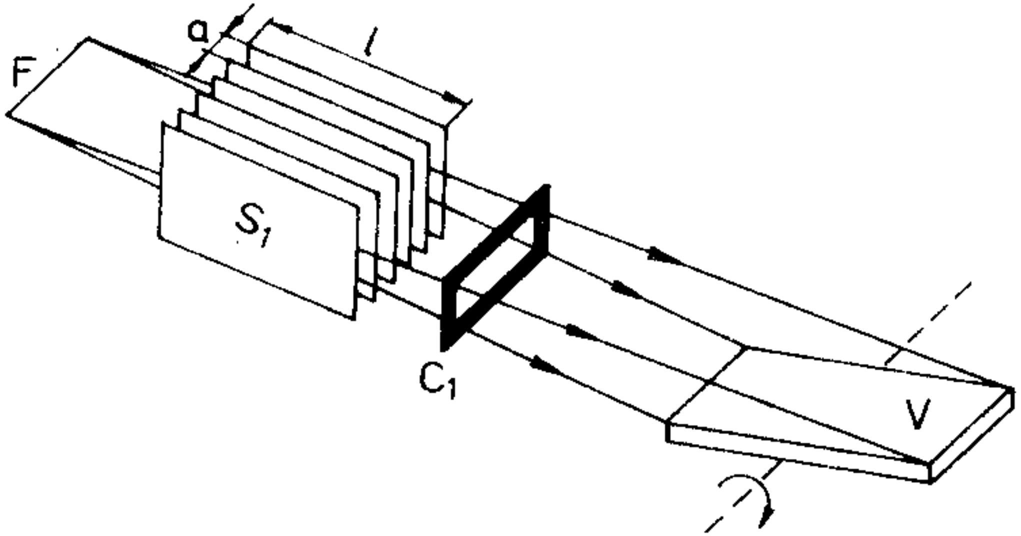
Debye-Scherrer

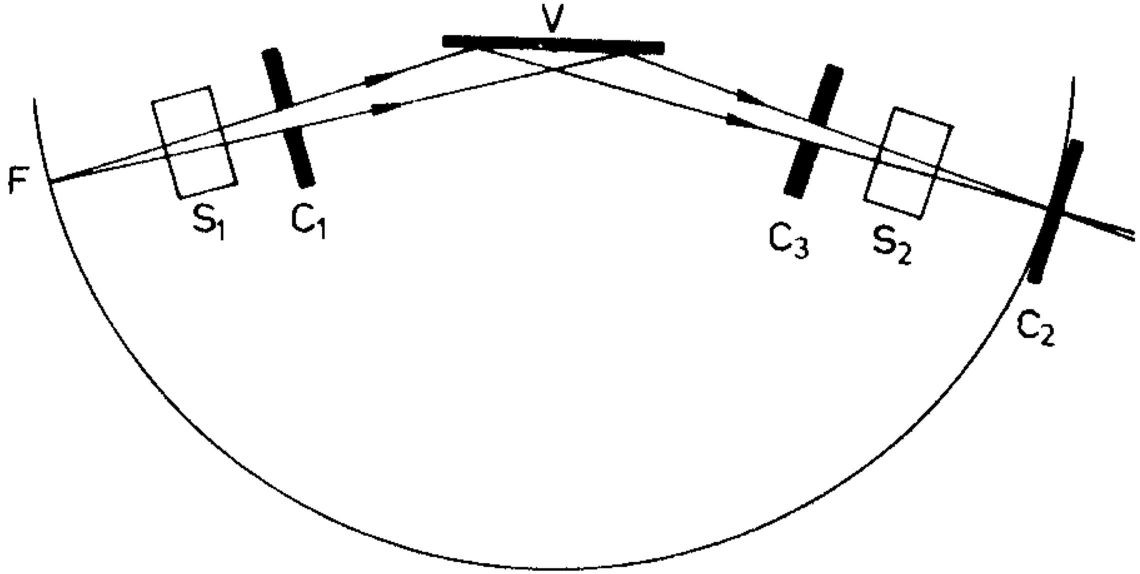


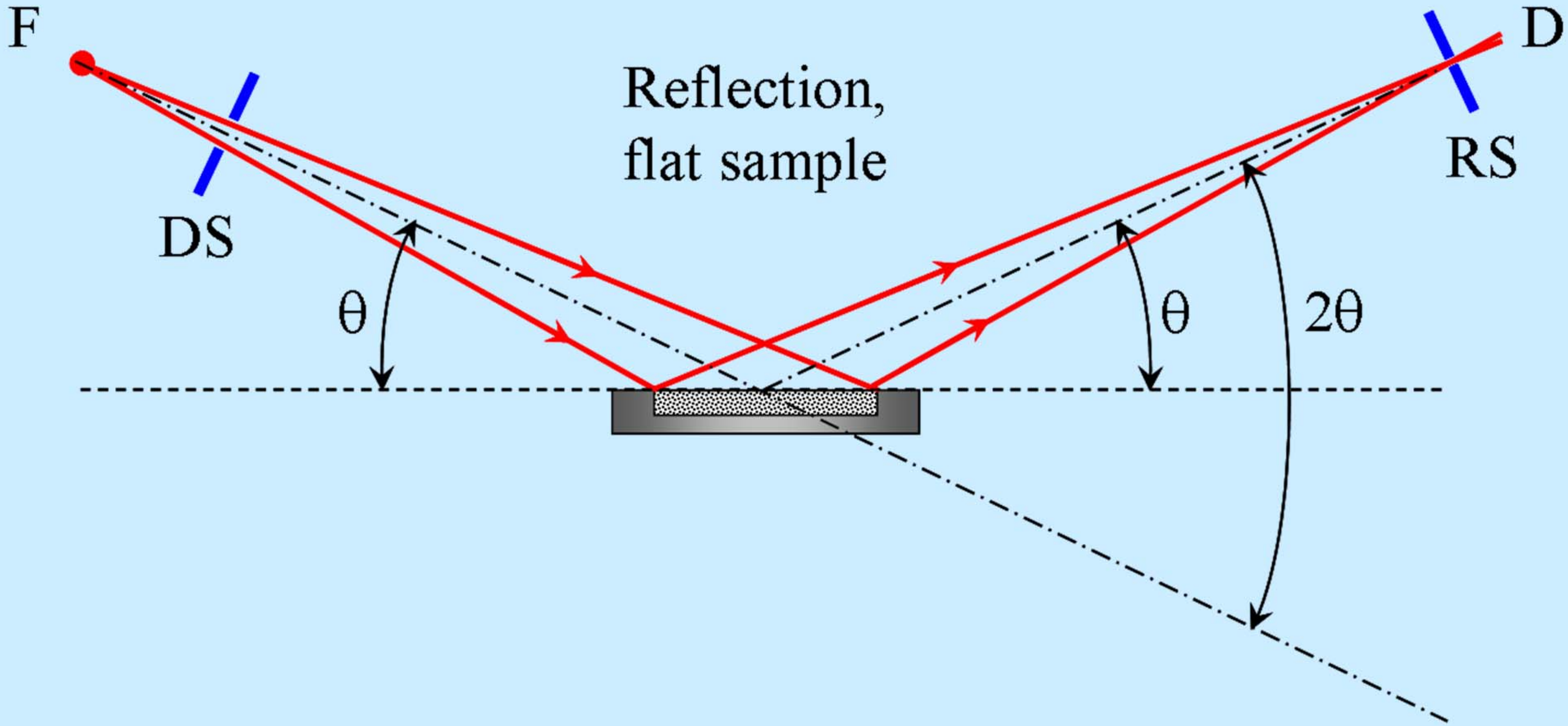
Bragg-Brentano

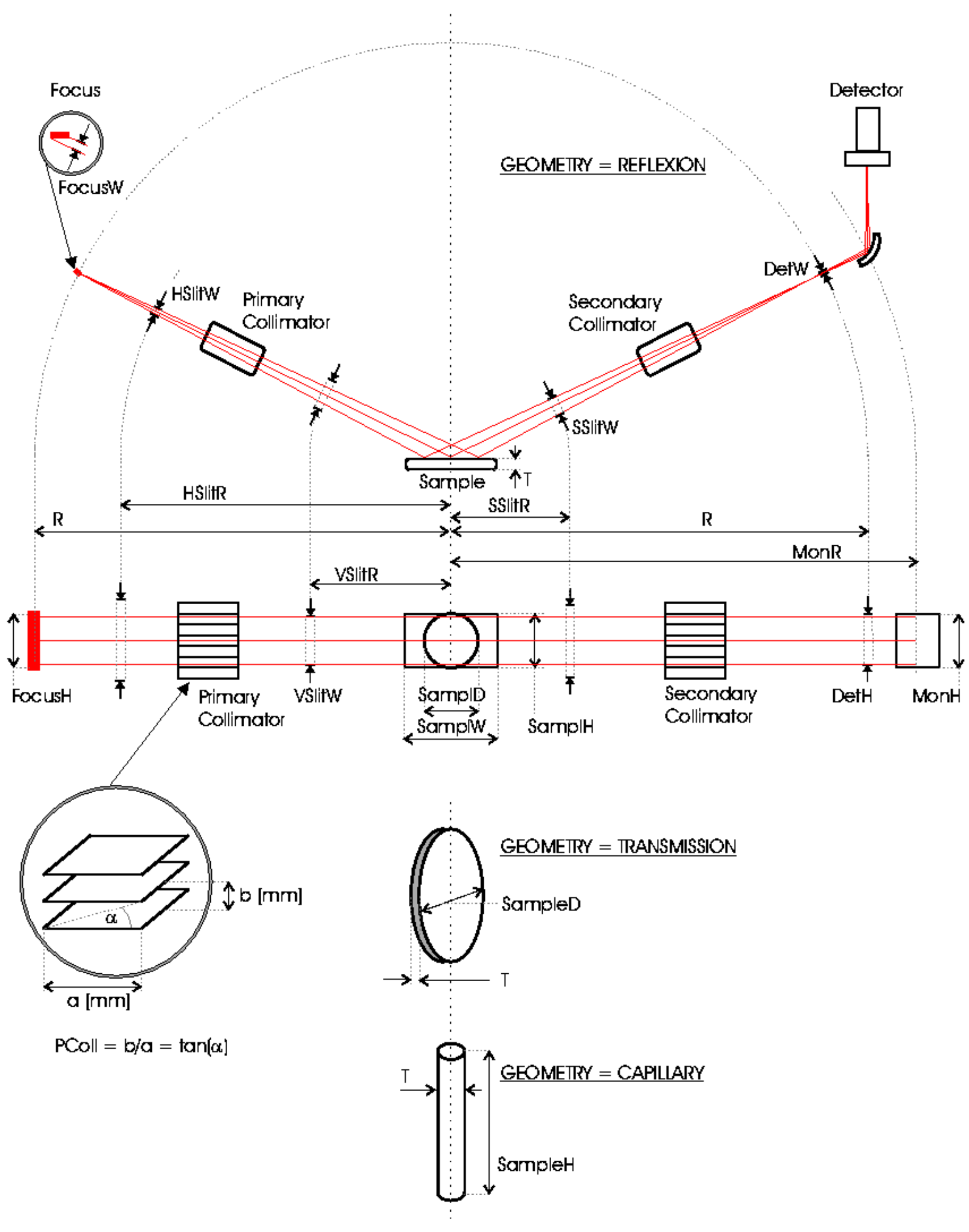


Bragg-Brentano

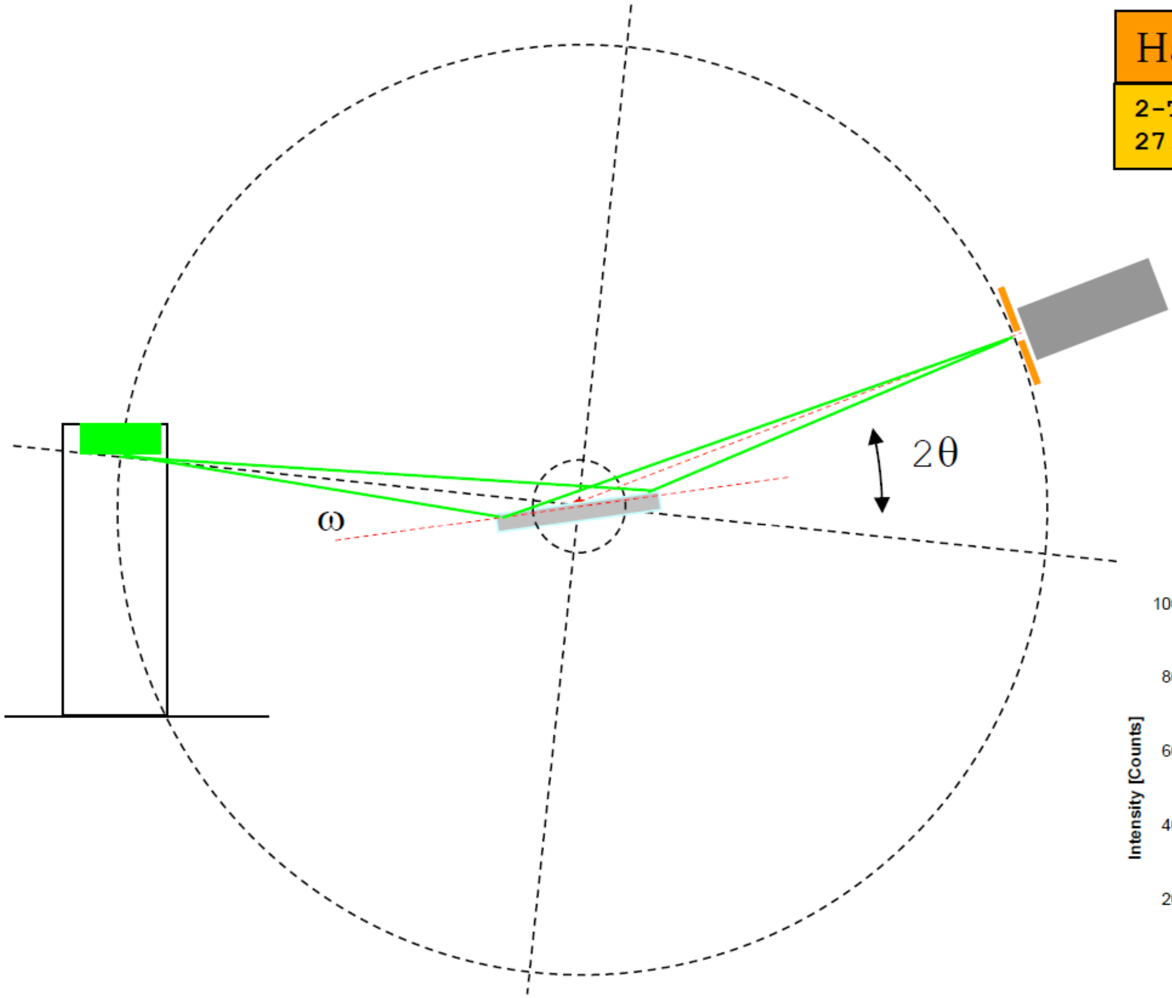





F
D
Reflection,
flat sample
DS
RS
θ
θ
2θ


Focus
FocusW
Detector
GEOMETRY = REFLEXION
DetW
HSlitW
Primary Collimator
Secondary Collimator
SSlitW
Sample
T
HSlitR
SSlitR
R
R
MonR
VSlitR
FocusH
Primary Collimator
VSlitW
SampID
SamplW
SamplH
Secondary Collimator
DetH
MonH
b [mm]
α
a [mm]
PColl = b/a = tan(α)
GEOMETRY = TRANSMISSION
SampleD
T
T
GEOMETRY = CAPILLARY
SampleH

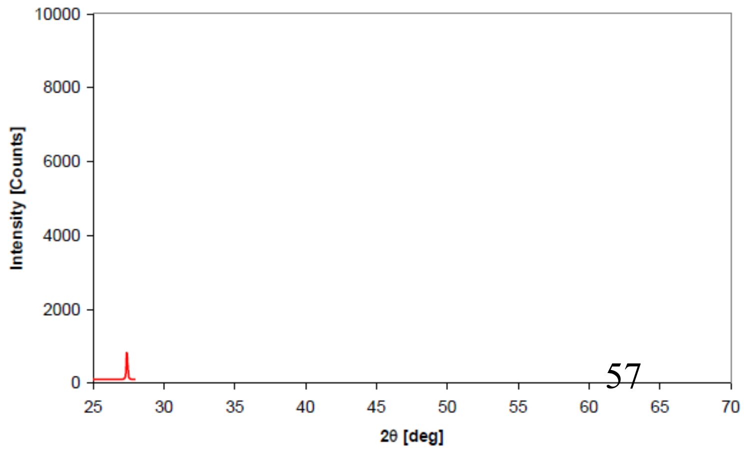
X-ray Powder Diffraction



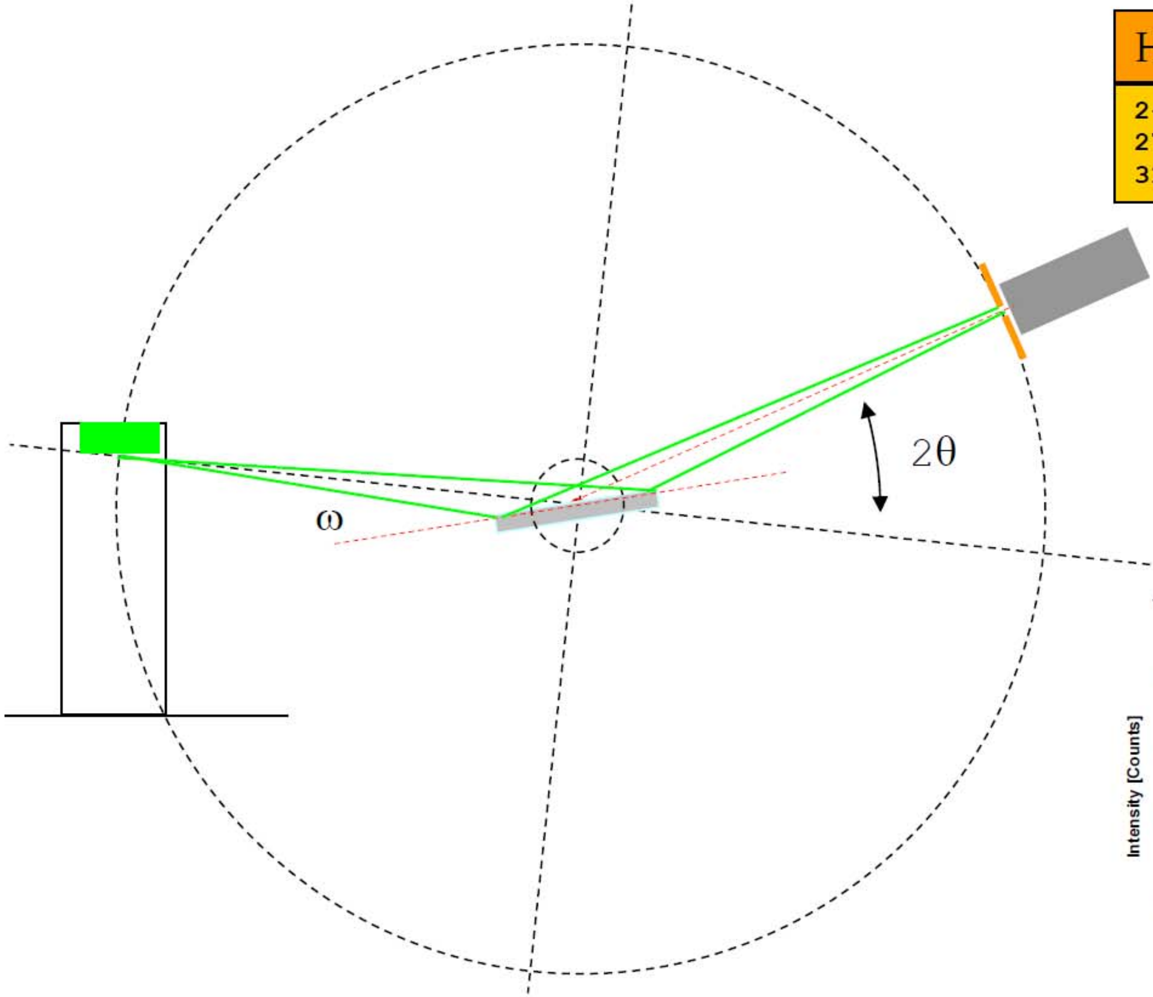
Halite (NaCl)

2-THETA	INTENSITY	D-SPACING	H	K	L
27.39	8.77	3.2563	1	1	1

When **Bragg's law** is satisfied a **peak** appears



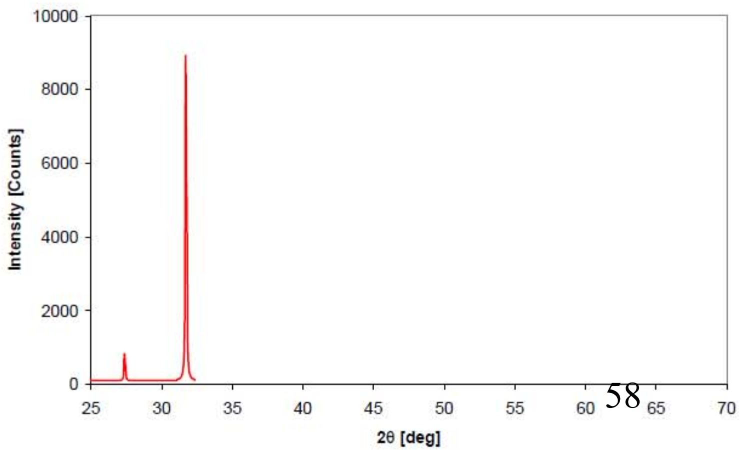
X-ray Powder Diffraction



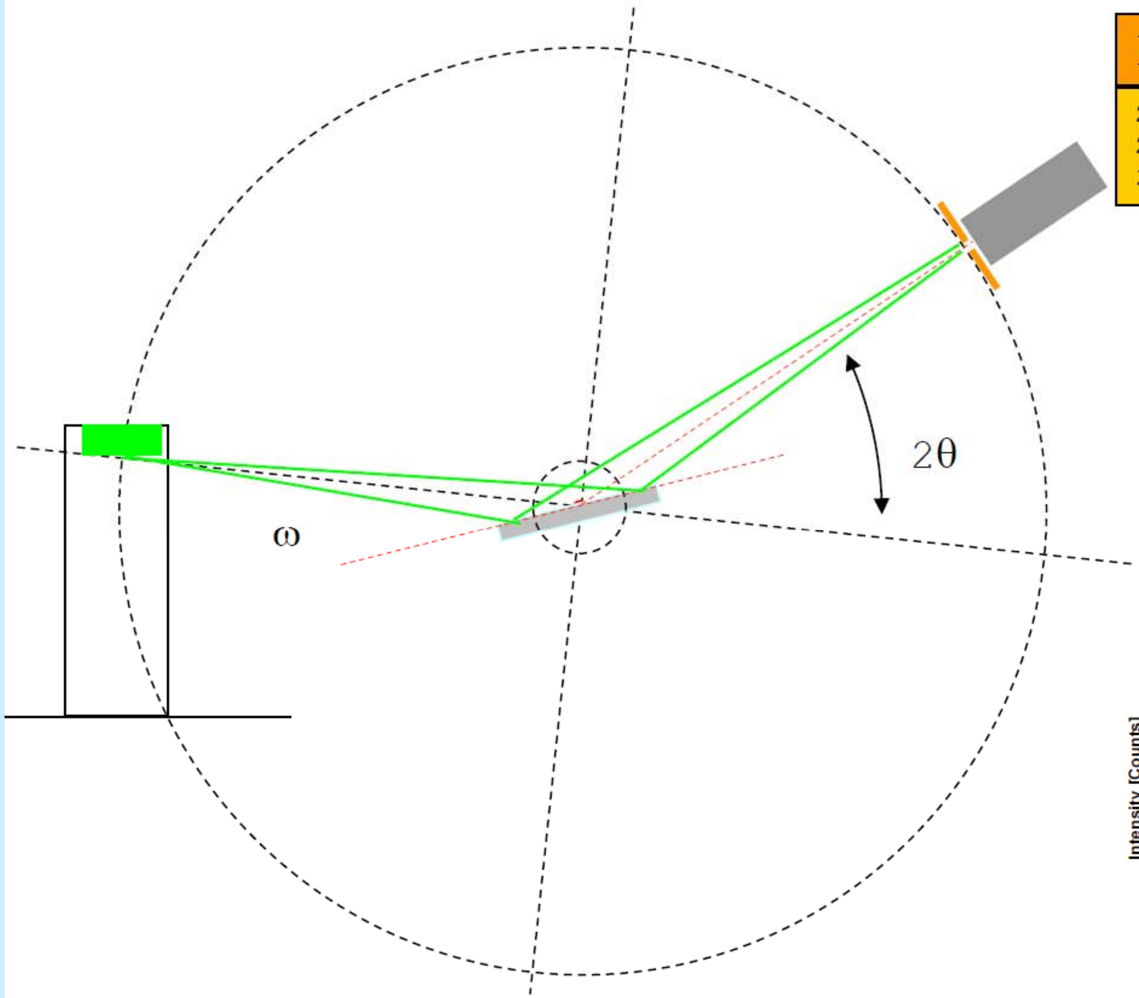
Halite (NaCl)

2-THETA	INTENSITY	D-SPACING	H	K	L
27.39	8.77	3.2563	1	1	1
31.73	100.00	2.8201	2	0	0

When **Bragg's law** is satisfied a **peak** appears



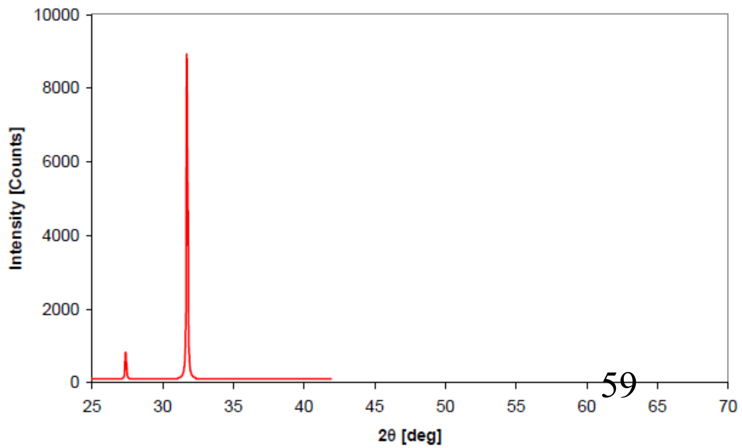
X-ray Powder Diffraction



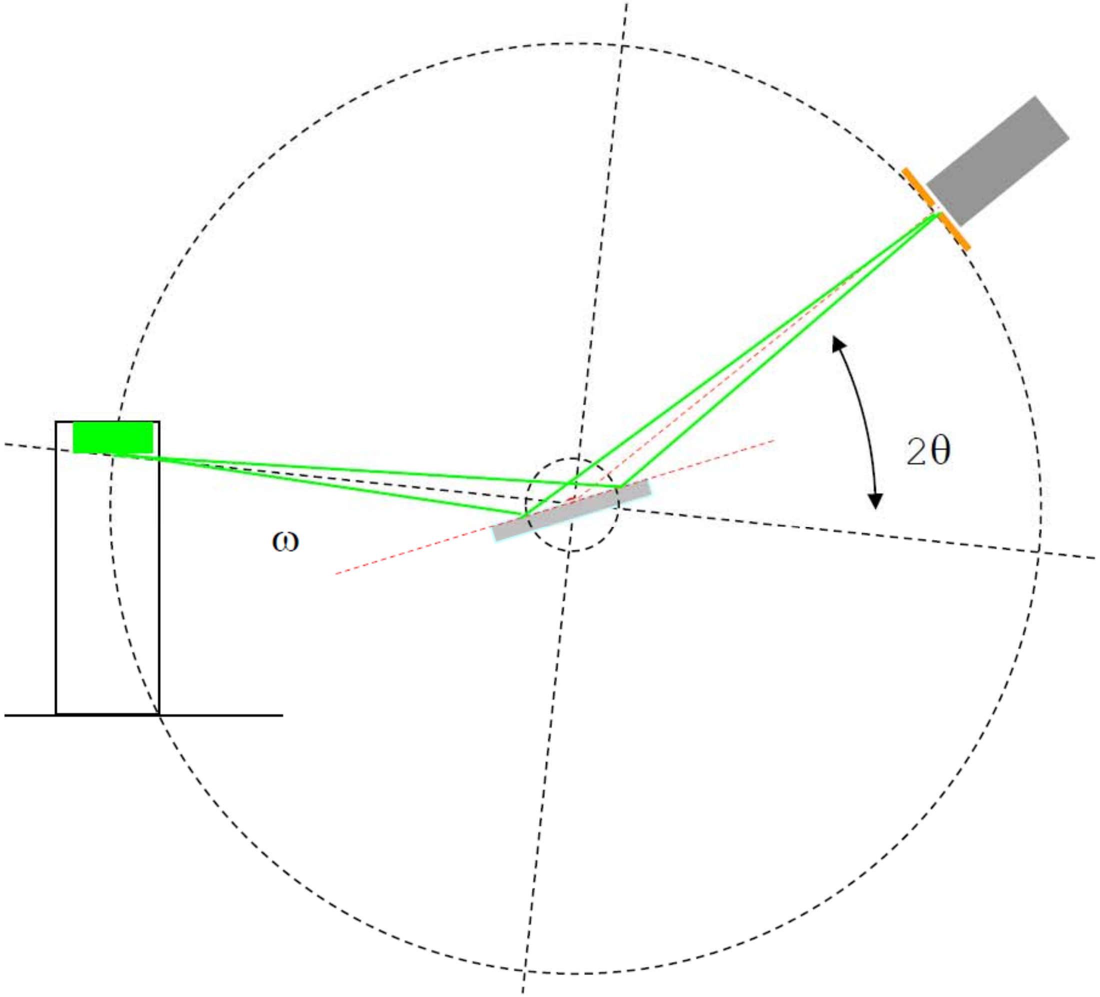
Halite (NaCl)

2-THETA	INTENSITY	D-SPACING	H	K	L
27.39	8.77	3.2563	1	1	1
31.73	100.00	2.8201	2	0	0

When **Bragg's law** is satisfied a **peak** appears



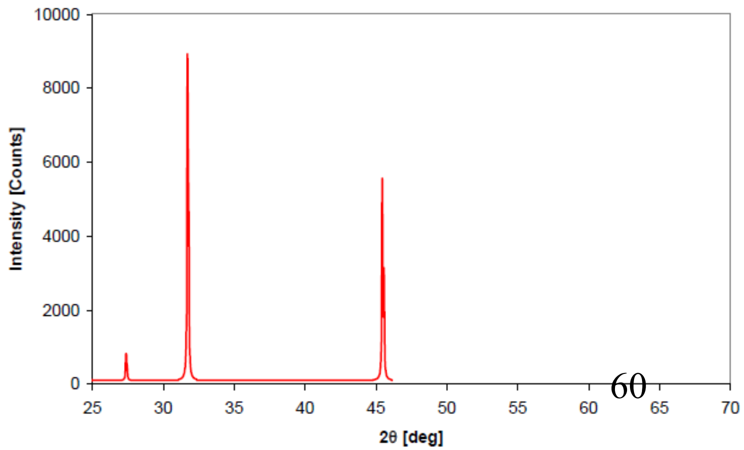
X-ray Powder Diffraction



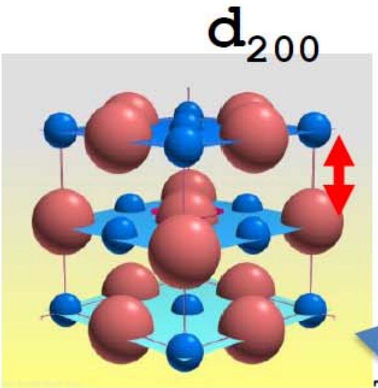
Halite (NaCl)

2-THETA	INTENSITY	D-SPACING	H	K	L
27.39	8.77	3.2563	1	1	1
31.73	100.00	2.8201	2	0	0
45.49	61.00	1.9941	2	2	0

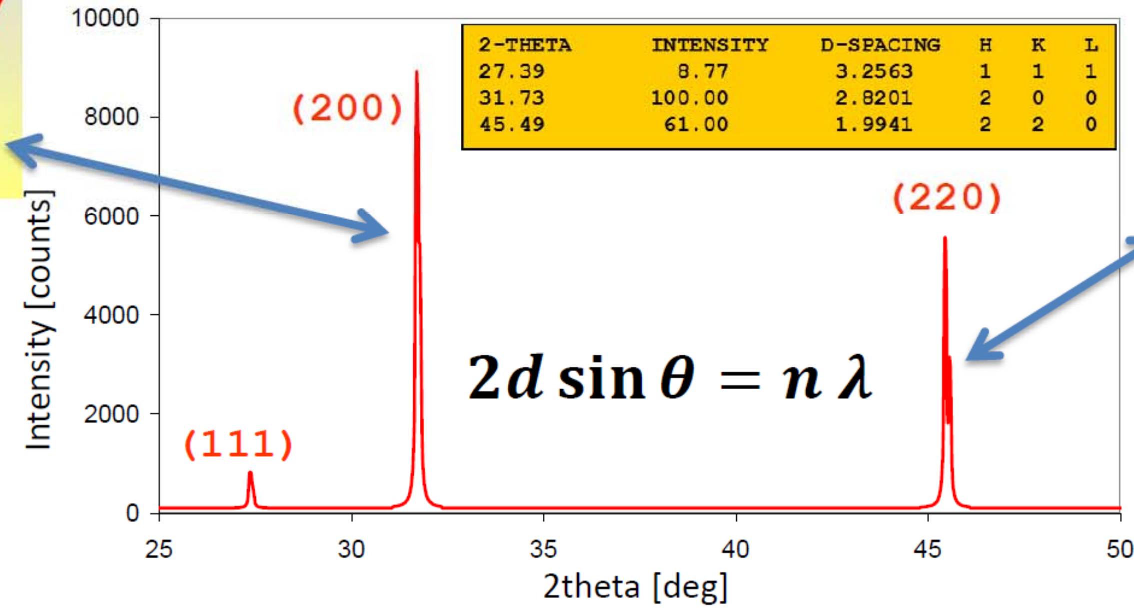
When **Bragg's law** is satisfied a **peak** appears



X-ray Powder Diffraction

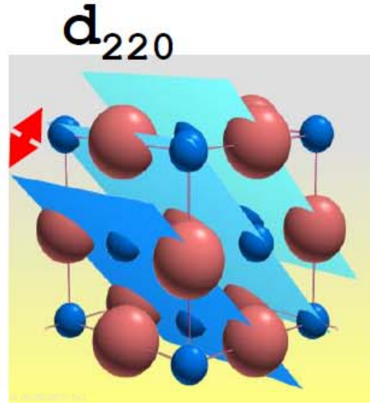


There is a **correnspondence** between each **peak** and atomic **set of planes** with distance ***d*** in the sample.



2-THETA	INTENSITY	D-SPACING	H	K	L
27.39	8.77	3.2563	1	1	1
31.73	100.00	2.8201	2	0	0
45.49	61.00	1.9941	2	2	0

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

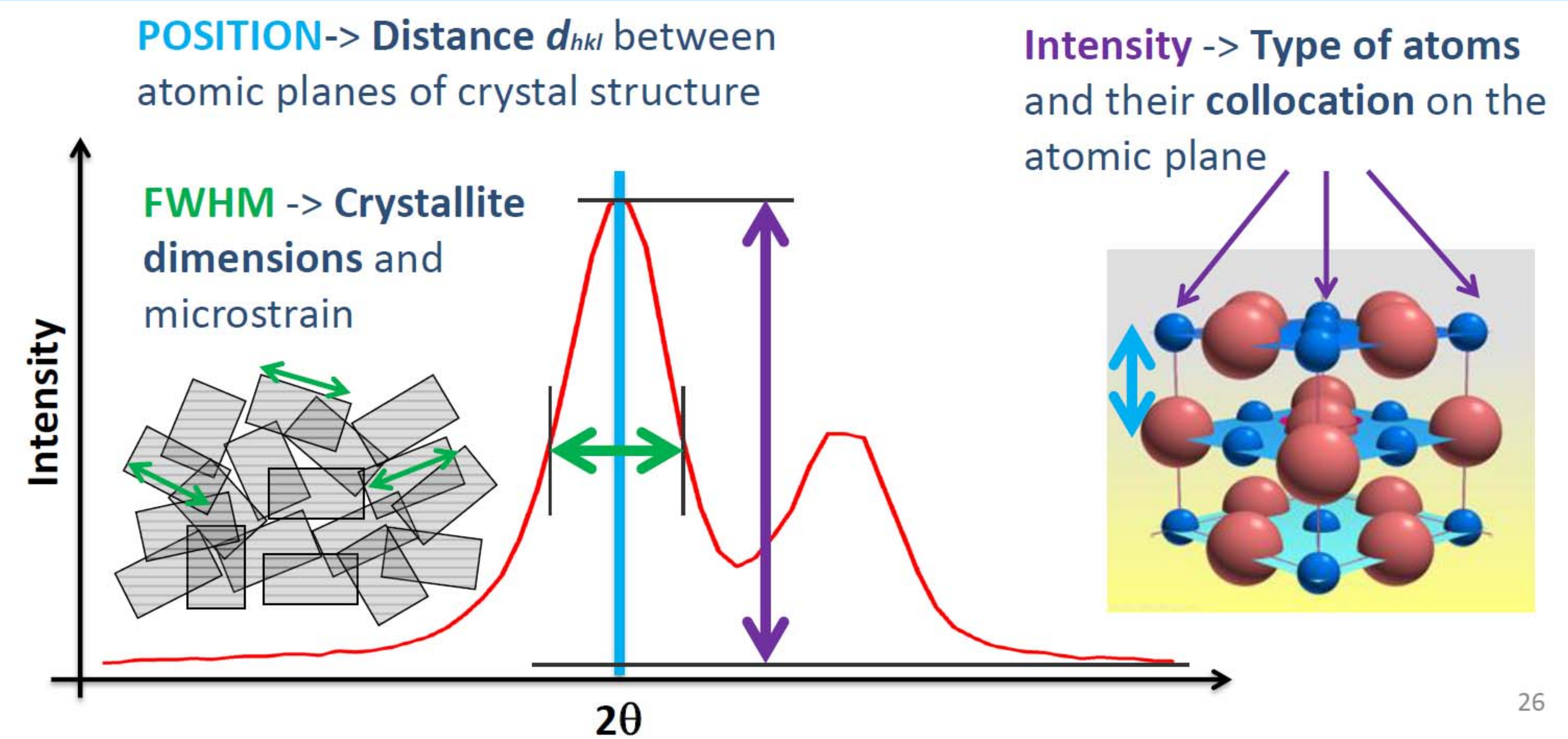


27

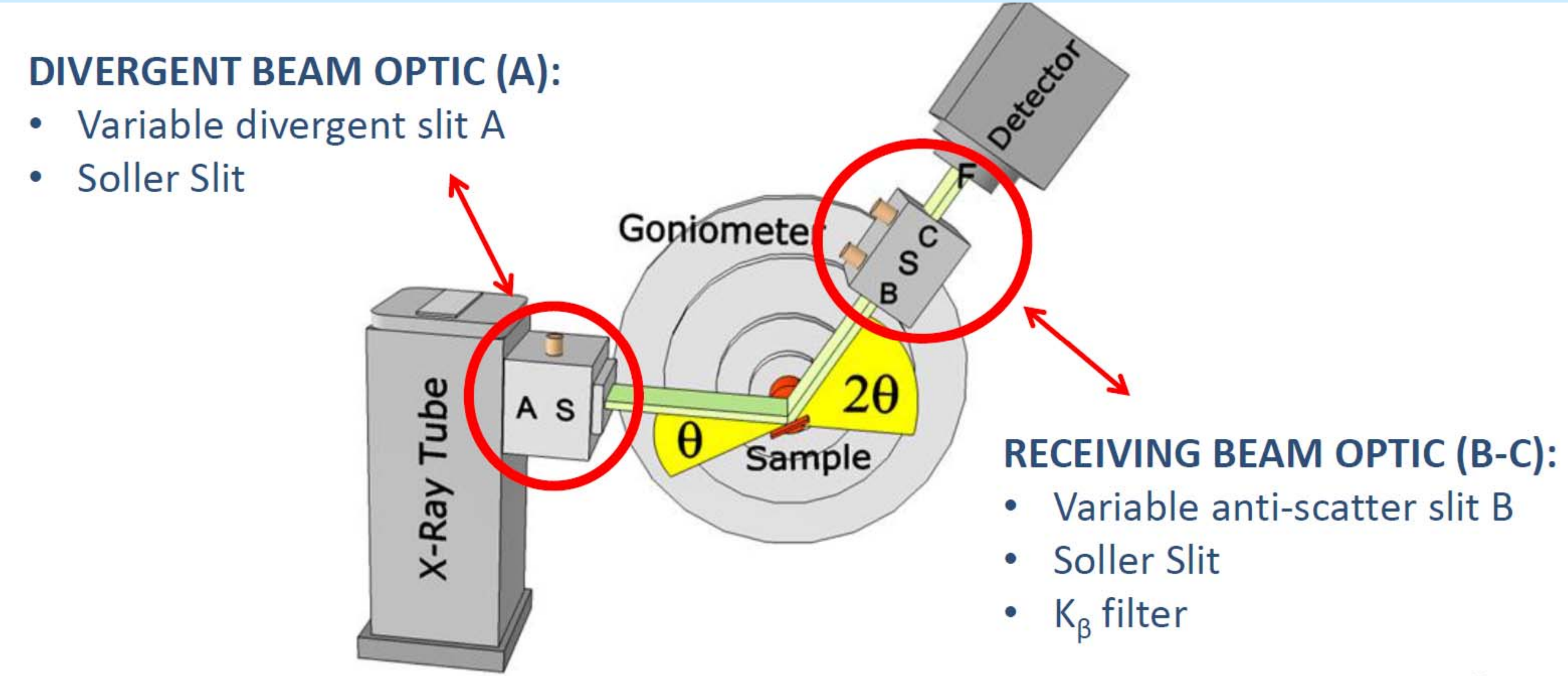
increasing θ, decreasing d

Minimum d: $d_{min} = \lambda / 2$, $\theta_{max} = 90°$

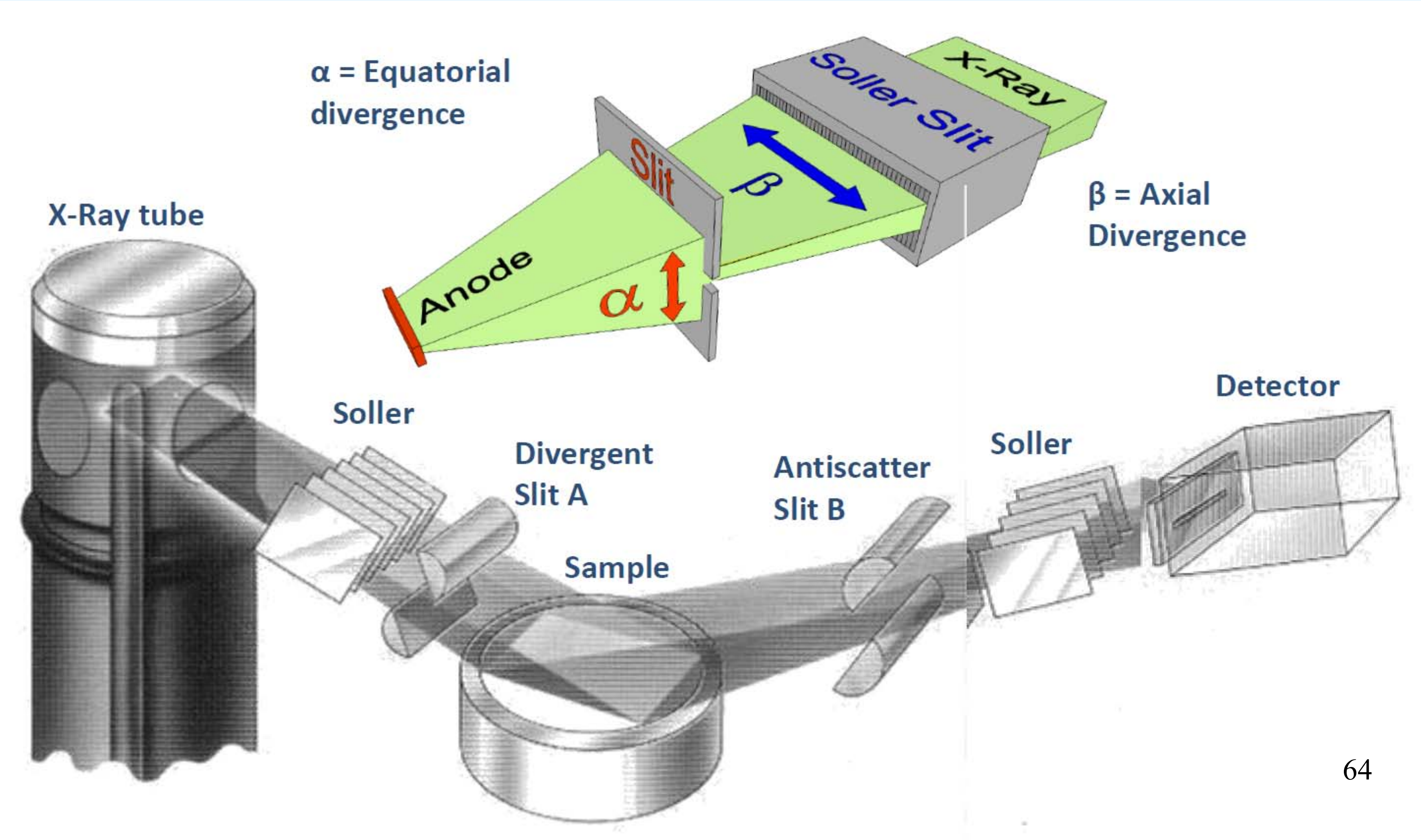
Results


POSITION-> Distance d_{hkl} between atomic planes of crystal structure
Intensity -> Type of atoms and their collocation on the atomic plane
FWHM -> Crystallite dimensions and microstrain
Intensity
2θ
26

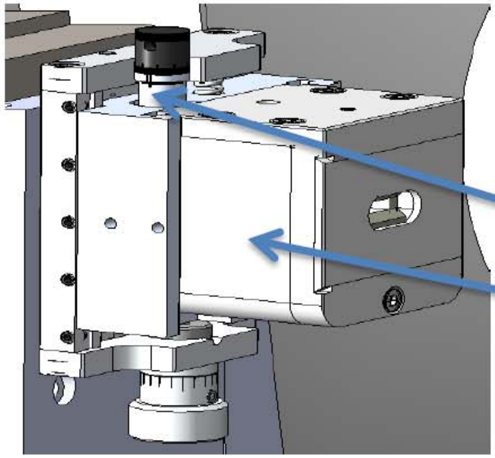
X-Ray Optics


DIVERGENT BEAM OPTIC (A):
• Variable divergent slit A
• Soller Slit
Goniometer
Detector
F
C
S
B
A S
X-Ray Tube
θ
2θ
Sample
RECEIVING BEAM OPTIC (B-C):
• Variable anti-scatter slit B
• Soller Slit
• K_β filter

X-Ray Optics

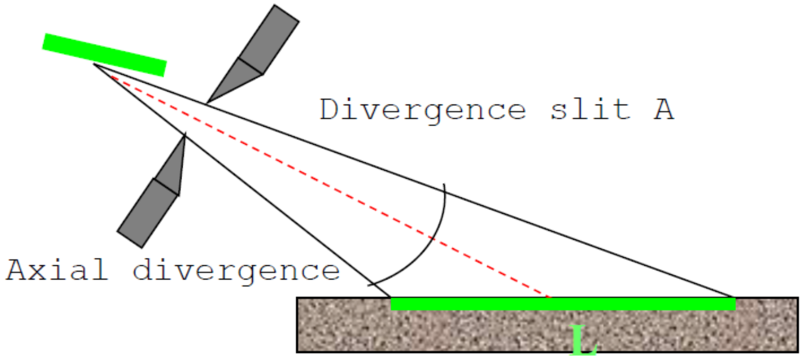

α = Equatorial
divergence
Soller Slit
X-Ray
Slit
β
Anode
α
β = Axial
Divergence
X-Ray tube
Soller
Divergent
Slit A
Sample
Antiscatter
Slit B
Soller
Detector

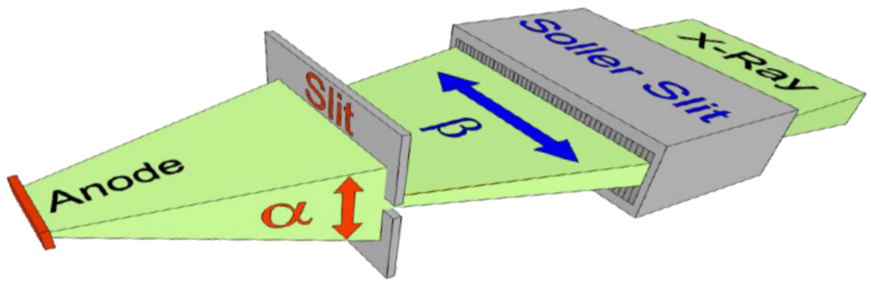
X-Ray Optics



DIVERGENT BEAM OPTIC (A) conditions X-Ray beam from the **tube** and is composed by:

- **Variable Divergent Slit A** (controlls equatorial divergence **α** and X-ray beam projection **L** on the sample)
  variable from 0° to 4°
- **Soller slit** (reduces axial divergence **β**)
  fixed 2.3°

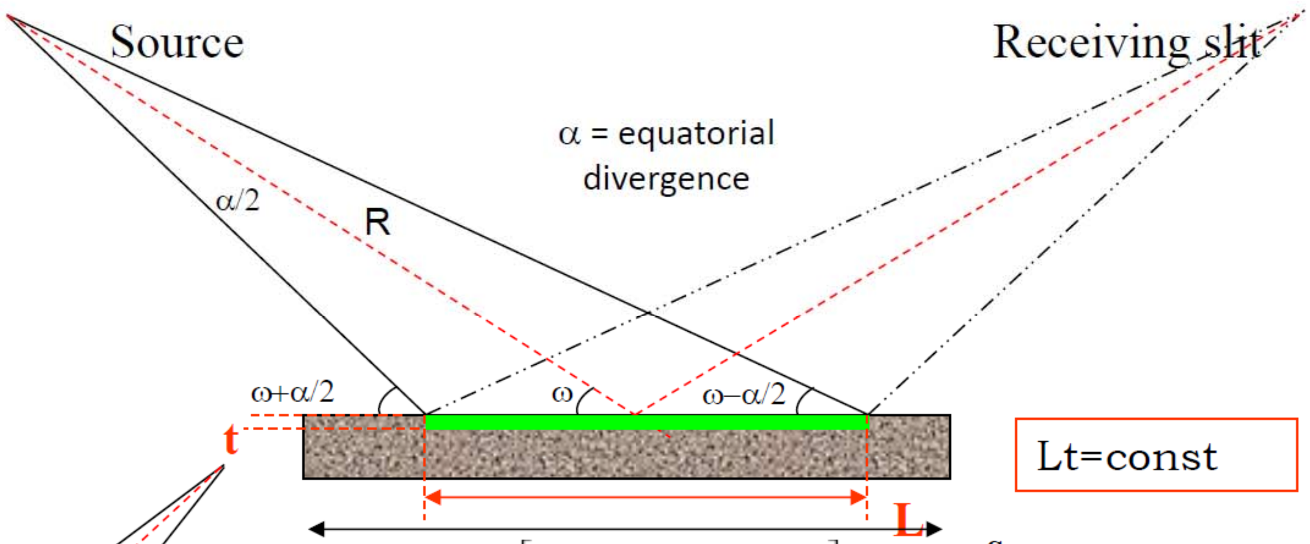




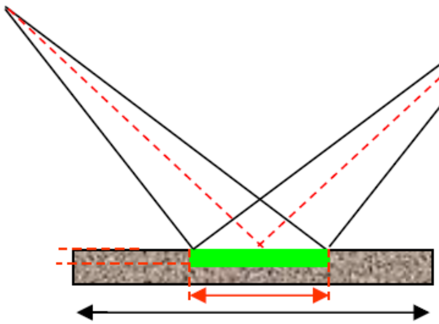
X-Ray Optics

Divergence Slit A:

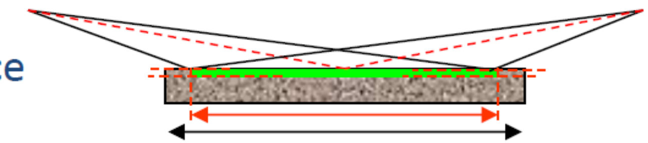
- L = Beam projection on the sample
- t = Depth illuminated



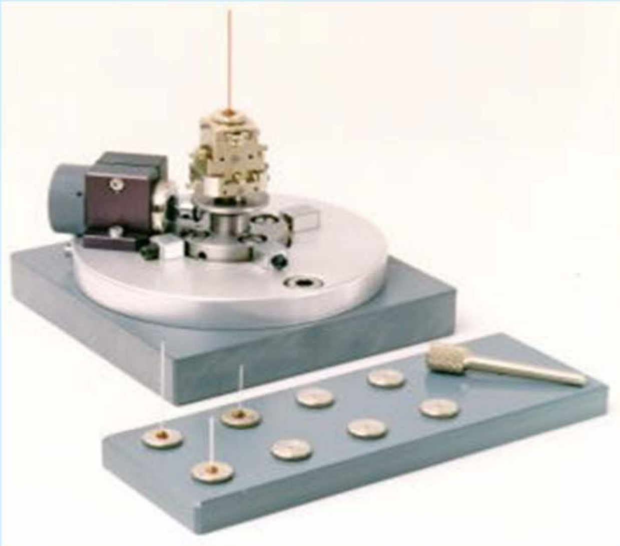
$$L = R\sin(\omega)\left[\frac{1}{\tan\left(\omega-\frac{\alpha}{2}\right)}-\frac{1}{\tan\left(\omega+\frac{\alpha}{2}\right)}\right]$$



Pay **attention** when setting the divergence **slit A**: **L(ω)<s (in particular for low ω)**



Sample Holders

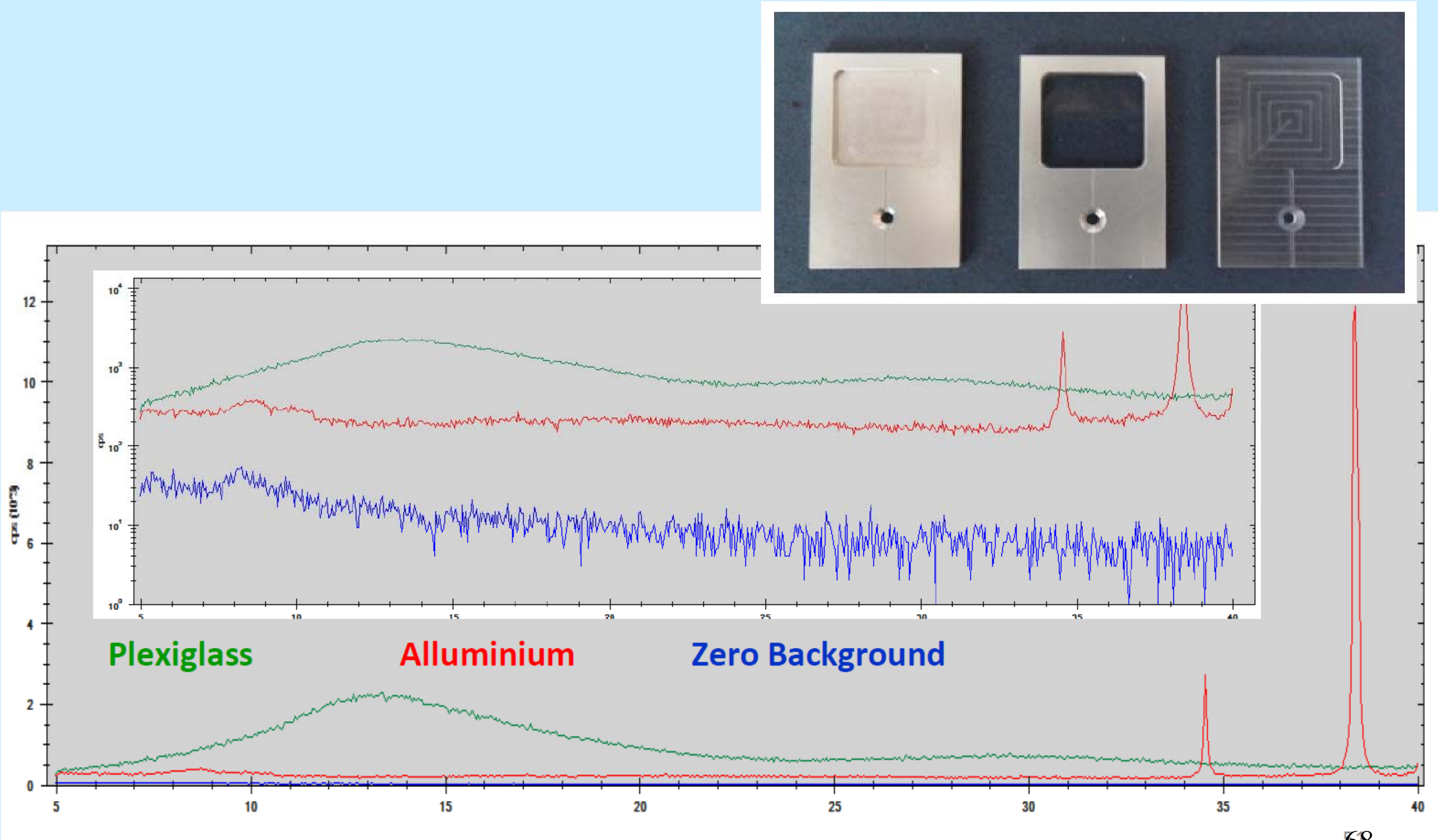


Capillary

Transmission

Reflection

Sample Holders



Detection of X-rays

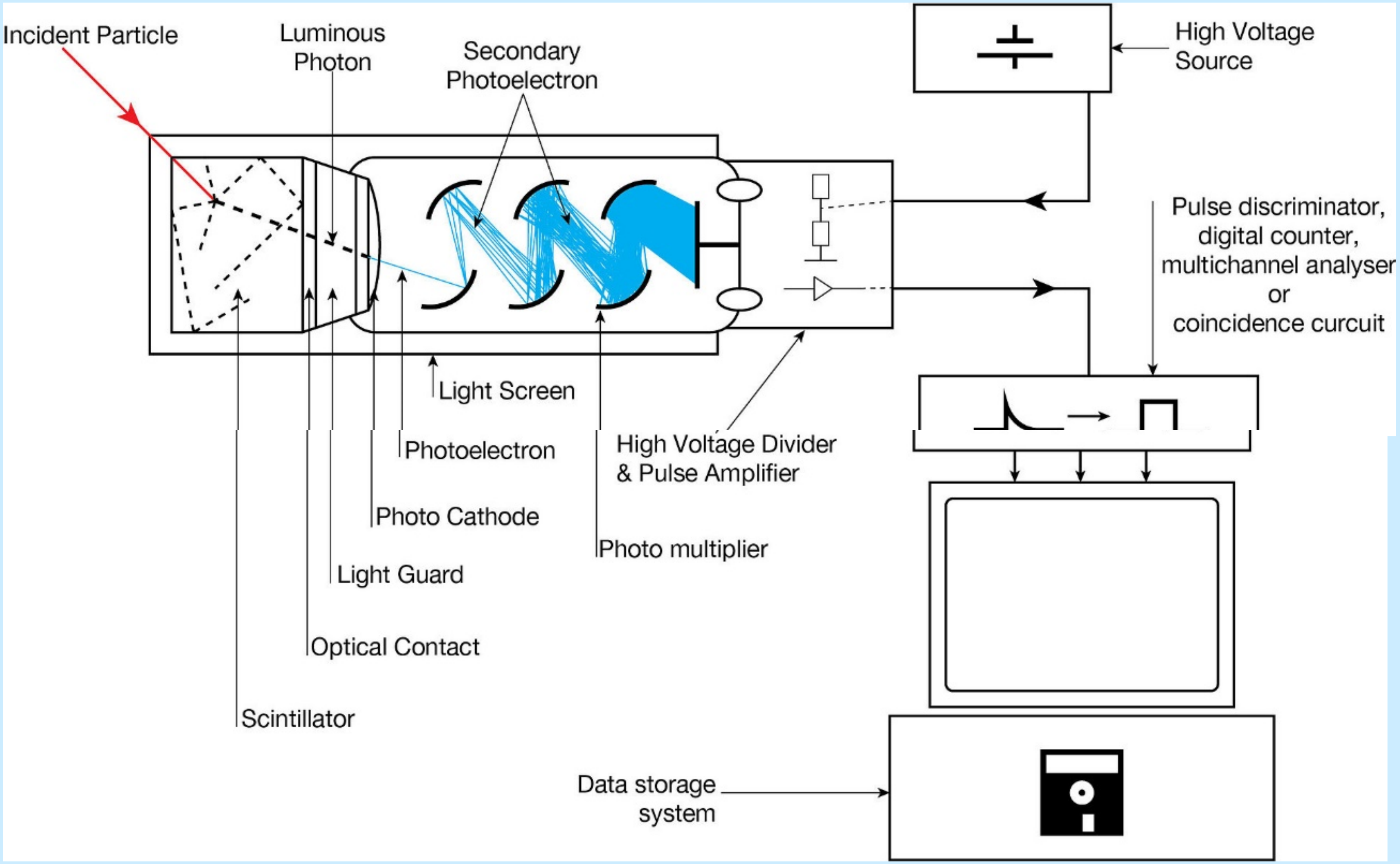
Detectors

•convert energies of individual photons to electric current
•convert current into voltage pulses that are counted

- Film (in the linear range, Guinier, Debye-Scherrer, precession cameras)
- Gas Proportional Counter
- Si(Li) solid state detector (powder diffractometers)
- Scintillation counter (photocathode, dynodes, 4-circle diffractometer, Stoe powder diffractometer)
- Position Sensitive Detectors (1D or 2D)
- Image Plate Detectors (2D detection)
- CCD Detectors (Bruker SMART system)

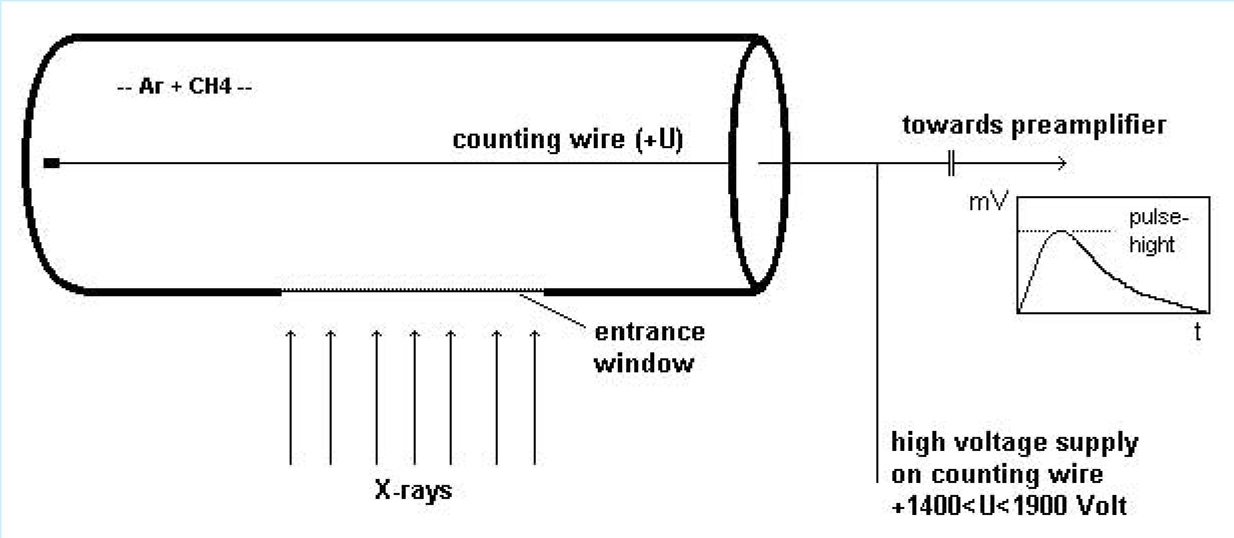
Point Detectors

Scintillation counters



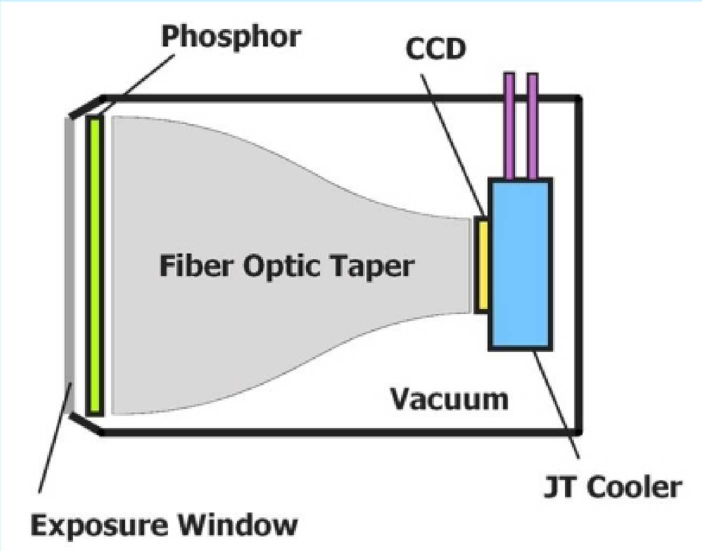
Point Detectors

Gas proportional counters



Area Detectors

Charge-coupled devices



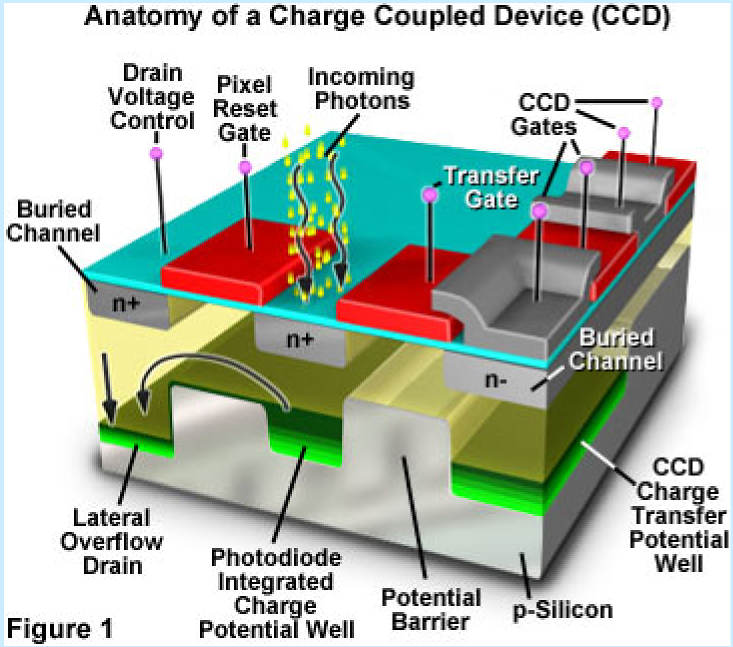
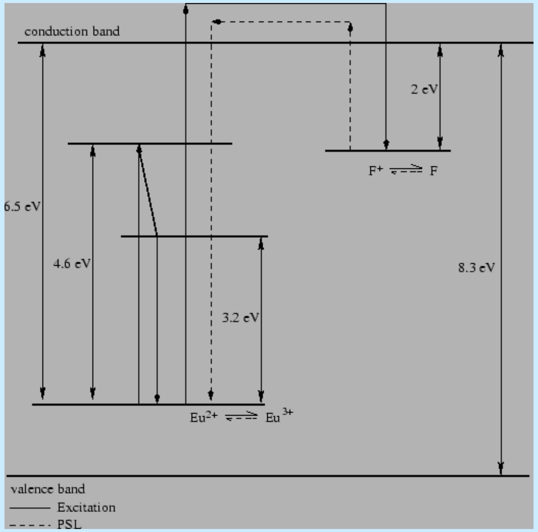
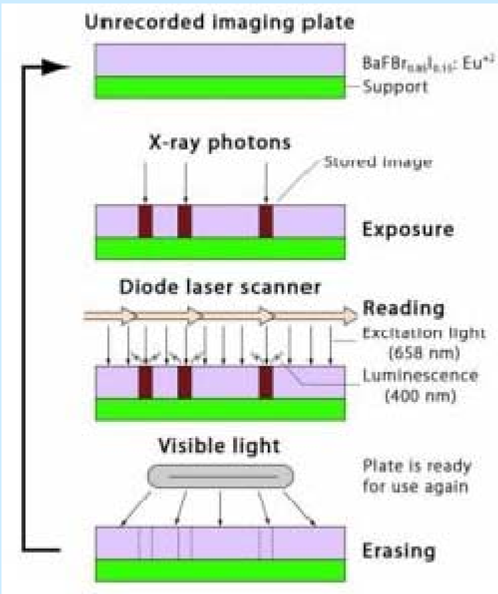


Image Plate Detectors



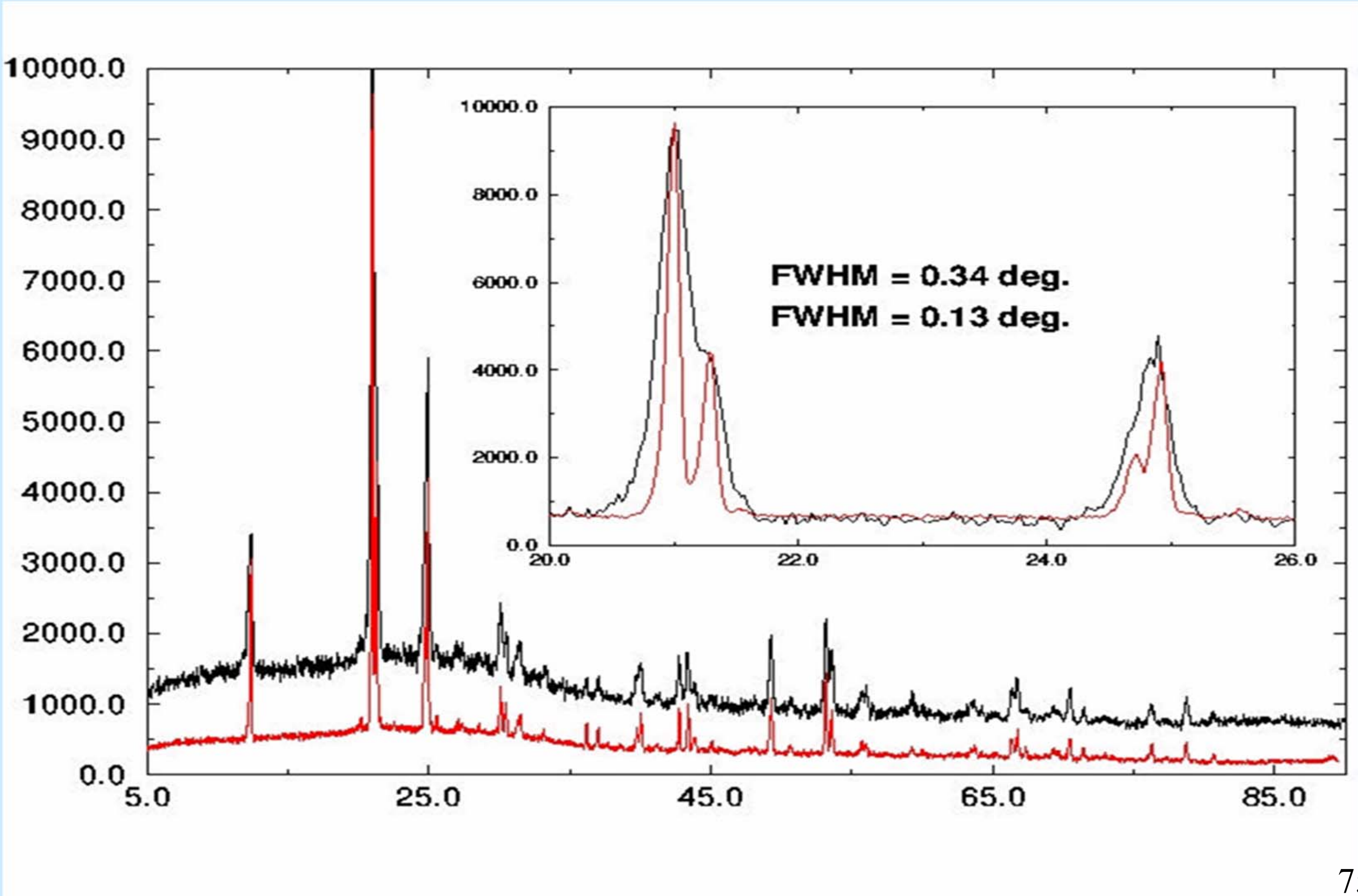
- Metal plate, 18 cm diameter, coated with Eu^{2+}doped BaFBr
- X-rays ionize Eu^{2+} to Eu^{3+} and the electrons are trapped in color centers
- Read out process with red laser leads to emission of blue light, when electrons return to ground state
- The blue light is amplified by a photomultiplier and recorded as a pixel image



Detector properties

- quantum-counting efficiency
- linearity
- energy proportionality
- resolution

Resolution



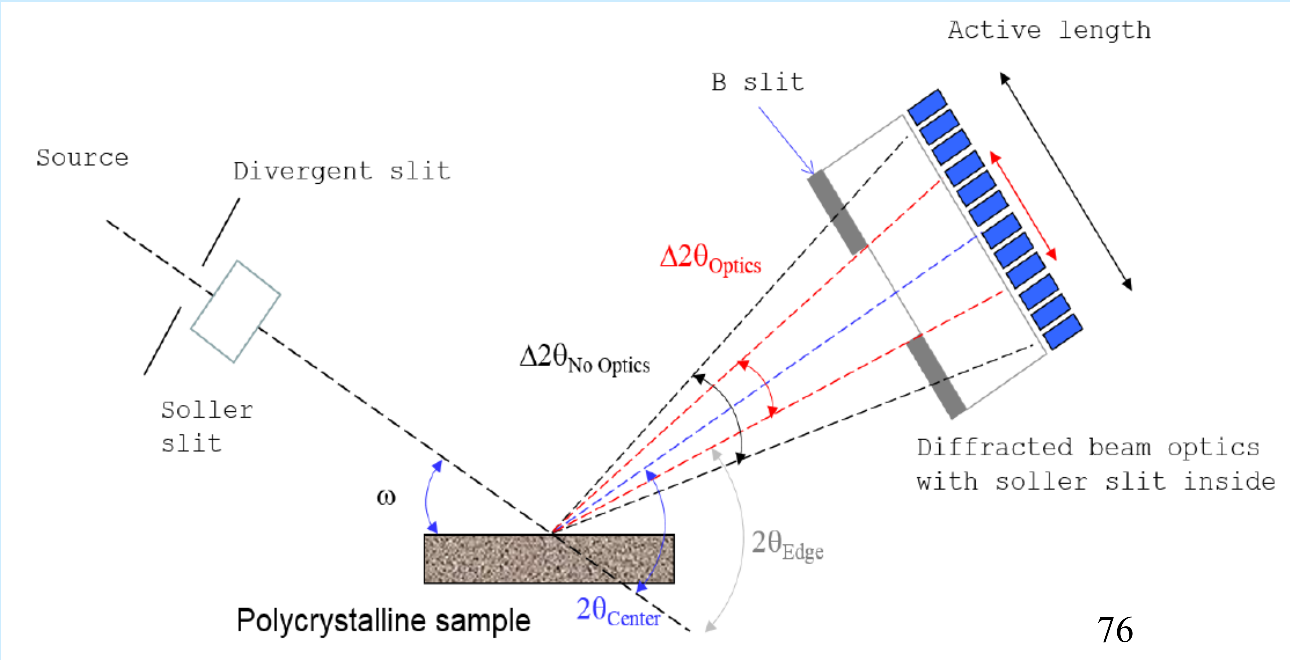
10000.0
9000.0
8000.0
7000.0
6000.0
5000.0
4000.0
3000.0
2000.0
1000.0
0.0
5.0
25.0
45.0
65.0
85.0
10000.0
8000.0
6000.0
4000.0
2000.0
0.0
20.0
22.0
24.0
26.0
FWHM = 0.34 deg.
FWHM = 0.13 deg.

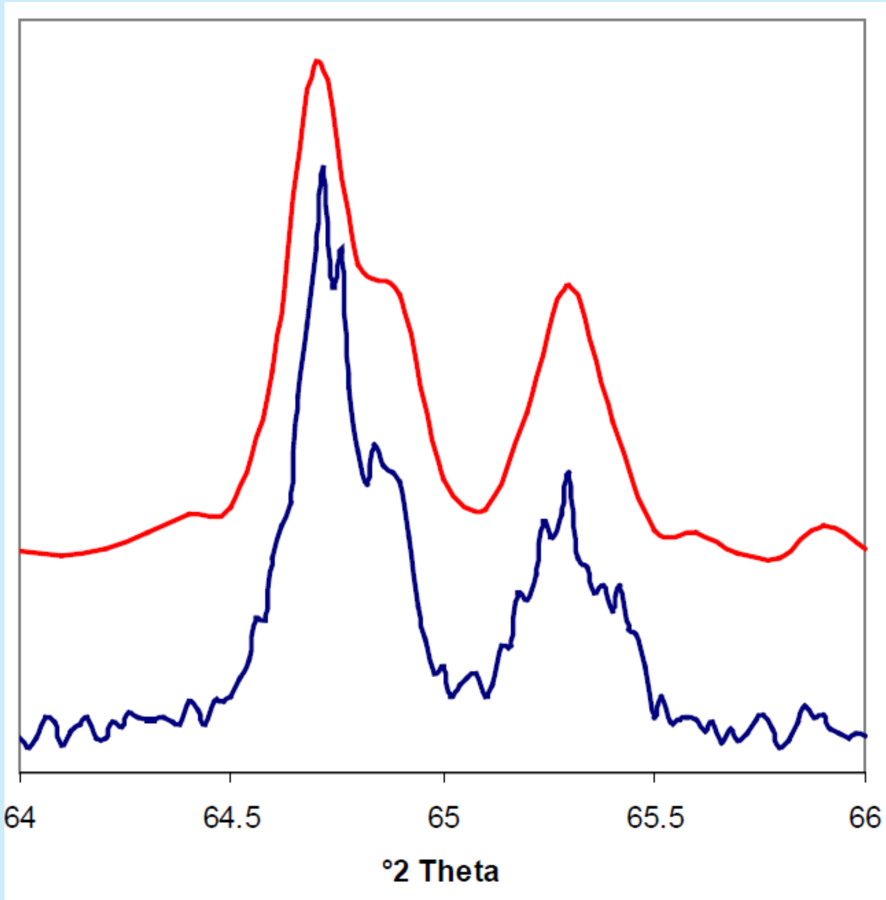
Linear Sensitive Position Detector

Single-photon-counting silicon microstrip

Detector active area made by many single point detectors (pixels)

Energy range 4 – 40 keV



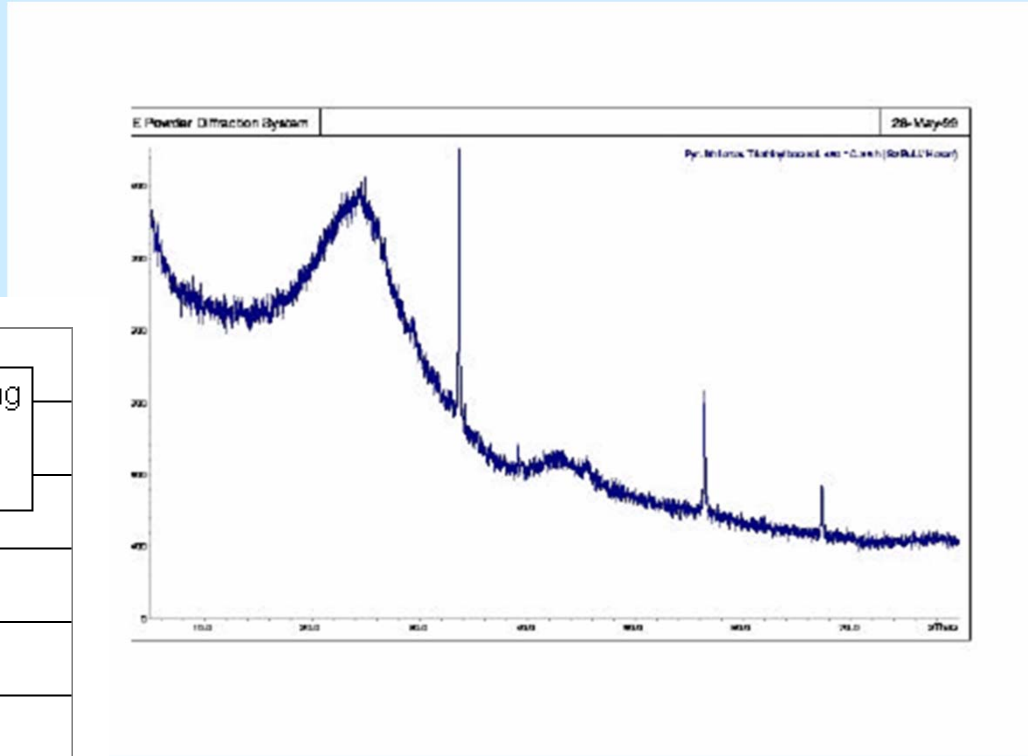


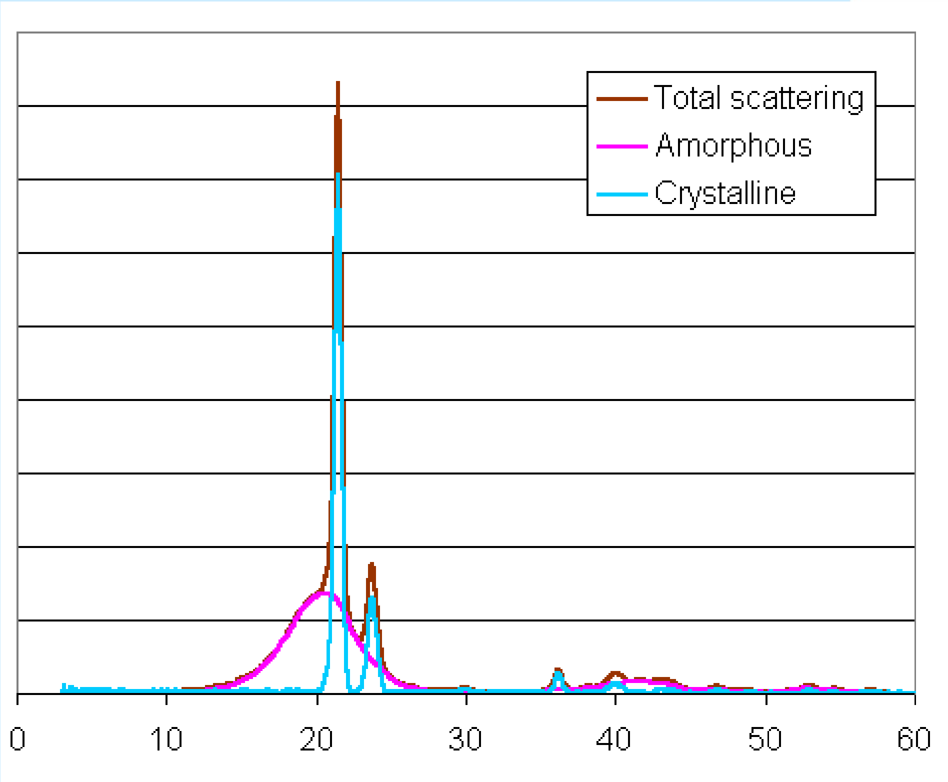
Red = Step 0.1 °2 theta
Blue = Step 0.02 °2 theta

Information Extracted from Diffraction Experiments

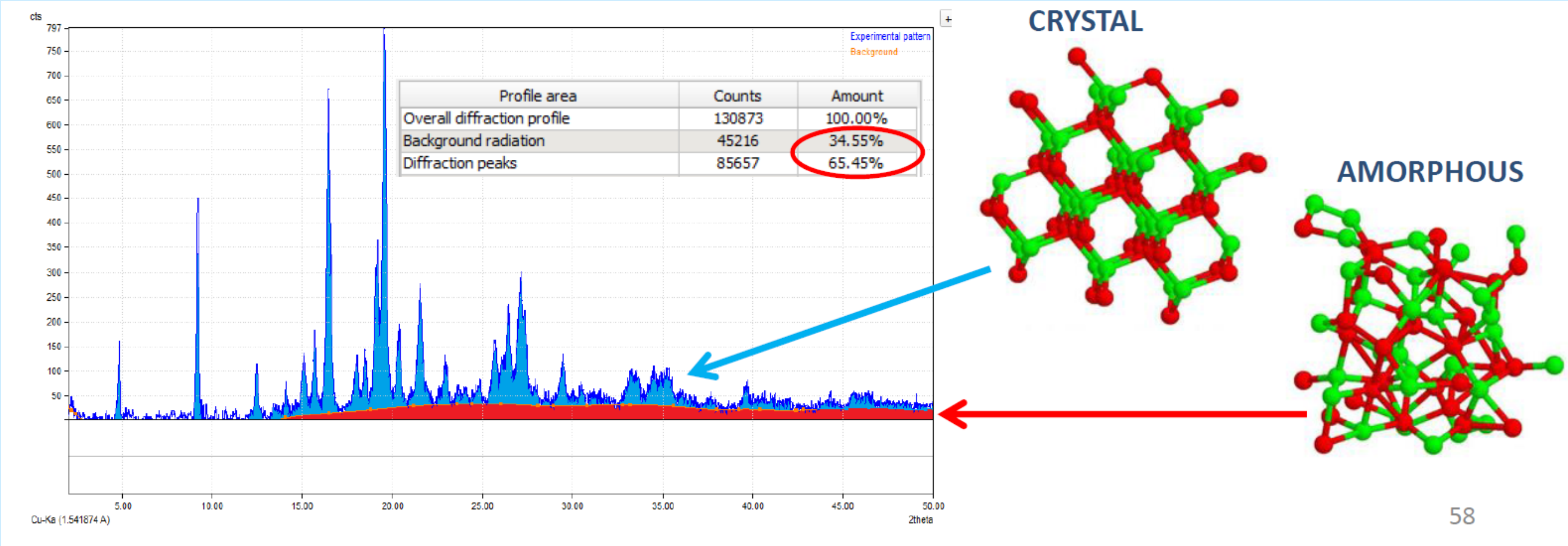
- Crystallinity
- Identification of known phases in databases (PDF)
- Determination of lattice constants
- Domain size - particle size
- Microstrain
- Quantitative analysis – Rietveld refinement
- Structure solution – Rietveld refinement
- In-situ measurements – temperature, pressure, atmosphere, kinetics

Crystalline and Amorphous Phases



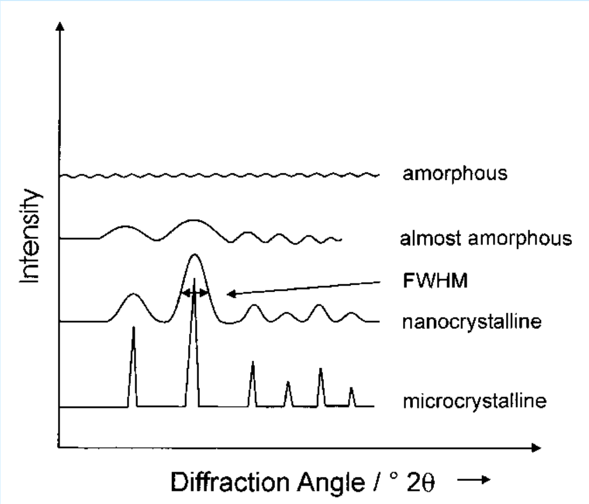


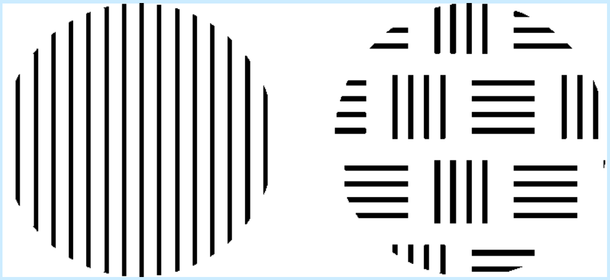
Crystallinity Degree



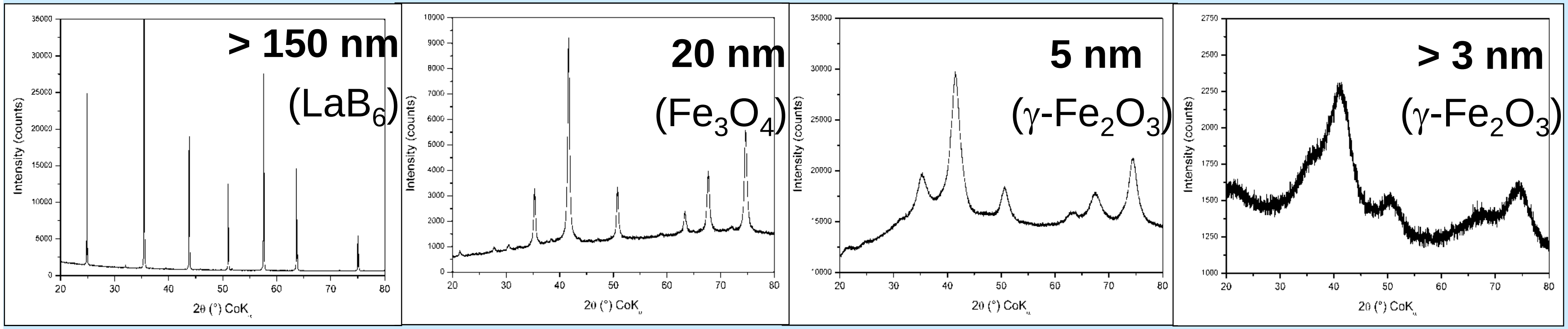
Profile area	Counts	Amount
Overall diffraction profile	130873	100.00%
Background radiation	45216	34.55%
Diffraction peaks	85657	65.45%

Domain size - particle size





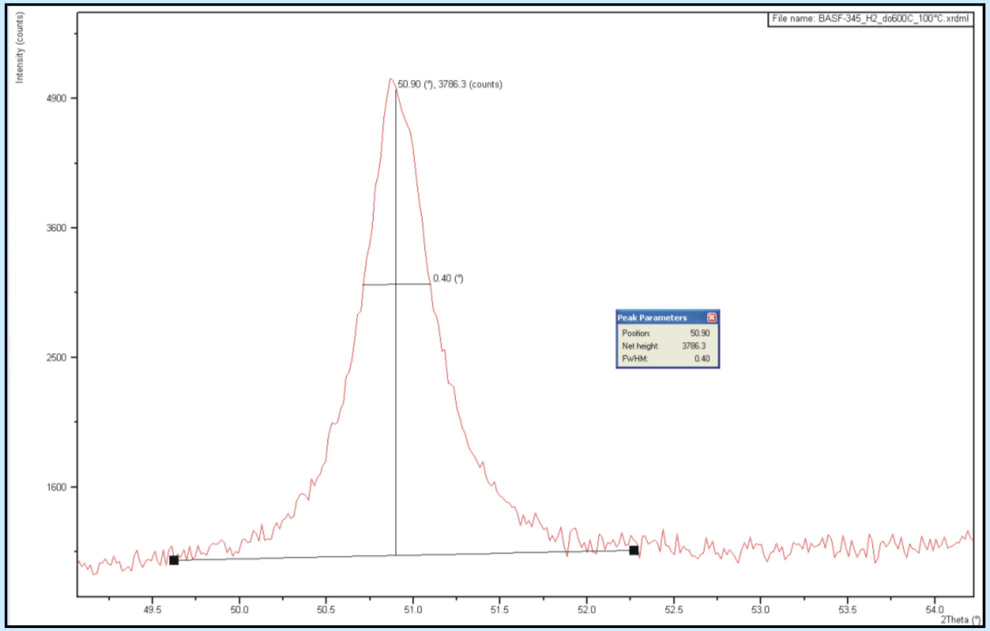
Coherent domain size
- Scherrer method
- Rietveld analysis

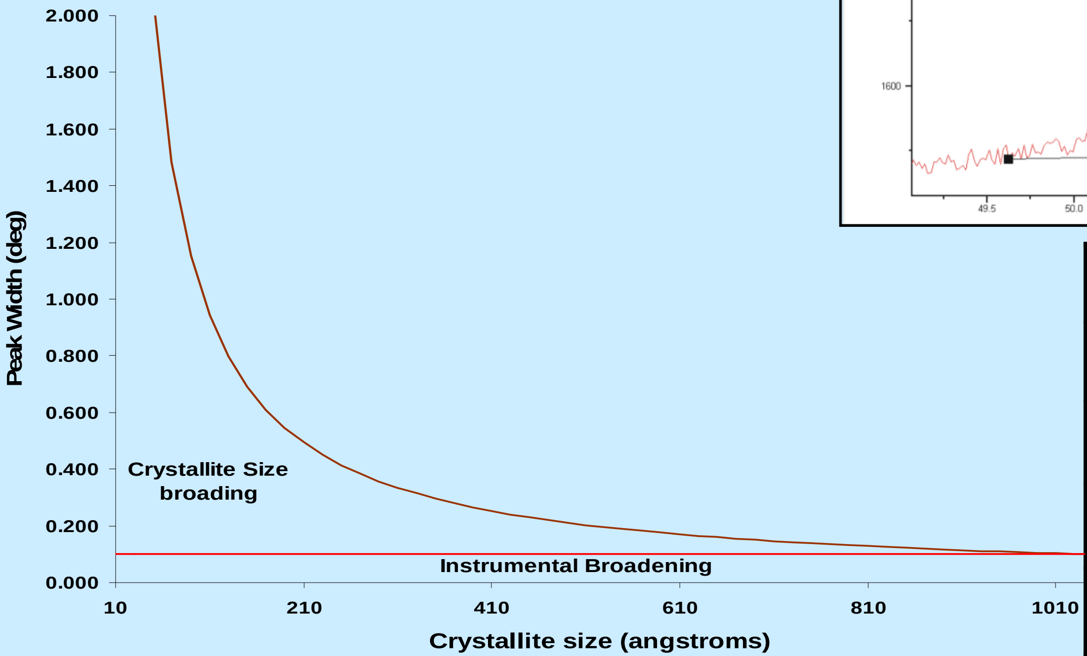


Scherrer method

$$C = K \lambda / (B \cos \theta)$$

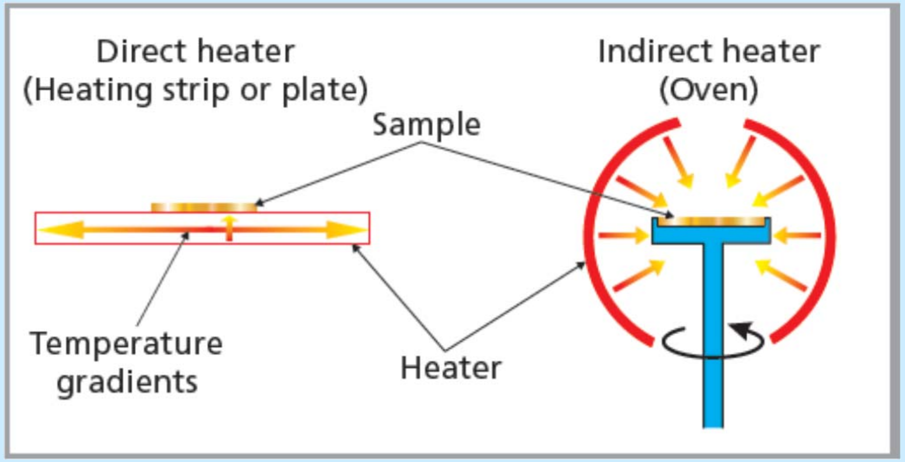
B – FWHM

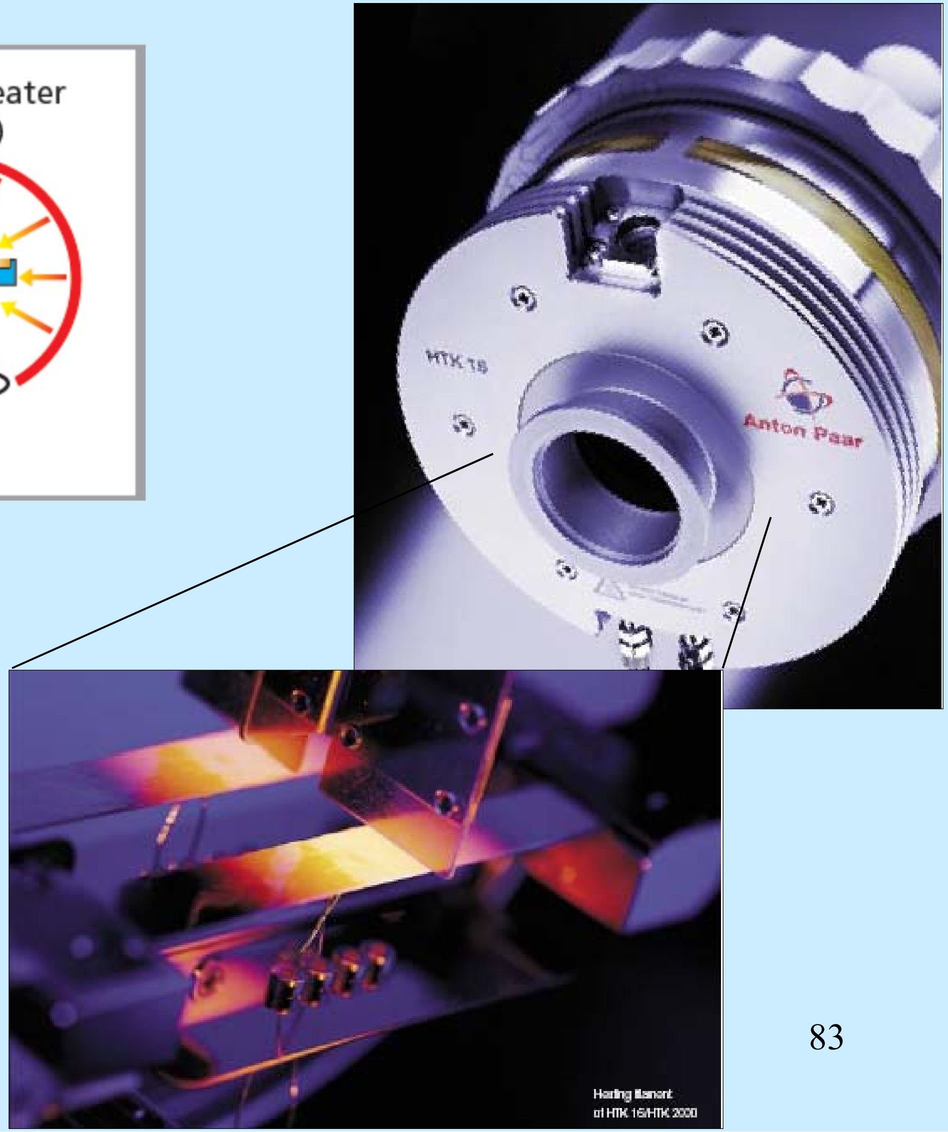




Particle	Shape factor K
sphere	0.89
cube	0.83 - 0.91
tetrahedron	0.73 - 1.03
octahedron	0.82 - 0.93

High-temperature XRD

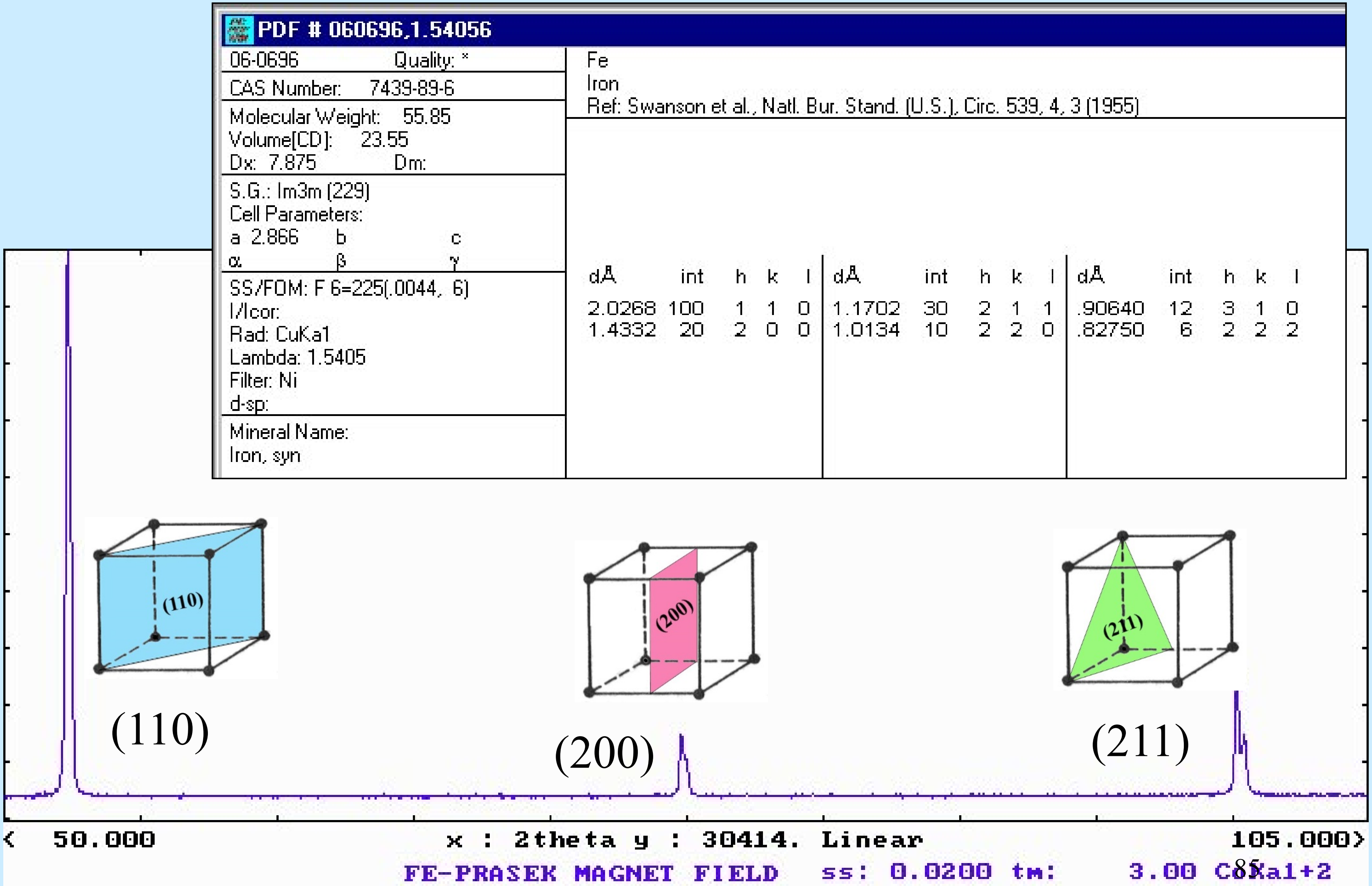




Databases

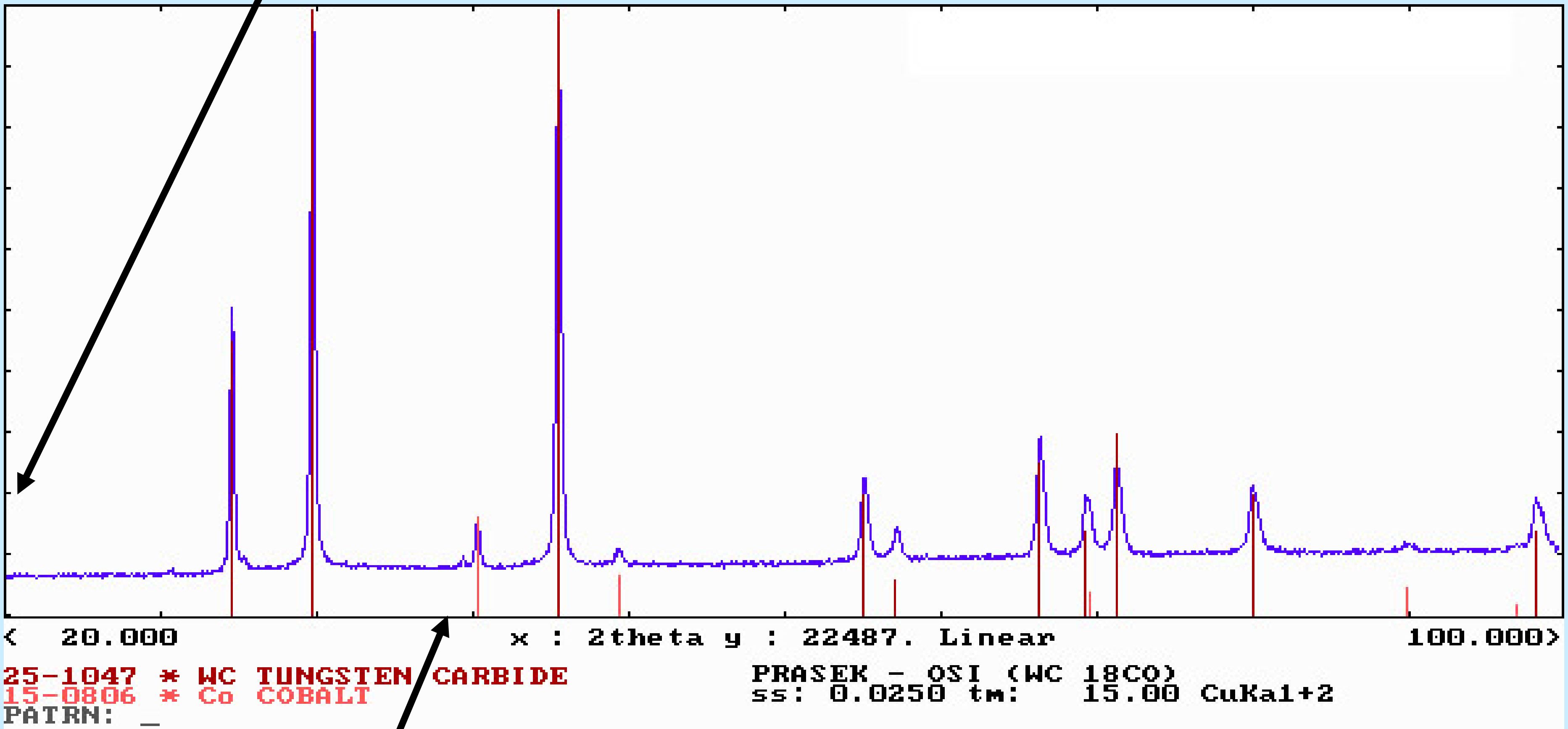
- ICSD (Karlsruhe, inorganics, single crystal data)
- CSD (Cambridge, organics, organometallics, sc data)
- NRCC CRYSTMET (metals)
- PDB (proteins, Brookhaven)
- NIST (NBS)
- JCPDS = ICDD (PDF files, 60000 patterns)

X-ray powder diffraction pattern of Fe



Quantity

More complicated, volume fraction



Quality

$$d = \lambda / 2 \sin \Theta$$

Line position is given by interplanar distance d and wavelenght λ

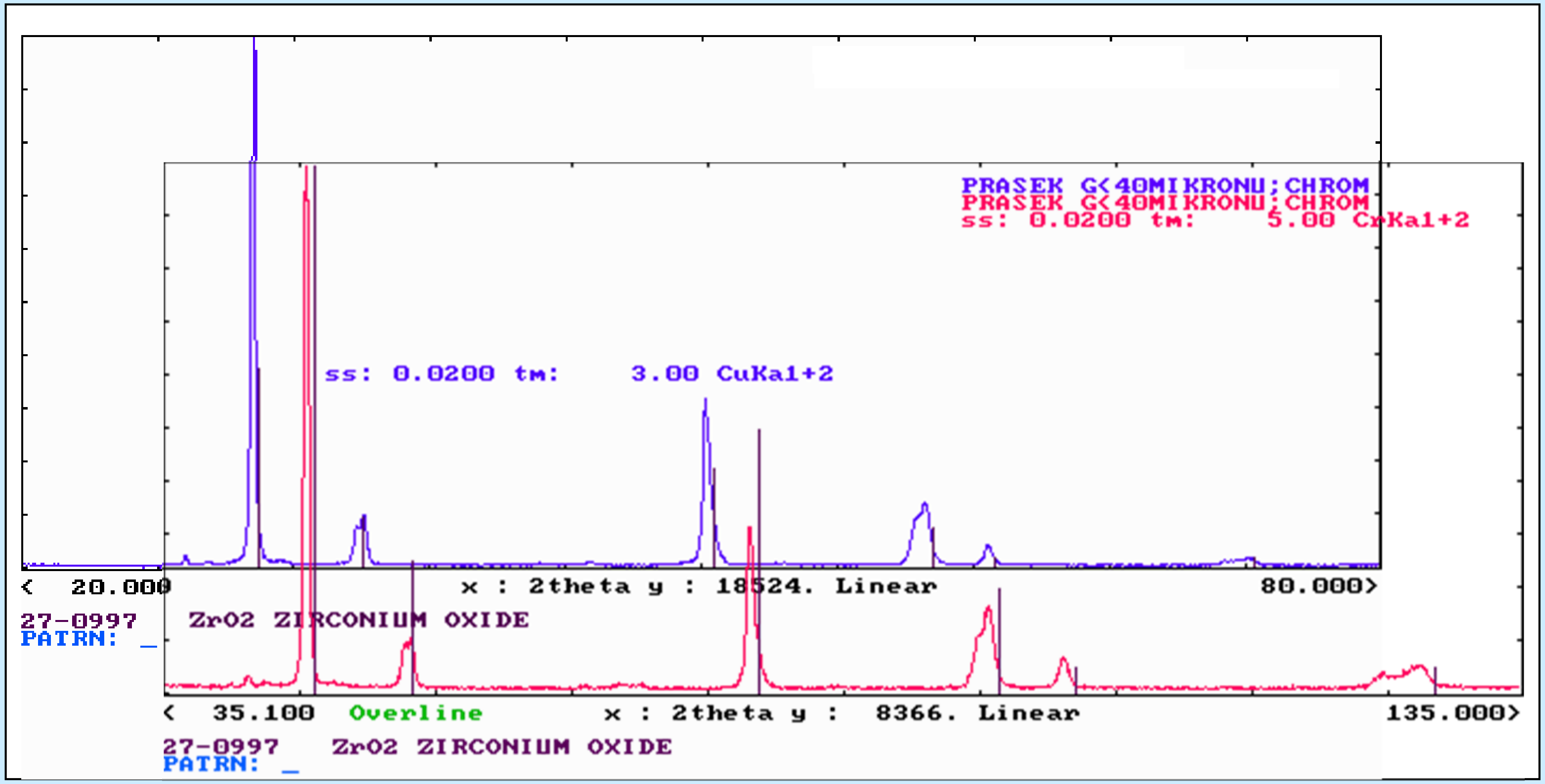
Selecting radiation

Anode	Wavelength [nm]			Beta filter
	$K\alpha_1$ [100]	$K\alpha_2$ [50]	$K\beta_1$	
Cr	0.228970	0.229361	0.208487	V
Fe	0.193604	0.193998	0.175661	Mn
Co	0.178897	0.179285	0.162079	Fe
Cu	0.154056	0.154439	0.139222	Ni
Mo	0.070930	0.071359	0.063229	Zr

$d = \lambda / 2 \sin \Theta$ ... longer λ ... better multiplet separation
... shorter λ ... more lines

Bcc crystal, Cu radiation

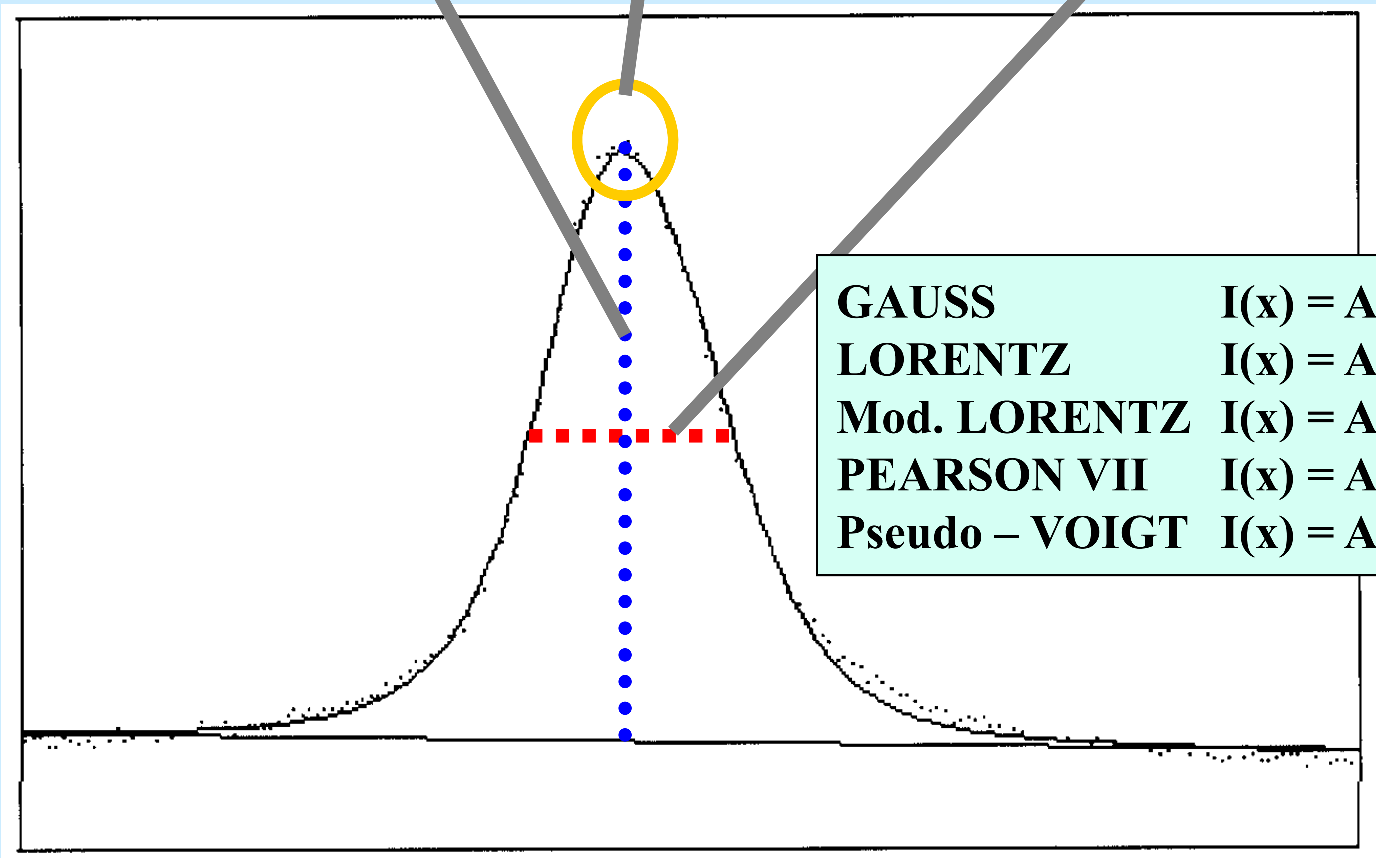
a = 1.5 nm --> 2Θ = 11.8
a = 1.2 nm --> 2Θ = 14.8
a = 0.9 nm --> 2Θ = 19.7
a = 0.6 nm --> 2Θ = 29.8
a = 0.3 nm --> 2Θ = 61.8



LINE HEIGHT
- integral intensity
- quantitative analysis
- texture

LINIE POSITION
- qualitative (phase) analysis
- lattice macrodistortions

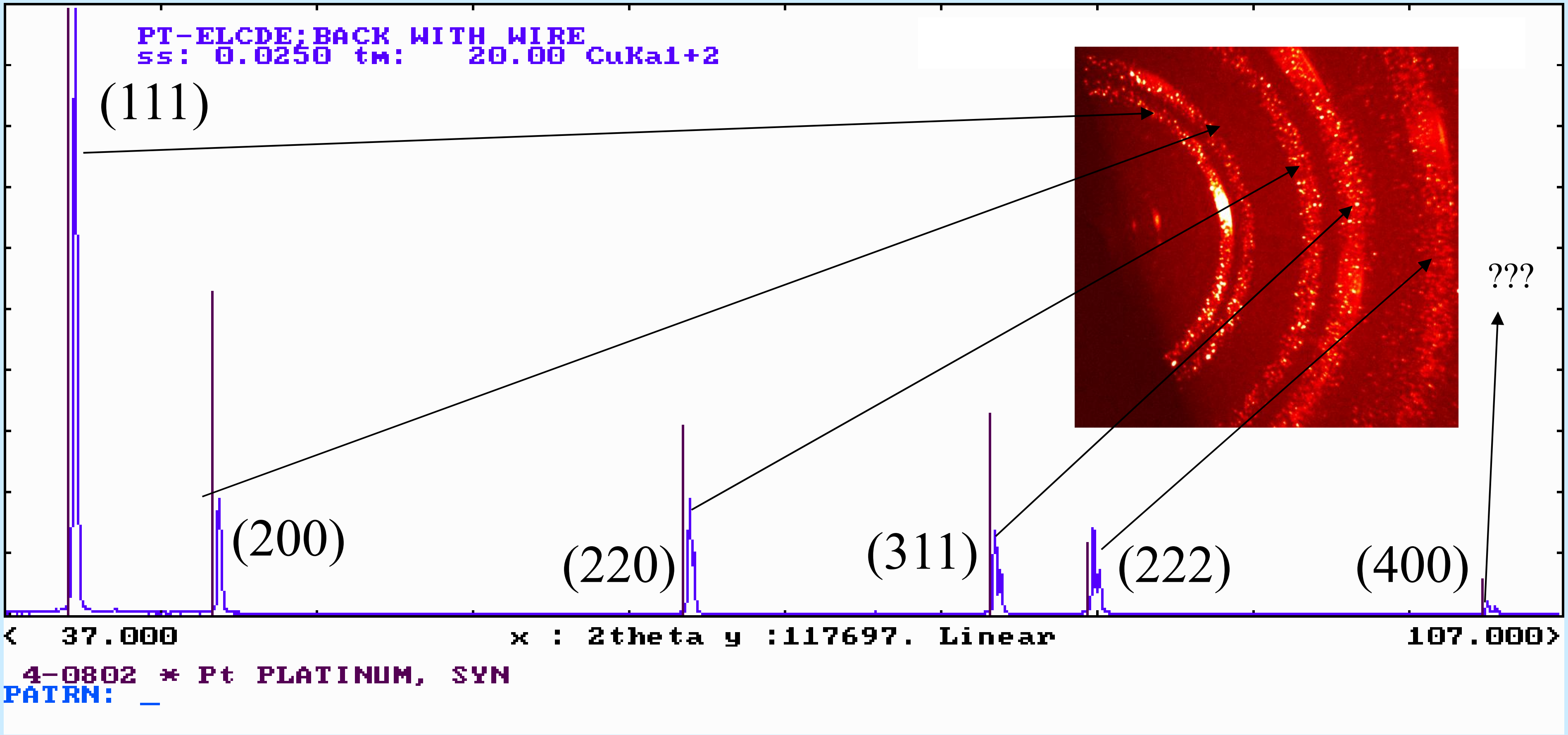
LINIE WIDTH
- size of diffracting domains
- lattice microdistortions



GAUSS	$I(x) = A \exp(-x^2/a^2)$
LORENTZ	$I(x) = A \exp[1+(x^2/a^2)]^{-1}$
Mod. LORENTZ	$I(x) = A \exp[1+(x^2/a^2)]^{-2}$
PEARSON VII	$I(x) = A \exp[1+(x^2/a^2)]^{-n}$
Pseudo – VOIGT	$I(x) = A [cL(x) + (1-c)G(x)]$

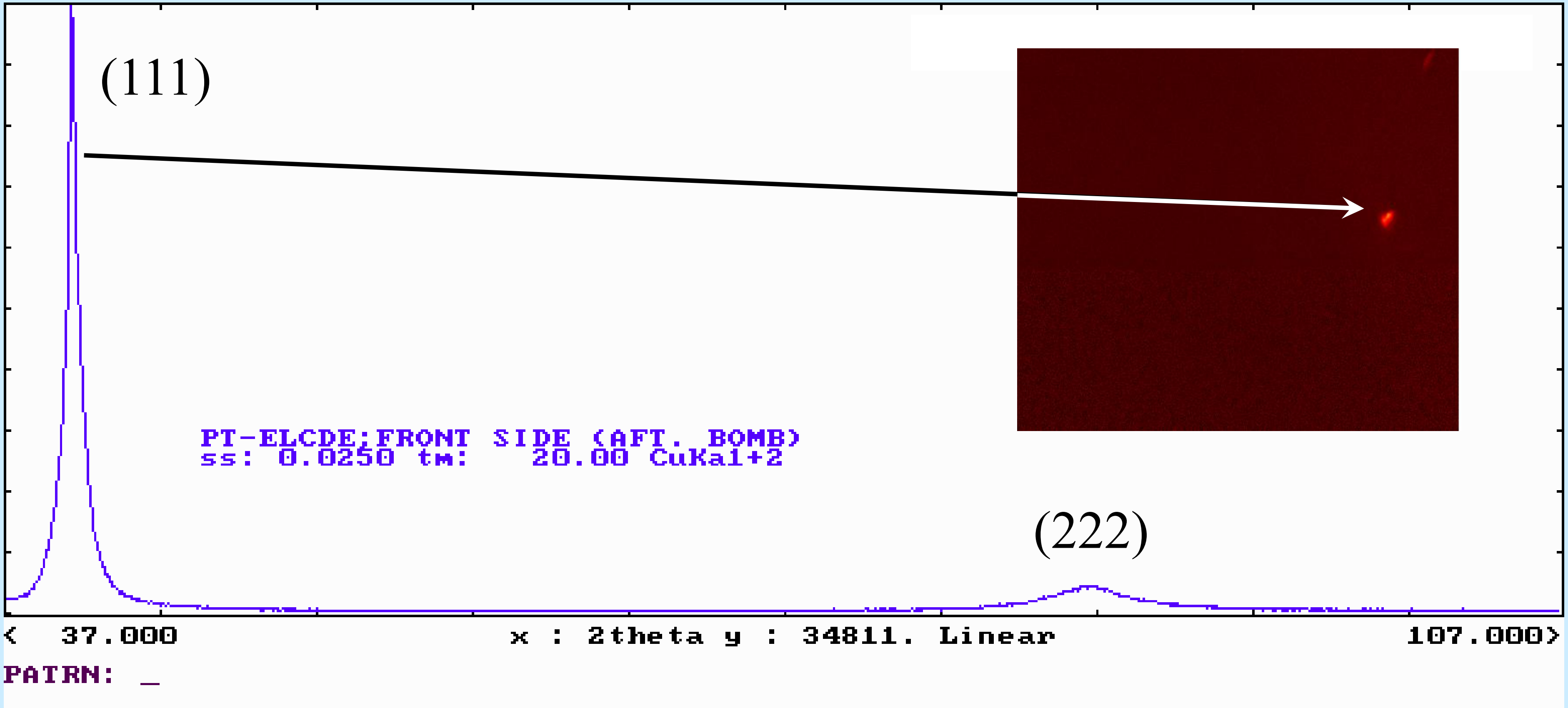
Comparison of Debye-Scherrer versus diffractometer

Polycrystalline sample



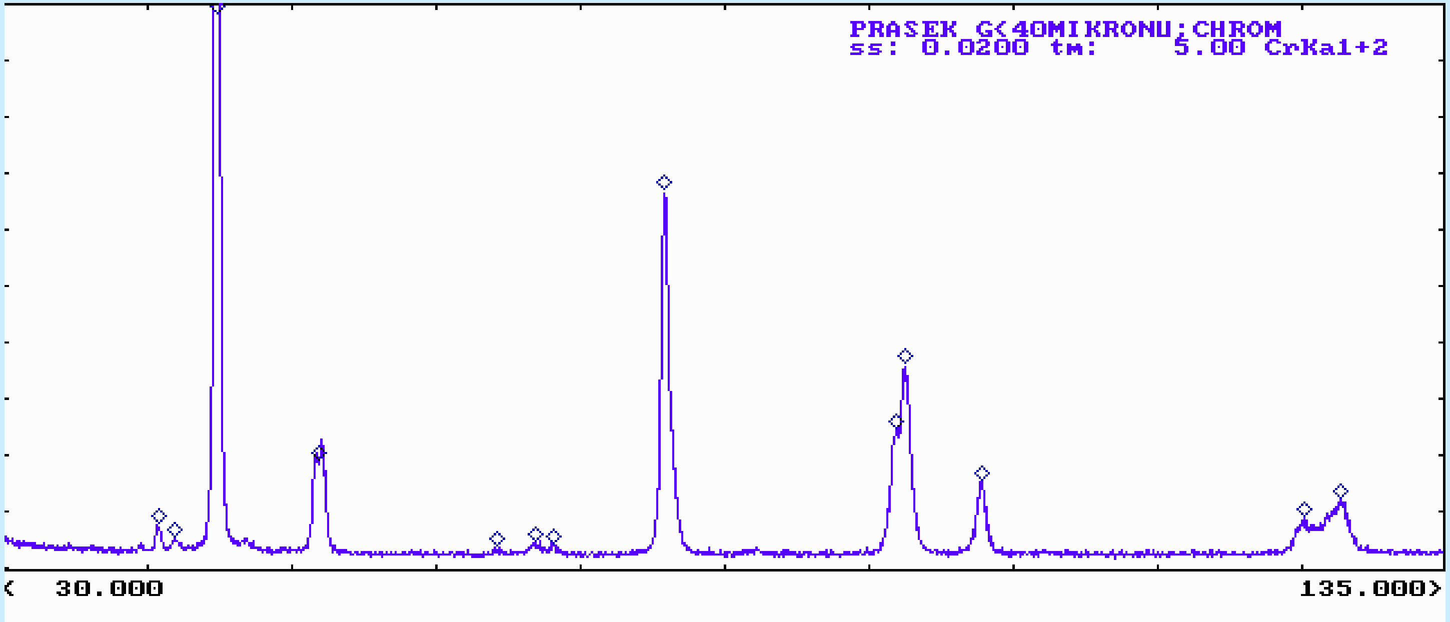
Comparison of Debye-Scherrer versus diffractometer

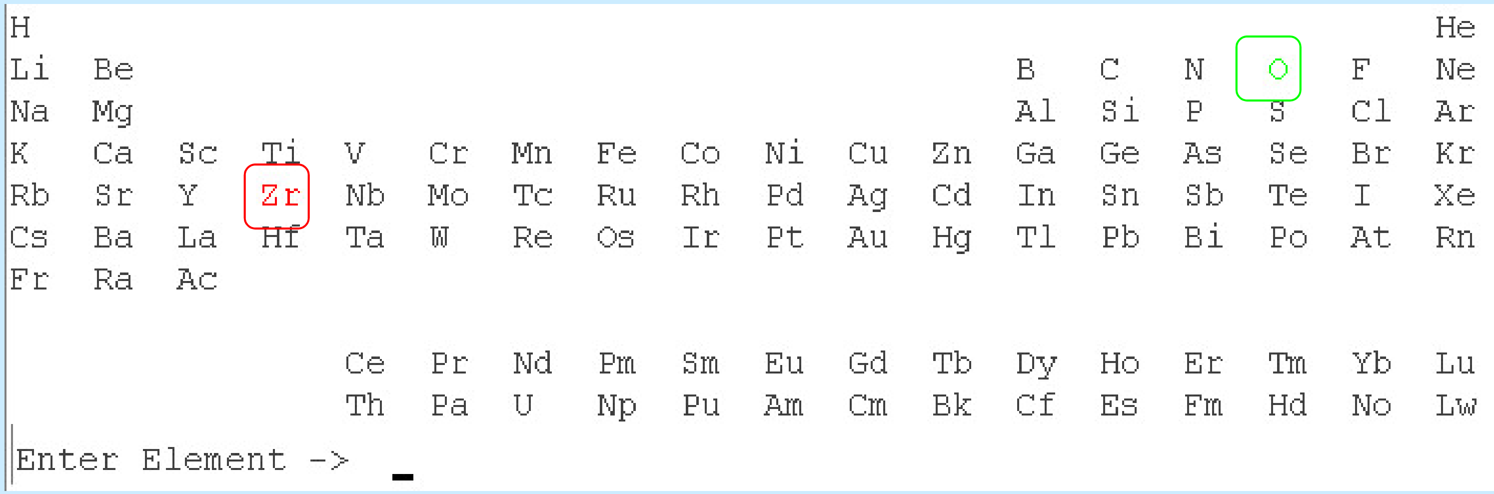
Single crystal



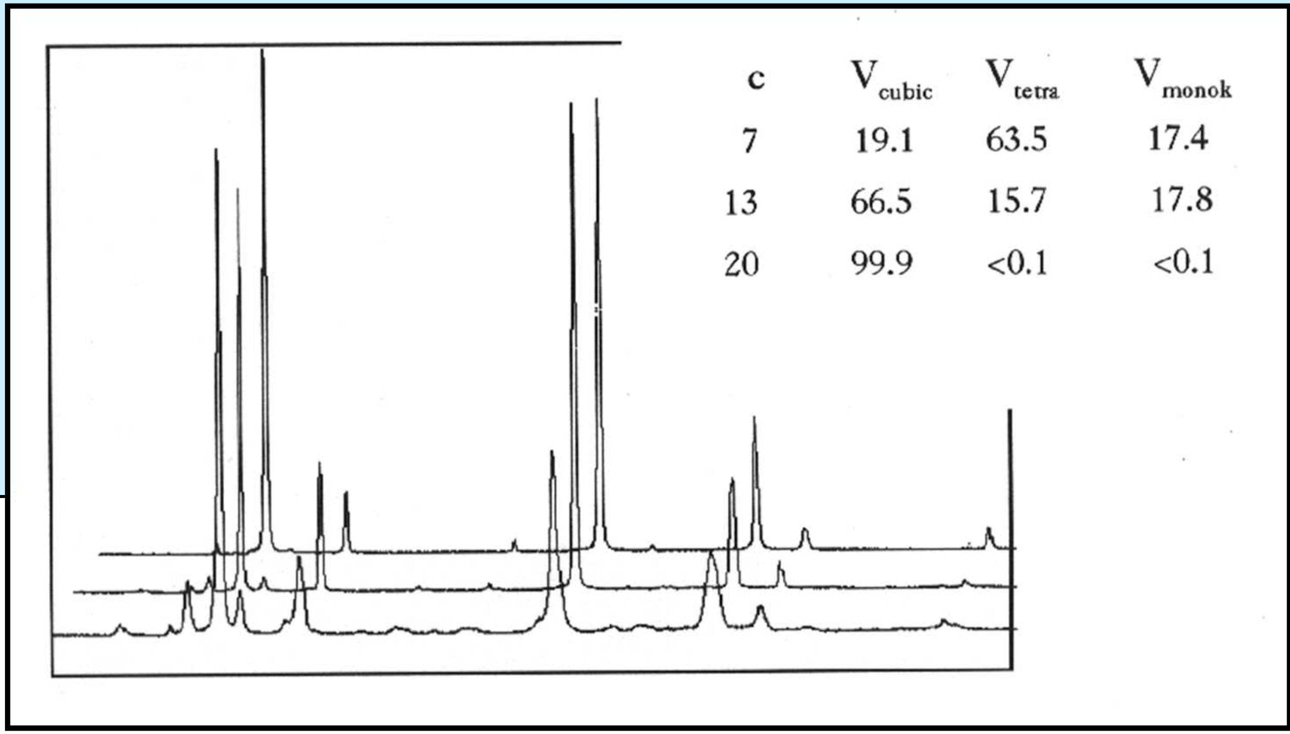
Phase analysis

$ZrO_2 + Y_2O_3$

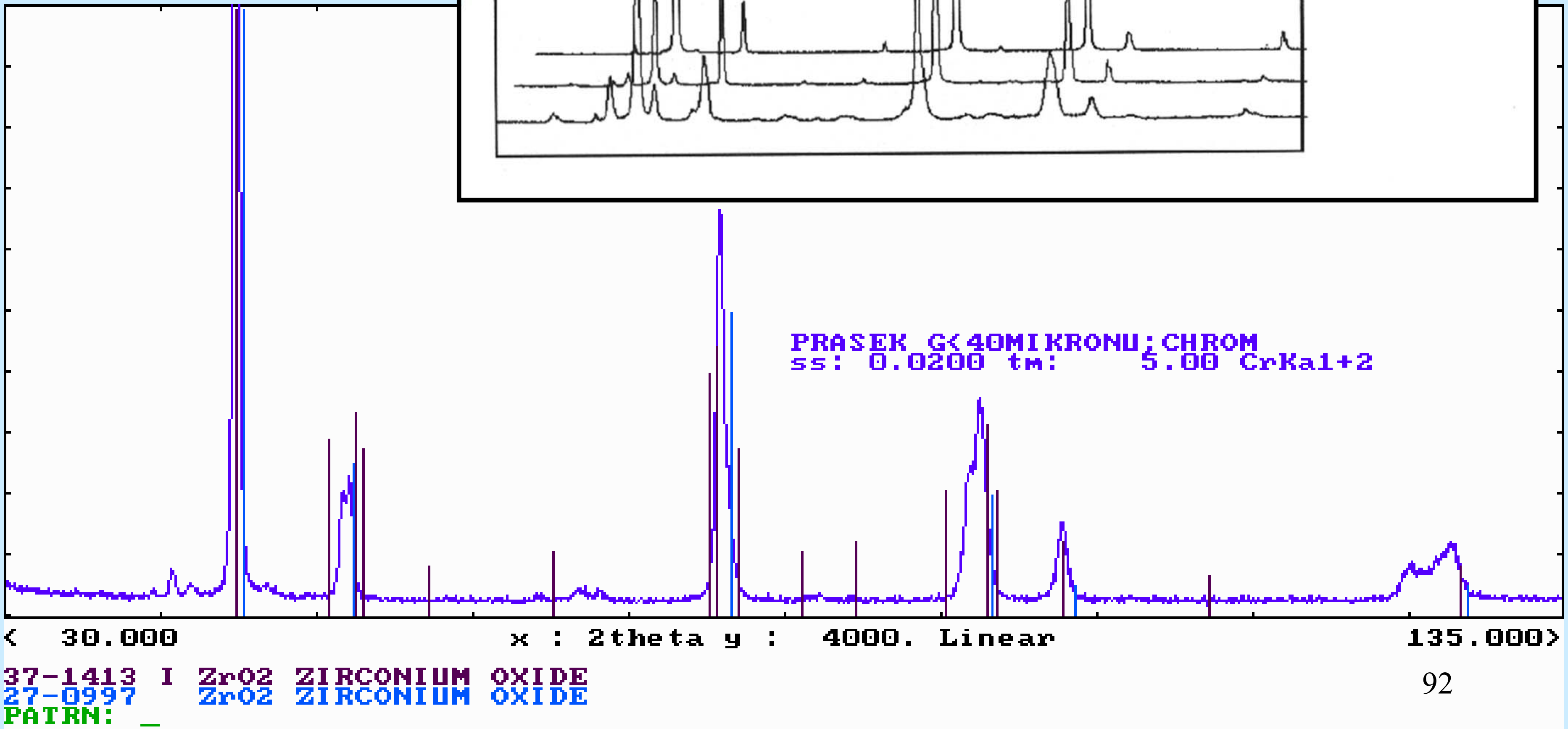




Results of phase analysis



c	V_{cubic}	V_{tetra}	V_{monok}
7	19.1	63.5	17.4
13	66.5	15.7	17.8
20	99.9	<0.1	<0.1



Which of these is *not* involved in the diffraction of X-rays through a crystal?

a	Electron transitions
b	Crystallographic planes
c	Nuclear interactions
d	Constructive interference

What is the *largest* wavelength of radiation that will be diffracted by a lattice plane of the interplanar spacing *d*?

a	0.5*d*
b	*d*
c	2*d*
d	No limit