Lesson 1
X-Rays & Diffraction

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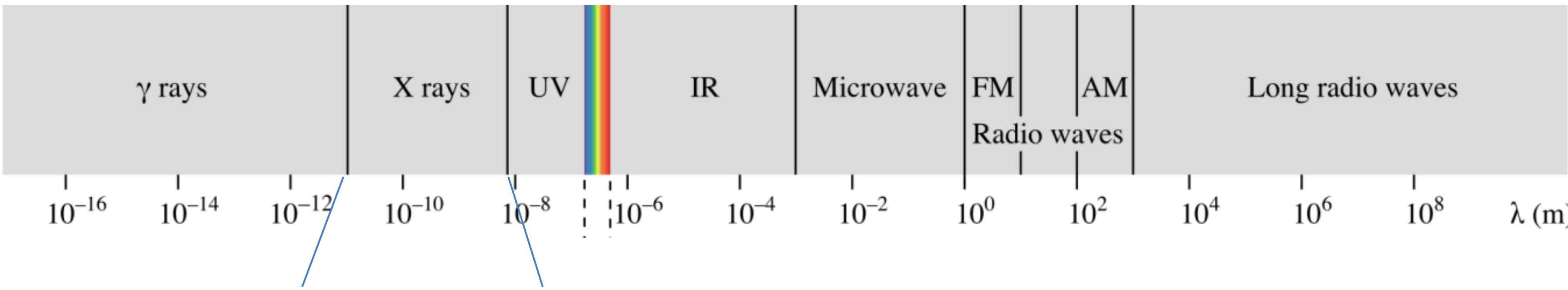
Electromagnetic Spectrum



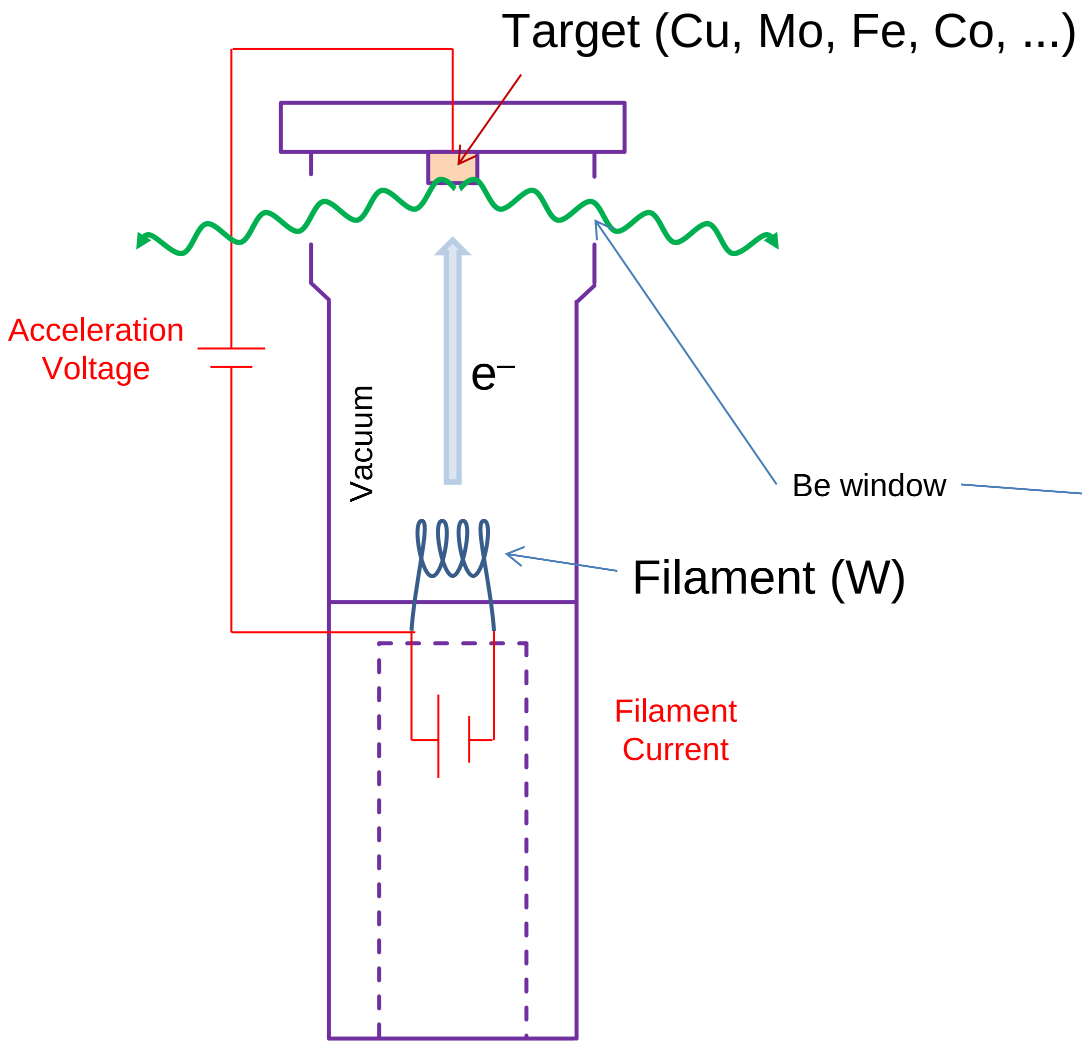
X rays:
Wavelength λ: 0.01 – 10 nm
Energy: 100 eV – 100 keV

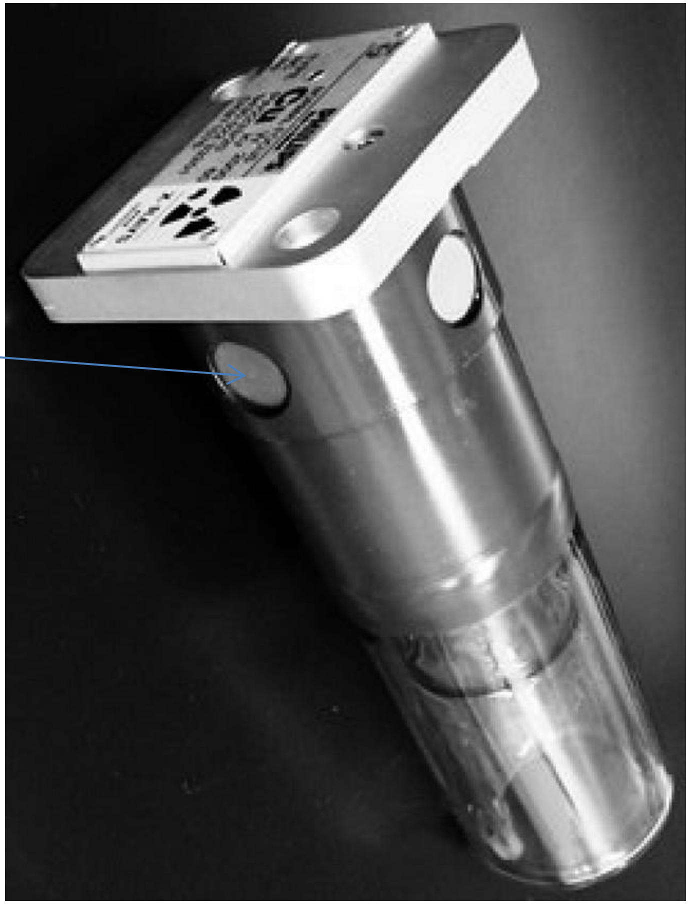
Interatomic distances in crystals:
typically 0.15 – 0.4 nm

Interference phenomena only
for features ≈ λ

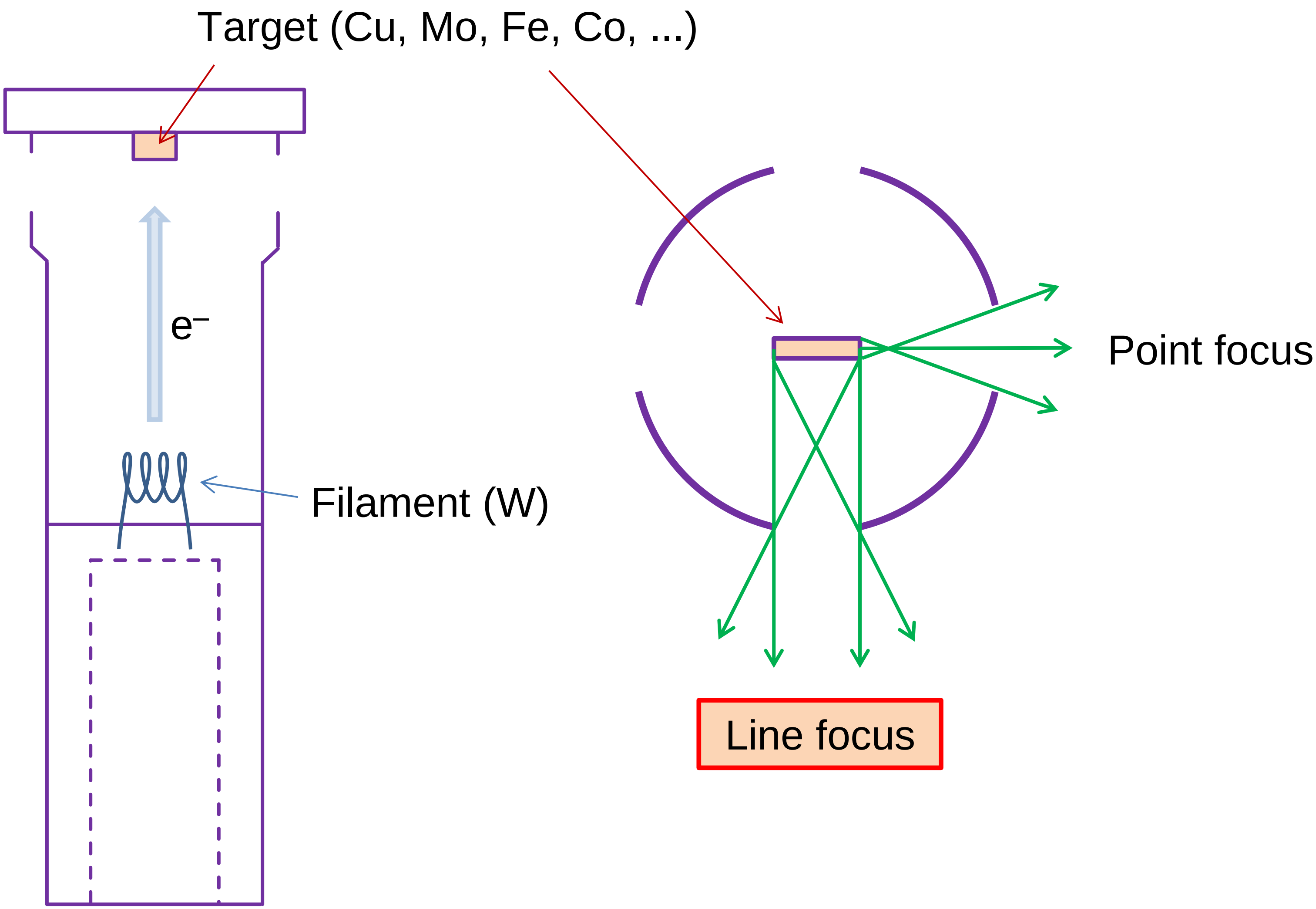
Generation of X-radiation:
Shoot electrons on matter

X-ray Tube


Target (Cu, Mo, Fe, Co, ...)
Acceleration Voltage
Vacuum
e⁻
Be window
Filament (W)
Filament Current

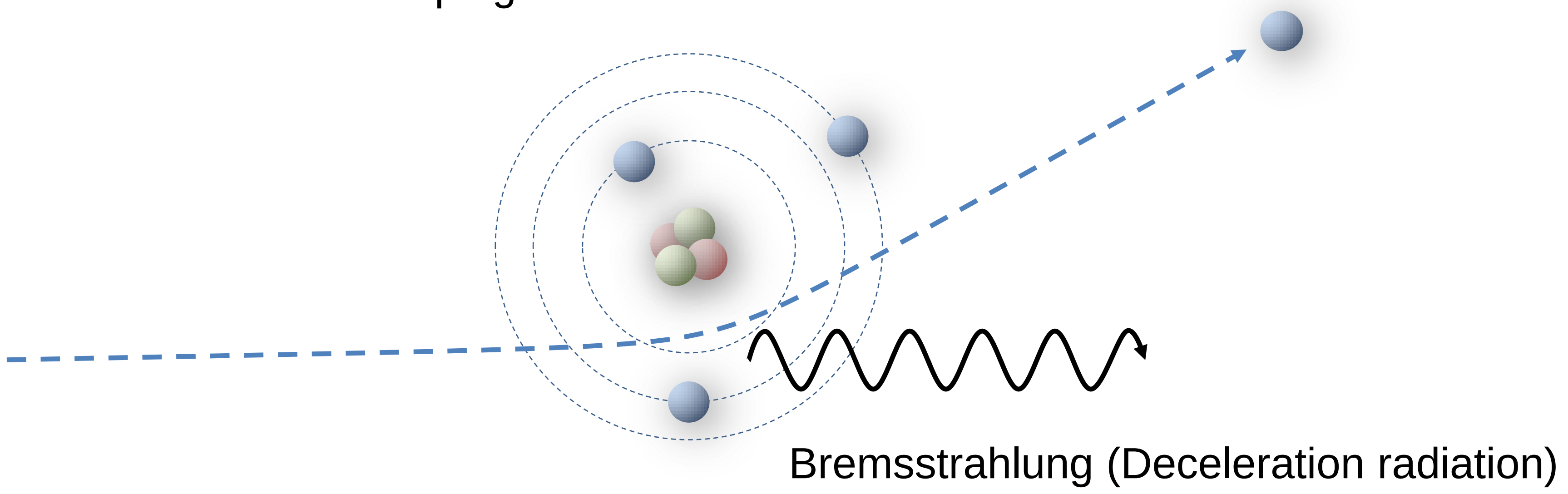


X-ray Tube



Generation of X-rays

Accelerated electron impinges on matter:

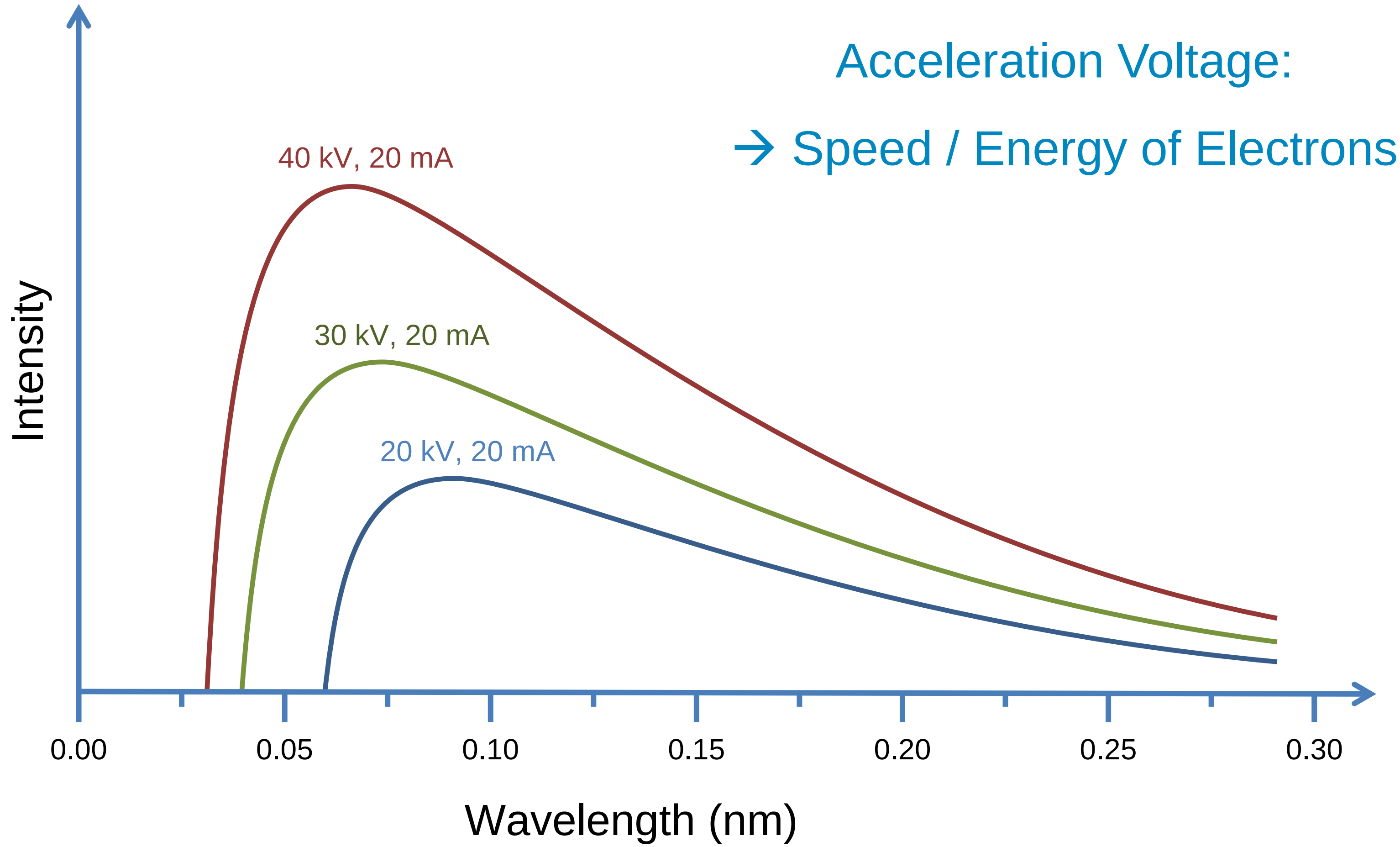


Electron is deflected and decelerated by the atomic nucleus.
(Inelastic scattering)

Deflected electron emits electromagnetic radiation.
Wavelength depends on the loss of energy.

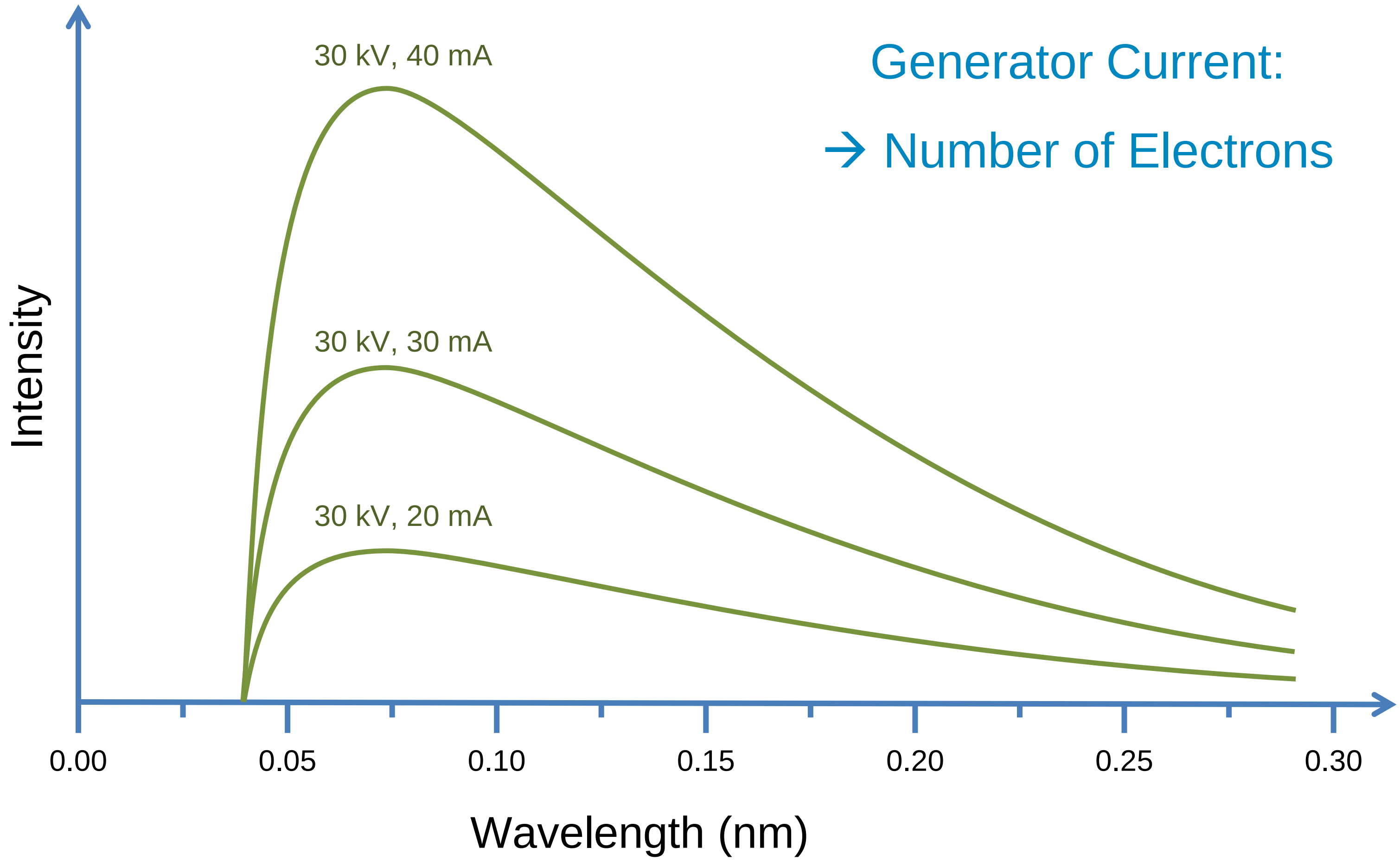
Bremsstrahlung

Continuous spectrum



Bremsstrahlung

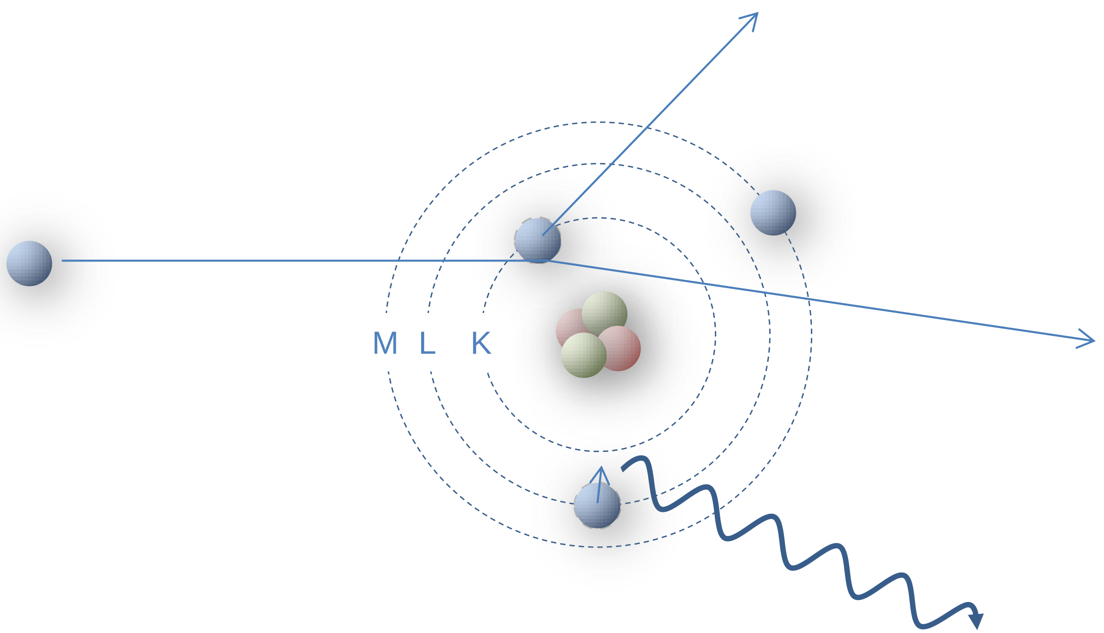
Continuous spectrum

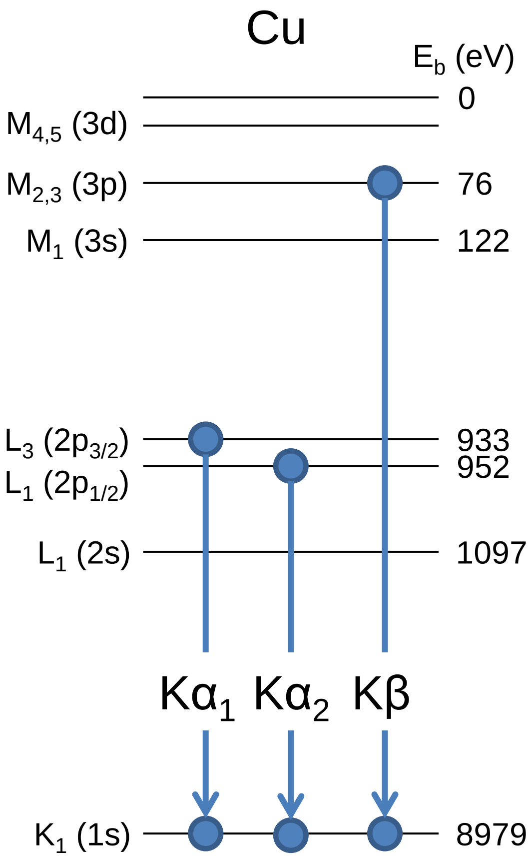


Generator Current:

→ Number of Electrons

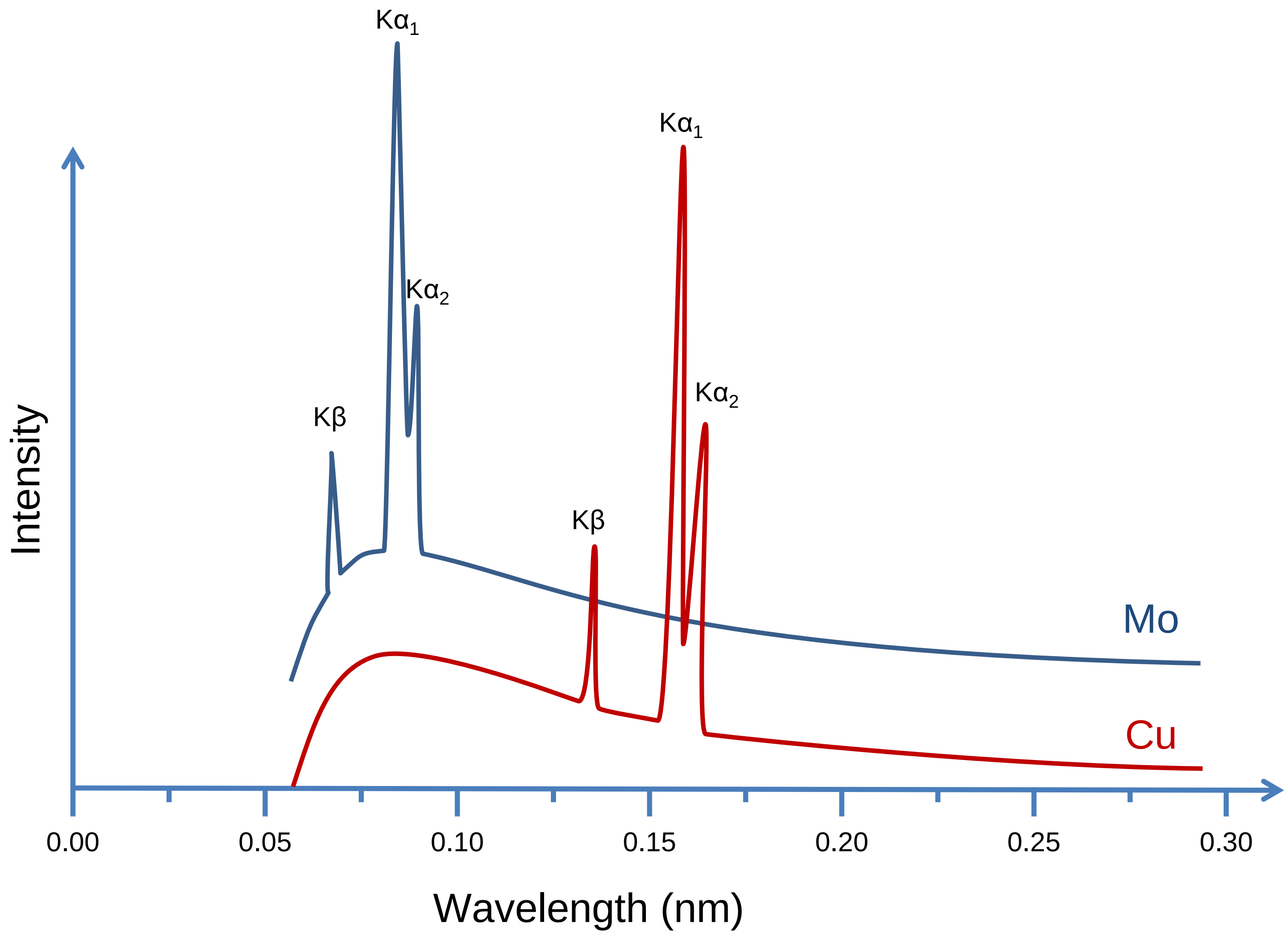
Characteristic Radiation





Wavelength of $K\alpha_1$, $K\alpha_2$, Kβ, Lα... are characteristic for the atomic species.

X-rays: Spectrum



Old X-ray tubes

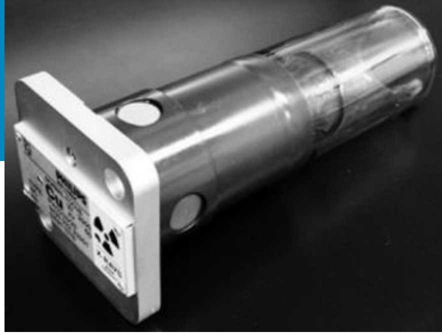
Lifetime of a few years:

- Vacuum decreases
  → loss of intensity
- Tungsten from filament deposits on target
  → contaminated spectrum (characteristic W spectrum starts to appear)

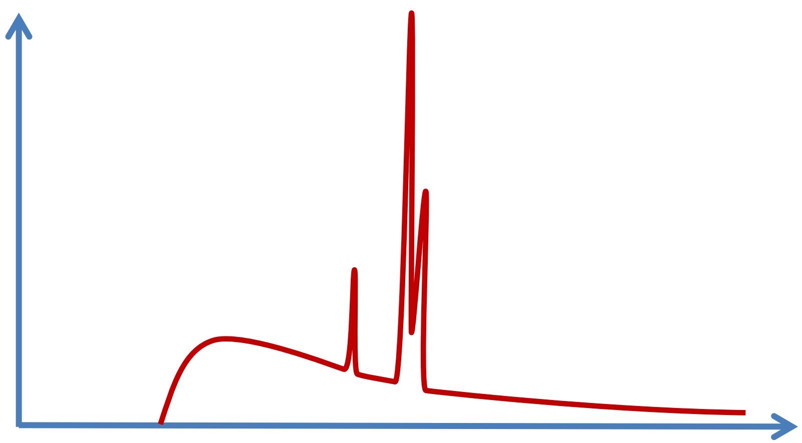
- Monitor the intensity
- Replace old tubes

Caution:
Beryllium is toxic & carcinogenic!
- Never touch the windows!
- Use appropriate covers!

X-rays: Summary



- Generated in an X-ray tube
- Spectrum contains Bremsstrahlung (continuous) and characteristic radiation ($K\alpha_1$, $K\alpha_2$, $K\beta$) of target material
- Tube is characterized by:
  - Target material
  - Size and shape of target
  - Aceleration voltage and current

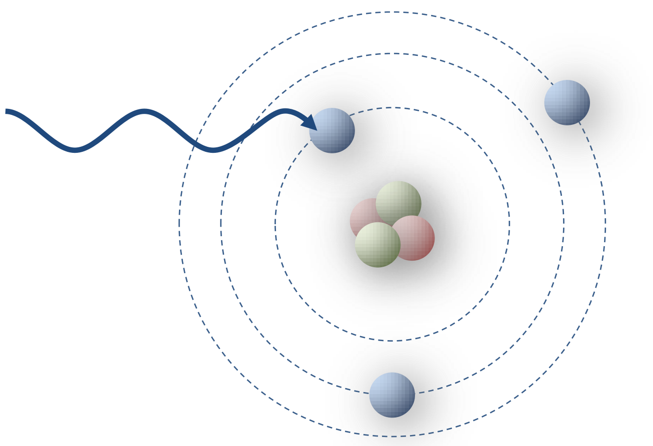


Diffraction Basics

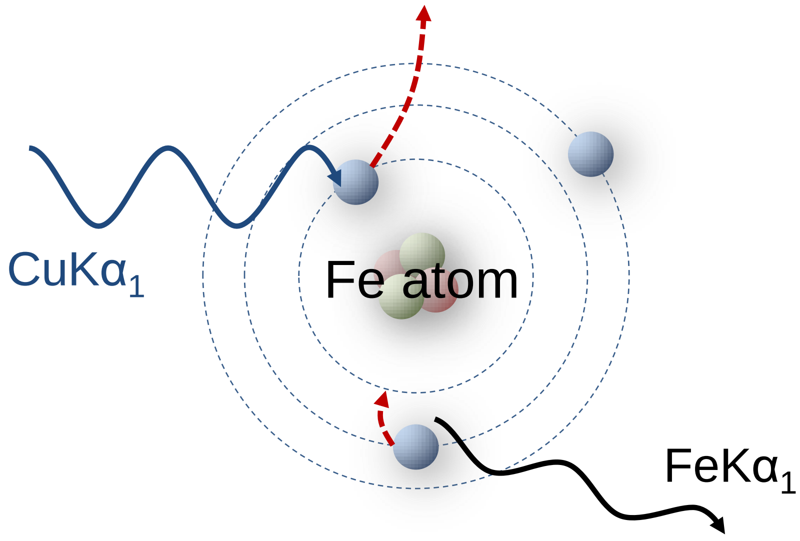
Interaction of X-rays with matter:

- Absorption (photoelectric effect, giving rise to fluorescence)
- Elastic scattering (Thomson scattering)
- ~~Inelastic scattering (Compton scattering)~~

Absorption

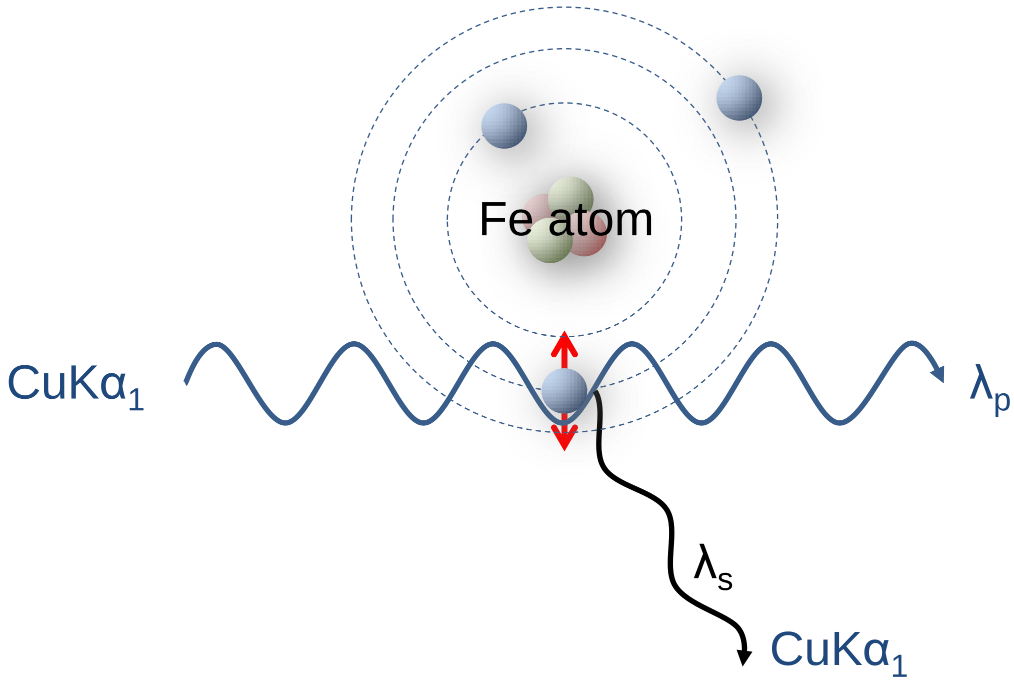


Photoelectric effect, Fluorescence



1. Absorption and ionization
2. Relaxation and emission of characteristic radiation

Elastic Scattering

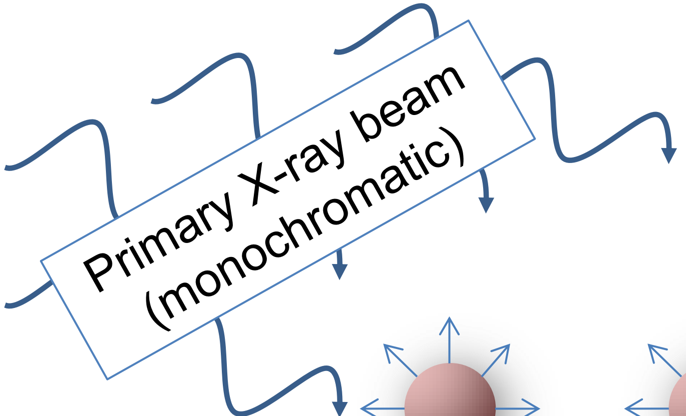


Electron oscillates in the electric field, emits photons of the same wavelength as the incoming radiation ($\lambda_s = \lambda_p$).

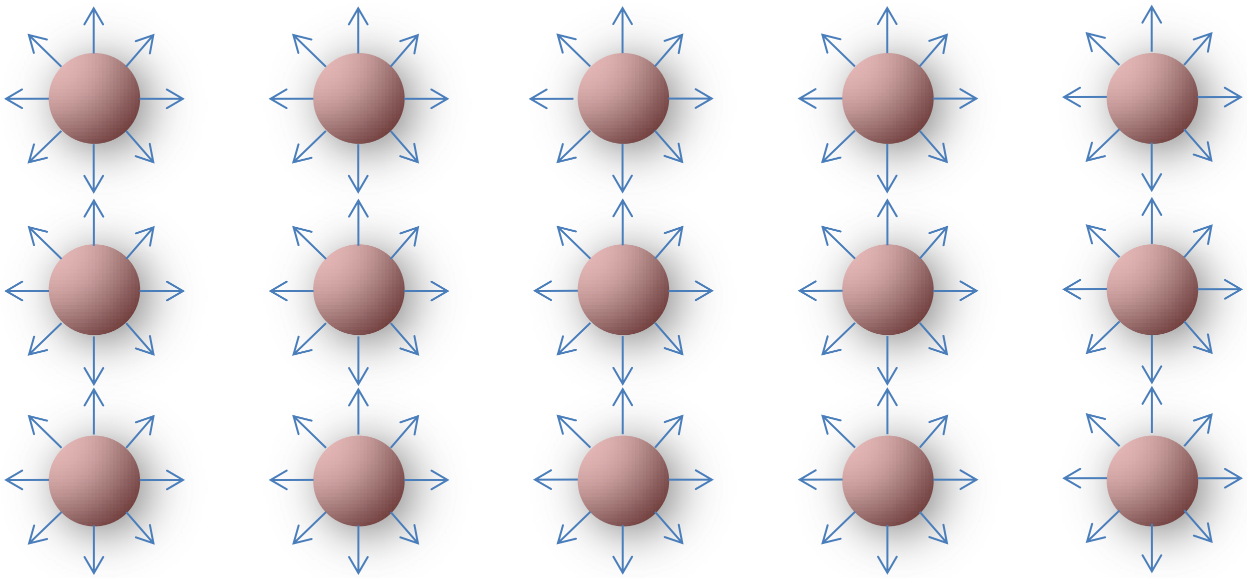
Secondary wave is in phase (+ 180°) with primary wave.

Crystal Lattice

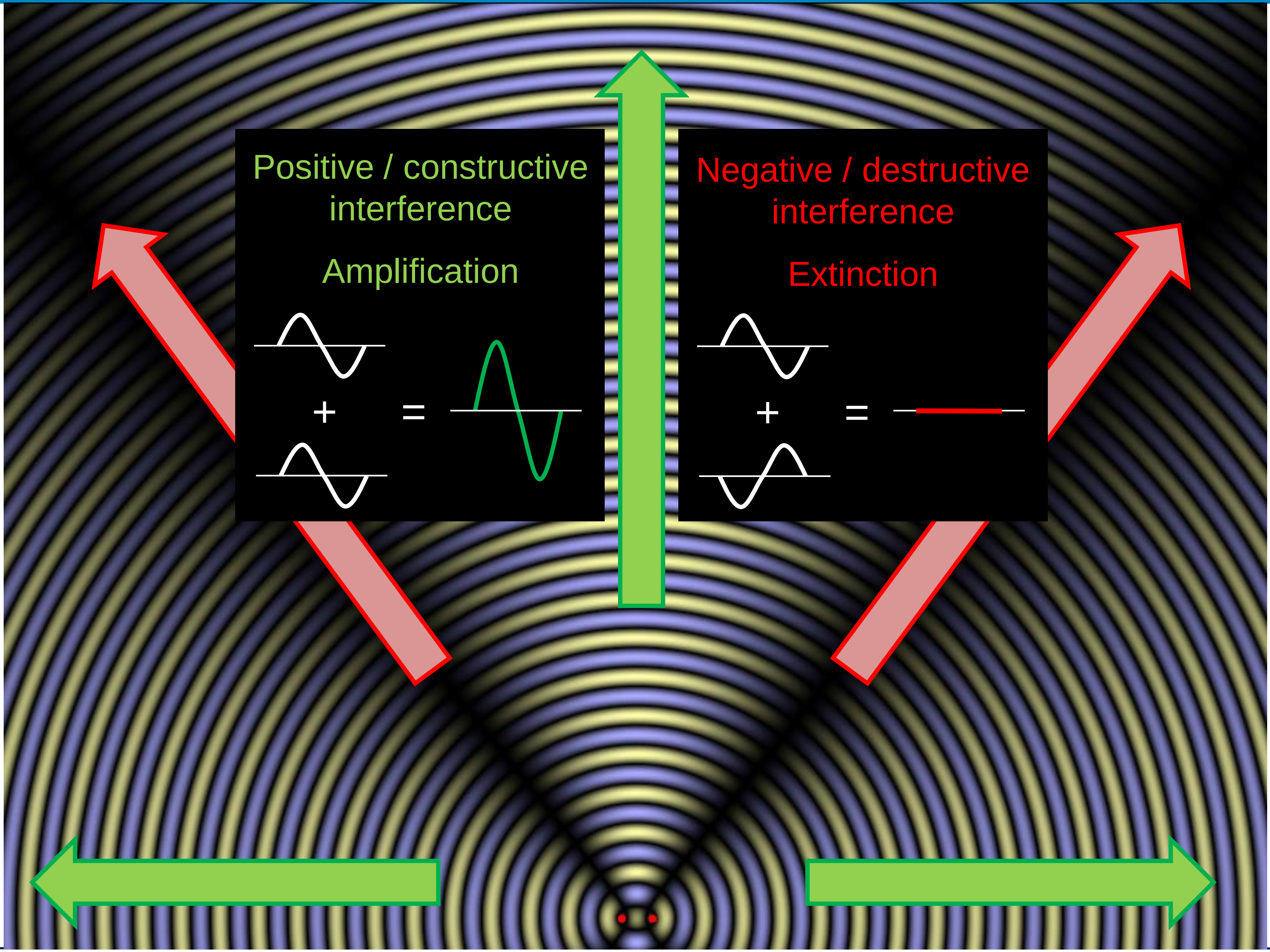
Crystal: Periodic arrangement of atoms/ions/molecules in 3 dimensions.



Electrons of each atom become a source of scattered radiation (spherical waves)

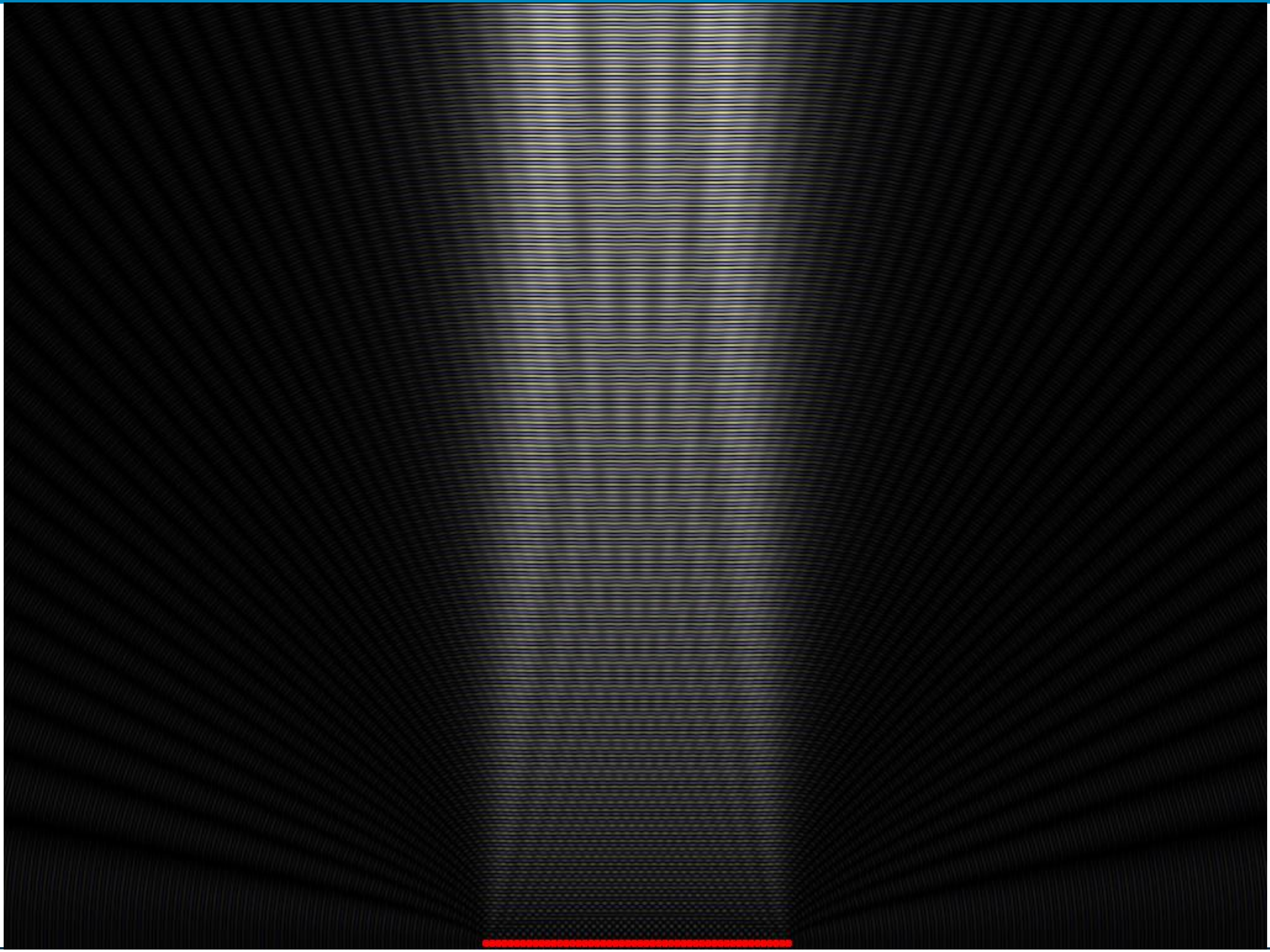


Interference pattern



n=2

Interference pattern

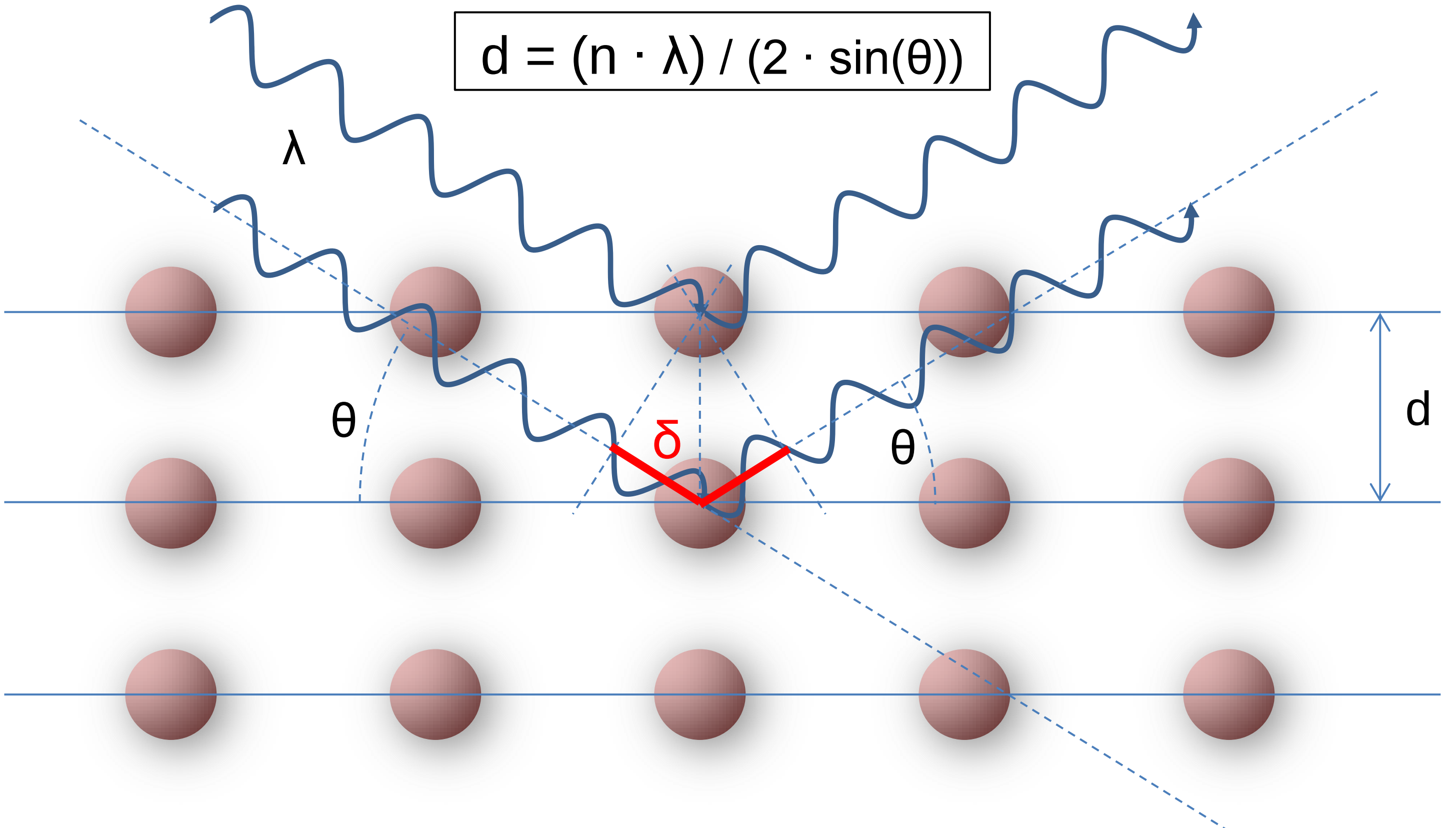


n=50

Bragg's Law

$$n \cdot \lambda = 2 \cdot d \cdot \sin(\theta)$$

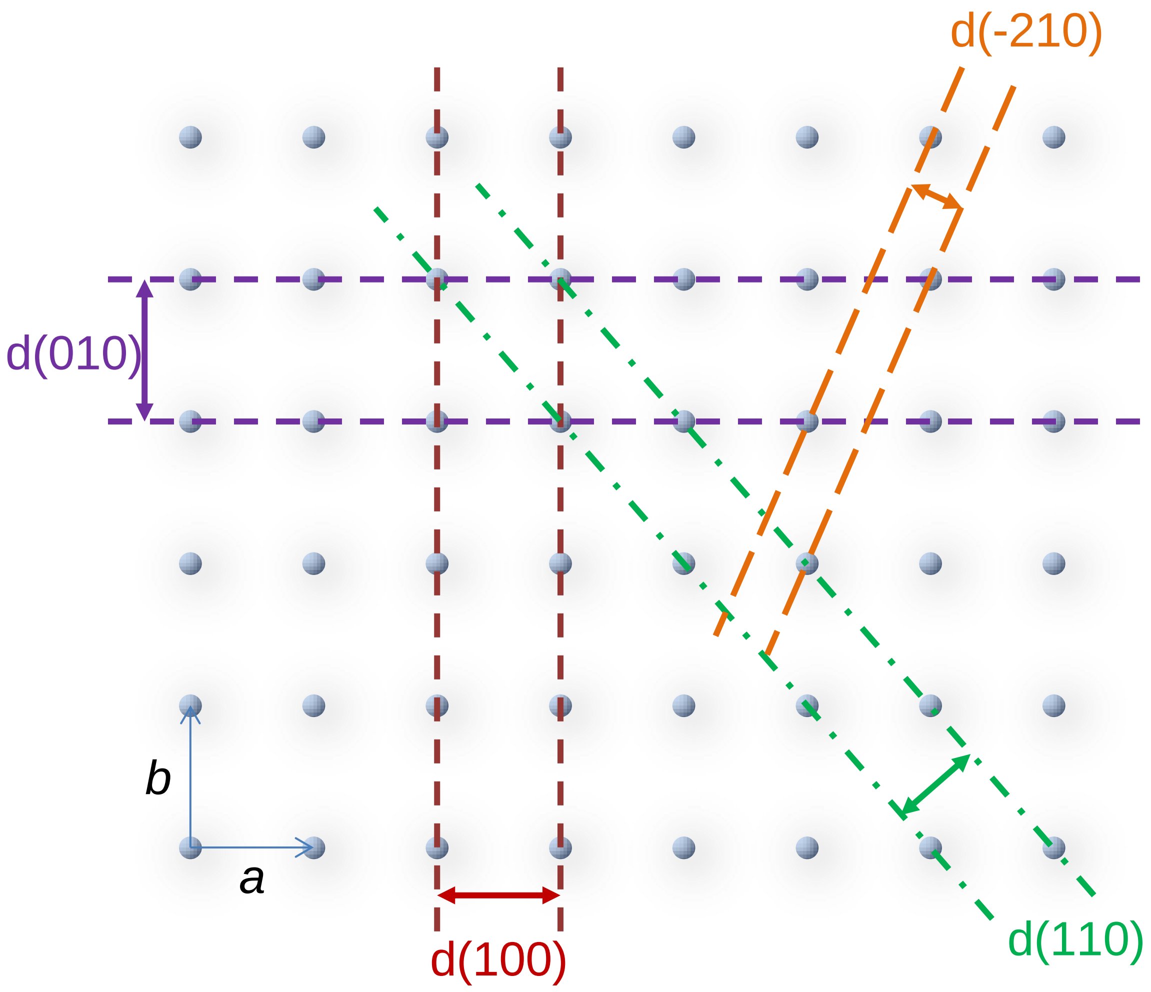
$$d = (n \cdot \lambda) / (2 \cdot \sin(\theta))$$



$$2\delta = n \cdot \lambda$$

$$\delta = d \cdot \sin(\theta)$$

Lattice Planes and Miller Indices

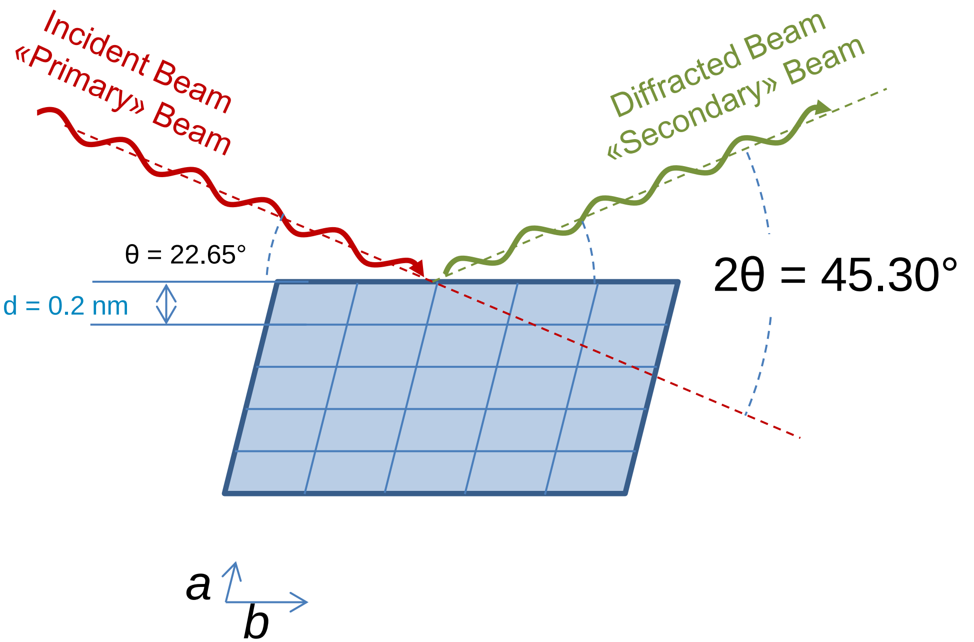


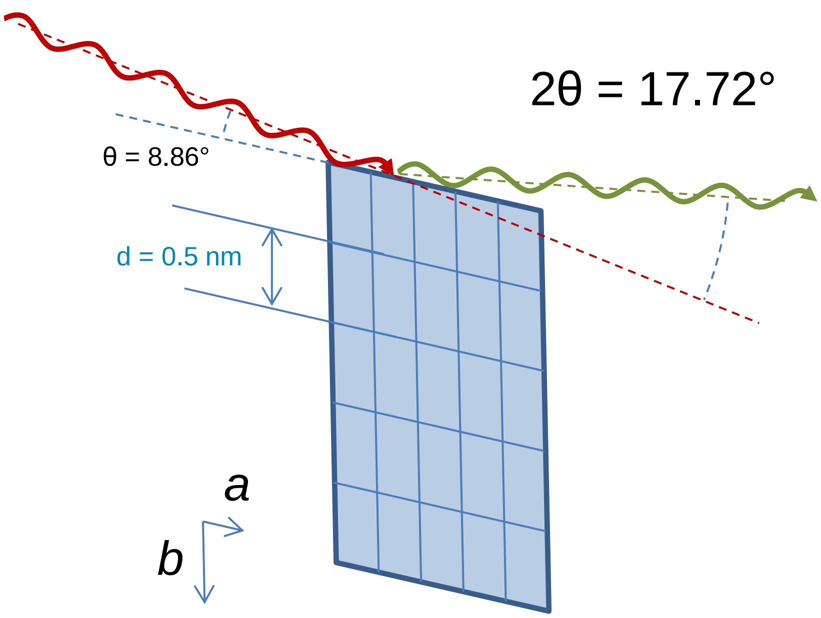
Definition:
A lattice plane is a plane which intersects atoms of a unit cell across the whole 3-dimensional lattice.

- Each lattice plane generates a diffraction peak.
- The 2θ angle of the peak depends on the plane's d-spacing.
- Diffraction peaks can be labelled with the plane's Miller index.

Bragg’s Law

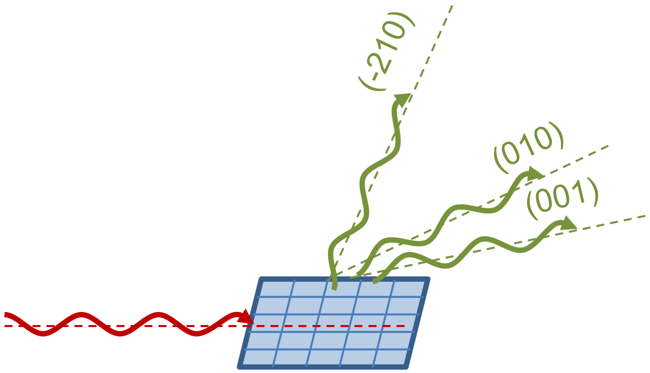
$CuK\alpha_1$ = 0.154056 nm
a = 0.2 nm
b = 0.5 nm





Single Crystal

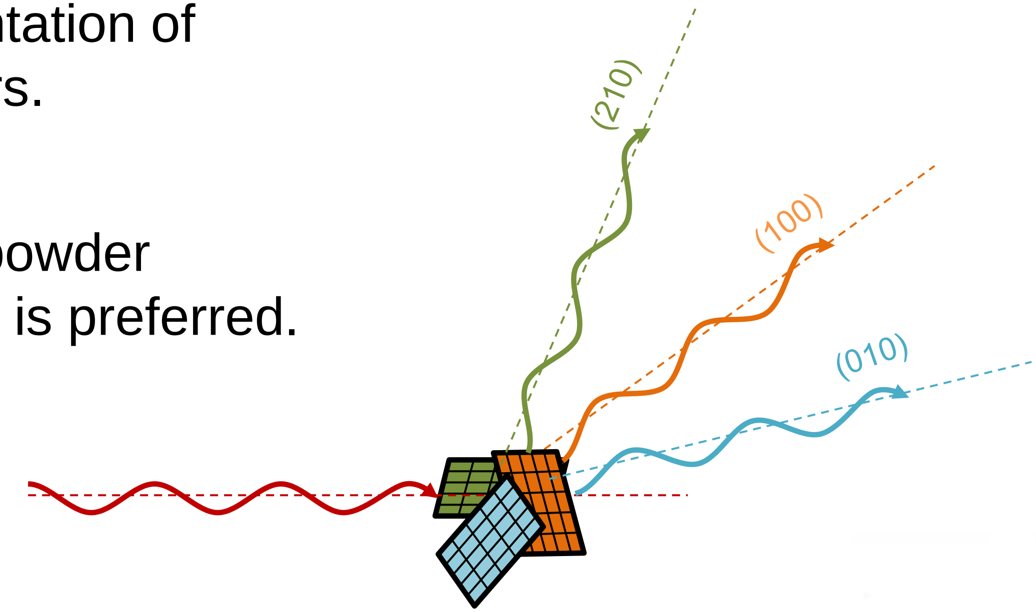
A single crystal must be rotated to bring each lattice plane in diffraction condition.



Polycrystals, Powders

In an ideal powder every possible orientation of crystals occurs.

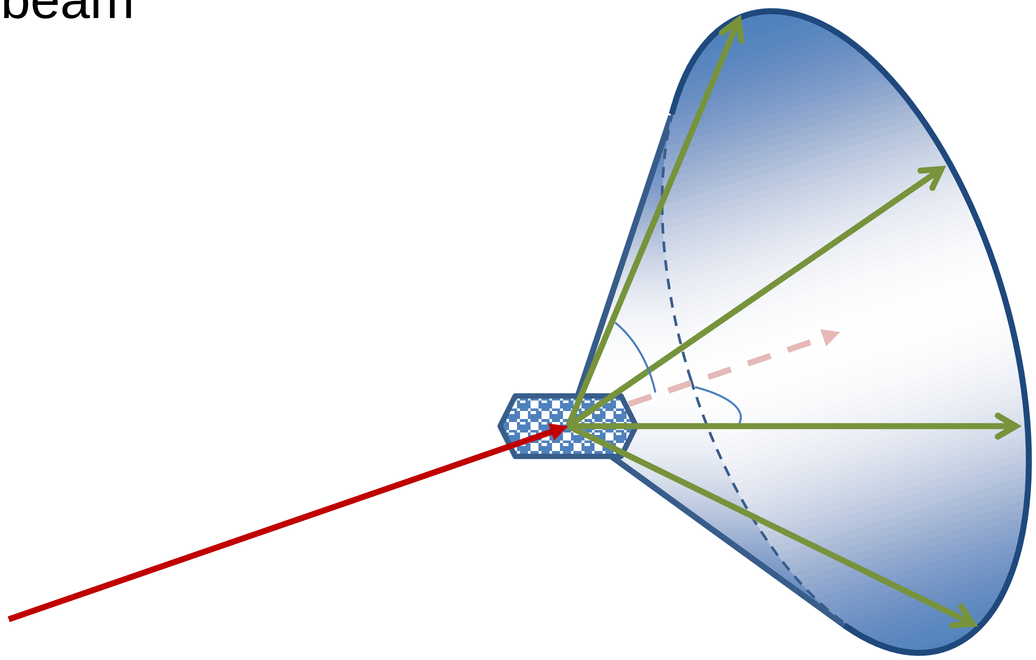
In a random powder
no orientation is preferred.



In an ideal powder all possible diffraction peaks are generated, regardless of sample orientation.

Diffraction Cones

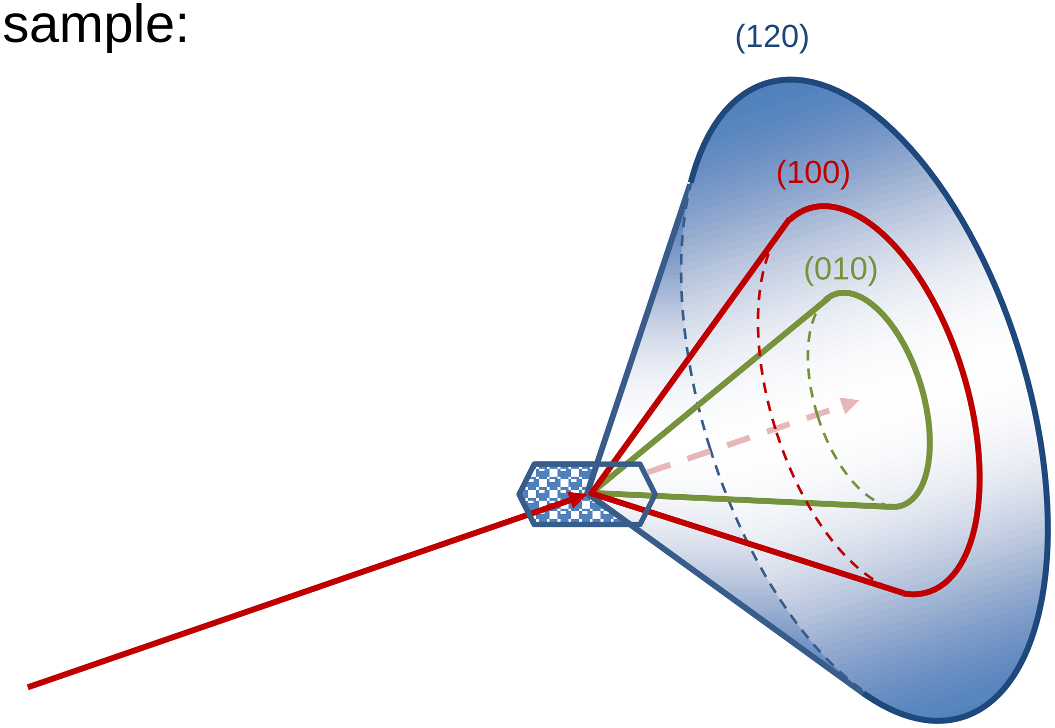
Diffraction at an angle 2θ° from the primary beam



All possible rays form a cone = diffraction cone = Debye cone

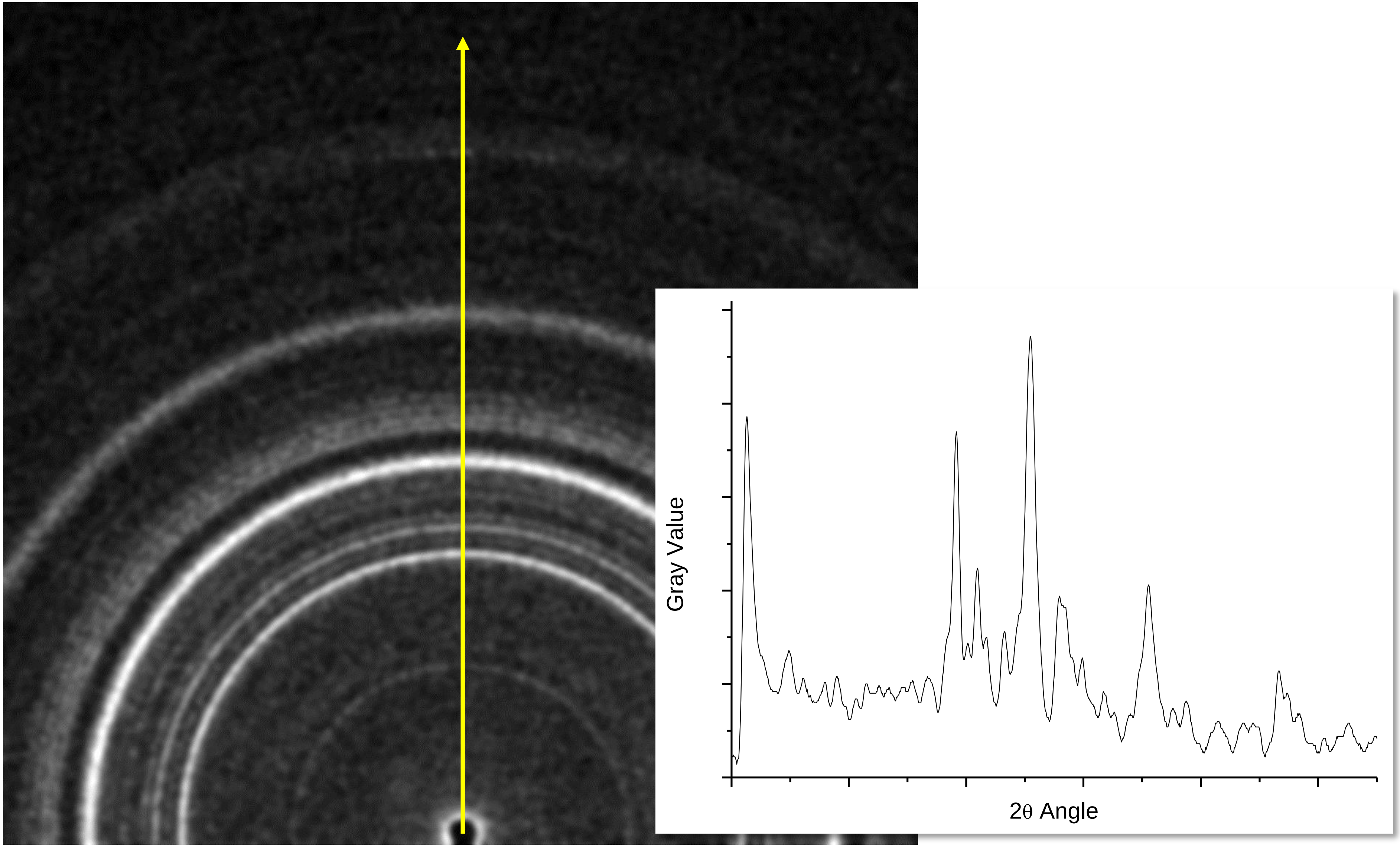
Diffraction Cones

Powder sample:

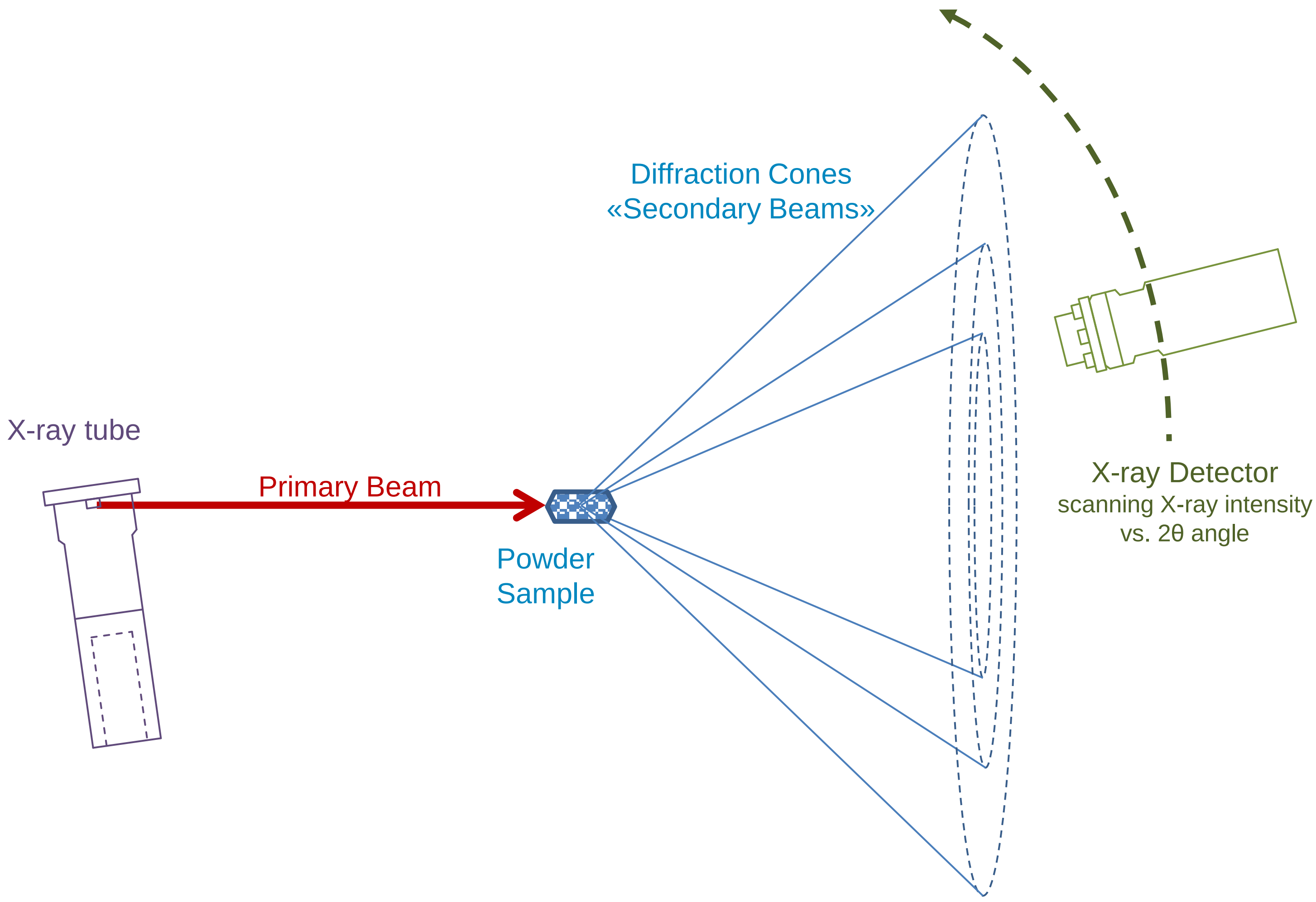


One Debye Cone for each lattice plane spacing (d value)

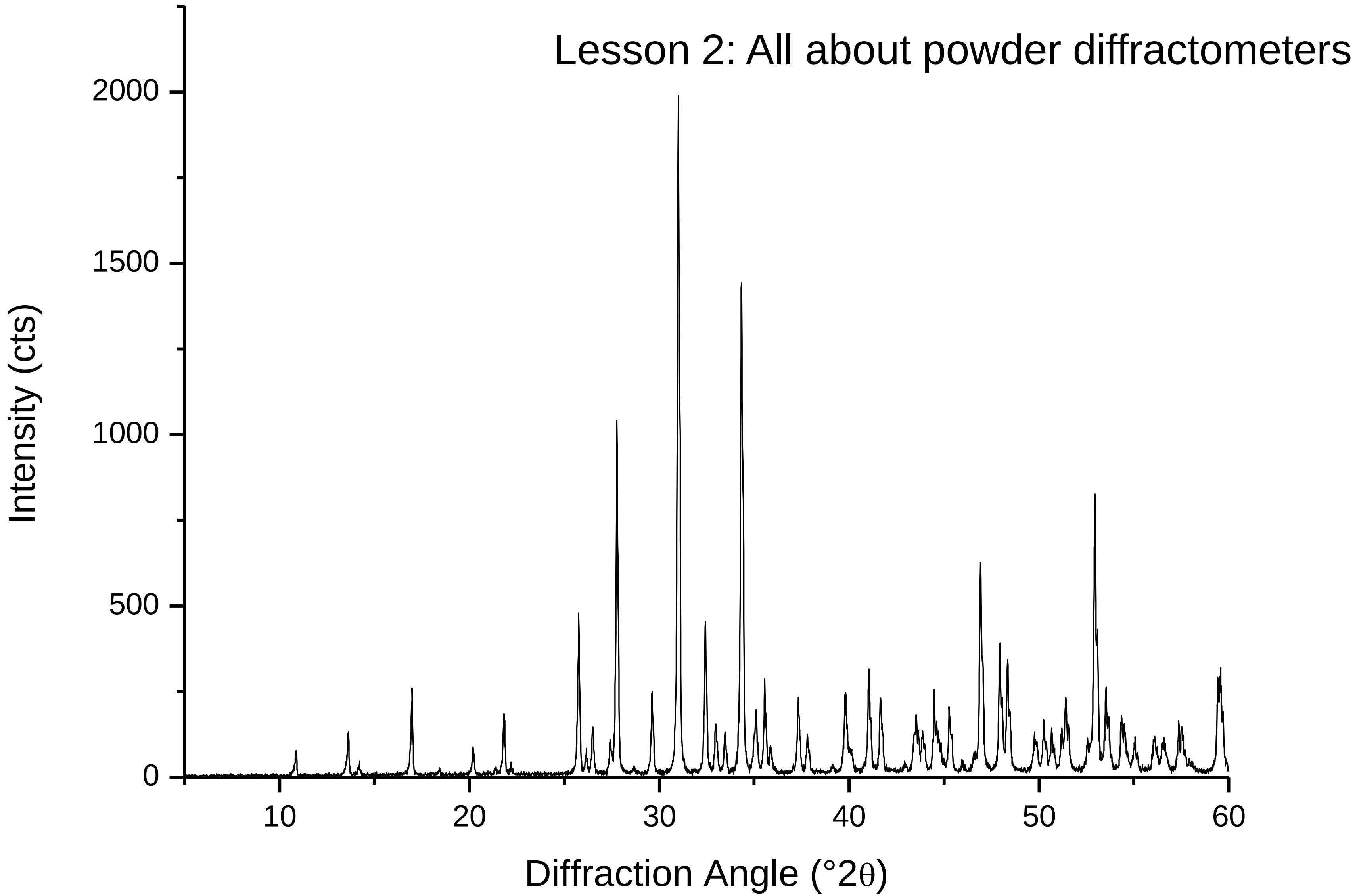
Debye Ring



Powder Diffractometer



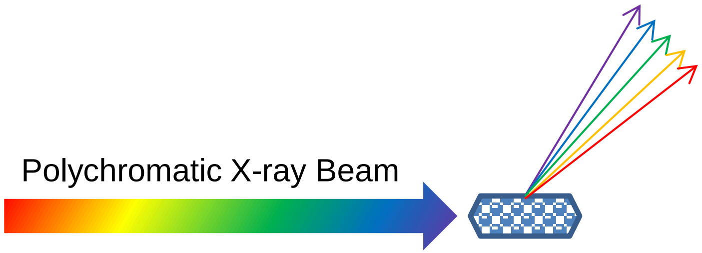
Powder Diffraction Pattern



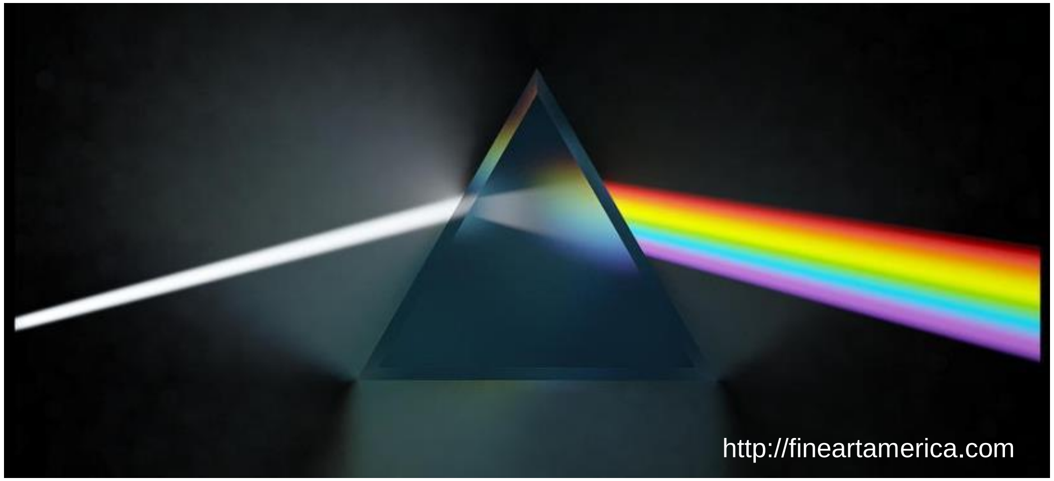
Monochromatic X-radiation

Diffraction angle θ depends on wavelength λ:

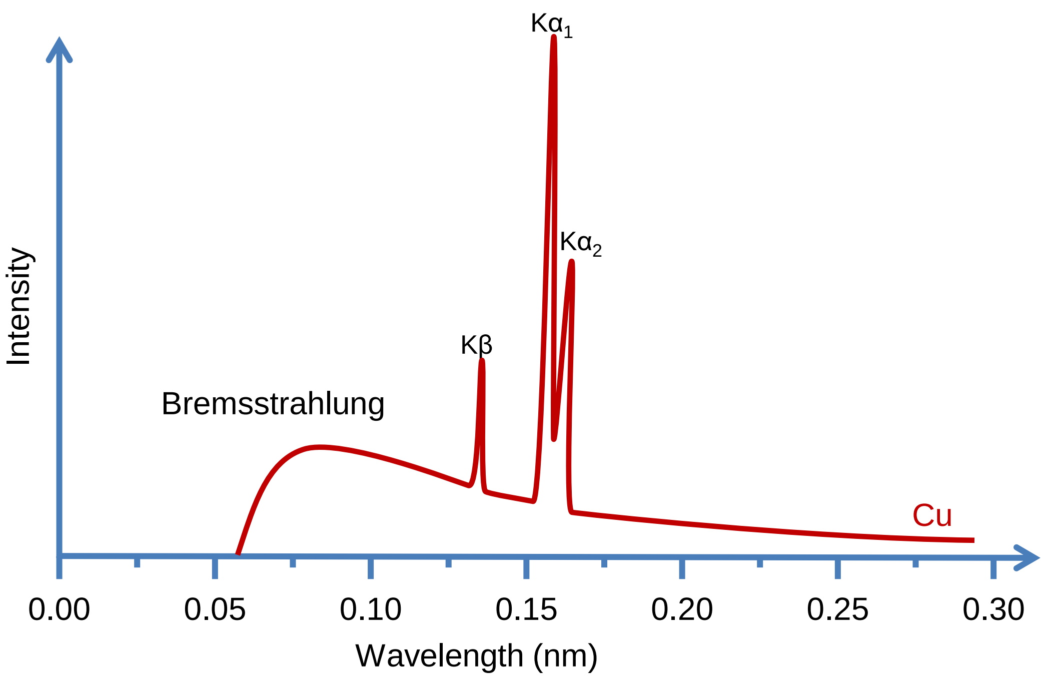
$$n \cdot \lambda = 2 \cdot d \cdot \sin(\theta)$$

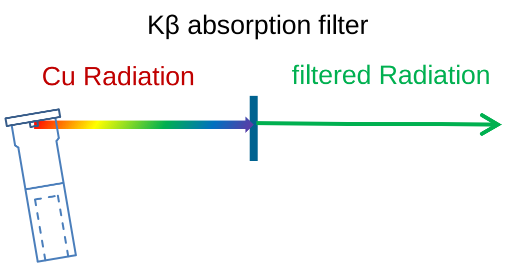


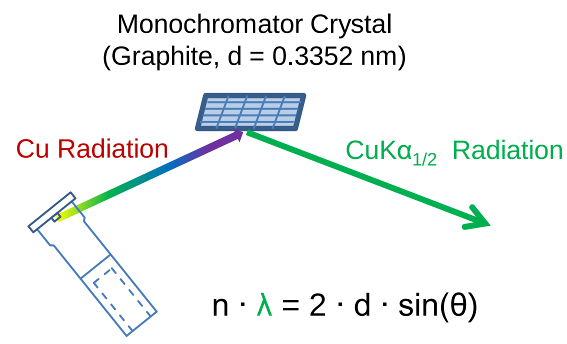
We need monochromatic X-radiation!

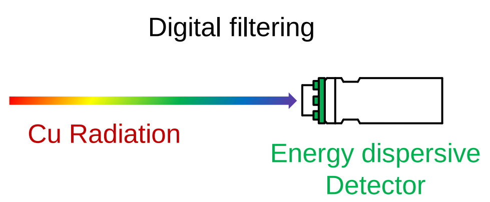


Monochromatic X-Radiation





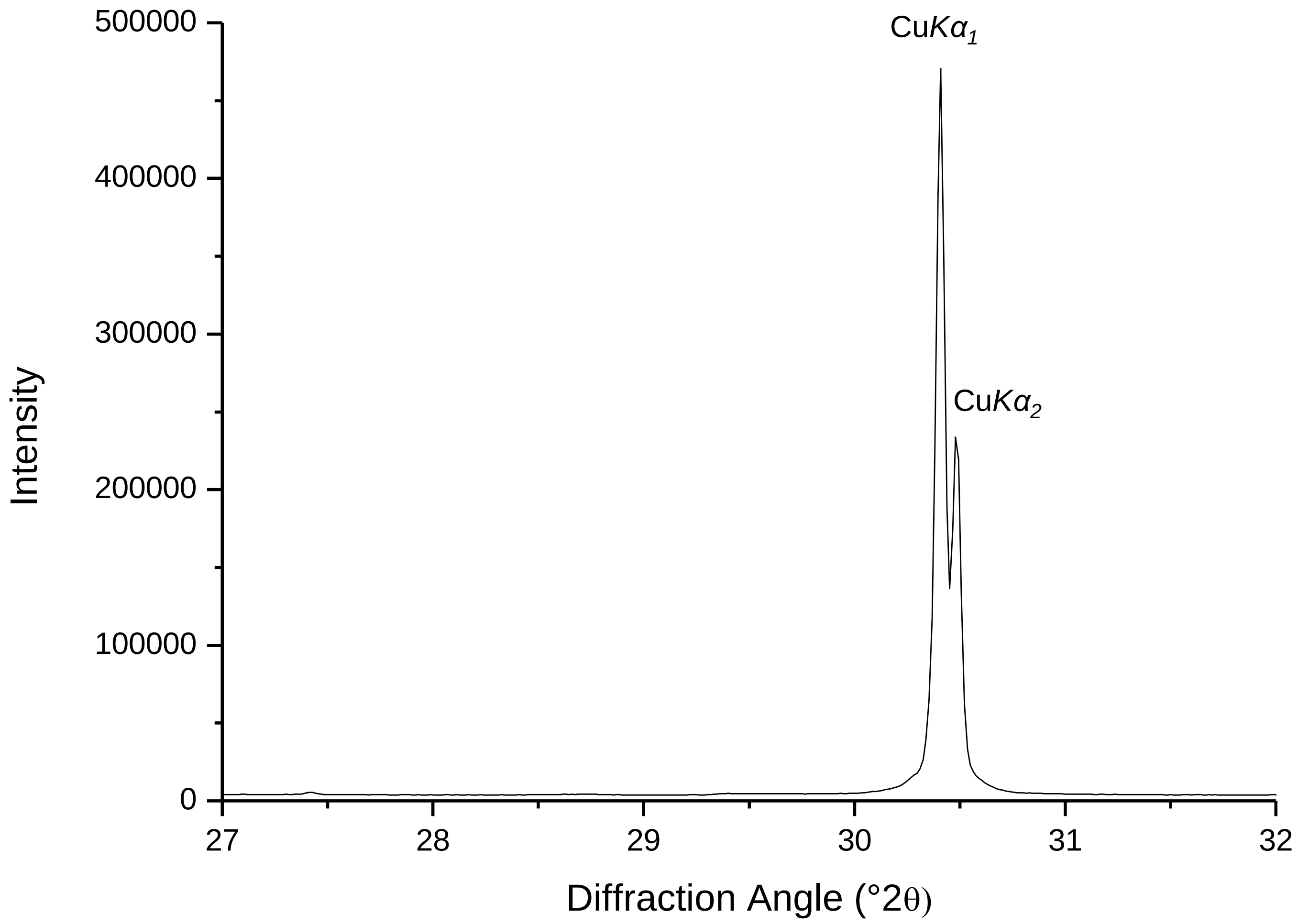




Ideally: Isolate $K\alpha_1$

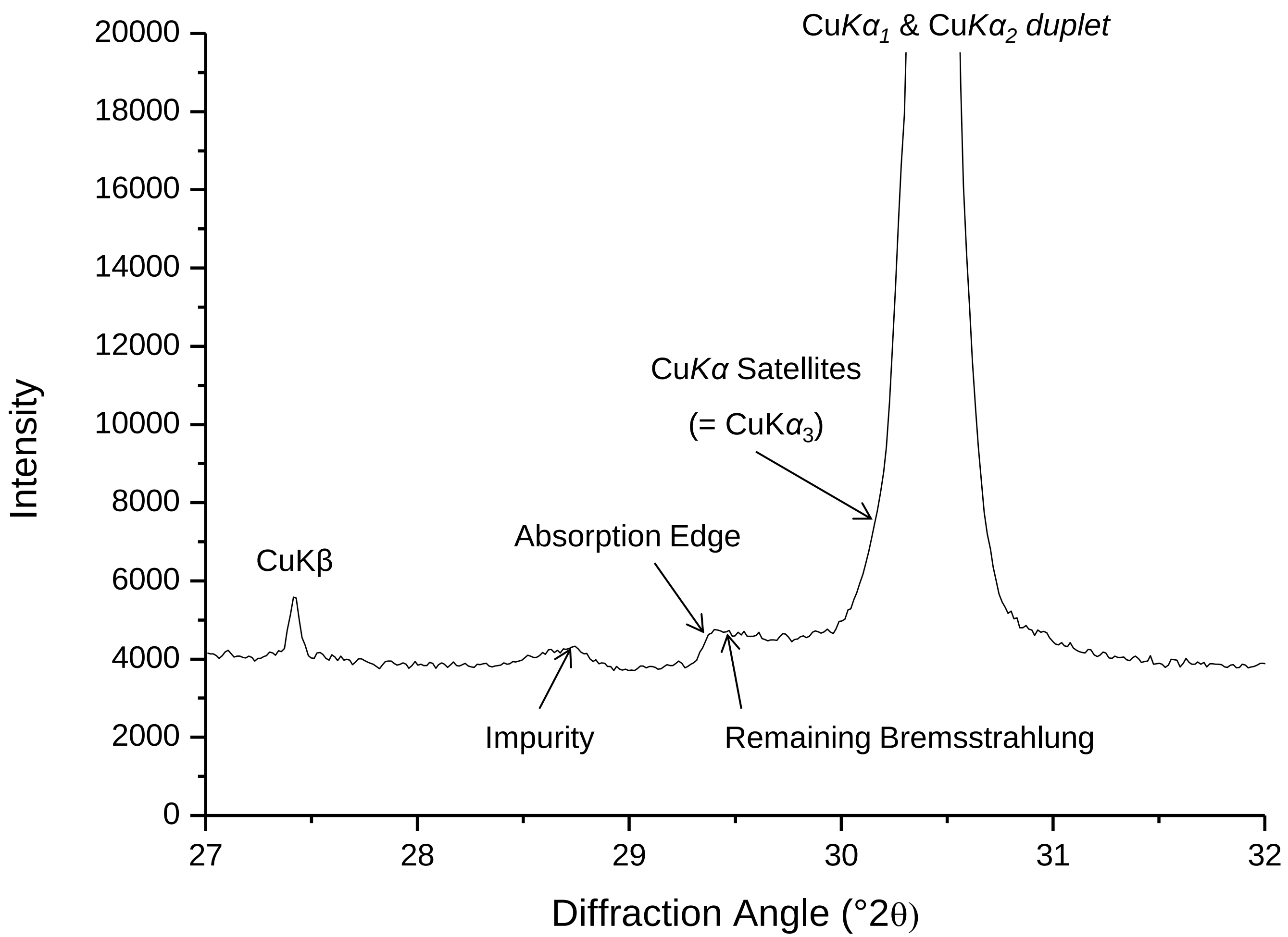
Reality: Suppress Kβ and Bremsstrahlung

Kβ-filtered Diffraction Pattern



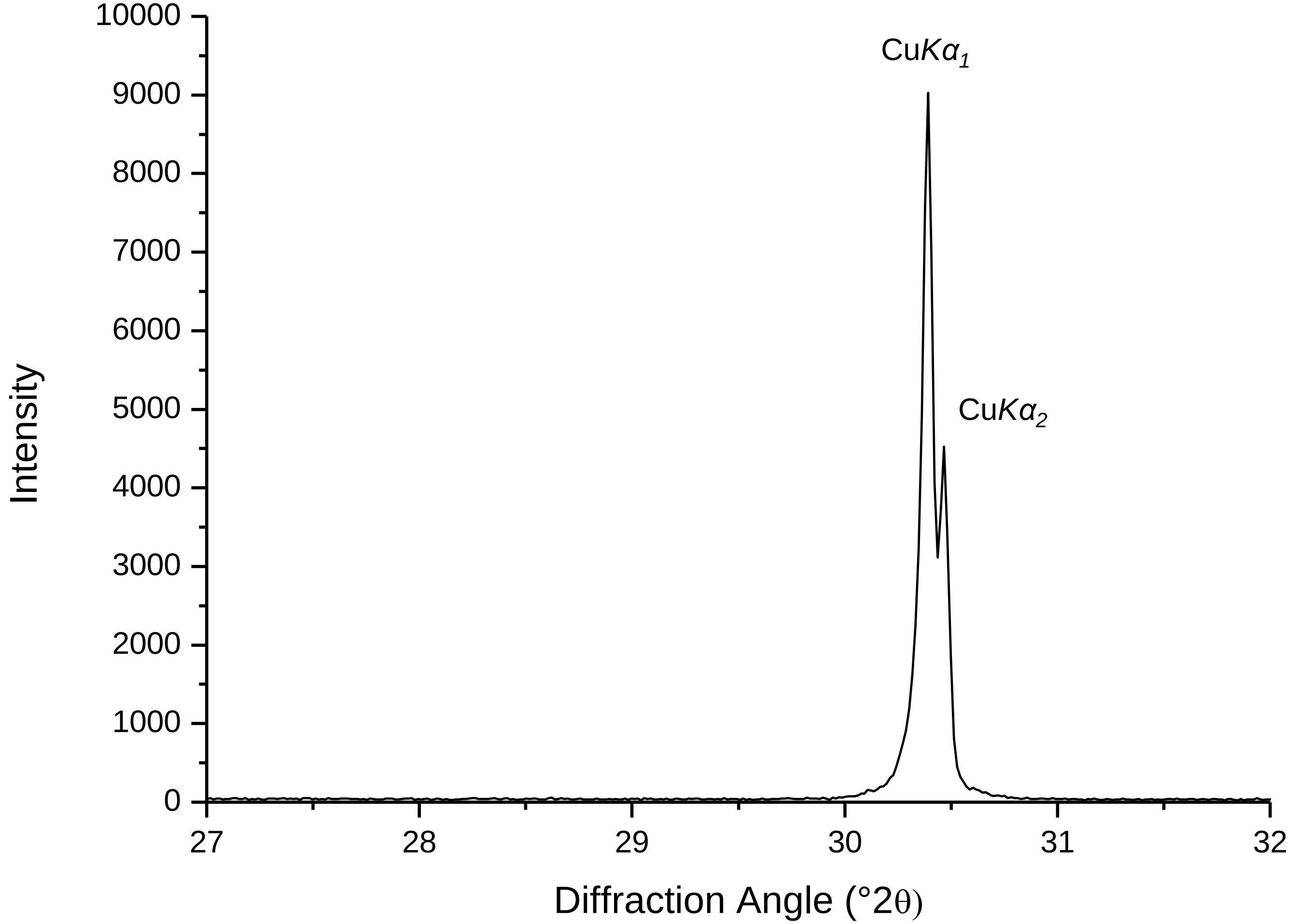
LaB_6 pattern, Cu radiation, Ni filter in primary beam (Bruker D8 Advance)

Kβ-filtered Diffraction Pattern



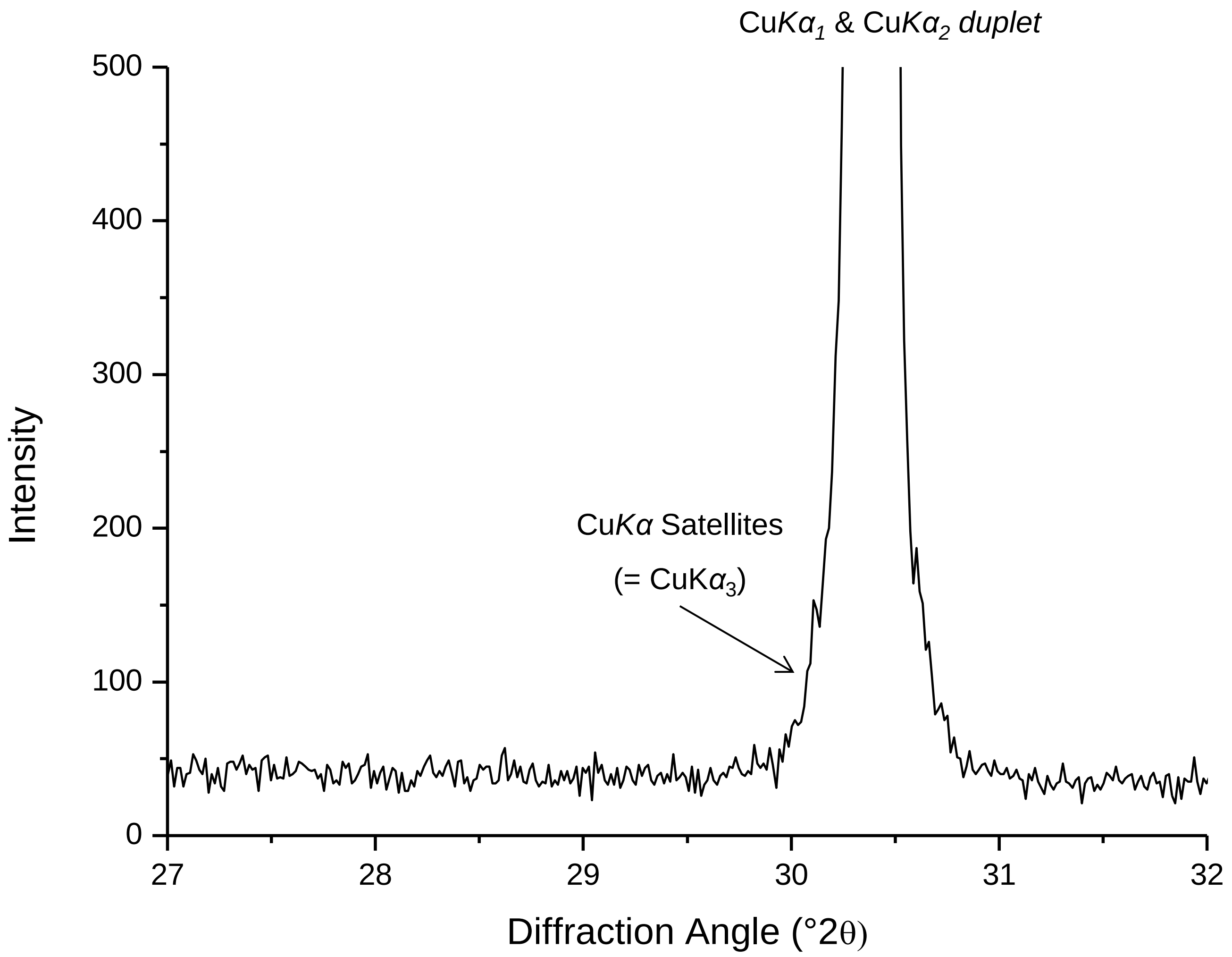
LaB_6 pattern, Cu radiation, Ni filter in primary beam (Bruker D8 Advance)

Graphite Monochromator



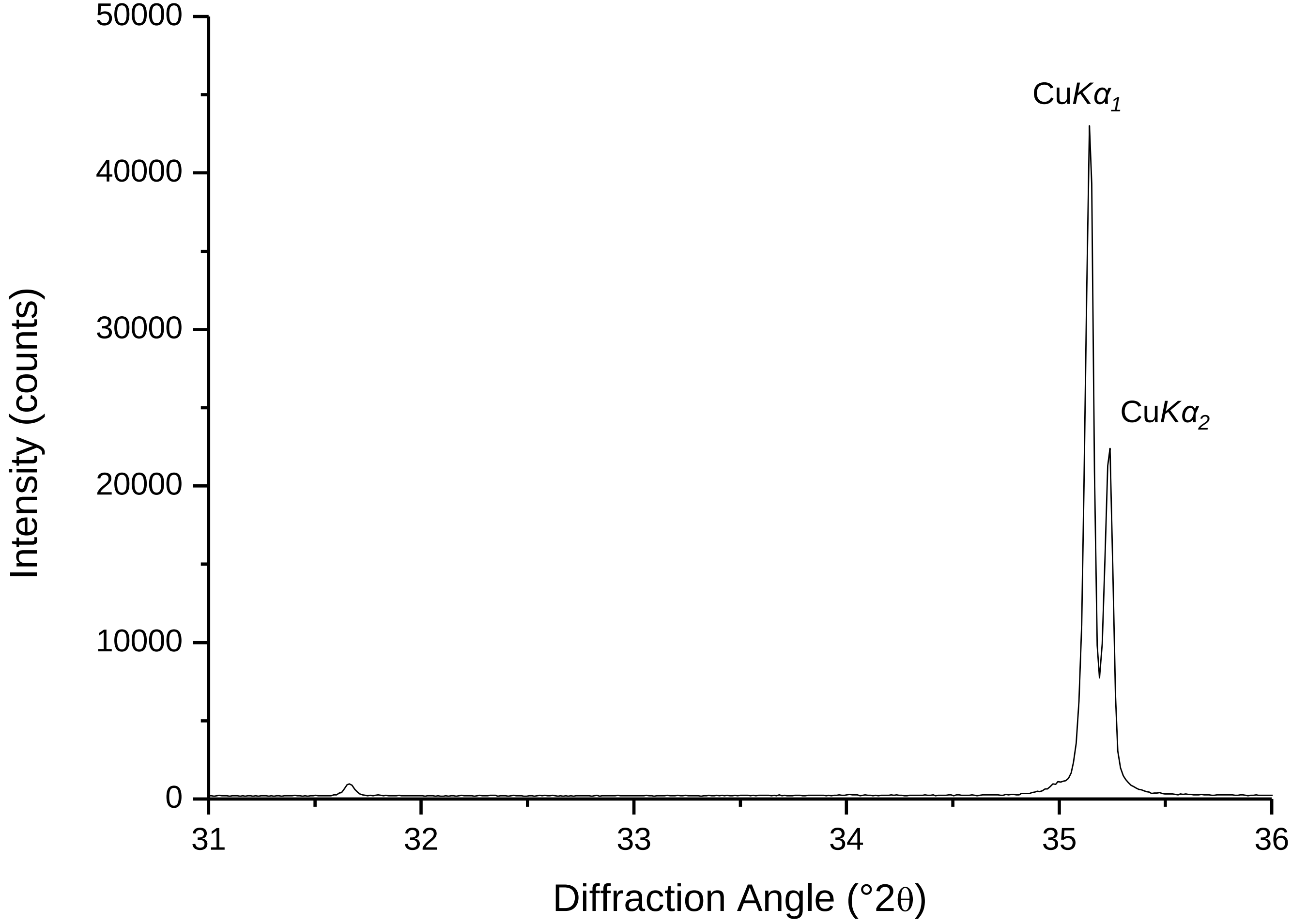
LaB_6 pattern, Cu radiation, Graphite monochromator, secondary beam (PANalytical CubiX[3])

Graphite Monochromator



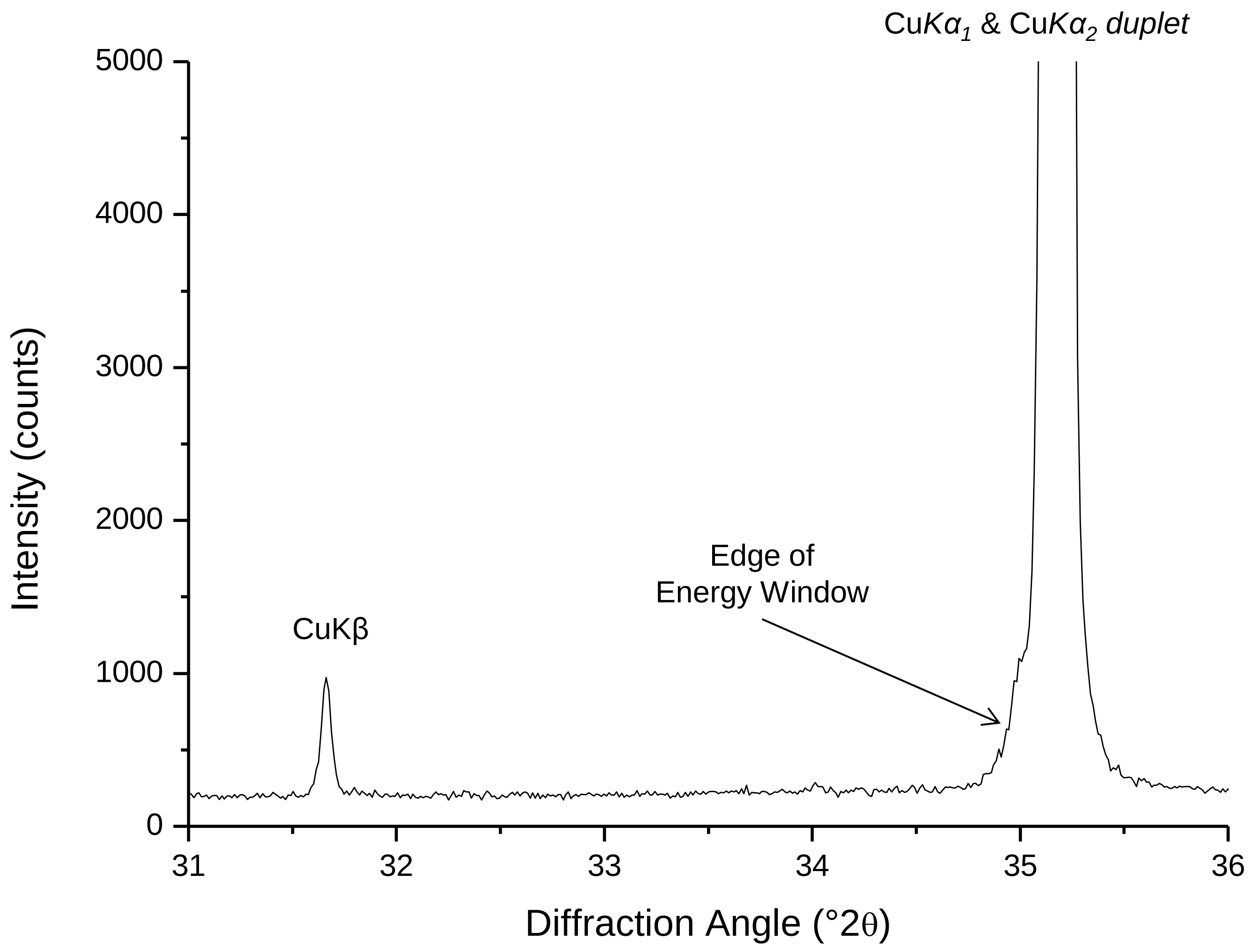
LaB_6 pattern, Cu radiation, Graphite monochromator, secondary beam (PANalytical CubiX^3)

Energy-Dispersive Detector



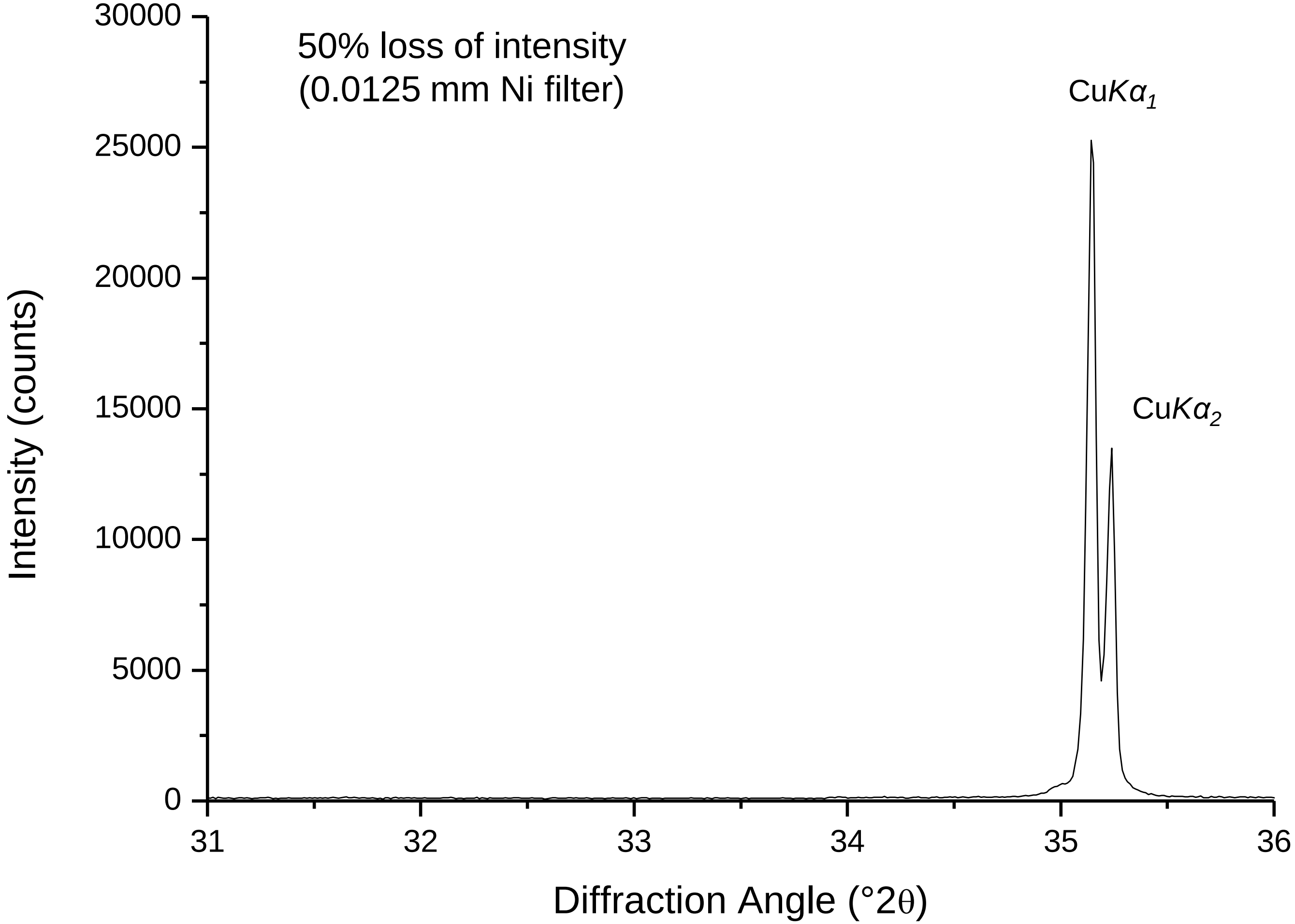
Al_2O_3 pattern, Cu radiation, LynxEyeXE detector (Bruker D8 Advance)

Energy-Dispersive Detector



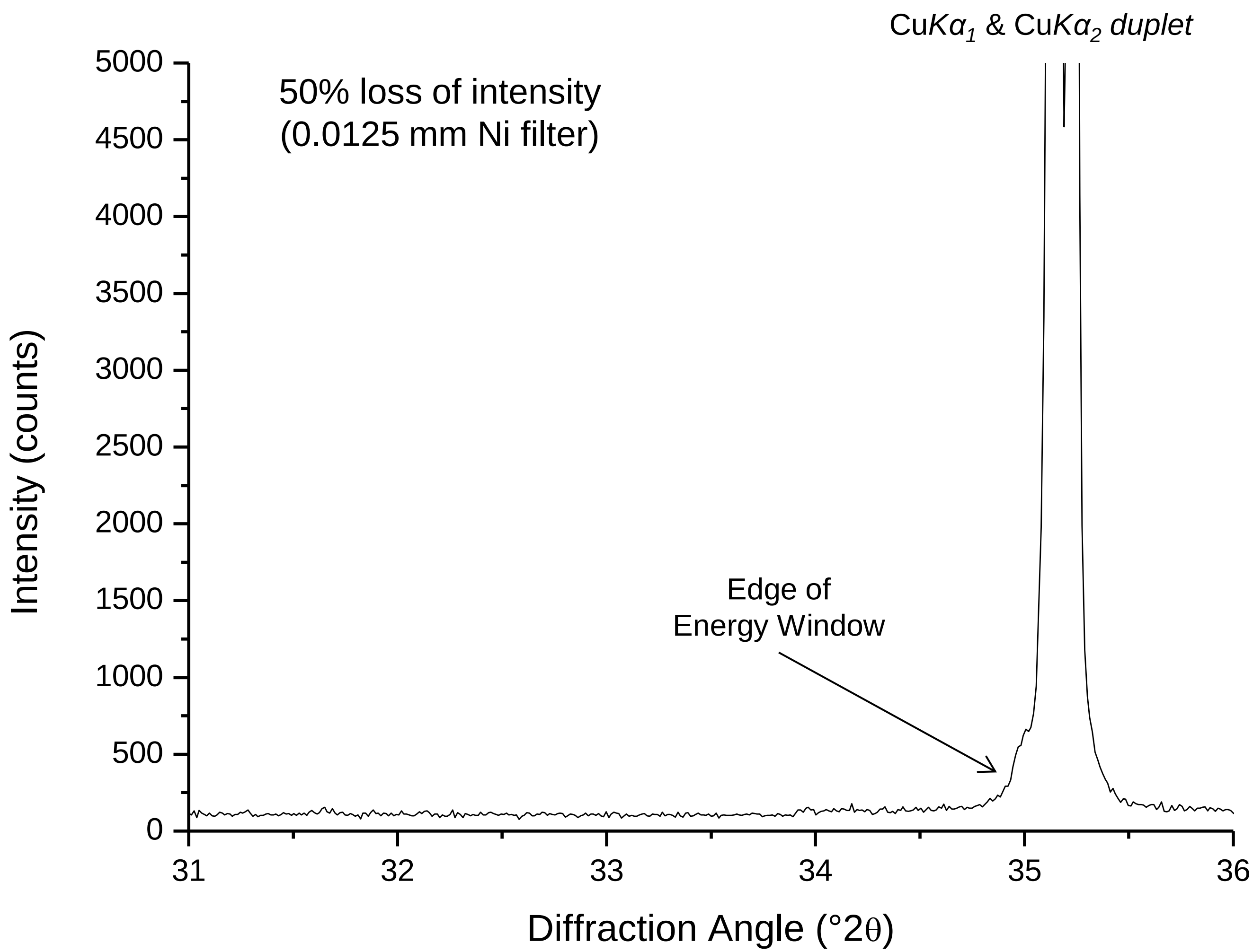
Al_2O_3 pattern, Cu radiation, LynxEyeXE detector (Bruker D8 Advance)

Energy-Dispersive Detector + Kβ filter



Al_2O_3 pattern, Cu radiation, LynxEyeXE detector (Bruker D8 Advance)

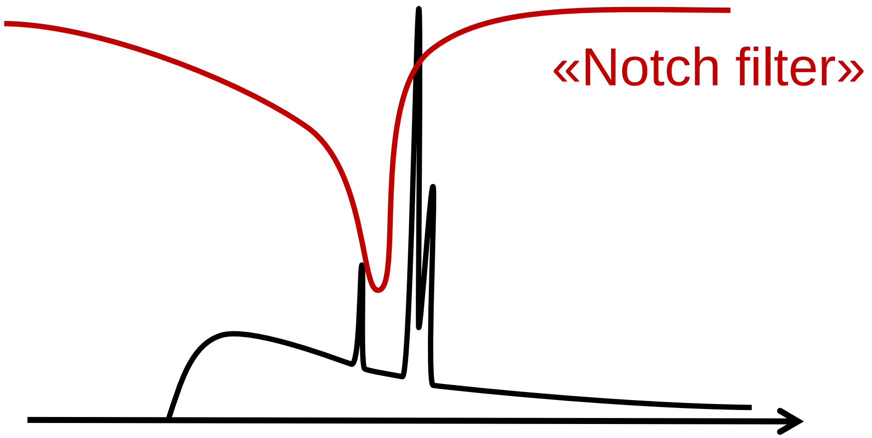
Energy-Dispersive Detector + Kβ filter



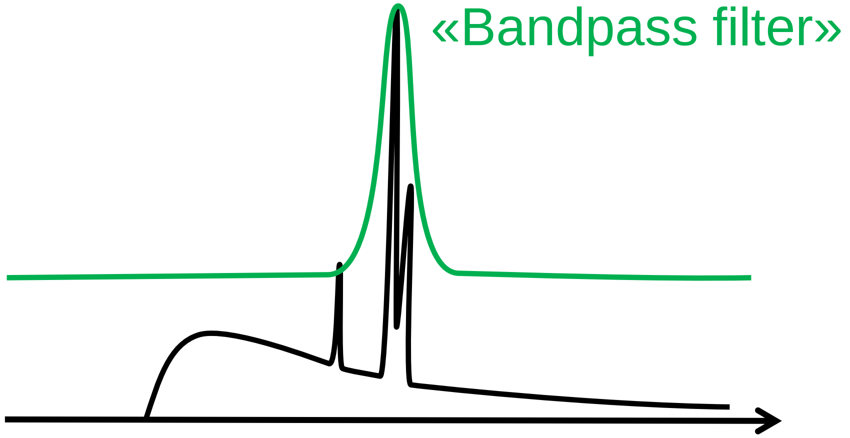
Al_2O_3 pattern, Cu radiation, LynxEyeXE detector (Bruker D8 Advance)

Monochromators

Kβ Filter:
Selectively suppresses Kβ and parts of Bremsstrahlung

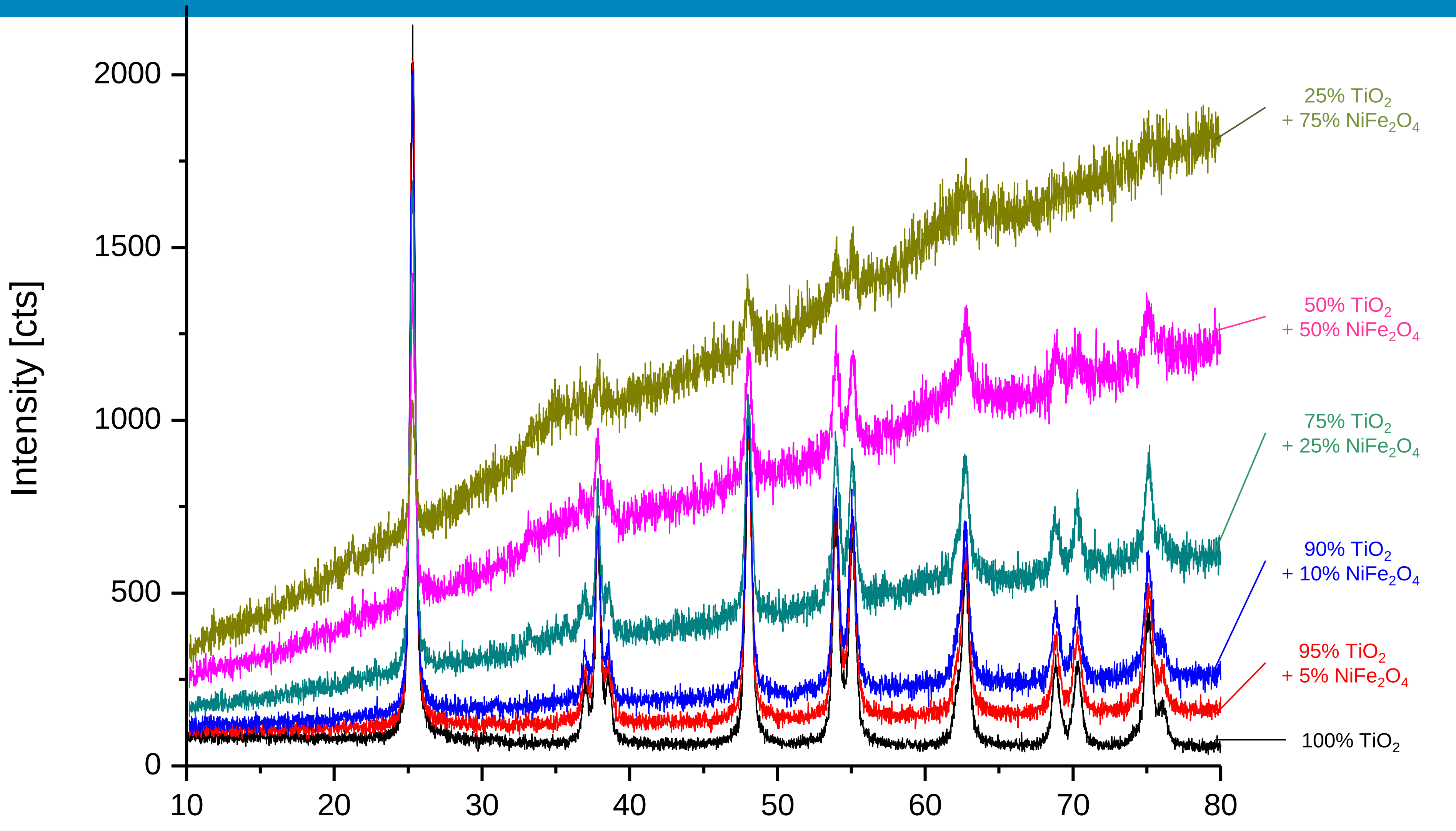


Monochromator crystal and energy dispersive detector:
Suppress everything BUT Kα



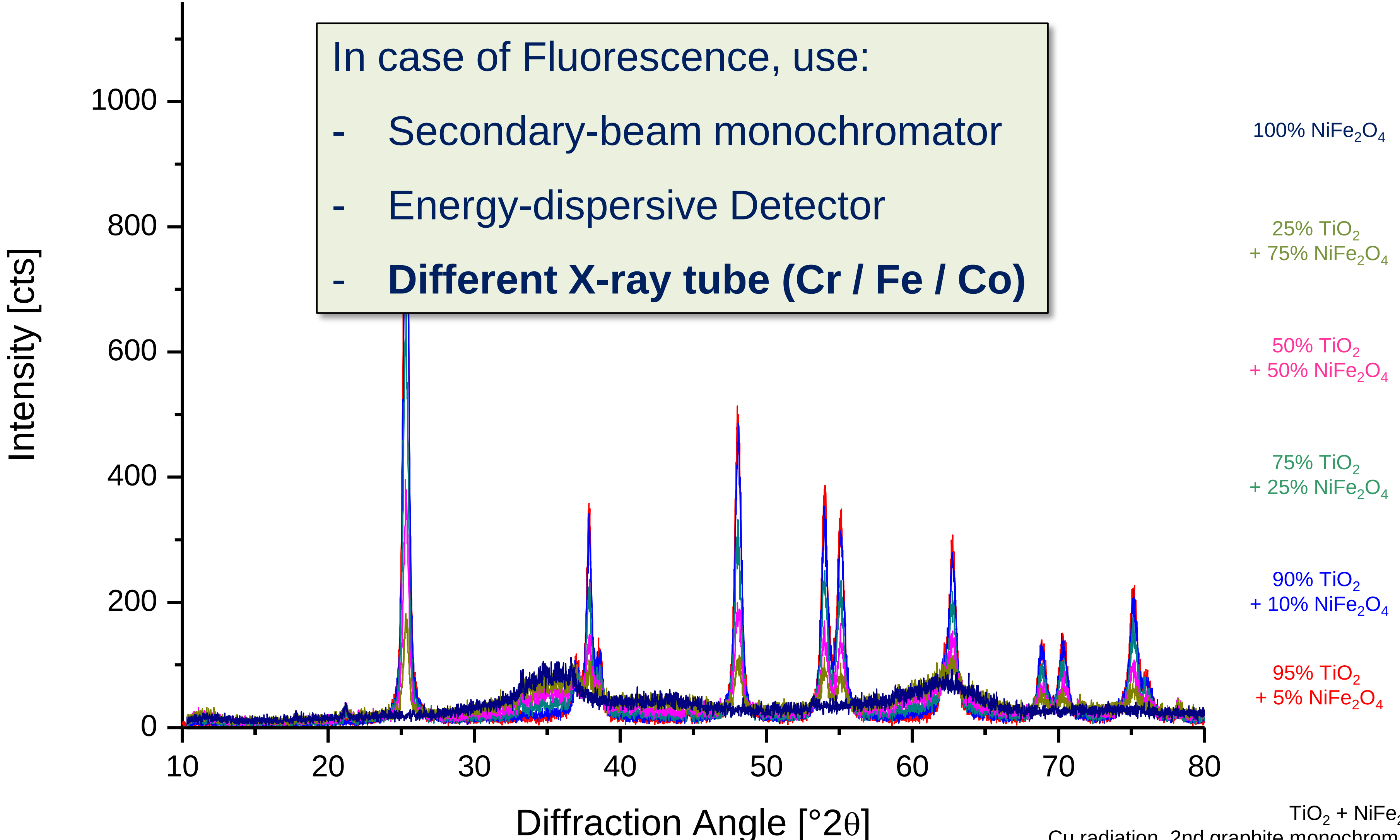
Important difference for fluorescent samples

Ni-Filtered Cu Radiation, Fe Fluorescence



Cu radiation, Ni filter in 2nd beam
(PANalytical X'Pert Pro)

Secondary-monochromated Cu-Radiation



TiO_2 + $NiFe_2O_4$,
Cu radiation, 2nd graphite monochromator
(PANalytical CubiX[3])

Summary: Monochromators

Optical Element	Effect on Spectrum	Effect on Intensity
Kβ Filter	Reduces Kβ peaks	Moderate loss
Graphite Monochromator	Eliminates Kβ peaks Eliminates Fluorescence	Strong loss
Multi-bounce Monochromator	Eliminates Kβ and $K\alpha_2$ Eliminates Fluorescence	Massive loss (mostly used on Synchrotrons)
Energy dispersive Detector	Reduces Kβ peaks Eliminates Fluorescence	No loss

Overview of Instruments

Lab	Instrument	Monochromator
RMS Foundation	Bruker D8	Energy dispersive Detector
Uni Bern	Panalytical X'Pert	Kβ-Filter
Uni Bern	Panalytical CubiX	Graphite Monochromator

Bruker D8

Panalytical X'Pert

Panalytical CubiX