Testing • Research • Consulting

Workshop „Rietveld Refinement with Profex"

Lesson 1: Introduction to Powder X-ray Diffraction

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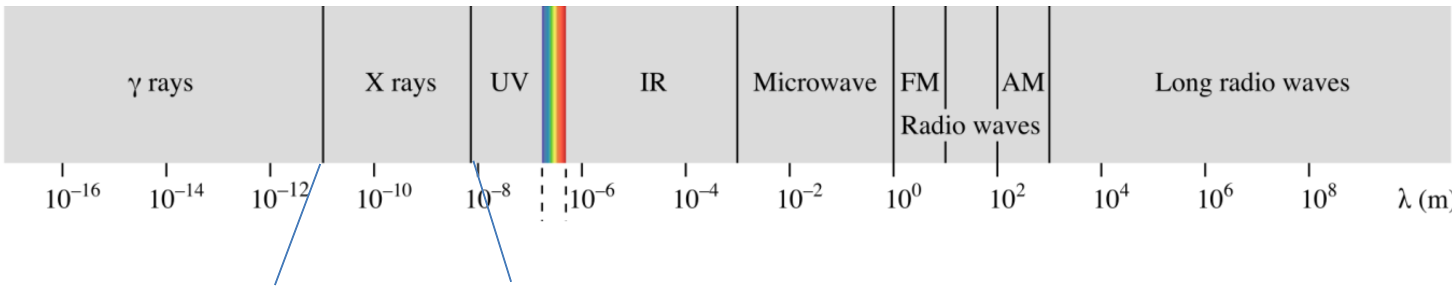
Forschungszentrum Jülich, Germany

Electromagnetic Spectrum



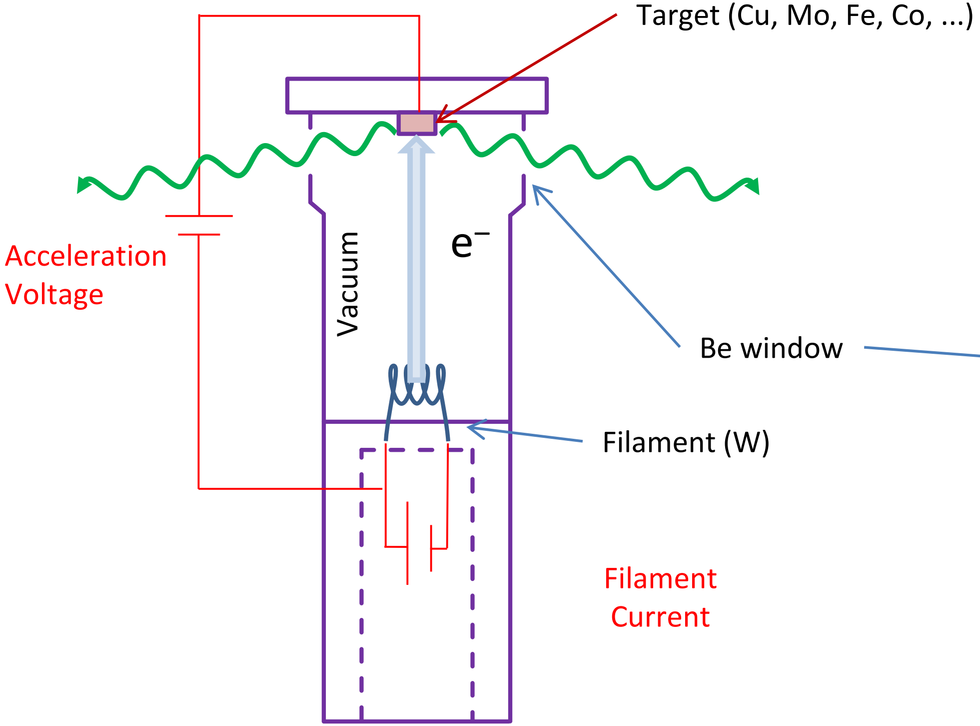
X rays:
Wavelength λ: 0.01 – 10 nm
Energy: 100 eV – 100 keV

Generation of X-radiation:
Shoot electrons on matter

Interatomic distances in crystals:
typically 0.15 – 0.4 nm

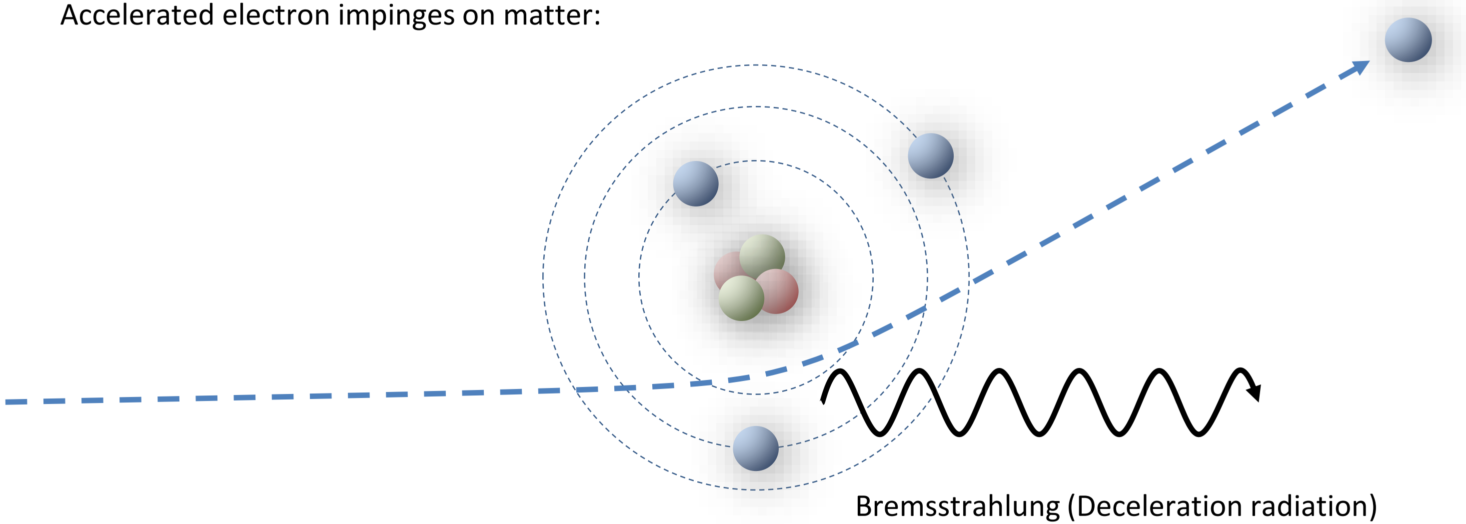
Interference phenomena only
for features ≈ λ

X-Ray Tube


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

Generation of X-Rays: Bremsstrahlung (Deceleration Radiation)

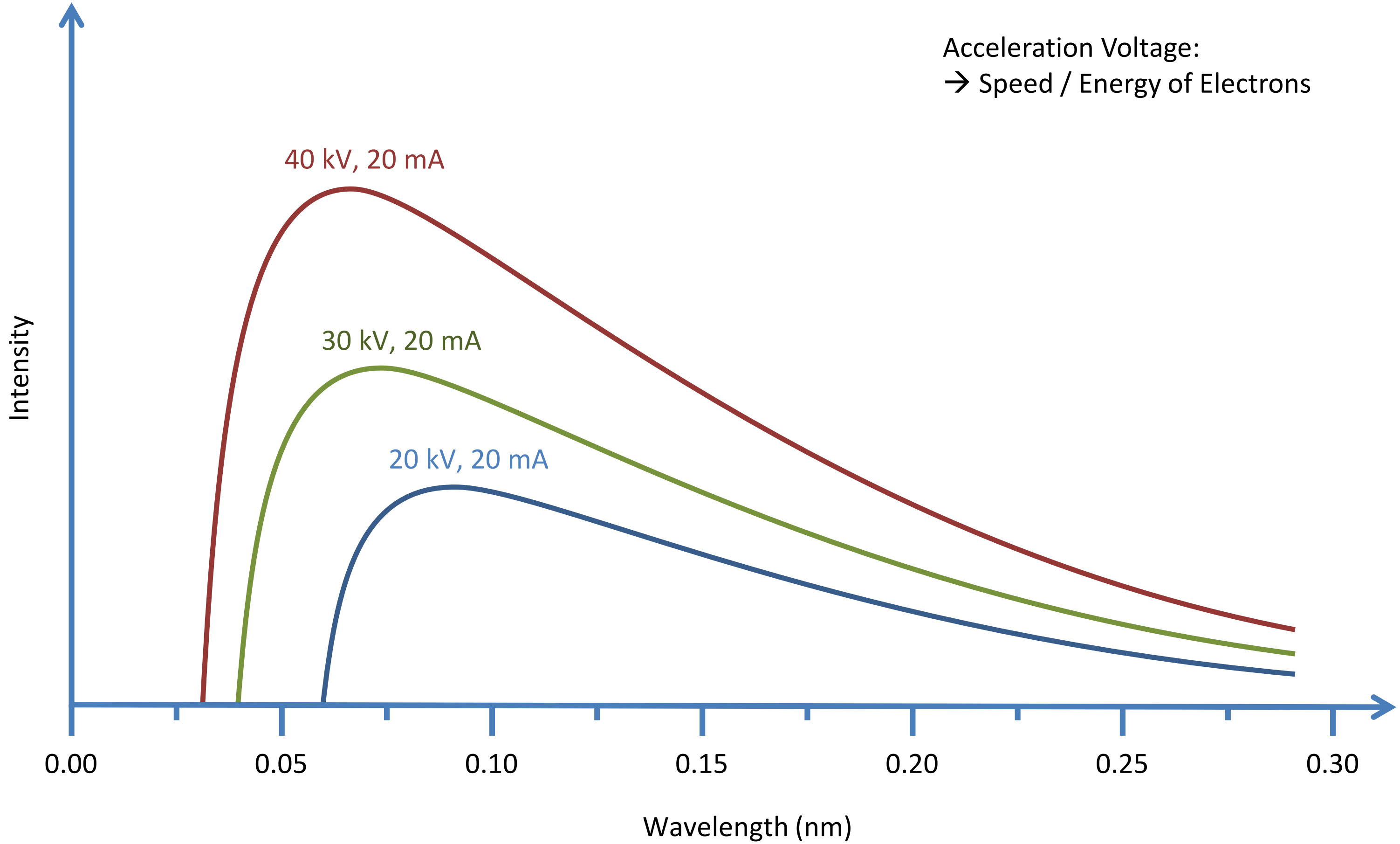
Accelerated electron impinges on matter:



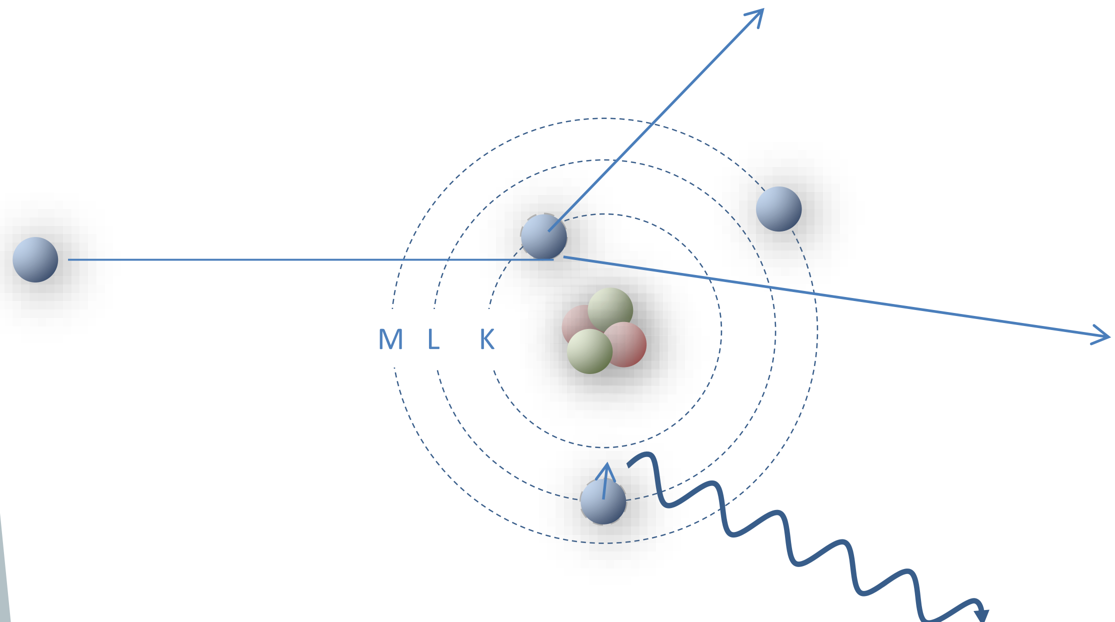
Electron is deflected and decelerated by the atomic nucleus.
(Inelastic scattering)

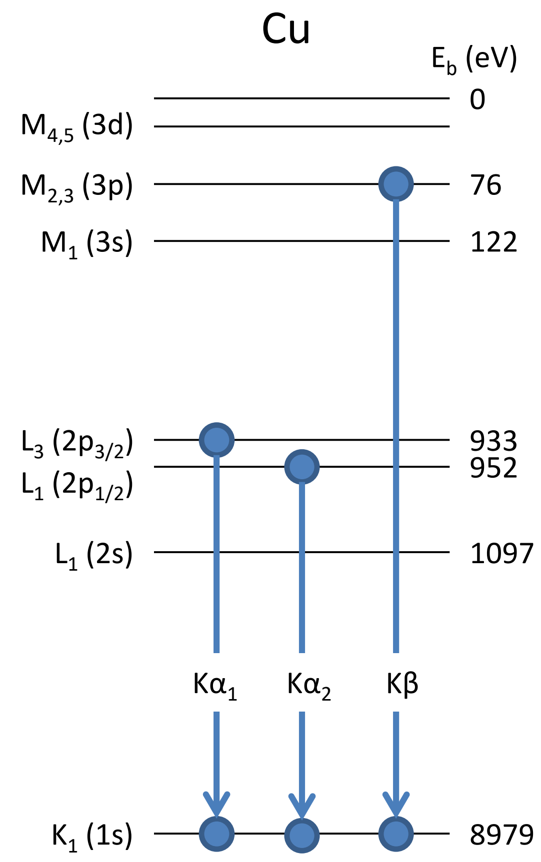
Deflected electron emits electromagnetic radiation.
Wavelength depends on the loss of energy.

Beneration of X-Rays: Bremsstrahlung (Deceleration Radiation)



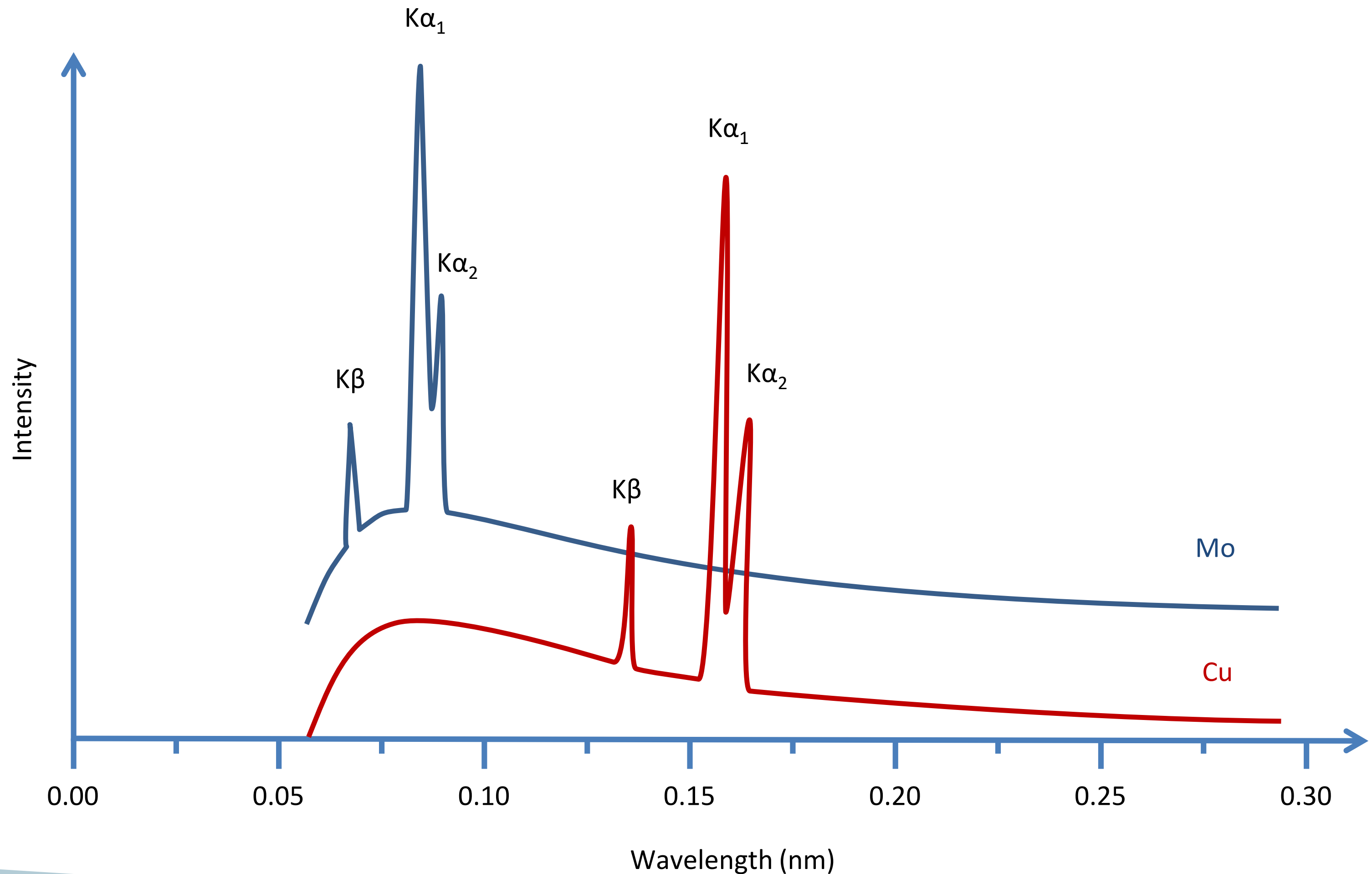
Generation of X-Rays: Characteristic Radiation



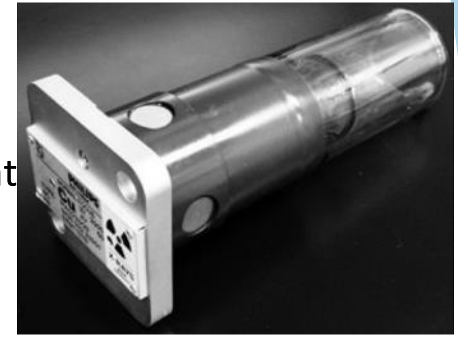


Wavelength of $K\alpha_1$, $K\alpha_2$, $K\beta$, $L\alpha$...
are characteristic for the atomic species.

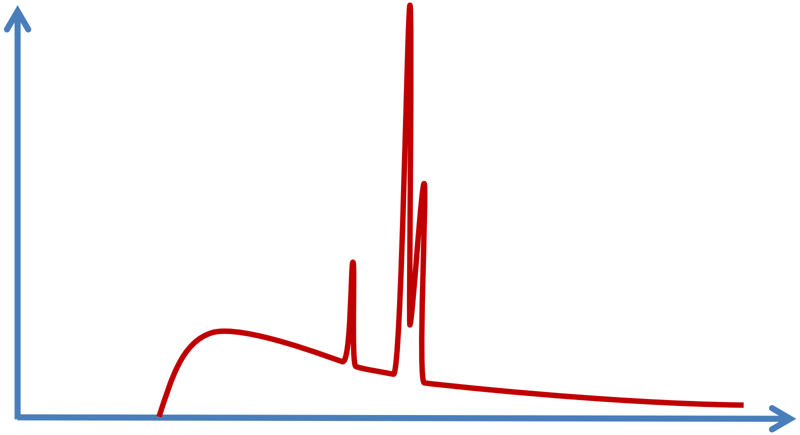
Generation of X-Rays: Characteristic Spectrum



Generation of X-Rays: Summary

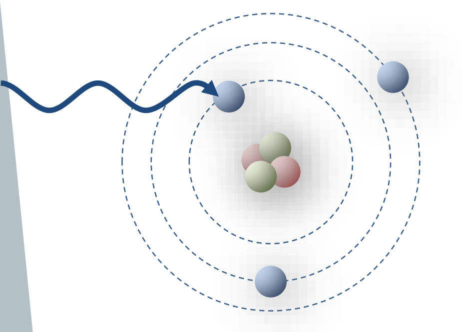


- Generated in an Cathod Ray Tube (X-Ray Tube)
- Spectrum contains Bremsstrahlung (continuous) and characteristic radiat the target material
- Tube is characterized by:
  - Target material (Cu, Co, Cr, Fe, Mo, …)
  - Size and shape of the target
  - Acceleration voltage and current



X-rays: Interaction with Matter

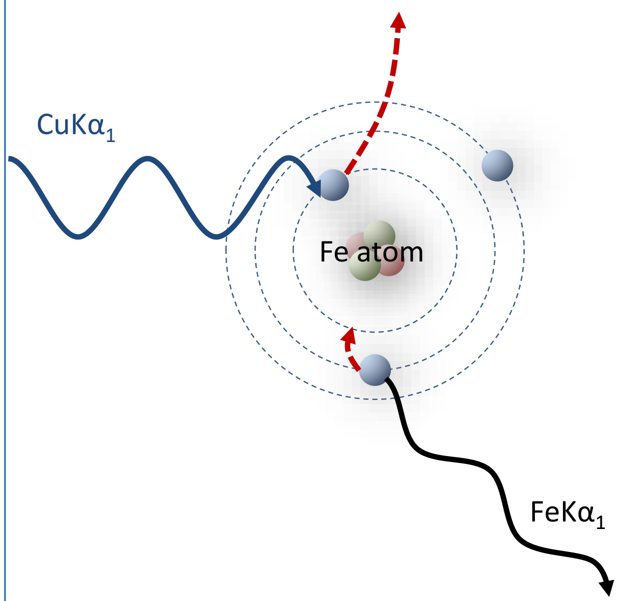
Absorption



1. Energy transfer to electrons (sample heats up)

XAS (X-ray absorption spectroscopy)

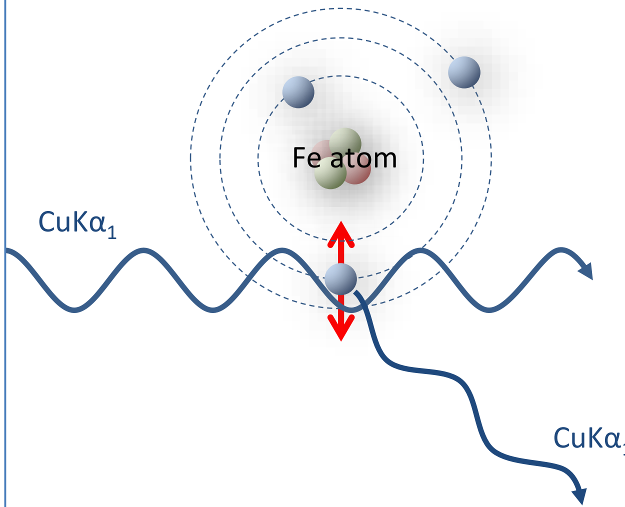
Photoelectric Effect



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

XRF (X-ray fluorescence)

Elastic Scattering



1. Electron oscillates in the electric field
2. Emits secondary radiation ($\lambda_s = \lambda_p$)
3. Φ_p and Φ_s are phase coherent (+180°)

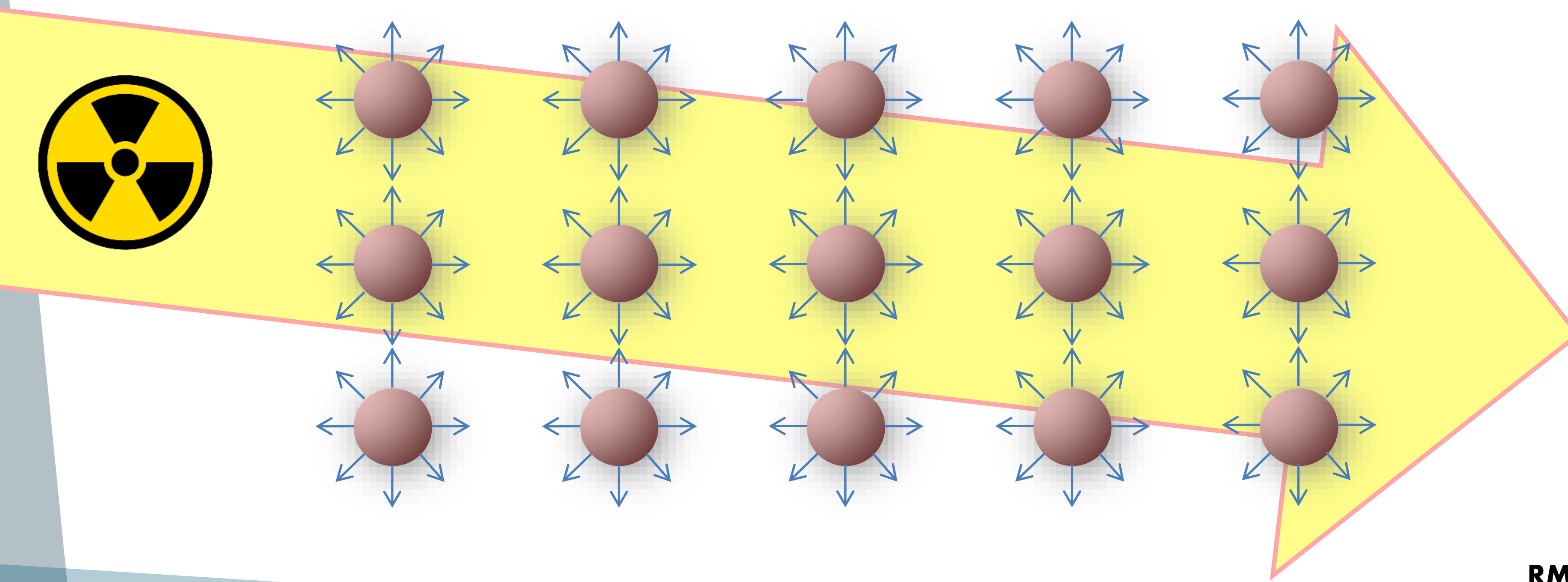
XRD (X-ray diffraction)

Diffraction: Interference

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

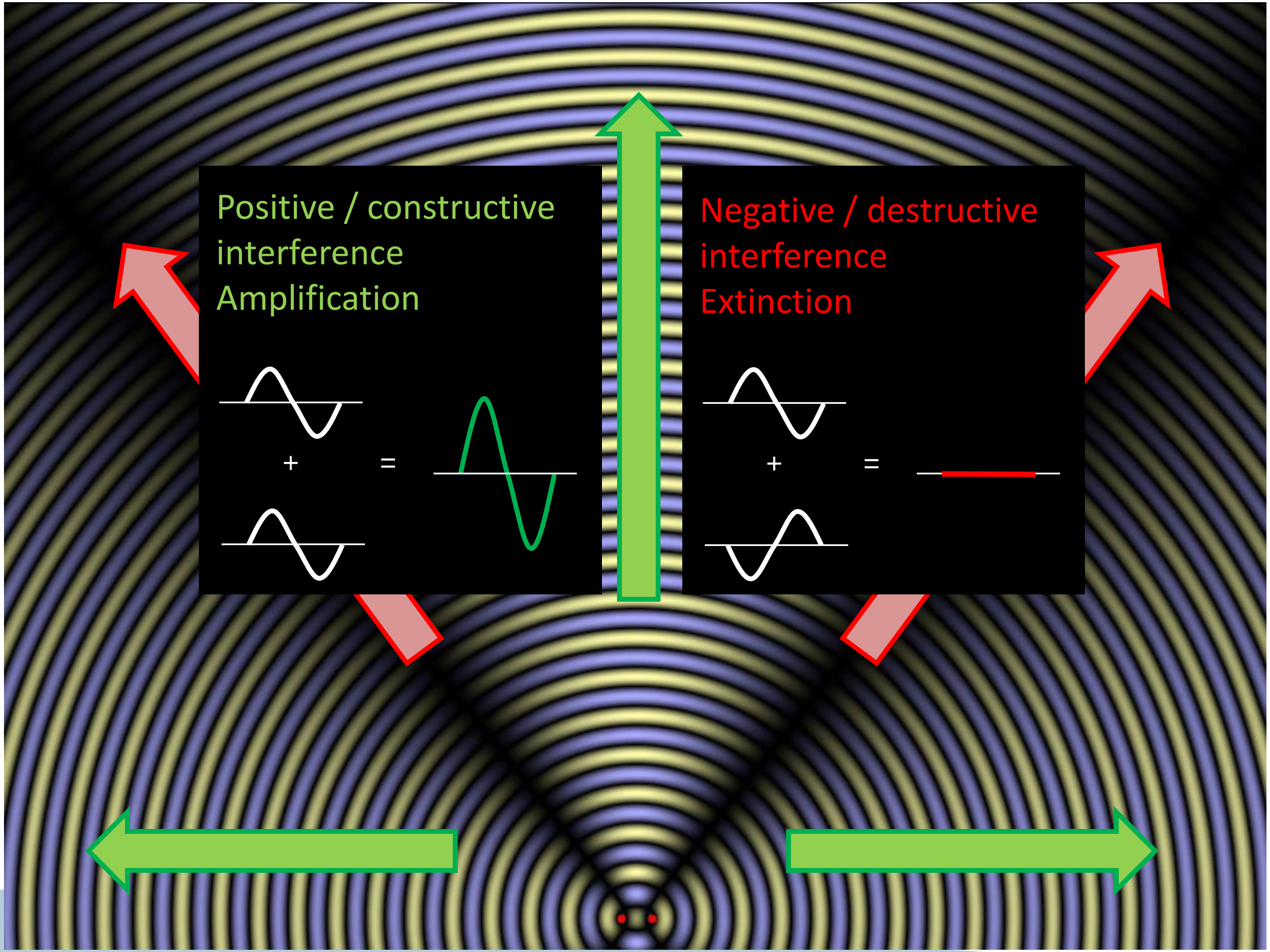
Each atom becomes a point source of secondary (undirected) radiation

→ Interference



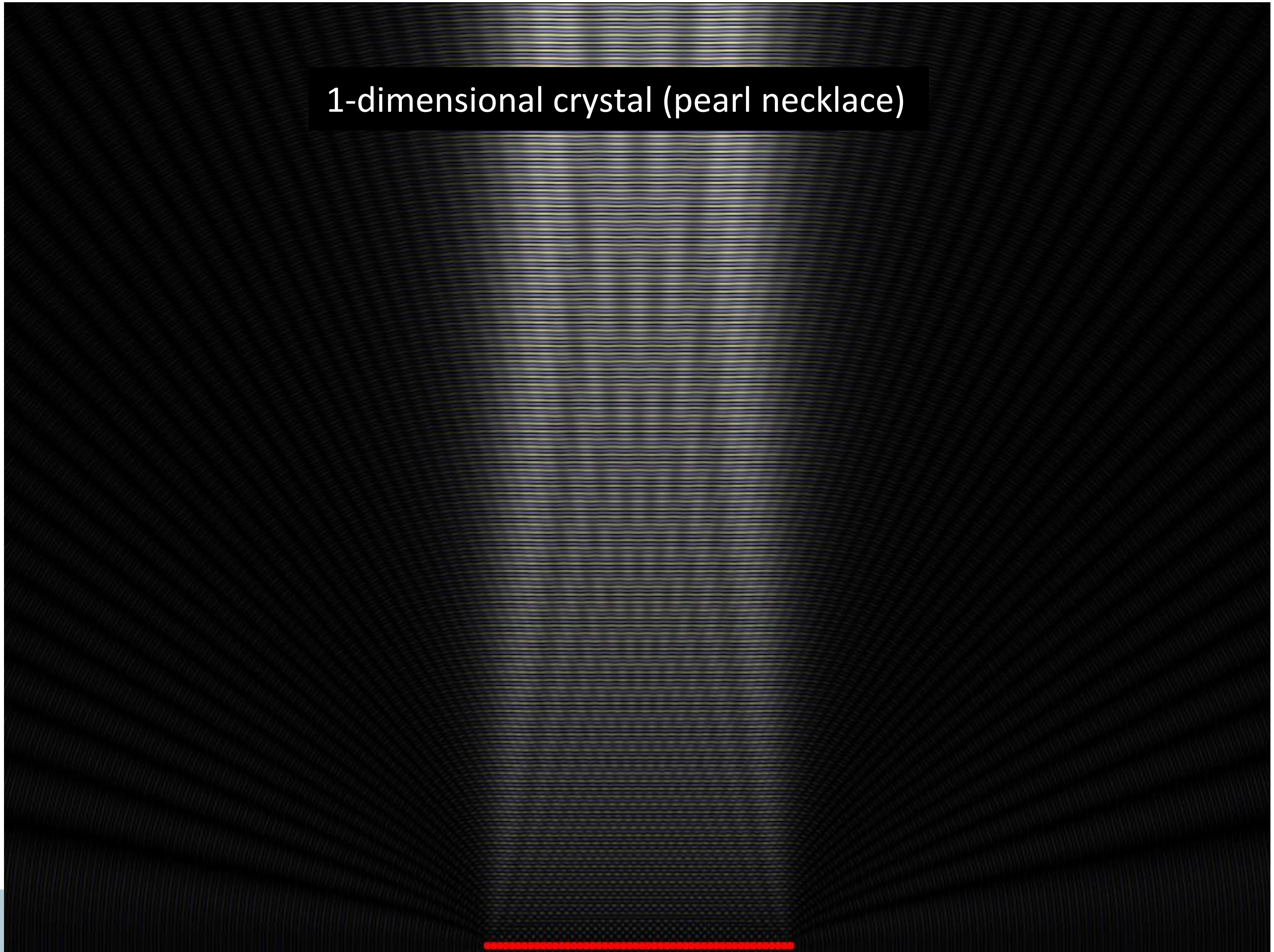
Diffraction: Interference

n=2



Diffraction: Interference

n=50

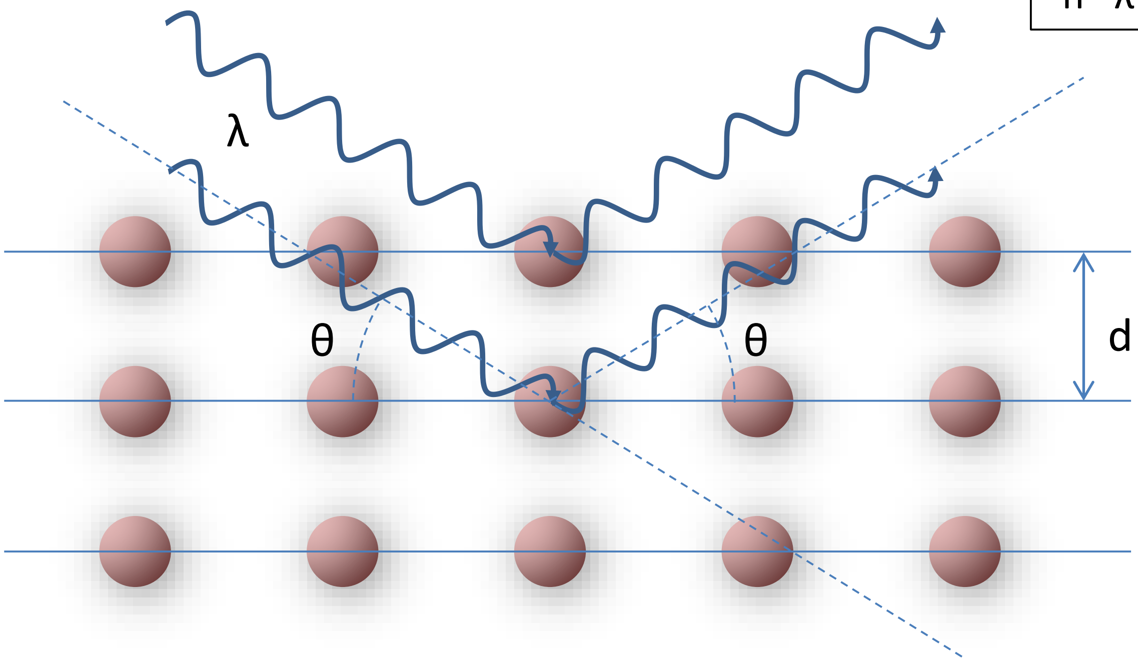


Diffraction: Bragg's Law

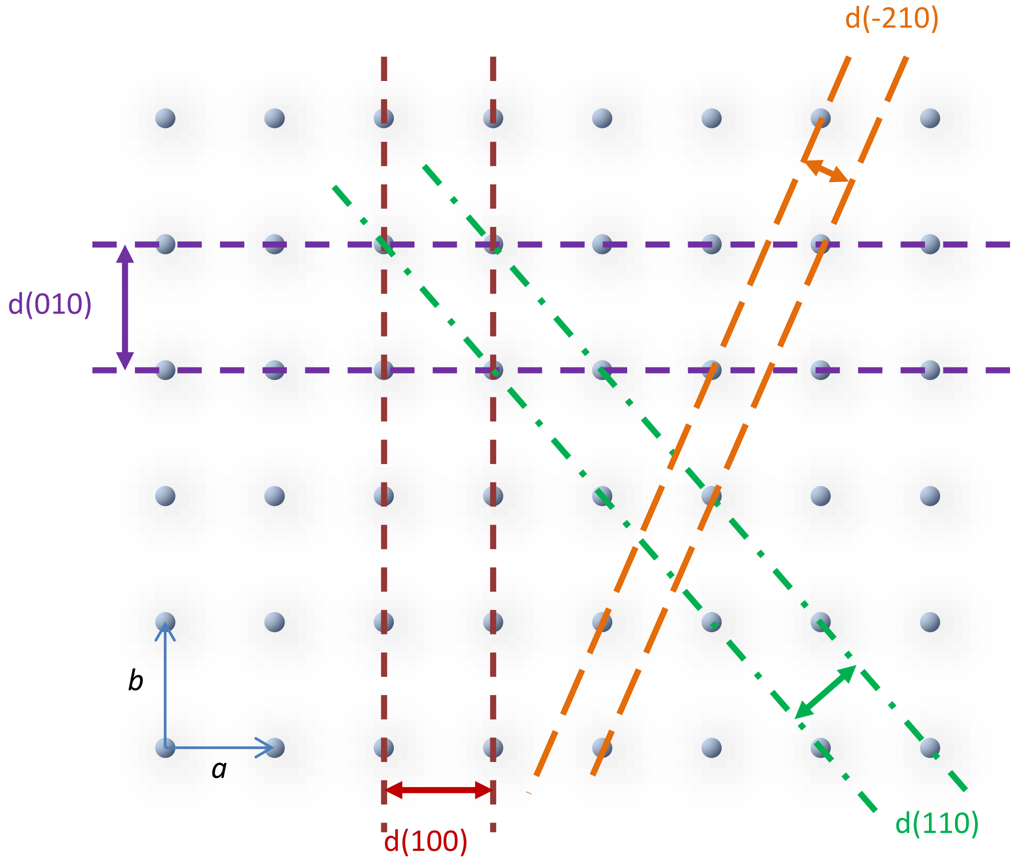
3-dimensional crystal:

- More complex conditions for positive interference to occur
- If interference conditions are not fulfilled: Extinction

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



Diffraction: Lattice Planes and Miller Indices



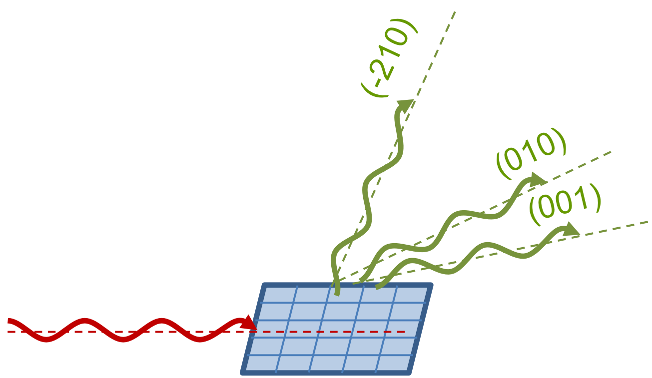
Definition:
A lattice plane is a plane which intersects atoms of a unit cell across the whole 3-dimensional lattice.

- Each lattice plane generates a diffraction peak.
- The plane's d-spacing determines at what 2θ angle diffraction occurs (Bragg's law)
- Diffraction peaks can be labelled with the plane's Miller indices.

Diffraction: Lattice Planes

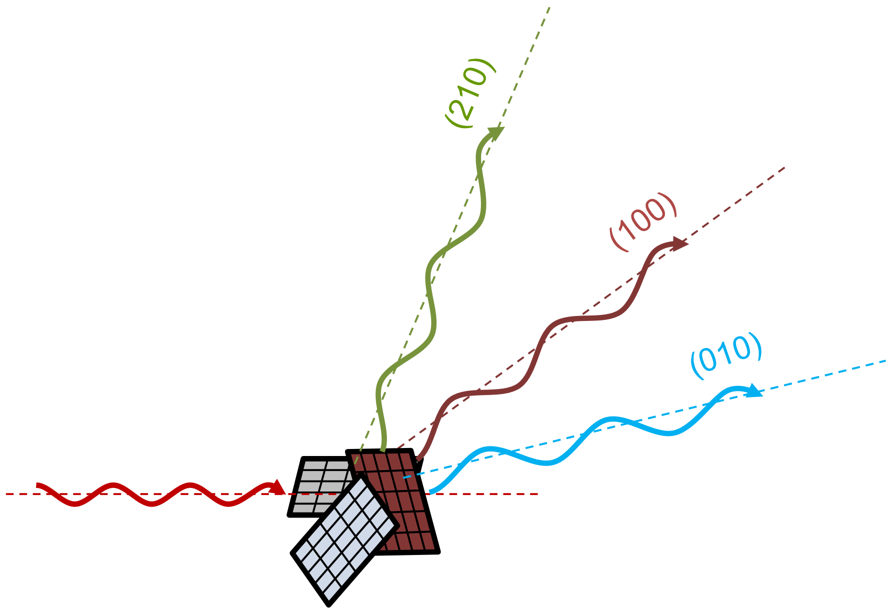
Single crystal:

- Rotate relative to primary beam to bring all lattice planes in diffraction conition:



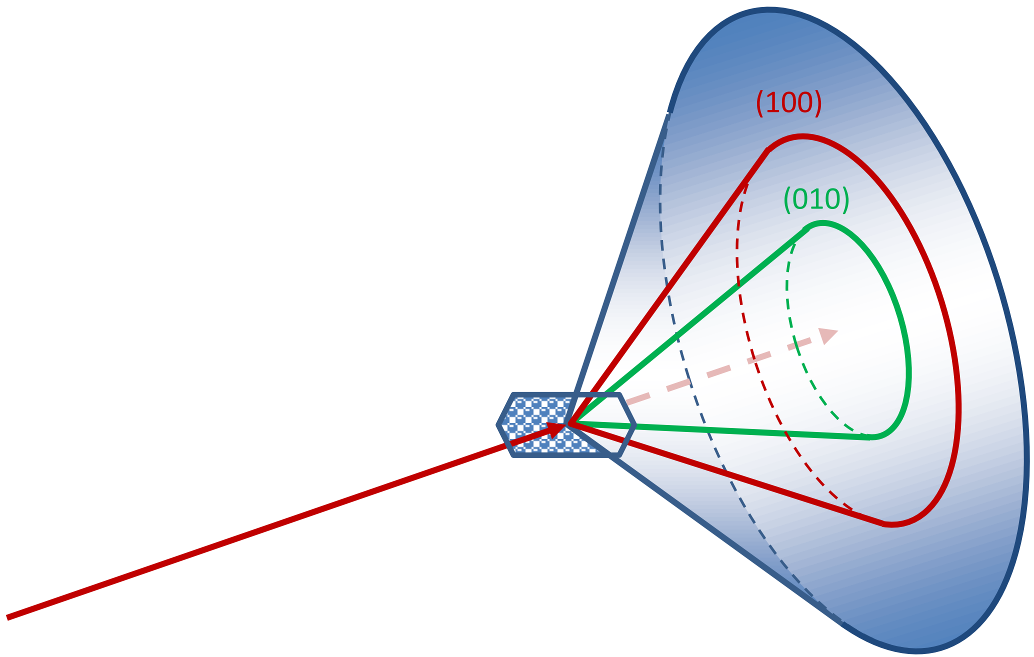
Randomized powder:

- Crystals in all possible orientations are always present:



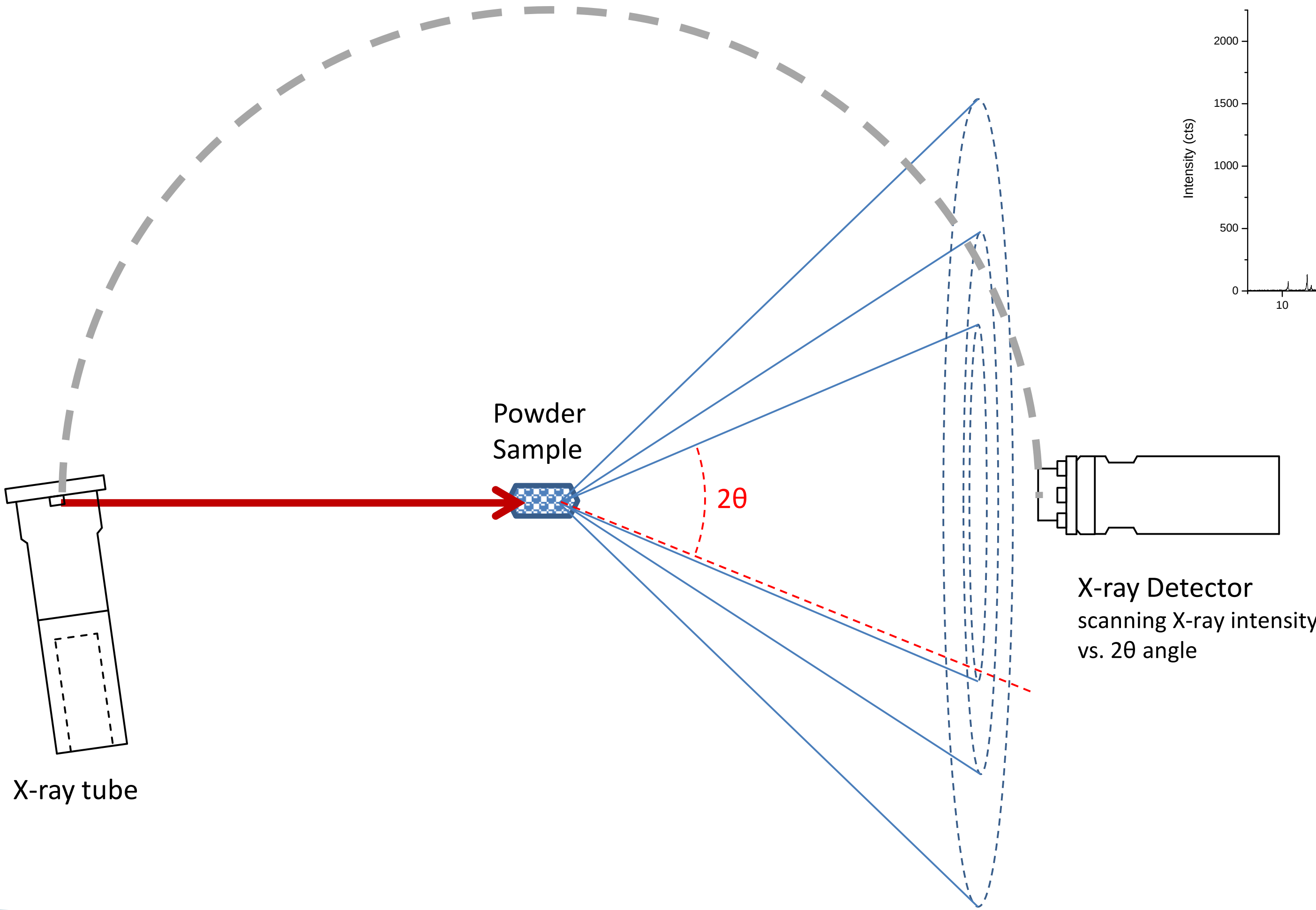
Diffraction: Debye Rings

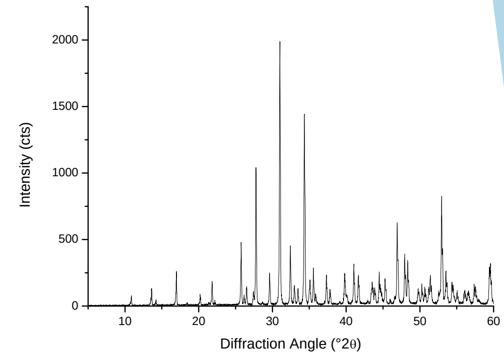
Powder sample:



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

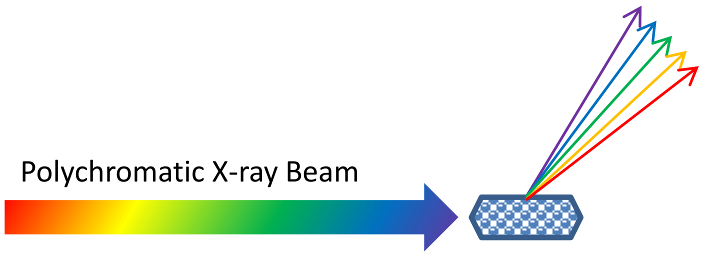
Diffraction: Data Collection

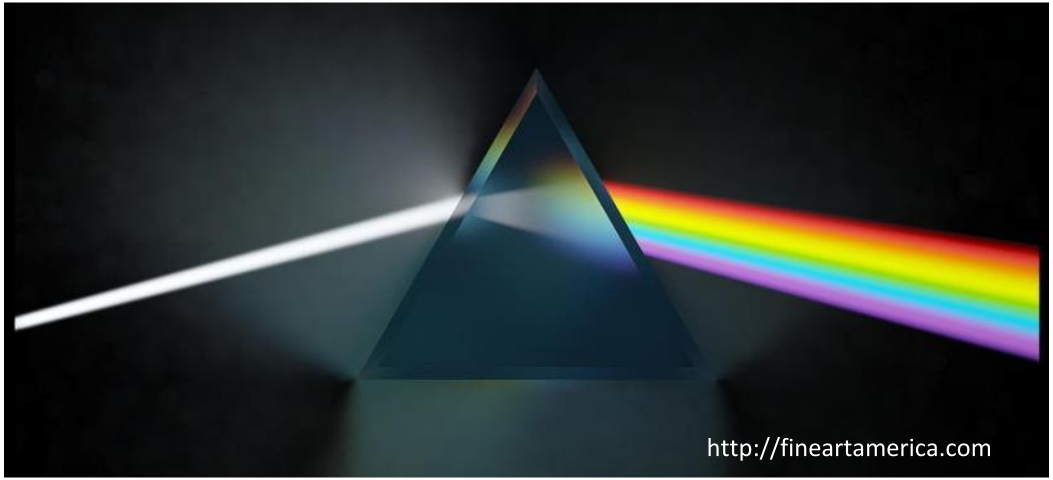




Peak Profile

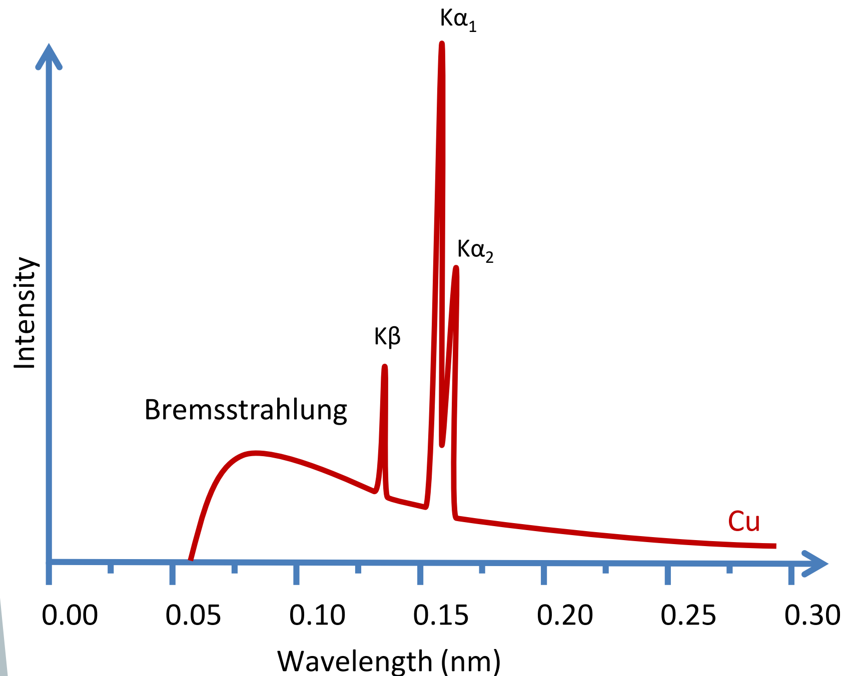
Diffraction angle θ depends on wavelength λ: $n \cdot \lambda = 2 \cdot d \cdot \sin(\theta)$



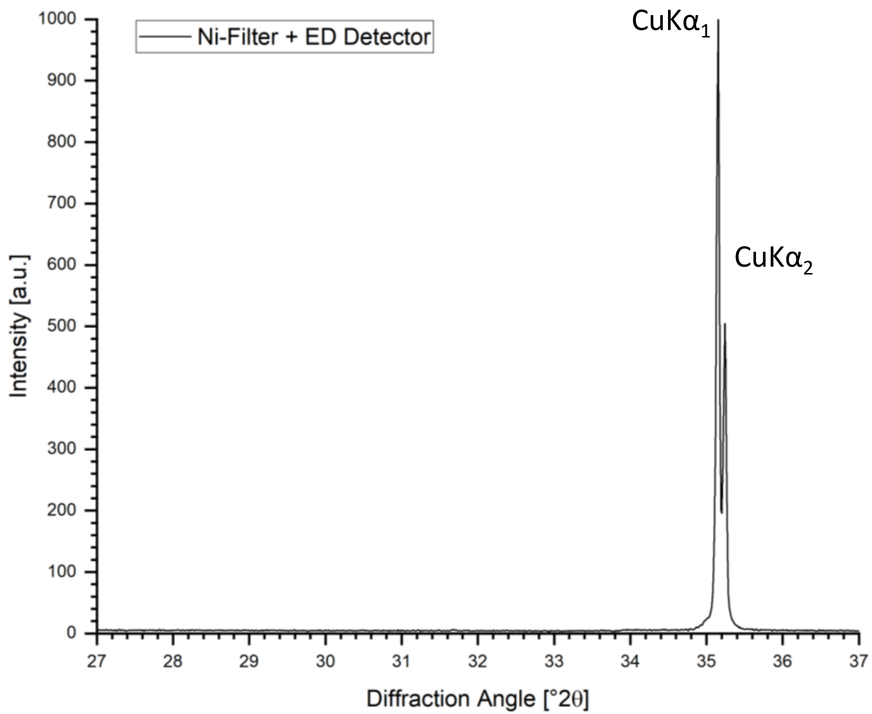


Peak Profile

Characteristic Radiation Spectrum



Diffraction Pattern of Al_2O_3 (104) Peak



Common Instrument Configurations

https://www.malvernpanalytical.com

https://www.thermofisher.com

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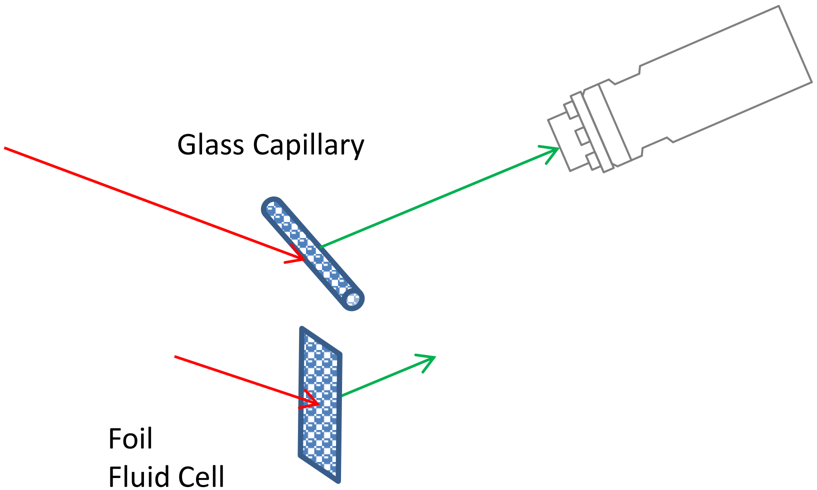
Instrument Configurations

Transmission Geometry

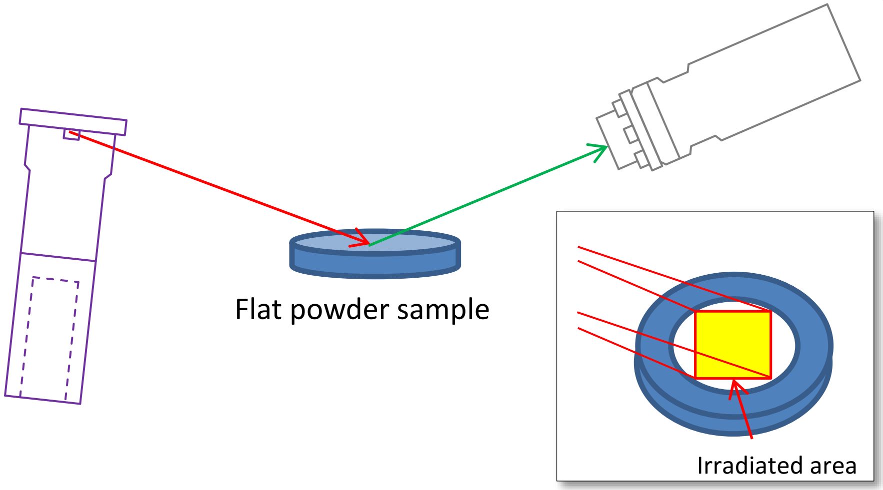


Capillaries are ideal for:

- Light materials (Polymers, Pharmaceuticals)
- Small amounts
- Hazardous materials
- Air-sensitive materials

Use characteristic radiation with **low** absorption coefficient (e.g. MoKα)

Reflective Geometry

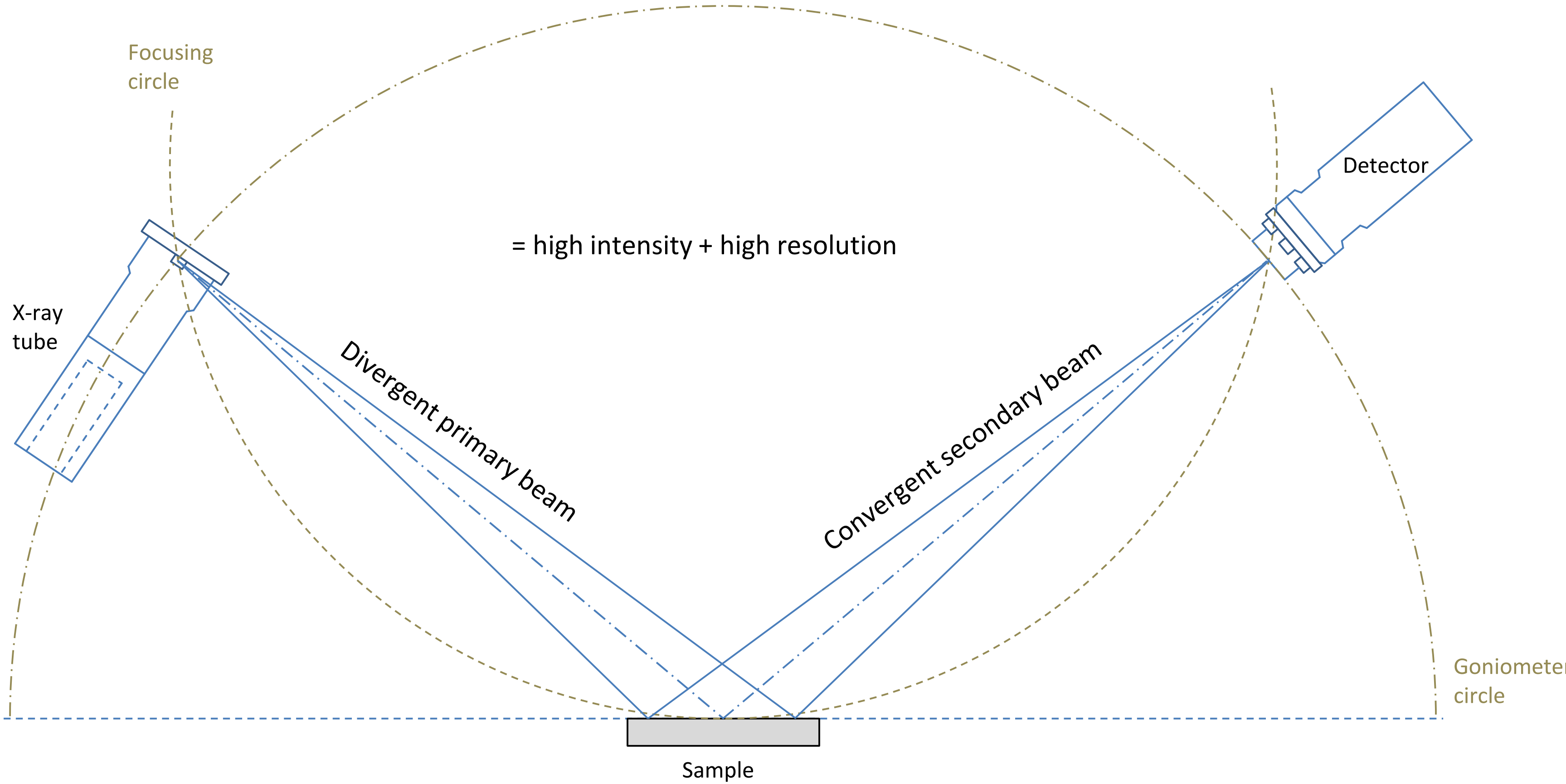


Reflective Geometry is ideal for:

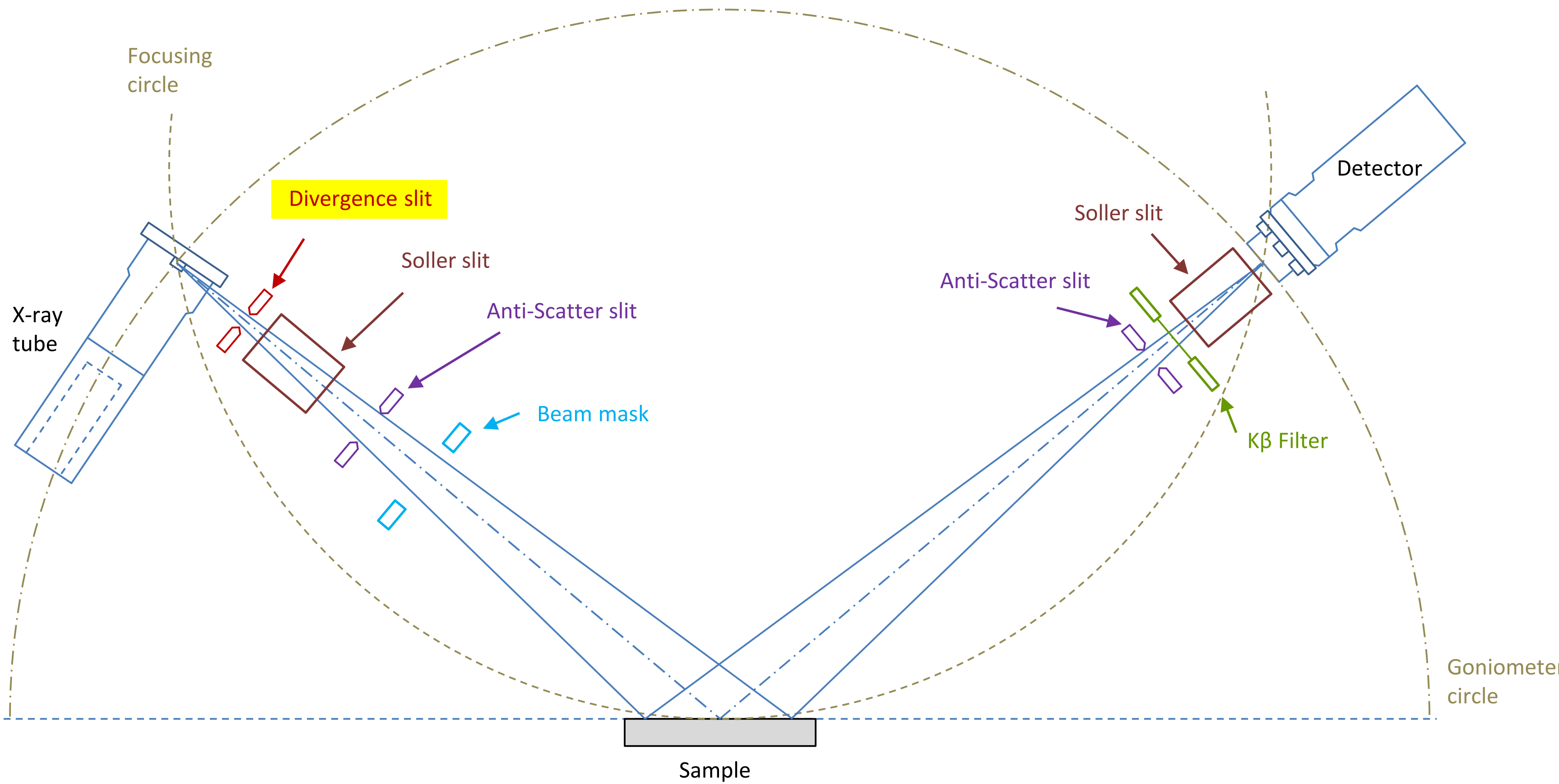
- Absorbing materials (Minerals, Ceramics, Metals)
- Thin films
- Texture analysis

Use characteristic radiation with **high** absorption coefficient (e.g. CuKα)

Instrument Configurations: Bragg-Brentano Parafocusing Geometry

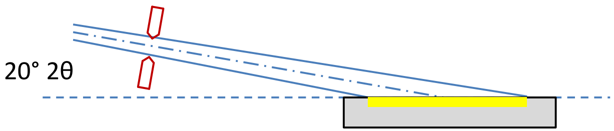


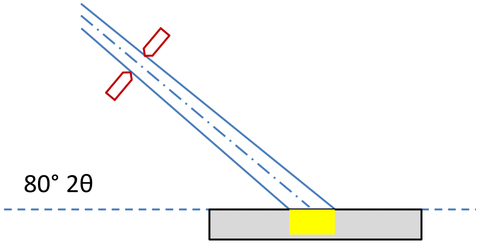
Instrument Configurations: Bragg-Brentano Parafocusing Geometry



Instrument Configurations: Divergence Slit

Fixed divergence slit:



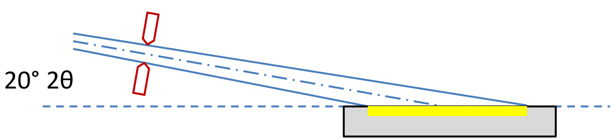


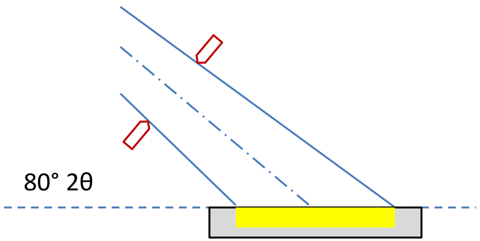
Low incident angle:
- Low penetration depth
- Large illuminated area

High incident angle:
- Deep penetration depth
- Small illuminated area

Irradiated **Volume** is constant
Constant intensity of diffraction pattern

Variable divergence slit:





Low incident angle:
- Narrow divergence slit
- Low penetration depth

High incident angle:
- Wide divergence slit
- Deep penetration depth

Irradiated **Area** is constant
Higher diffracted intensity at high 2θ angle

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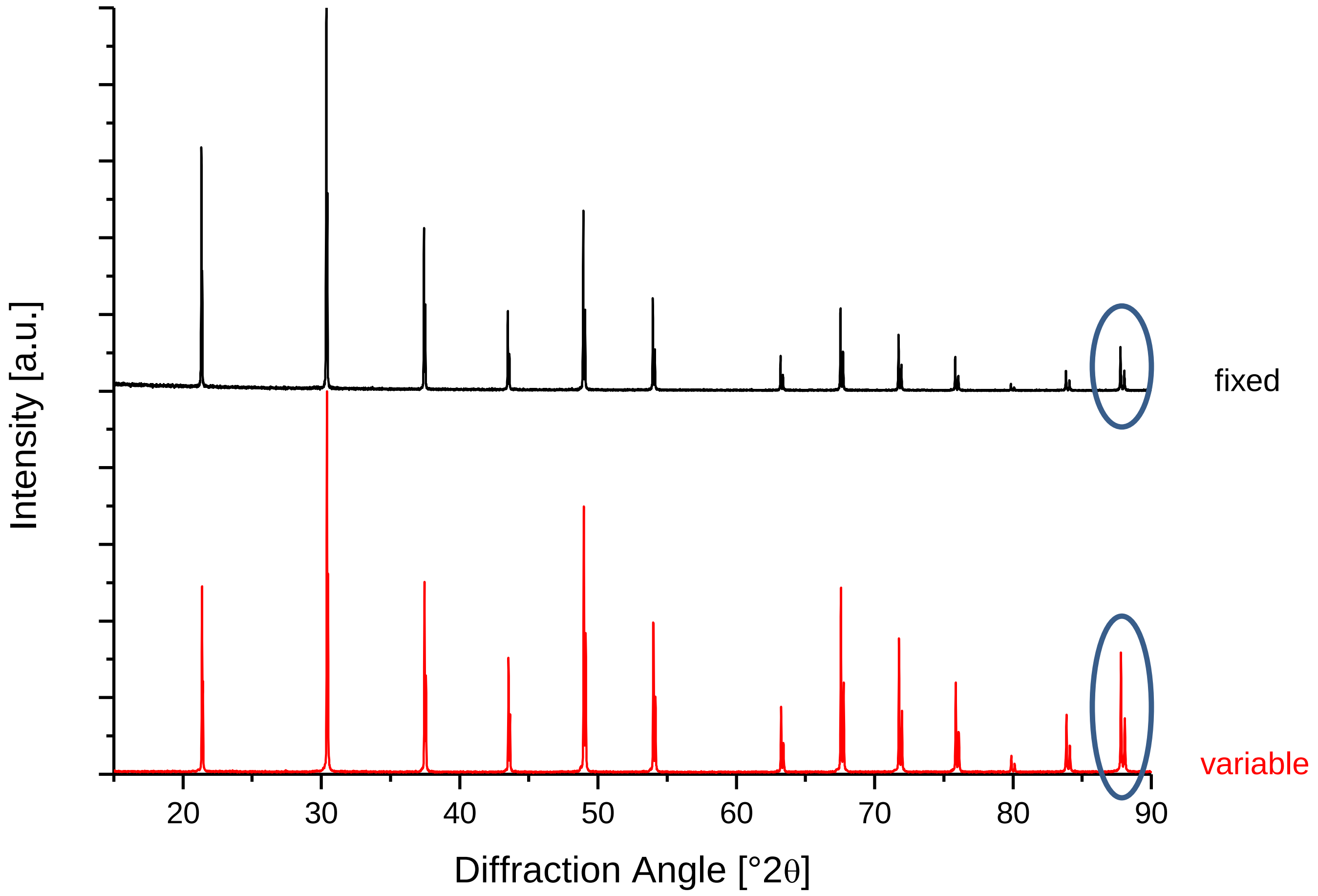
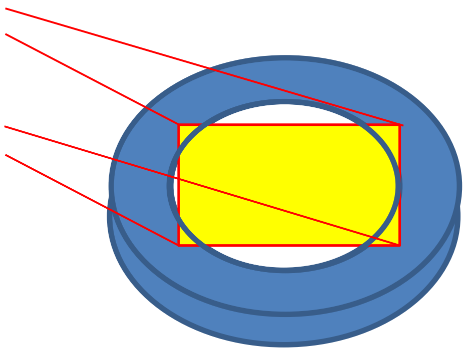
Instrument Configurations: Divergence Slit



Instrument Configurations: Optimum Setup

Wrong!

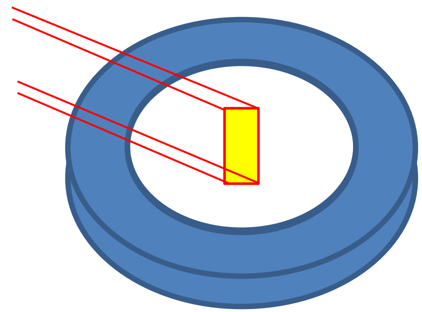
Beam overflow!
Generates signal from
sample holder material



Reduce «irradiated length»
or angle of divergence slit

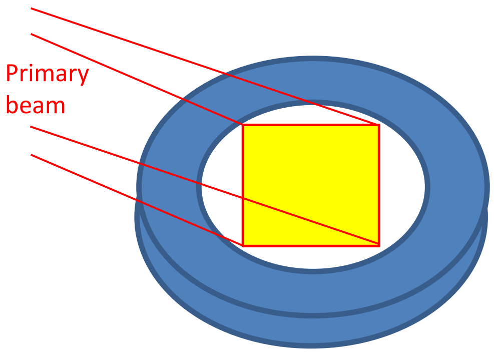
Wrong!

Waste of intensity



Adjust divergence slit (and beam mask)
to maximize irradiated length

Correct!



Instrument Configurations: Setup Checklist

		Optical Element	Ideal setup
Incident beam path	✔	Divergence Slit	Automatic Max irr. length w/o beam overflow
	✔	Soller Slit	Installed Small opening
	✔	Mask	Installed (if available) Max irr. width w/o beam overflow
	✔	Anti-scatter slit	Identical to divergence slit
	✔	Sample	Spinning
Diffracted beam path	✔	Anti-scatter slit	Wide open
	✔	Soller slit	Installed Small opening
	✔	Additional slits	Wide open
	✔	Kβ filter	Installed
	✔	Linear Detector	Maximum PSD opening

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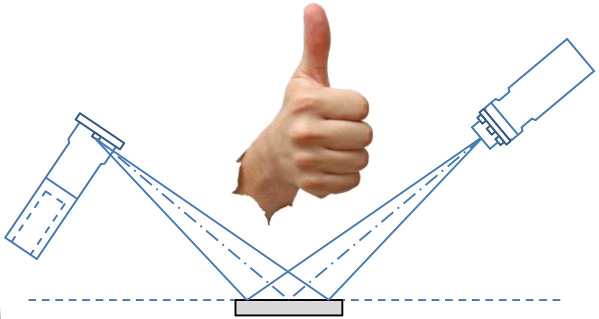
Instrument Configurations: Different Geometries

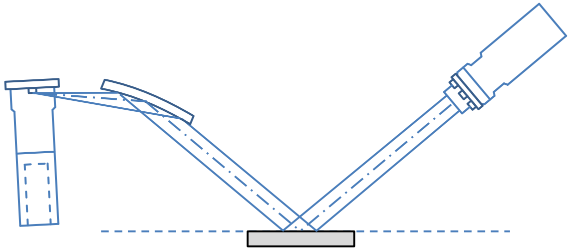
Bragg-Brentano Parafocusing



+ **Ideal for Rietveld Refinement** (phase and structure analysis)
+ High intensity
+ High resolution
+ Good particle statistics

- Large amount of sample material (> 0.5g)

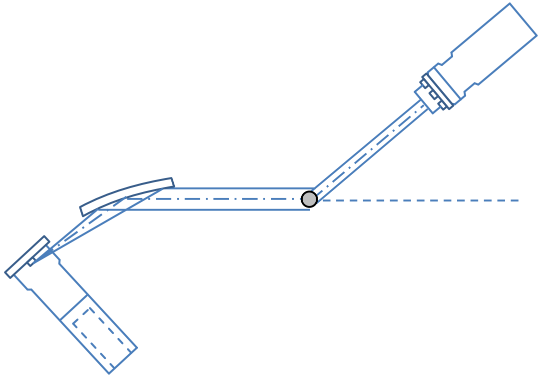
Parallel Beam Reflective



- **Not for Rietveld Refinement**
- Poor peak resolution

+ For other applications (e.g. GI-XRD)

Debye-Scherrer Parallel / Focusing Beam

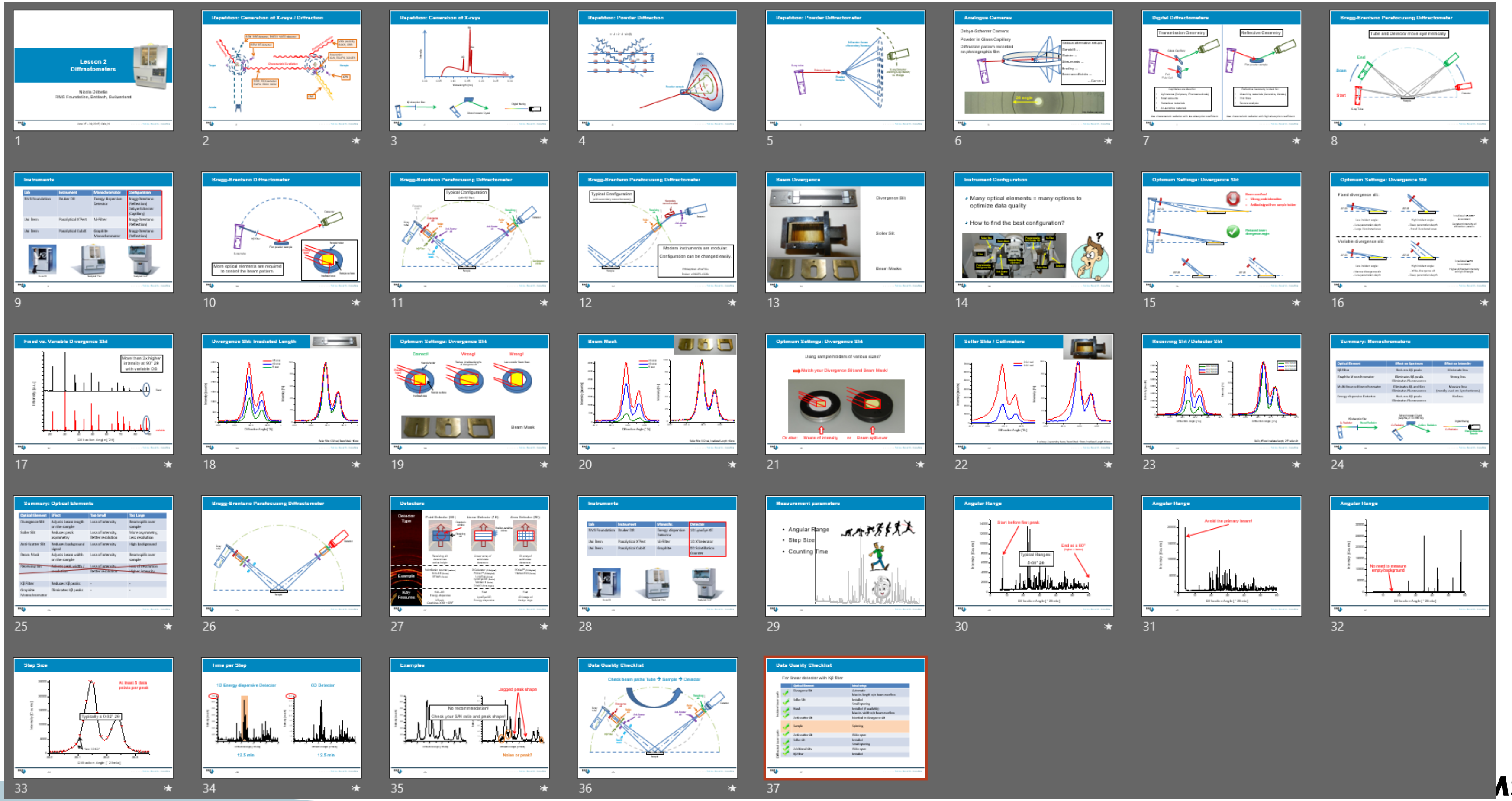


0 **Works for Rietveld Refinement** (but not ideal)
+ Small amount of sample material

- Poor particle statistics
- Sample-dependent peak profile (due to absorption)

Instrument Configurations: More Information

More detailed discussion and examples in previous workshops:



https://www.profex-xrd.org

Profex

Open Source XRD and Rietveld Refinement

Current Version: Profex 5.2.5 - **Released** December 29, 2023

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- Lesson 1: Rietveld Refinement (4.2 MB)
- Lesson 2: Instrument Configurations (2.7 MB)
- Lesson 3: Instrument Example (1.0 MB)
- Lesson 4: Structure Files (2.3 MB)
- Lesson 5: Advanced Refinements and Features (3.2 MB)

June 2017

- Lesson 1: X-rays and Diffraction (3.8 MB)
- Lesson 2: Diffractometers (2.1 MB)
- Lesson 3: Sample Preparation (2.7 MB)
- Lesson 4: Phase Identification (2.2 MB)
- Lesson 5: Rietveld Refinement (2.2 MB)
- Lesson 6: Profex (5.1 MB)
- Lesson 7: How-To Session (4.1 MB)
- Lesson 8: Structure and Device Files (3.6 MB)
- Lesson 9: Publishing XRD Data (4.0 MB)

Examples 2017-06 (1.0 MB)