SYNCHROTRON THAILAND CENTRAL LAB

XRD Forum: discussion panel for technologies for ferrous samples

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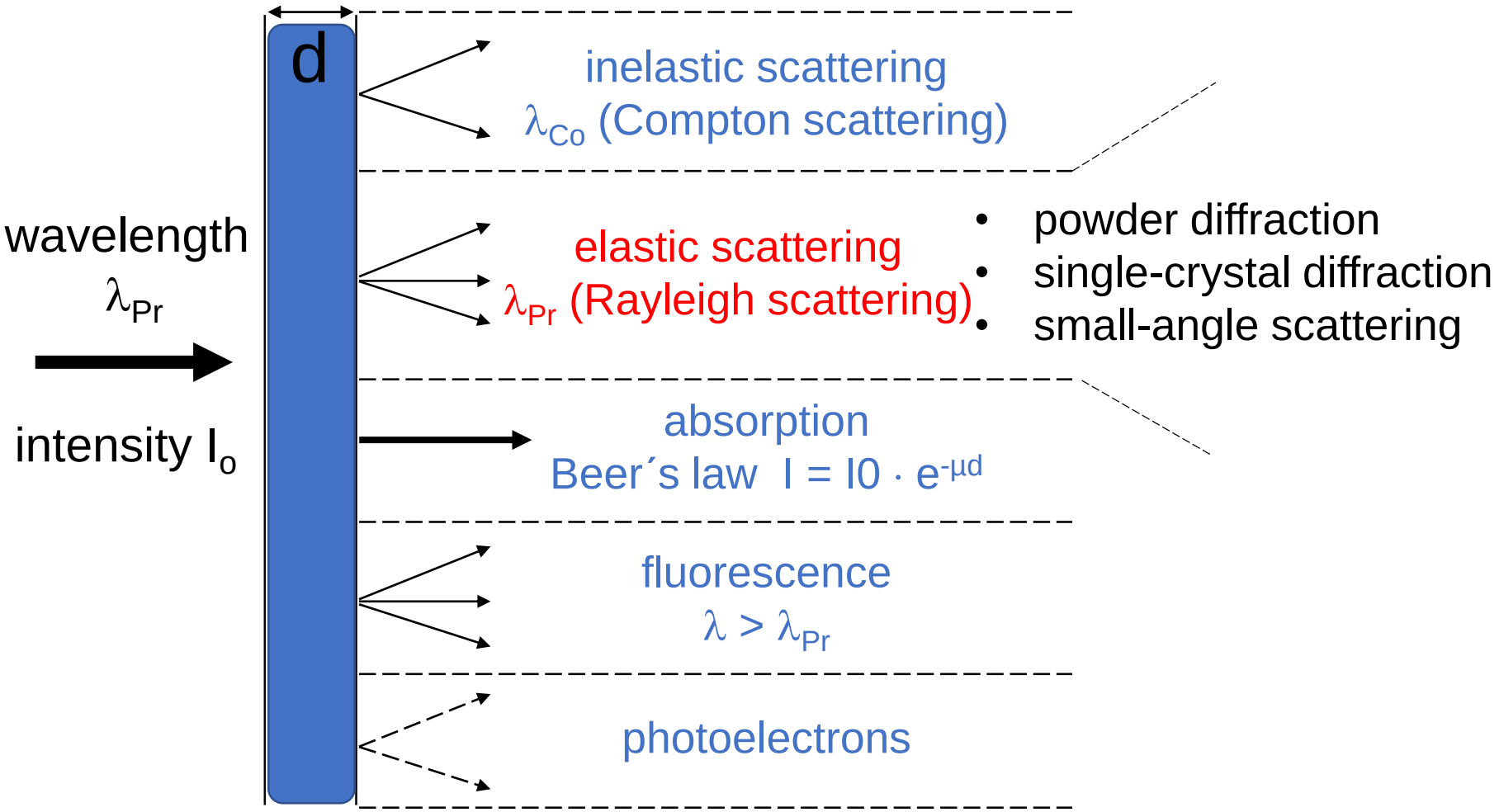
Siam Photon

Challenges and Scientific facts
X-ray diffraction of iron containing samples

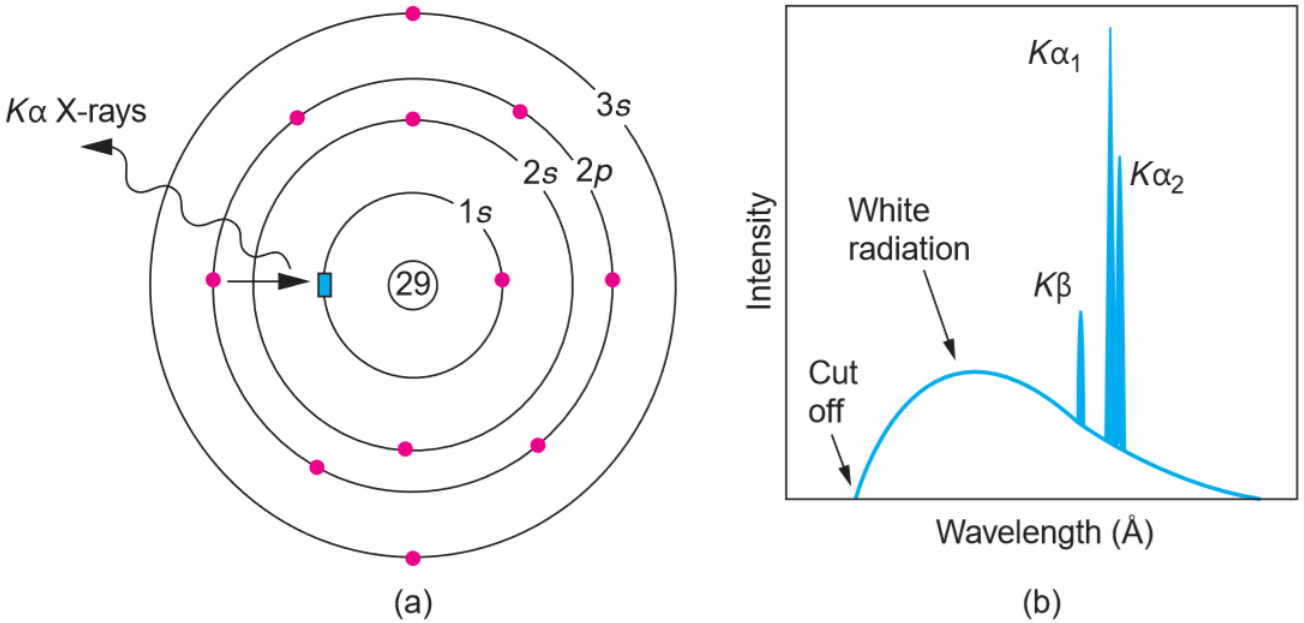
- High background signal / Moderate quality of XRD peaks when using Cu K_α radiation
- How to reduce fluorescence background?
- Alternative laboratory X-ray sources and/or synchrotron X-ray sources

Interaction of X-ray with matter



X-ray generated from X-ray tubes

X-rays are produced when high-energy electrons collide with matter.



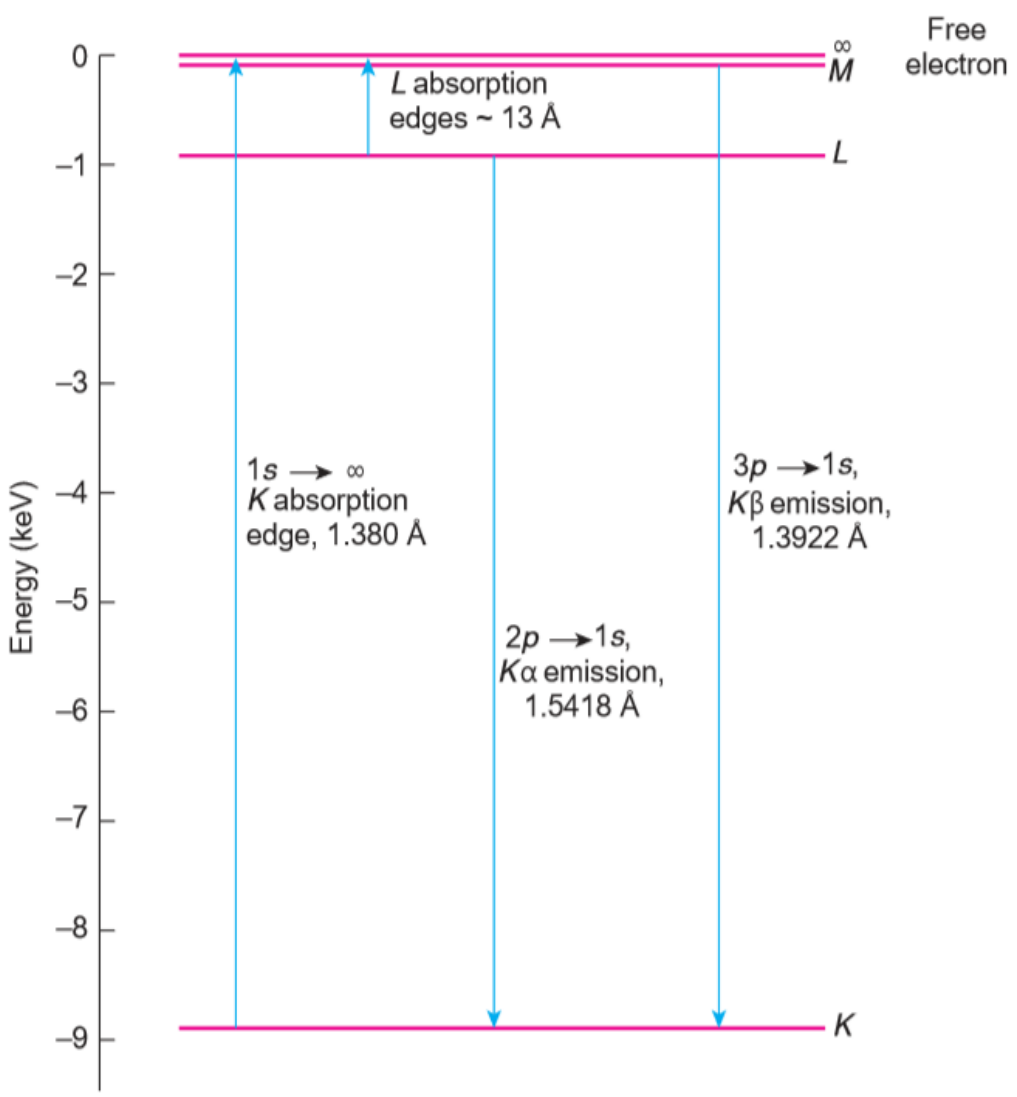
(a) Generation of Cu K_α X-rays. A 1s electron (K shell) is ionized; a 2p electron falls into the empty 1s level and the excess energy is released as X-rays.

(b) X-ray emission spectrum of Cu have two components;

i) a broad spectrum of wavelengths known as white radiation

ii) a number of fixed, or monochromatic, wavelengths (sharp and intense)

Electronic transition → photoelectric effect and X-ray emission (fluorescence)



The incident electrons have sufficient energy to ionize some of the Cu 1s (K shell) electrons.

An electron in an outer orbital (2p or 3p) immediately drops down to occupy the vacant 1s level and the energy released in the transition appears as X-radiation.

For Cu

2p → 1s transition, called Kα, has a wavelength of 1.5418 Å.

3p → 1s transition, Kβ, 1.3922 Å.

The electronic transitions involved in both the ionization of inner shell electrons and emission of X-rays

Unwanted phenomenon in XRD

- **Photoelectric effect** → X-ray knocks one of the electrons out of the inner shell of an atom, emitting a characteristic fluorescent radiation (XRF)
- However, this is an unwanted phenomenon in XRD;
  - A relatively large part of the energy of the incident beam is absorbed in this process.
  - Less intensity of the beam reaches the detector (the diffracted beam).
  - Lower signal of the peak is observed in the diffractogram.
  - The fluorescent radiation will be detected, causing a high background.
  - These two effects combined can cause peaks to become invisible, making it difficult to analyze the diffractogram.

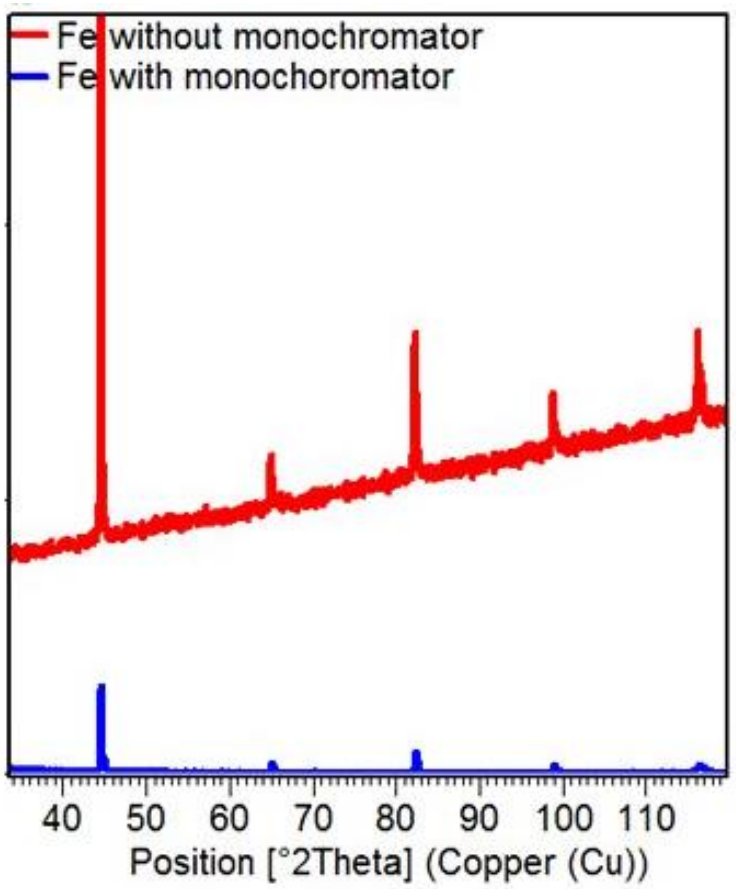
K_α radiation / Absorption edge / Fluorescence

Elements	Wavelength of $K_{\alpha 1}$ radiation (Å)	Characteristic energy (eV)	Absorption K-edge (eV)	Fluorescence $K_{\alpha 1}$ energy (eV)
Cu	1.5406	**8046.3**	8979	8046.3
Fe	1.9357	6405.2	**7112**	6405.2
Co	1.7889	6930.9	7709	6930.9
Cr	2.2897	5414.9	5989	5414.9

To ensure sufficient scattering (XRD), the energy of the K_α radiation should be lower than the K absorption edge of the materials, otherwise strong fluorescence is generated.

Cu K_α radiation and Fe K-edge absorption → not suitable at all

Cu K_α radiation & iron containing samples



Mismatching between choice of X-ray radiation and sample composition

- High background signal due to fluorescence phenomena
- Moderate or poor quality of XRD peaks, especially the low-intensity peaks
- Difficulty for phase identification and incorrect phase identification

  Example: magnetite / maghemite

  - Both can form in similar environments and be converted into one another (e.g. exposure to ambient air)
  - Diffractograms of these two minerals are only distinguishable by a few low intensity peaks.

Choices of compatible radiation → Diffractogram of good quality

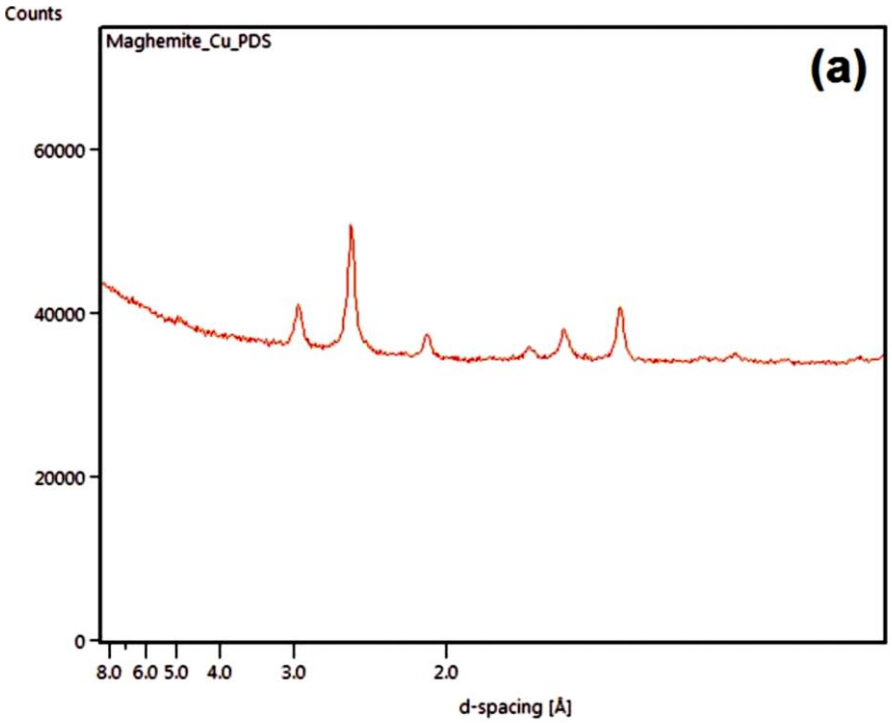
How to reduce fluorescence background?

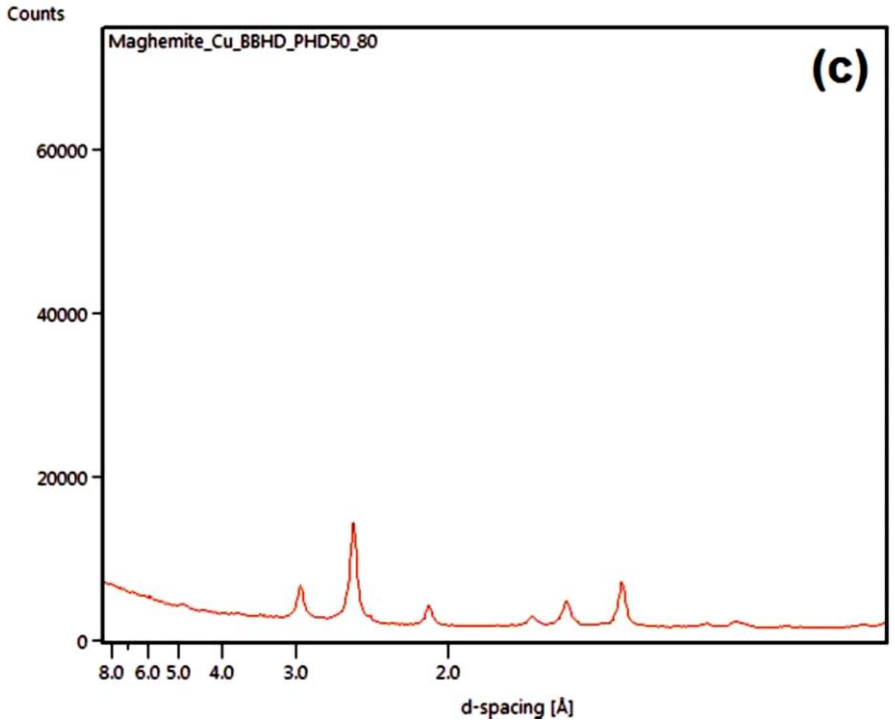
How to reduce fluorescence background of iron containing samples?

- Setting a sensitivity window for the detector to be higher
  - solves the problem for iron analysis with Mo radiation but not for Cu radiation
- Using additional optics
  - programable divergent slit (PDS)
  - monochromator (Germanium or Graphite crystal) both in the incidence beam and in the diffracted beam
    - ➢ eliminate radiation other than K_α
- Applying a suitable type of radiation
  - reducing fluorescence background
  - increasing penetration depth
  - e.g. Co anode, Cr anode

Additional optics for Cu K_α radiation

Maghemite (γ-Fe2O3)





Programable divergent slit (PDS)

Monochromator: Bragg-Bentano module (BBHD) + adjustable energy sensitivity using pulse height distribution (PHD)

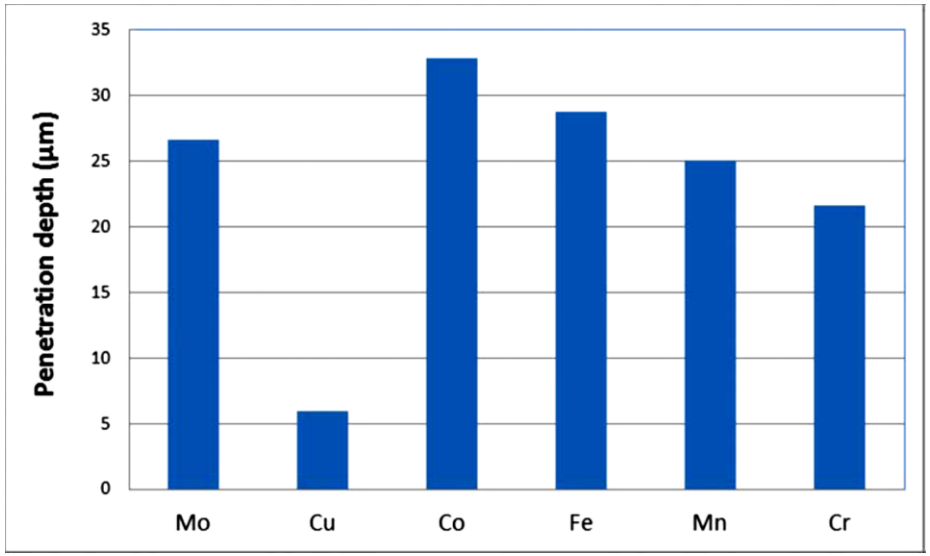
Ref. GEOMICROBIOLOGY JOURNAL, 2018, VOL. 35, NO. 6, 511–517.

Using Co K_α radiation instead

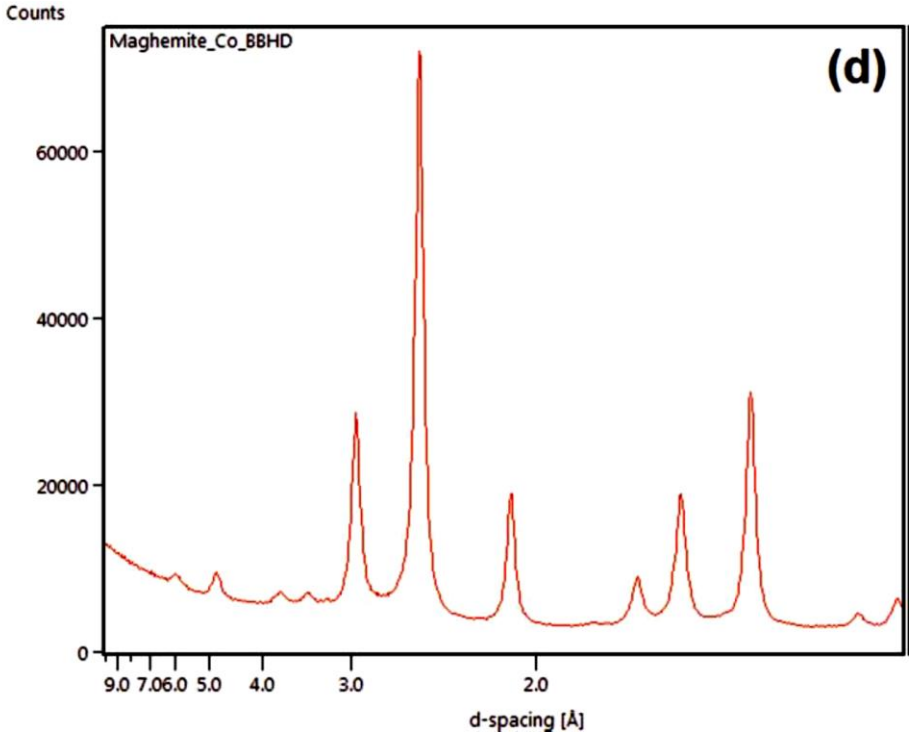
When using the same exposure time as in the case of Cu radiation

Co radiation:

- Reducing fluorescence background
- Increasing penetration depth



Maghemite (γ-Fe2O3)

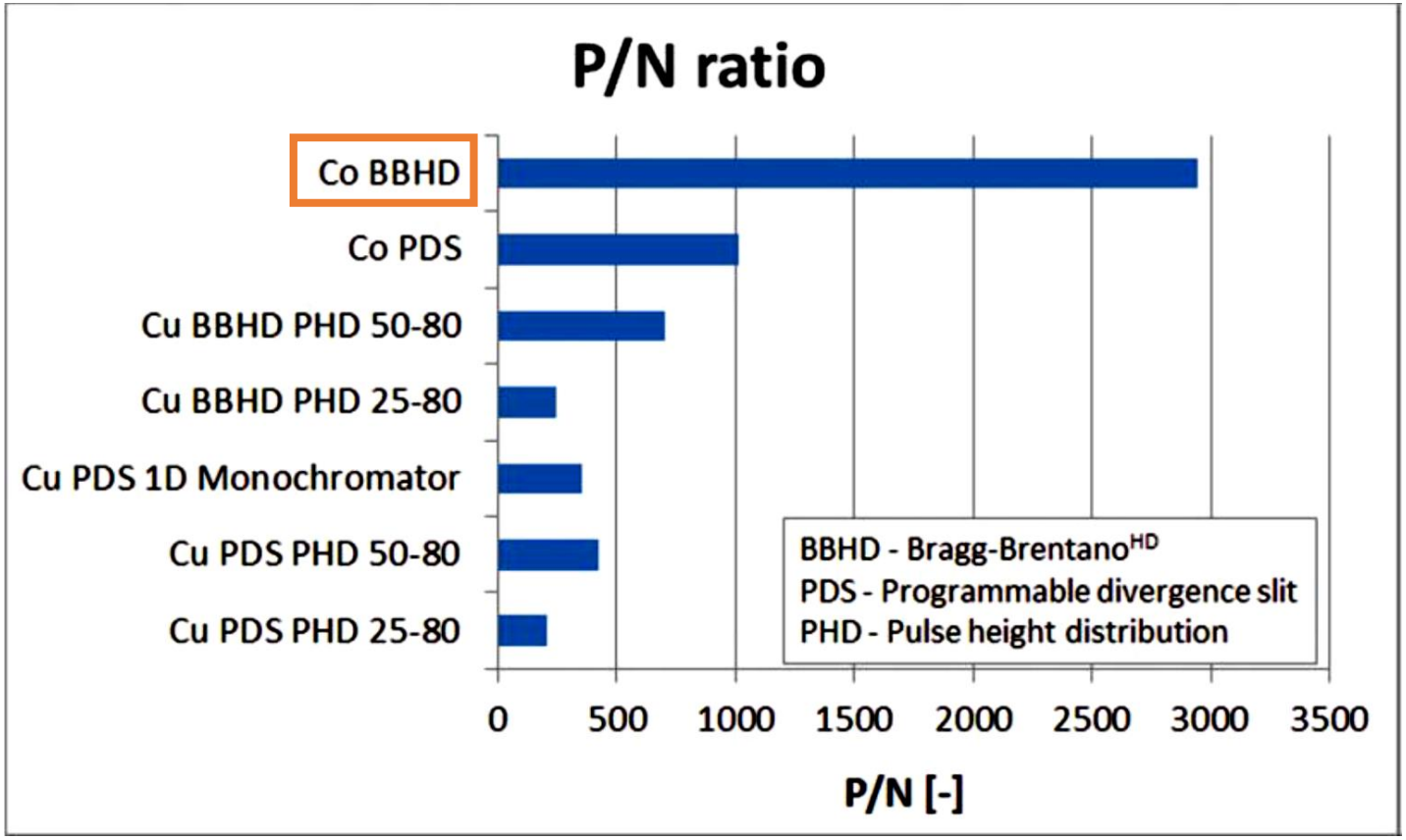


Bragg-Bentano module (BBHD) + pulse height distribution (PHD)

Ref. GEOMICROBIOLOGY JOURNAL, 2018, VOL. 35, NO. 6, 511–517.

Qualifying the diffractograms: Peak-to-noise ratio

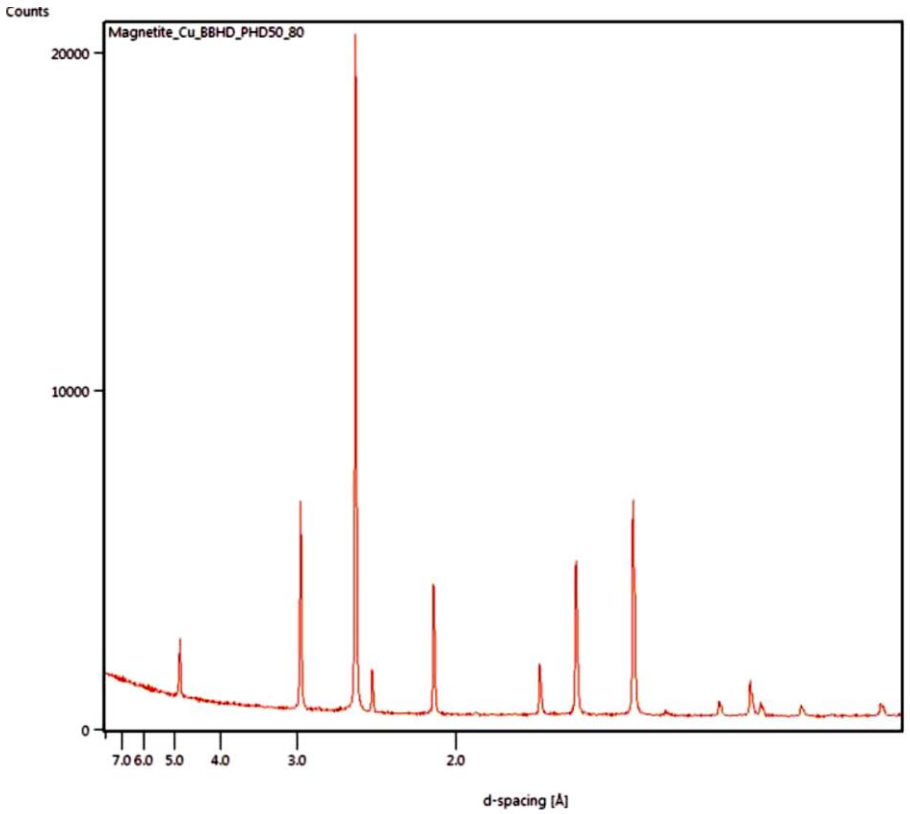
$$P/N = \frac{I_{net\ peak}}{\sigma\left(I_{background}\right)} = \frac{I_{net\ peak}}{\sqrt{I_{background}}}.$$



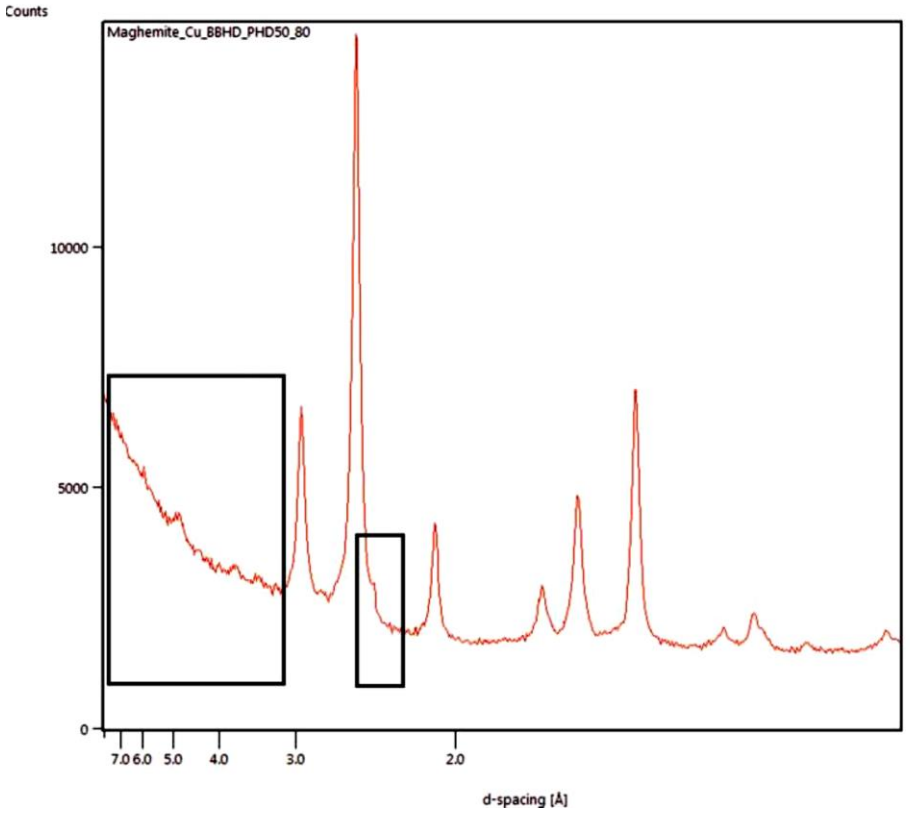
Ref. GEOMICROBIOLOGY JOURNAL, 2018, VOL. 35, NO. 6, 511–517.

Cu K_α radiation: phase identification

Magnetite (Fe_3O_4)



Maghemite (γ-Fe_2O_3)

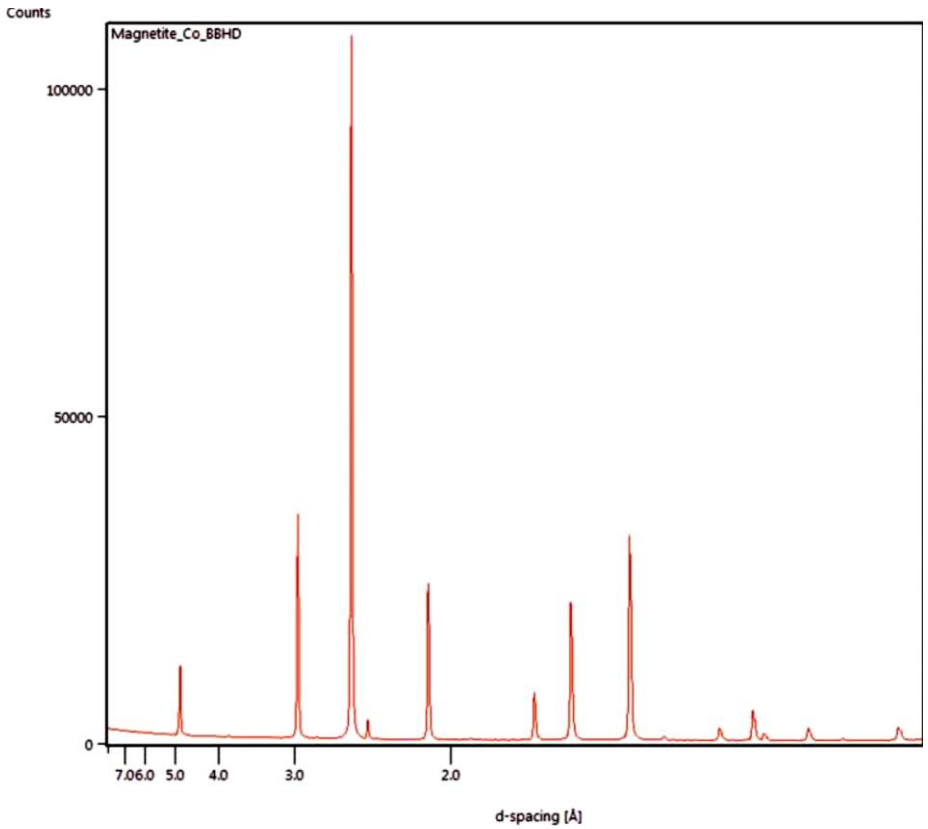


When using Cu radiation, it is ambiguous to identify the diffractogram in the “right figure” to be either magnetite or maghemite phase!!!

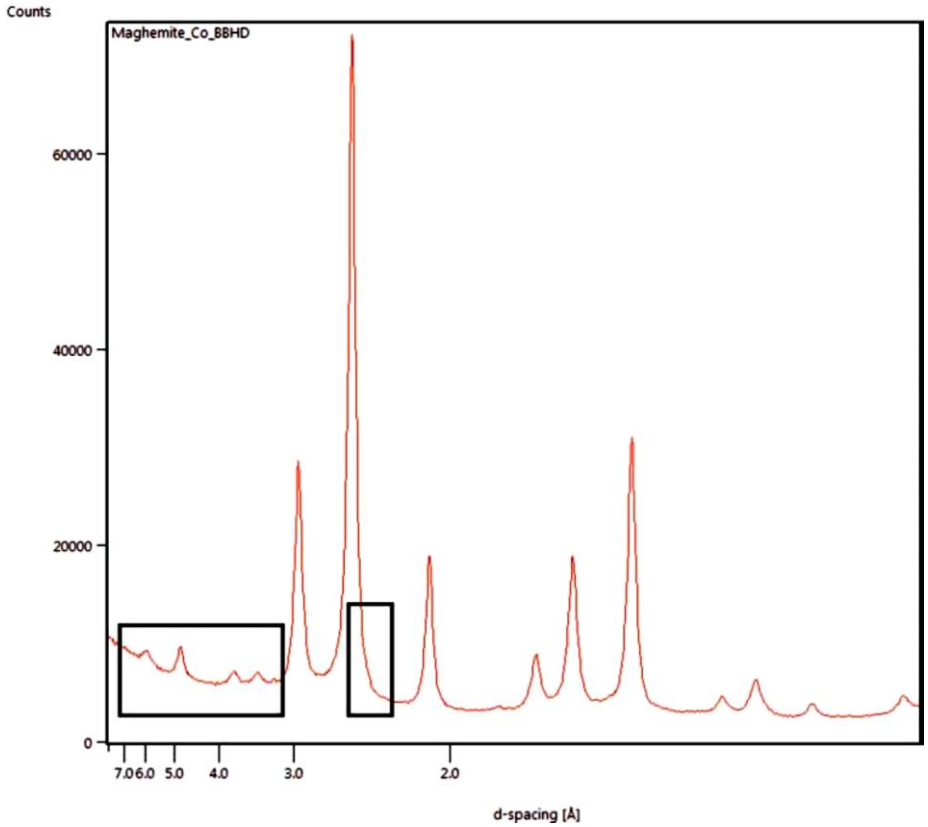
Ref. GEOMICROBIOLOGY JOURNAL, 2018, VOL. 35, NO. 6, 511–517.

Co K_α radiation: phase identification

Magnetite (Fe_3O_4)



Maghemite (γ-Fe_2O_3)

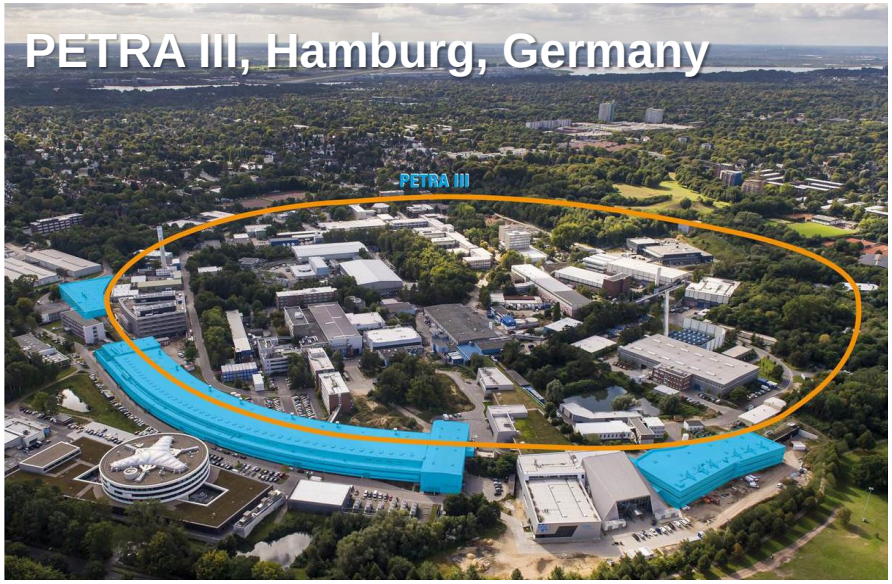


Changing to Co radiation, there are clearly distinguishable peaks present for identifying the maghemite phase at high d-spacing or low two-theta (Right figure).

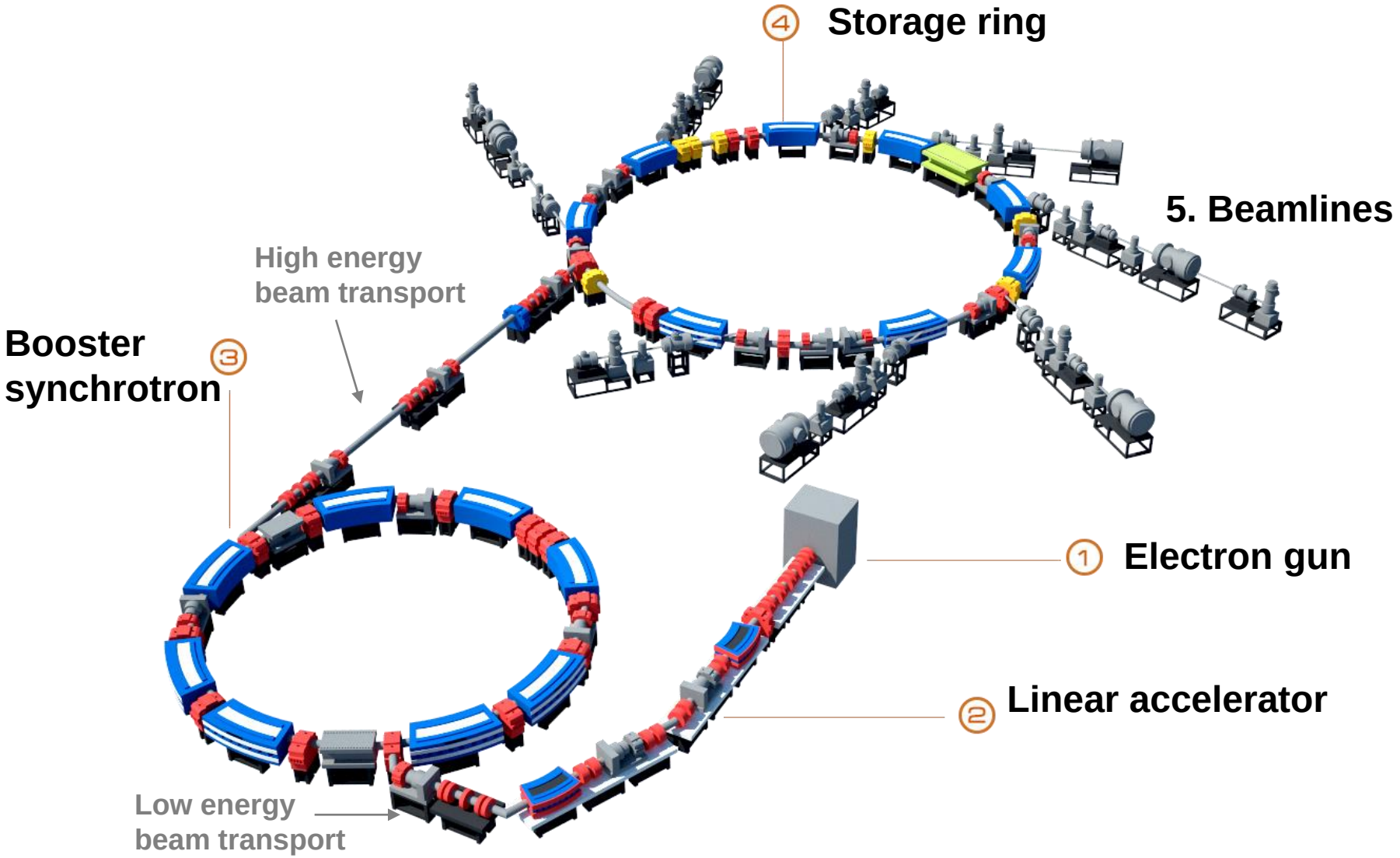
Ref. GEOMICROBIOLOGY JOURNAL, 2018, VOL. 35, NO. 6, 511–517.

Synchrotron X-ray diffraction

Synchrotron light (X-ray) sources

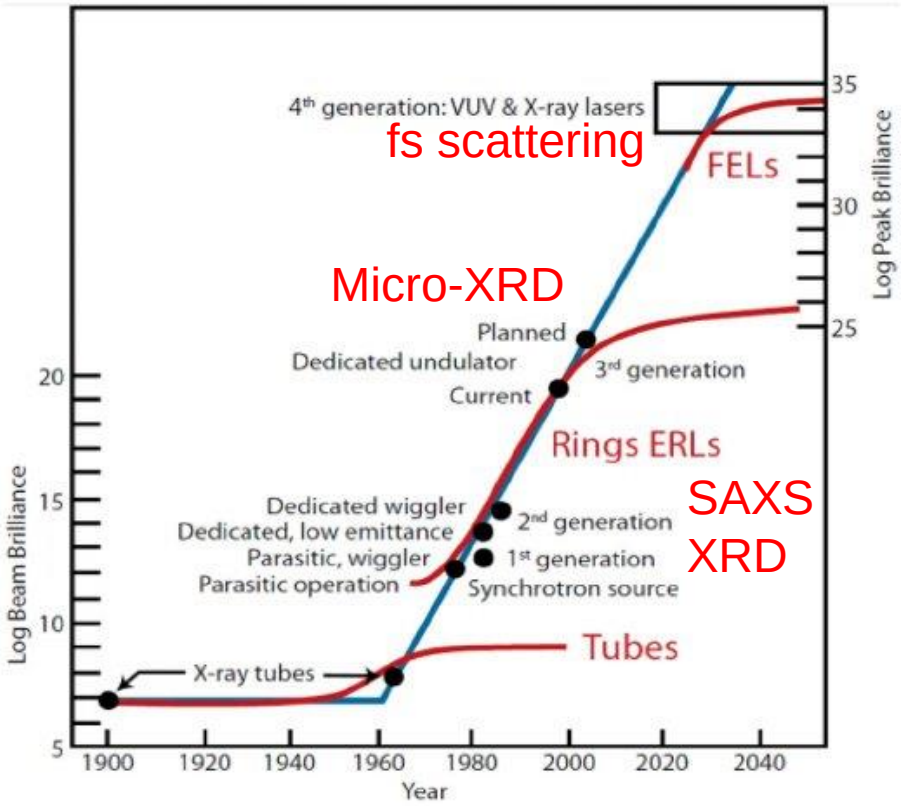


General components of synchrotron light source



Synchrotron Light Research Institute (SLRI), Thailand: www.slri.or.th

Why synchrotron powder X-ray diffraction?



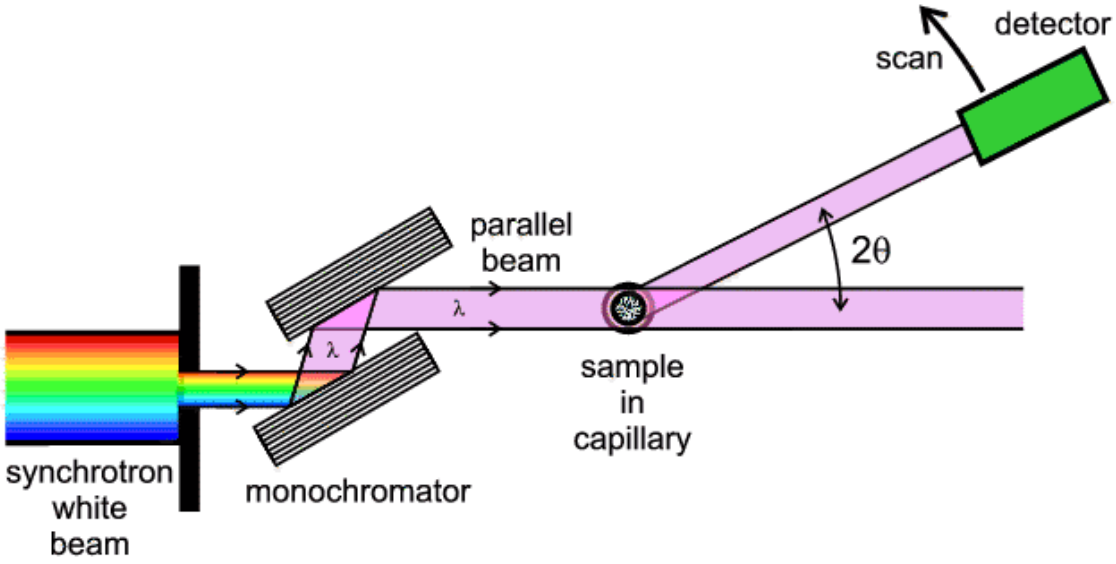
Ref. for figure: G. Shen, Y. Wang, *Reviews in Mineralogy and Geochemistry* **2014**, *78*, 745-777.

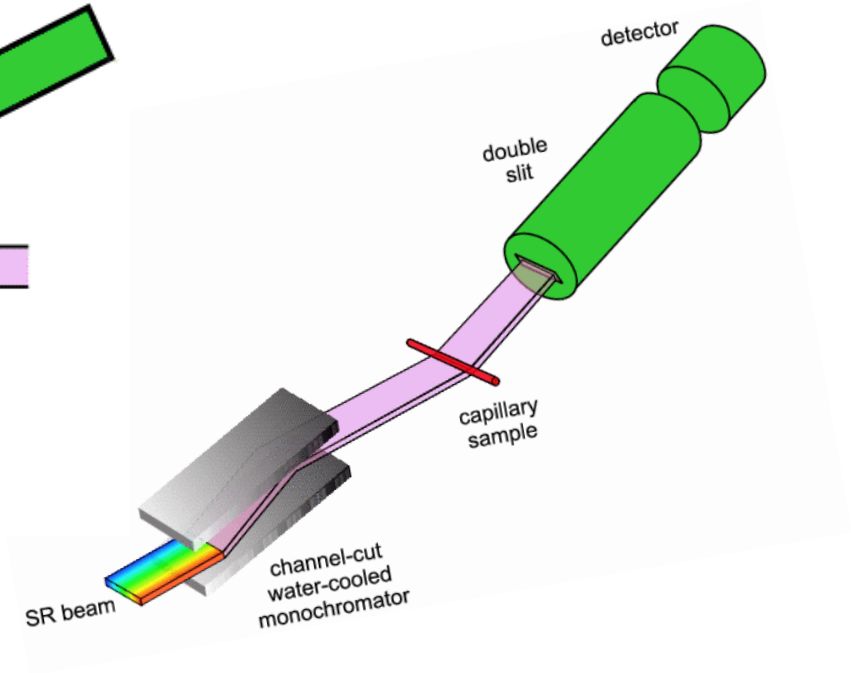
- ***well-defined wavelength*** selective (monochromator)
- ***choice of mode***: monochromatic (angle-scanning) or white radiation
- ***choice of wavelength*** from a continuous X-ray spectrum → avoid background fluorescence at specific wavelength
- ***intense X-ray beam*** (leading to superior statistics/speed) → in-situ monitoring of structural change upon external stimuli

- ***better spatial precision*** of the incident/diffracted X-ray beams (i.e. *resolution*)
- ***highly collimated*** nature of radiation (pre-sample optics)

  → eliminates a significant source of low angle peak broadening found in conventional laboratory XRD
- ***controlled sample environment*** (temperature, pressure, gas flow)

Synchrotron XRD: Debye-Scherrer Geometry





- uses a near-parallel incident beam of X-rays with sufficient cross-section to bathe the whole powder-sample

\+ relatively easy to use

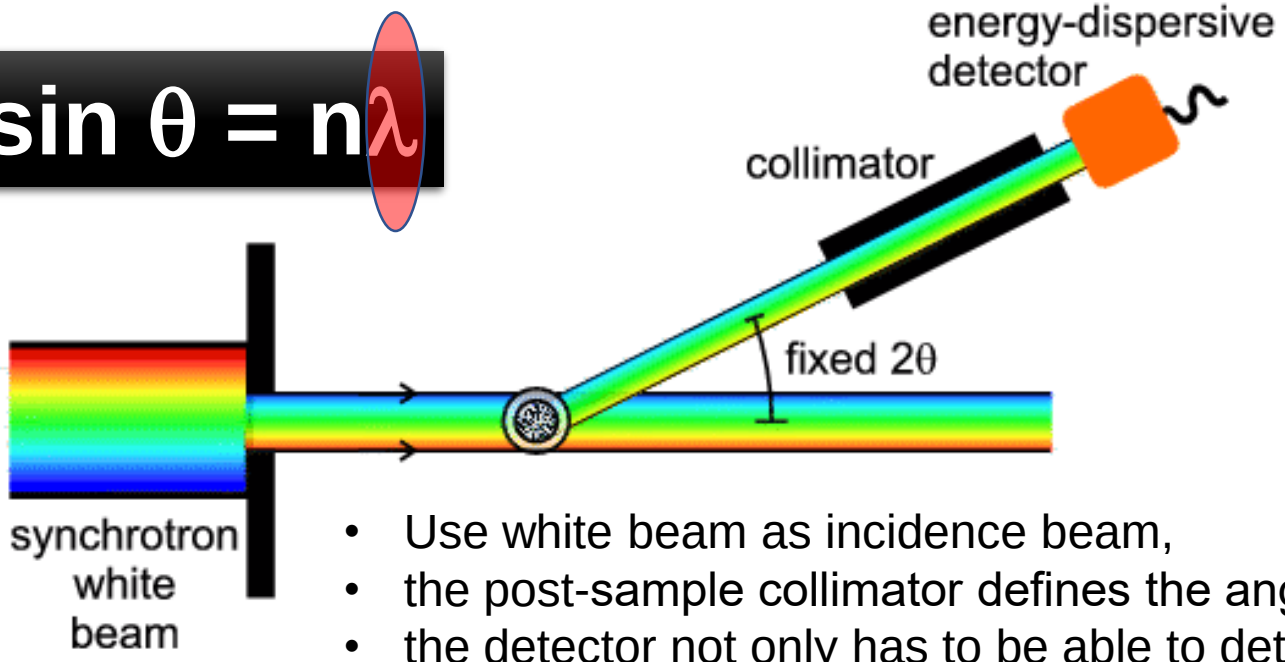
\+ produces a very good diffraction peak shape (for Rietveld refinement)

(-) inconvenience of loading their samples into a narrow capillary

Ref. for figures: http://pd.chem.ucl.ac.uk/pdnn/pdindex.htm#inst2

Energy dispersive diffraction (EDD)

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



- Use white beam as incidence beam,
- the post-sample collimator defines the angle 2θ
- the detector not only has to be able to detect X-ray photons but also measure their energy

\+ no moving parts with an EDD:
- data collection is simple and extremely rapid → rapid transformation study
- no angular scanning → much easier to design sample environment cells;
- White X-ray beam → very penetrating → good for truly bulk samples

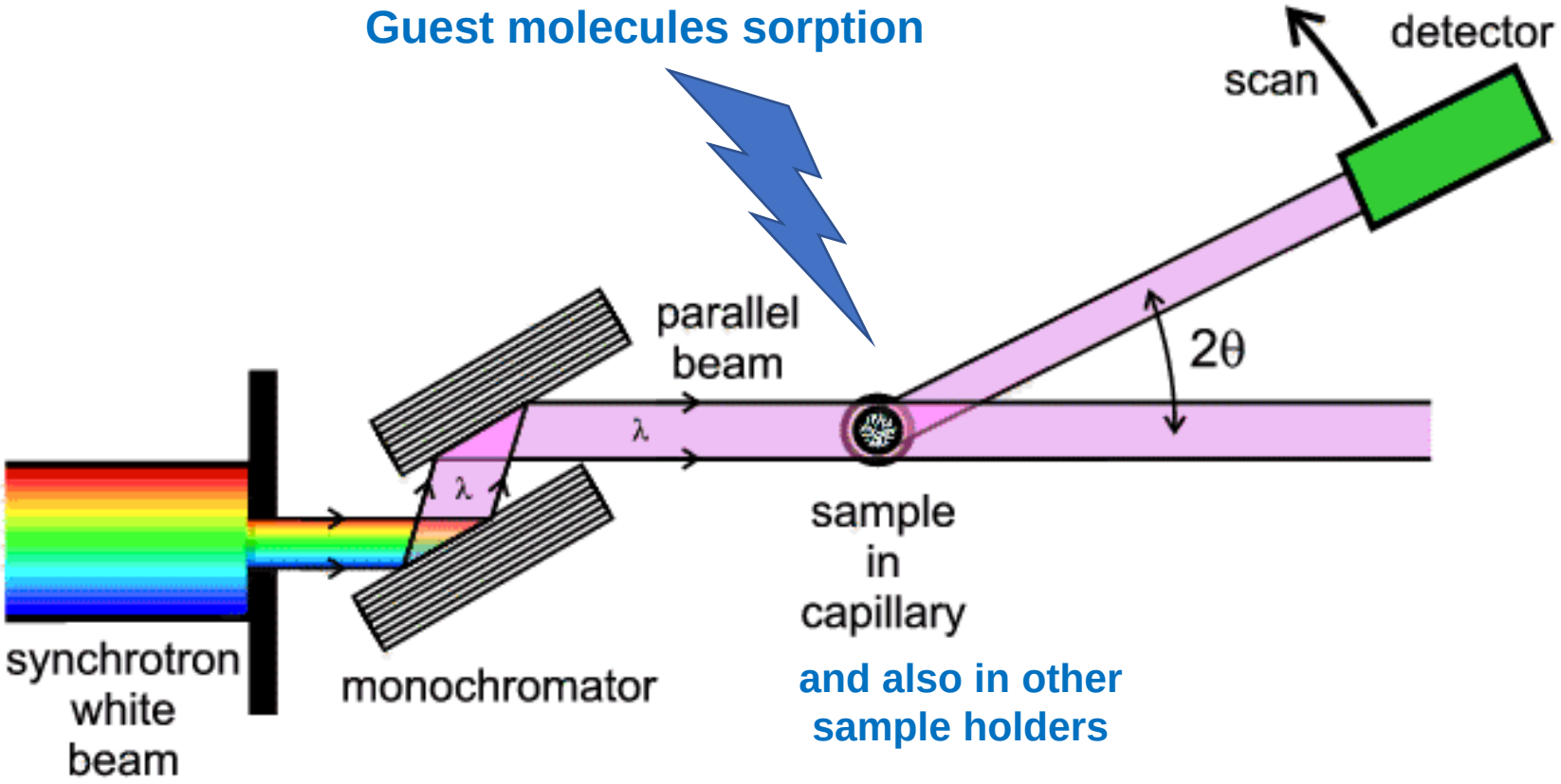
\- low quality of diffraction pattern (limited by ED-detector) → broader peak

\- difficult to perform structure refinement from EDD-data

Ref. for figures: http://pd.chem.ucl.ac.uk/pdnn/pdindex.htm#inst2

How to monitor long-range structural changes?

External stimuli
e.g. light, temperature change,
Guest molecules sorption



and also in other sample holders

In-situ X-ray diffraction (especially using synchrotron radiation)

BL1.1W: Multiple X-ray techniques

Synchrotron-based X-ray Techniques

1) X-ray Absorption Spectroscopy (XAS)
2) X-ray Fluorescence (XRF)
3) Wide Angle X-ray Scattering (WAXS)
4) X-ray Diffraction (XRD)

Beamline specification	
Radiation source	Multipole wiggler
Photon energy	4 – 18 keV
Photon flux	10^7 – 10^{10} Phs/sec/0.1% (@ 100 mA)
Optics	• Collimating mirror • Double crystal monochromator (Si111) • Toroidal focusing mirror • 4-Blades programmable slit
Detectors	• **Transmission XAS:** Ionization chambers • **Fluorescence XAS and XRF:** 19-element Ge detector • **WAXS**: Image plate • **XRD:** Strip detector

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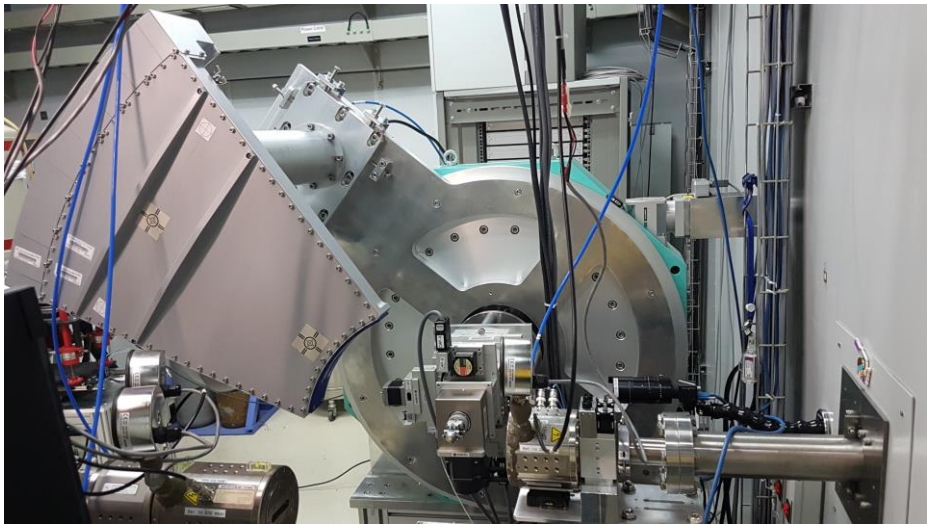
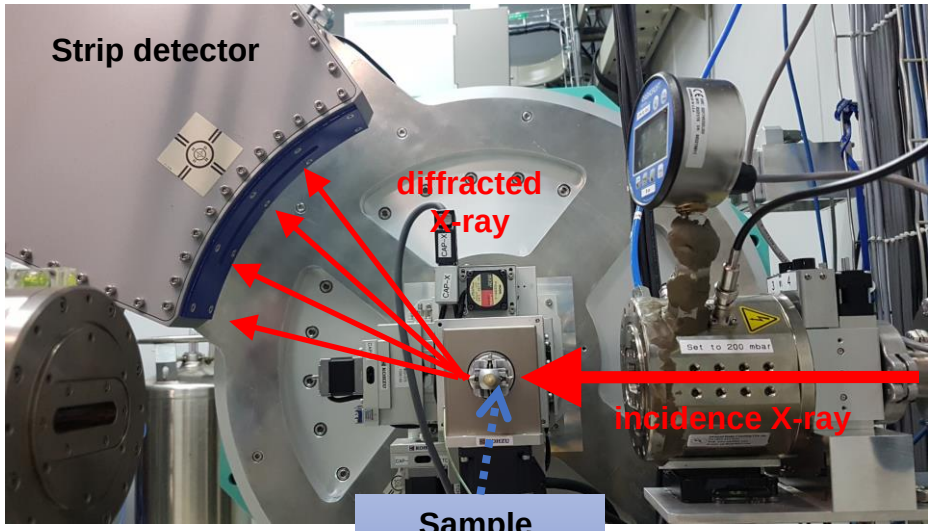
PXRD at BL1.1W, SLRI

Powder samples (in capillary)

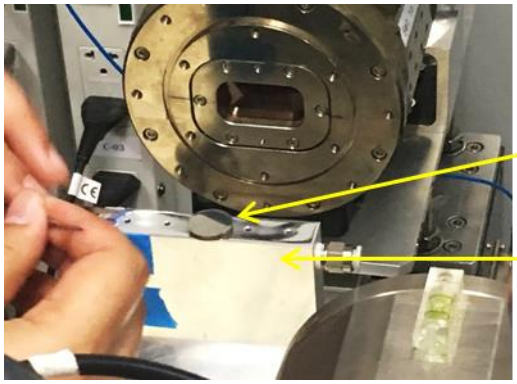


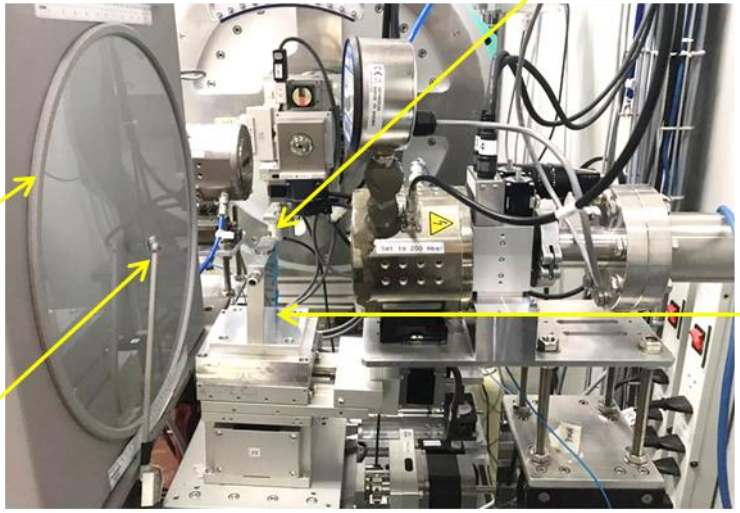


- Debye-Scherrer geometry
- Powder sample is packed in capillary (diameter 0.3 – 0.5 mm).
  - goniometer head / high speed spinner
- Strip detector: Mythen6K 450 (DECTRIS®)
  - 6 modules, 1280 × 6 channels
  - angular coverage ≈ 30°
  - sensor → reverse biased pn-junction array (Silicon)
  - readout time 0.3 ms

PXRD at BL1.1W, SLRI

Thin-film samples (Grazing incidence mode)





- Grazing incidence geometry
- Image Plate MAR345 detector
  - 2-dimensional detector
  - Sample-to-detector distance ≈ 170 mm
  - Angular coverage 5-70 degrees
  - Operated X-ray energy in normal run is 12 keV (possible to variable between 4-18 keV)

Thank you very much.

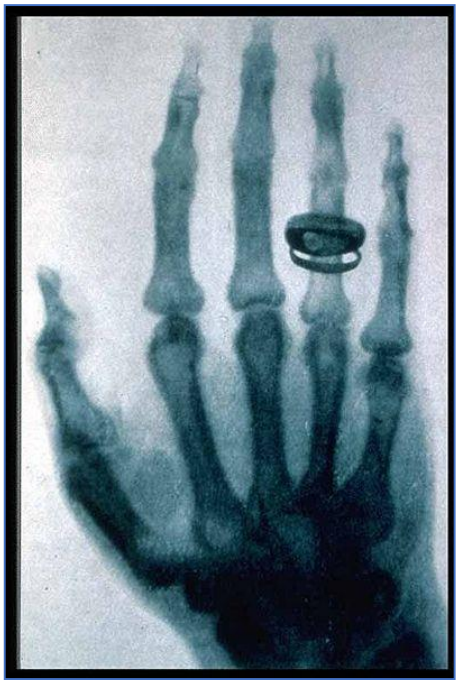
Q & A

Backup

Discovery of X-ray

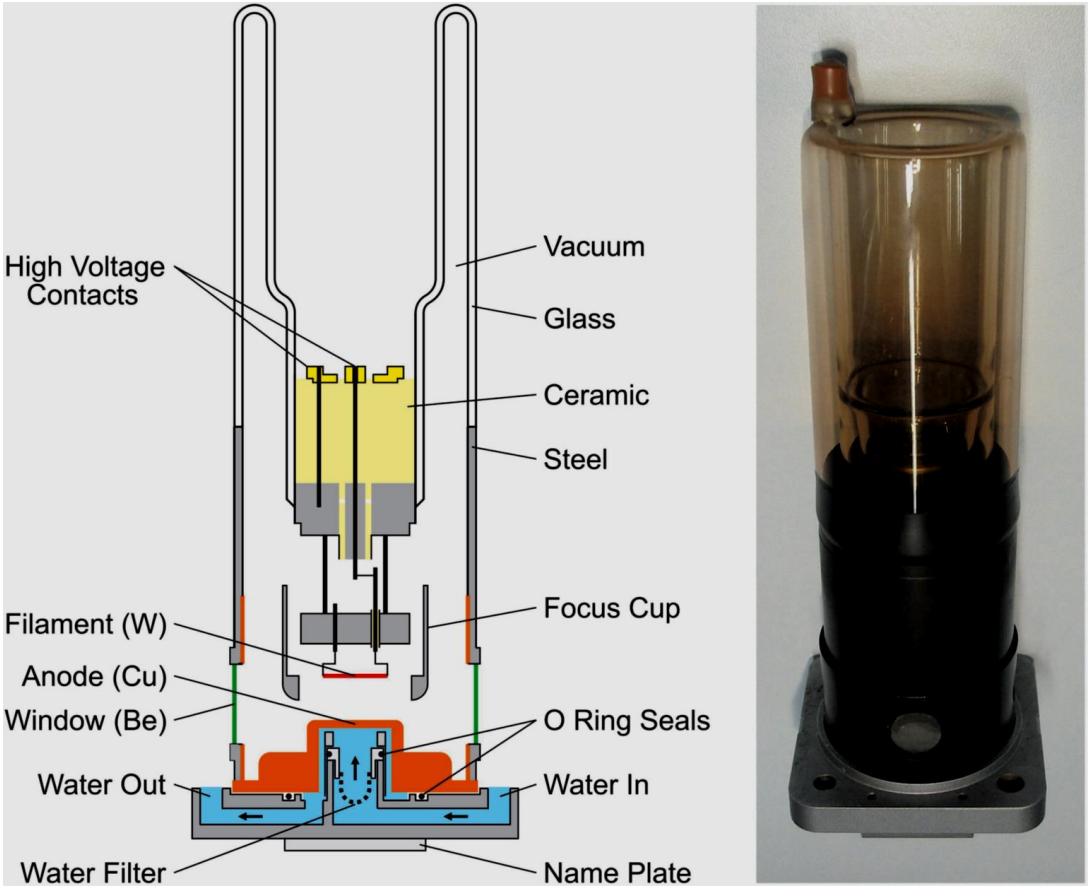
In 1895, *Röntgenstrahlung*, or X-rays were discovered by a German physicist, Wilhelm Conrad Röntgen, whilst investigating the effects of high tension electrical discharges in evacuated glass tubes.

He determined that these rays were invisible, traveled in a straight line, and affected photographic film like visible light, but they were much more penetrating.



Laboratory X-ray sources

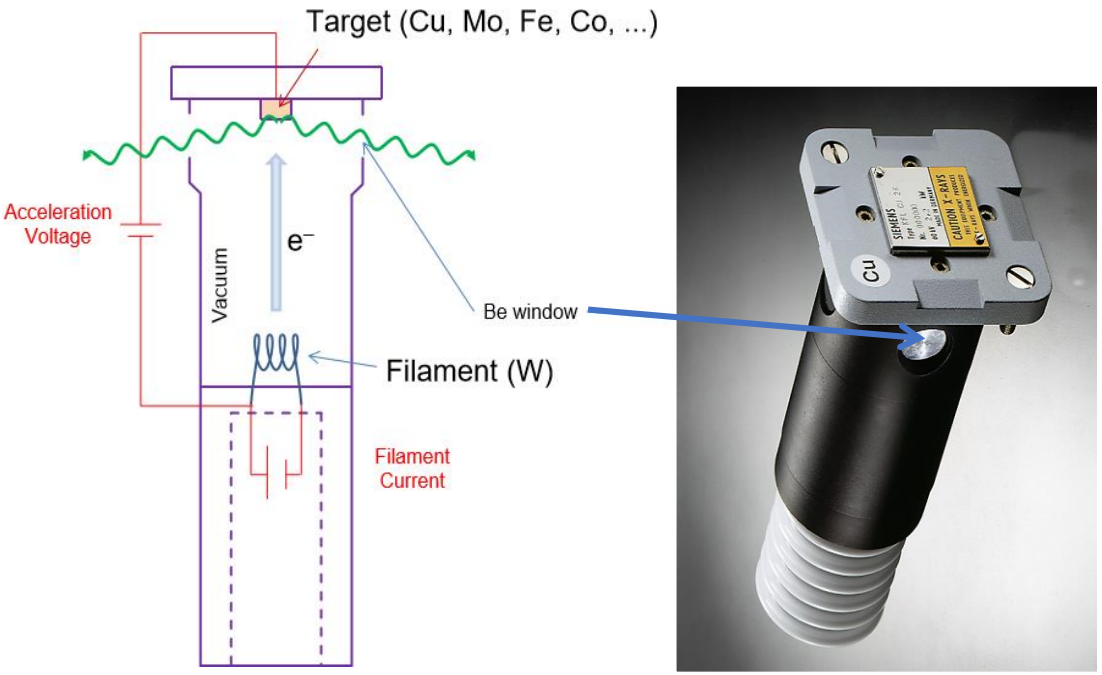
Sealed laboratory X-ray tubes



- X-Rays used for diffraction experiments are EM radiation with wavelengths in the approximate range 0.1 – 5 Å (equivalent to an energy range of about 125 keV to 2.5 keV)
- X-ray tube contains two metal electrodes: a cathode (filament as a source of electrons; W) and an anode (metal target).
- X-rays are produced in a sealed-tube source, where electrons accelerated by a potential difference of up to 60 kV bombard a metal anode inside a vacuum tube.

Ref. R.E. Dinnebier & S.J.L. Billinge, Powder diffraction theory and practice 2008.

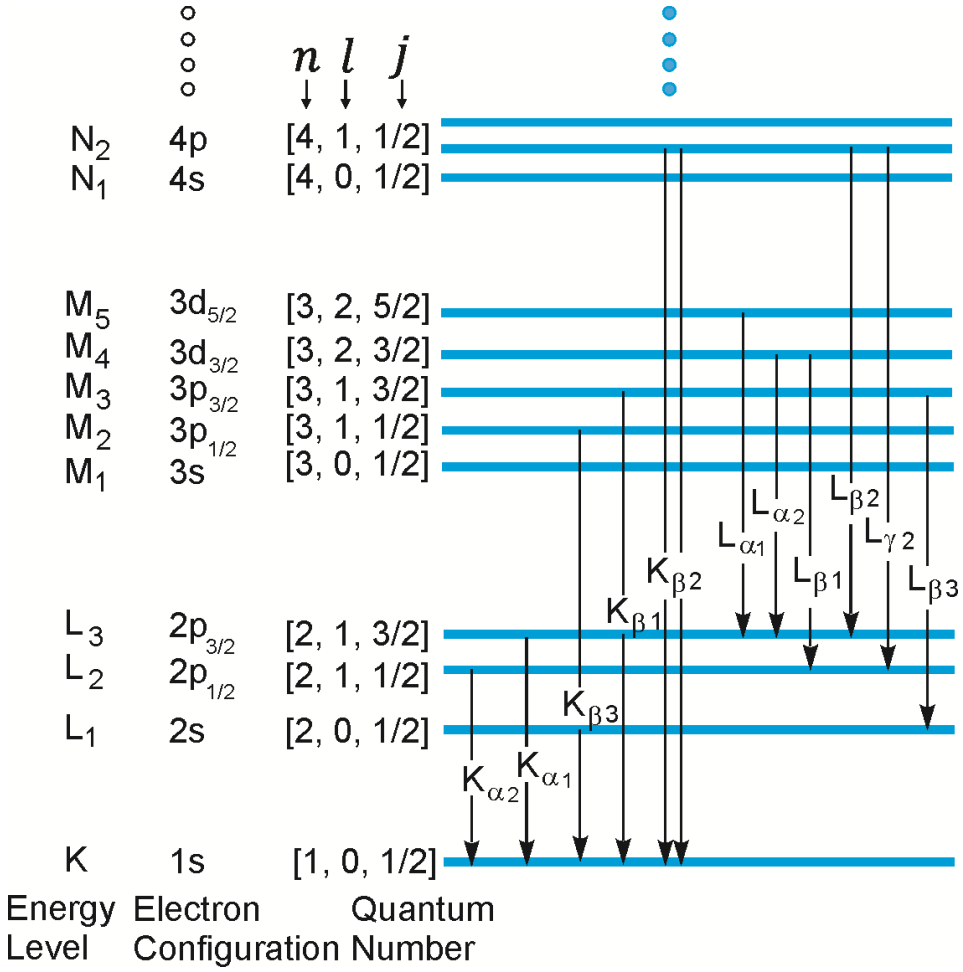
Laboratory X-ray sources



- The electrons induce a cascade of electronic transitions in the atoms of the target material, which emit electromagnetic radiation as they return to the ground state.
- Divergent X-rays exit the tube via beryllium windows in the casing.
- Anode materials must be good conductors of both electricity and heat, and have a suitably high melting point.
- The most common target elements are Cu and Mo, with Cr, Fe, Co, Ag, and W for specialist applications.

Selection Rules for XRF

XRF is a consequence of the ionization of atoms, for which the excited state returns to the ground state emitting x-ray photons of well-defined energies (characteristics).



Selection Rules

$\Delta n \neq 0$

$\Delta l = \pm 1$

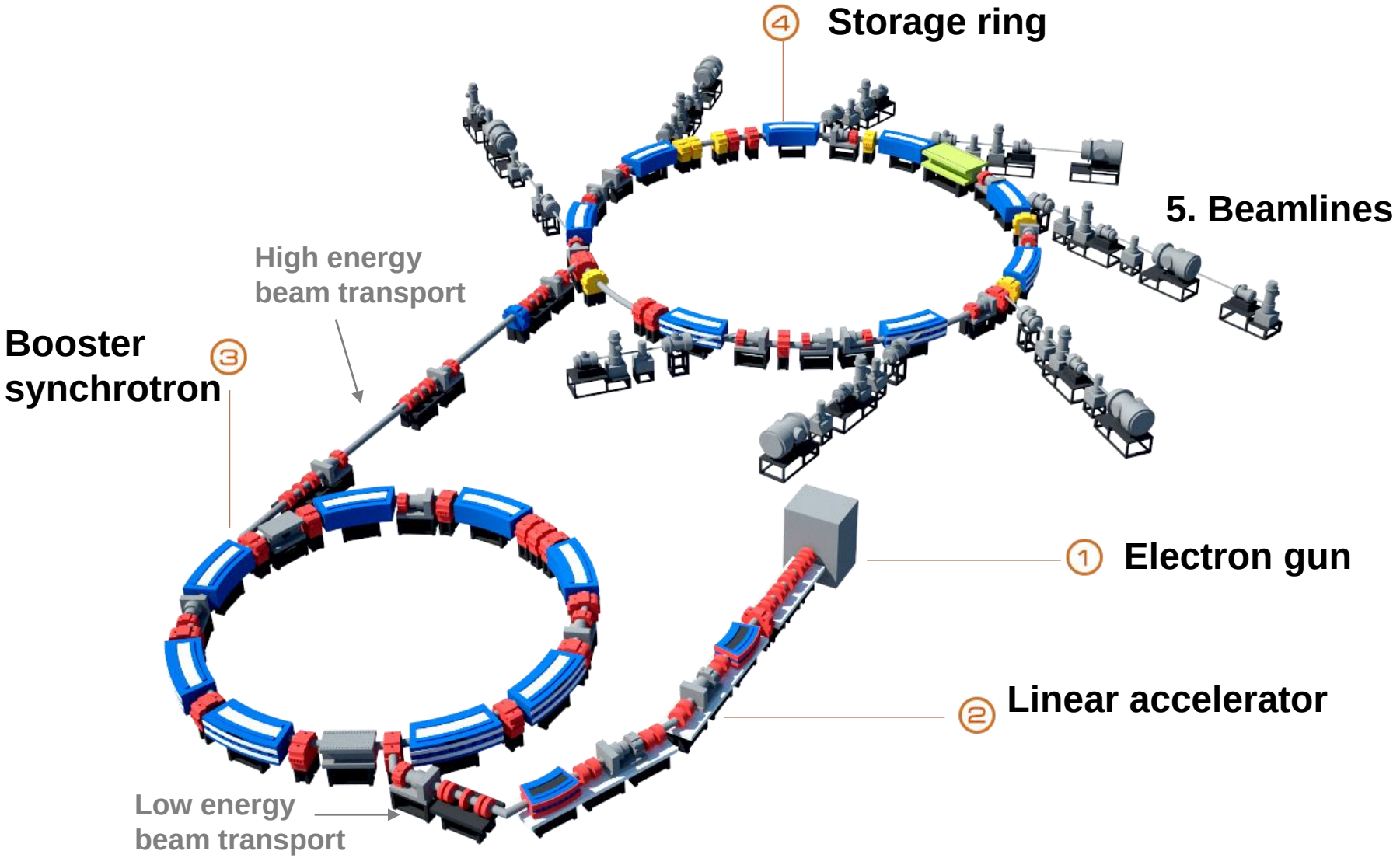
$\Delta j = 0, \pm 1$

** but if $j = 0$ initially, then $\Delta j = 0$ is forbidden

n is the principal quantum number,
$l = n - 1$ is the orbital quantum number,
$j = l \pm s$ is the total quantum number,
$s = \pm 1/2$ is the spin quantum number

Fig. credit: www.amptek.com/pdf/characteristic_xrays.pdf

General components of synchrotron light source

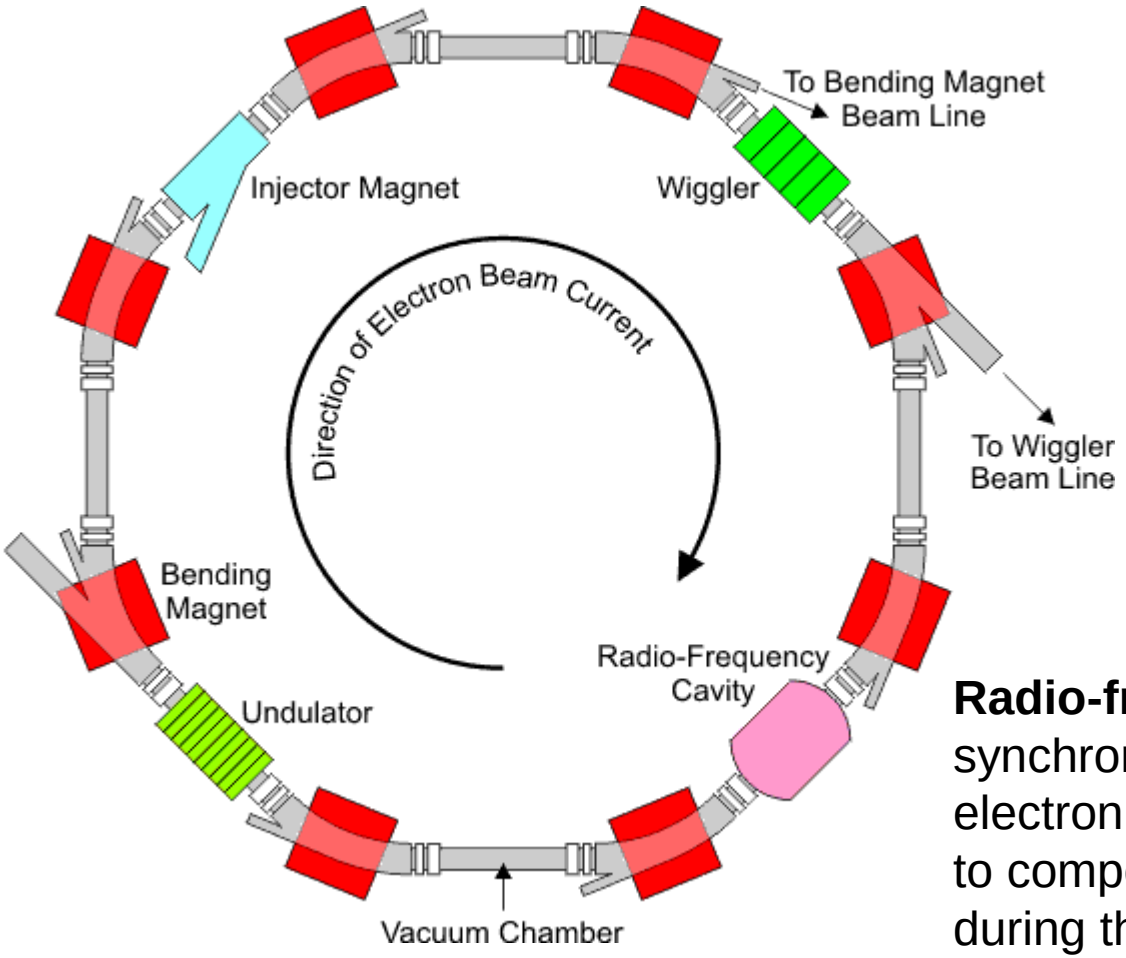


Synchrotron Light Research Institute (SLRI), Thailand: www.slri.or.th

General components of synchrotron light source

1. **Electron gun** → produces electrons by applying electricity to heat up the target metal at the cathode of electron gun
2. **Linear accelerator (Linac)**
   - → divides electrons into a groups called electron bunch
   - → accelerate the electron linear speed by microwaves to produce energetic electrons (MeV to GeV)
3. **Booster synchrotron (some synchrotron)**
   - → temporarily used during “start-up” (injection) to bridge energy gap between the output-MeV of the Linac and the input-GeV required for the storage ring
   - → increases the electron energy in a circular motion by radio waves until the electrons almost reaching the speed of light
4. **Storage ring**
   - → consists of various types of magnets including dipole, quadrupole and sextupole magnets
   - → force these high energy electrons to move in a vacuum tube
   - → release energy in the form of electromagnetic waves (synchrotron light)
5. **Beamlines**

Overview of 3rd generation synchrotron ring



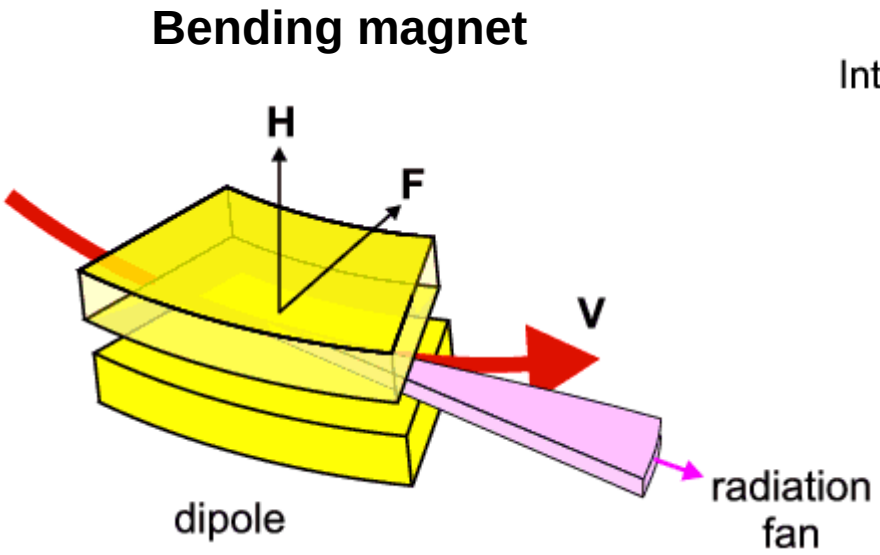
Electrons (or positrons) are injected in discrete *pulses* (100-200 bunches distributed around the whole ring).

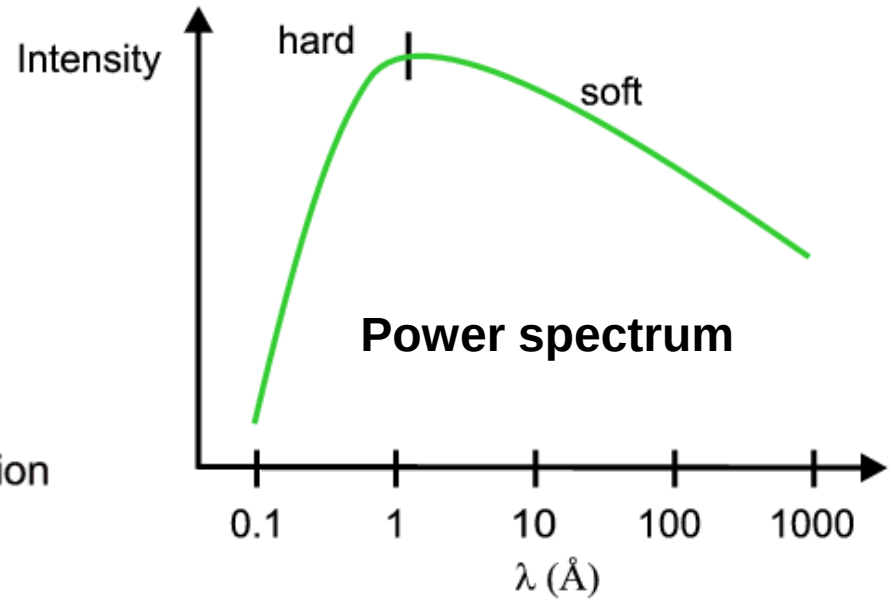
They are accelerated to speeds close to speed of light and circulate in ultrahigh vacuum tubes, guided by arrays of magnets.

Radio-frequency generator is used to synchronously feed energy to the electron bunches circulating in the ring to compensate for their energy losses during their emission of radiation.

This current of electron bunches slowly decays with time due to collisions between the electrons and any molecules contained within the ring; even with ultra-high vacuum conditions (typically 10^{-10} mbar) in the storage ring.

Synchrotron radiation

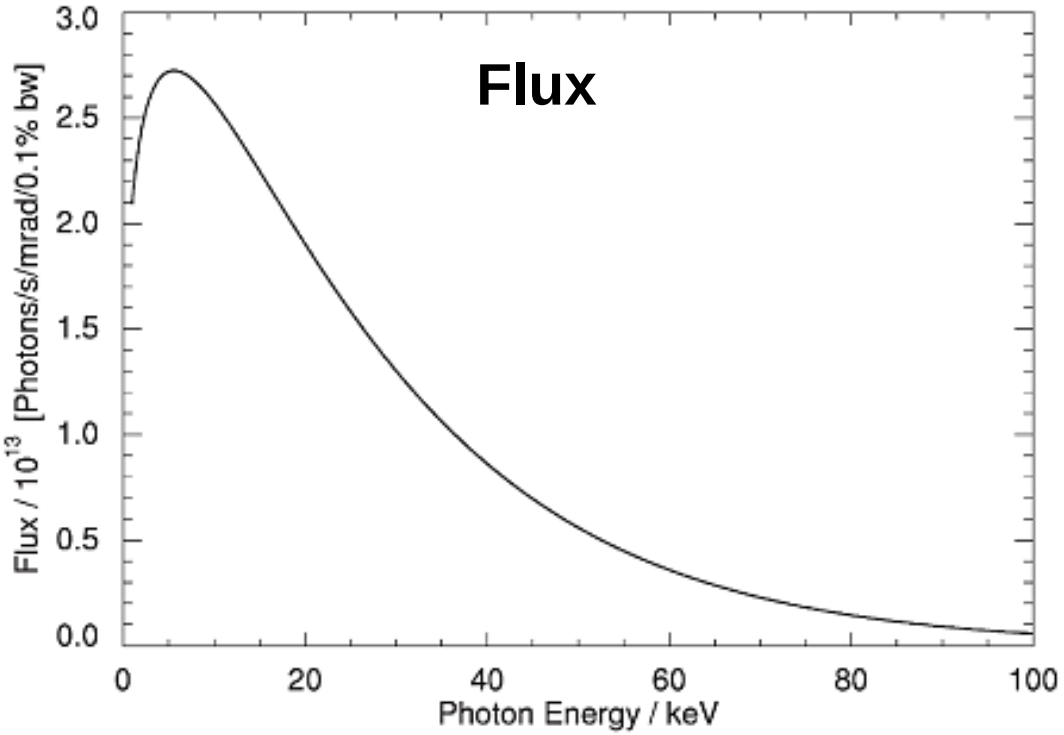




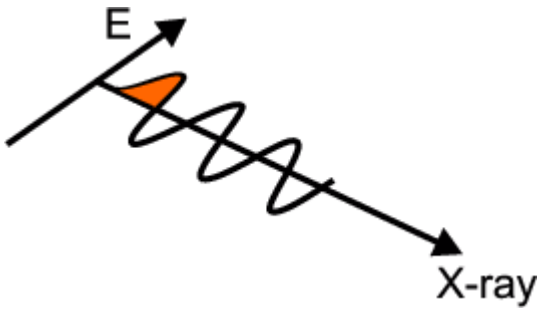
- Synchrotron radiation is emitted when **charged particles** travelling at **relativistic speeds** (e.g. 0.9999999964c in the 6 GeV storage ring of the ESRF in Grenoble) **change velocity**, such as when they are made to follow a curved trajectory by a magnetic field.

- The radiation is condensed into a **small angular fan**, thus imparting much **greater intensity and collimation** than can be obtained from conventional laboratory sources.

Synchrotron radiation from dipole magnet



- All forms of electromagnetic radiation show both wave-like and particle-like properties
- describe the radiation as a stream of particles (photons, which have discreate amount of energy E = hc / λ), rather than as a propagative wave
- **Flux** = amount of photons hitting a surface area in a unit of time



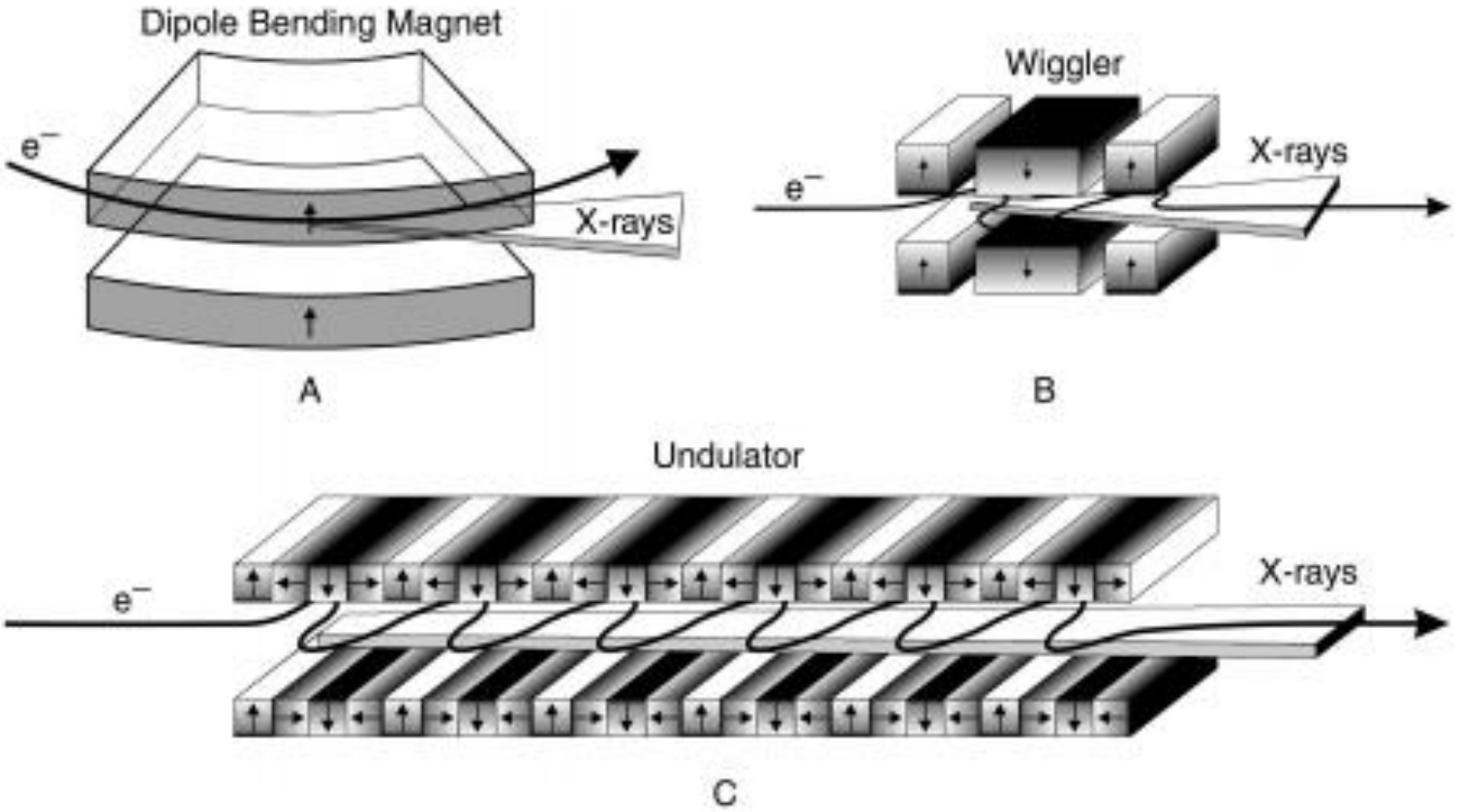
- horizontally polarized in the plane of the electron orbit
- circularly polarized above and below the orbit

→ Advantages for using in both synchrotron diffraction and spectroscopy

Advantages of synchrotron radiation

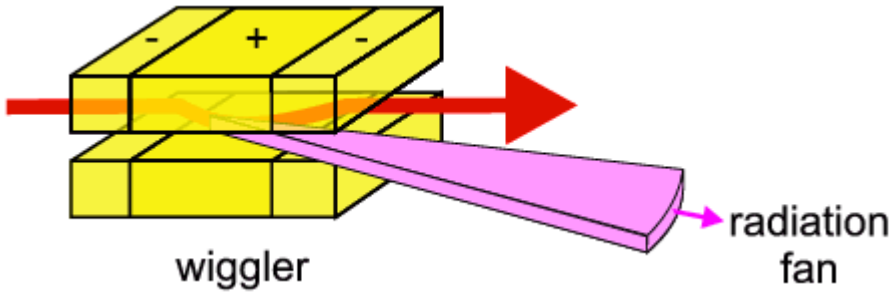
- **It is intense.** This can enable measurements to be conducted at great speed and with superior statistics.
- **It is highly *collimated*** (divergence in the order of mrads). This results in less wastage of radiation in its passage through the optical components towards the sample, and greater eventual resolution in measurement due to its spatial precision.
- It has a smooth **continuous spectrum**. This gives a choice of conducting experiments with *white radiation*, or offering any *single wavelength* by the use of monochromators
- **It is horizontally polarized**.
- It has **a precise "flashing" time structure.**

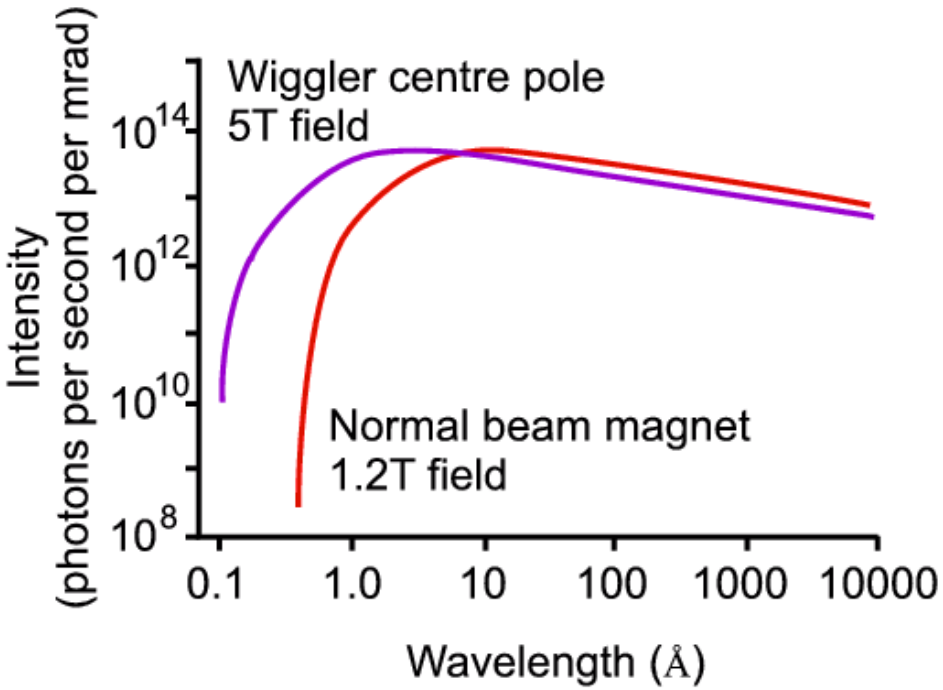
Insertion devices



- **For bending magnets** → radiation is emitted tangentially throughout the whole curved section → emission of a broad tangential fan of X-rays.
- **For insertion devices** → magnetic field varies sinusoidally → each oscillation of the electrons produces tangential bursts of synchrotron radiation.

Wiggler : higher intensity and energy

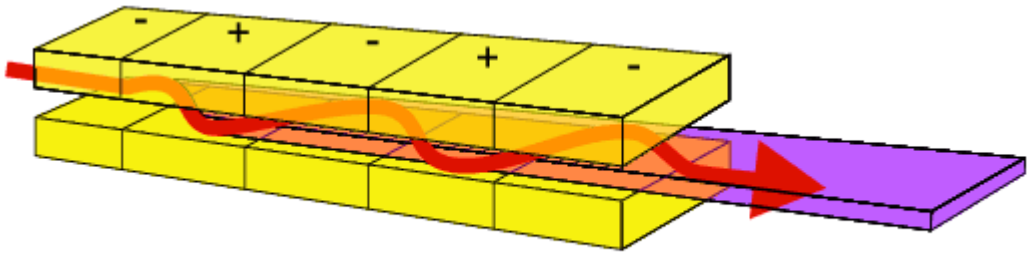




- a series of magnets designed to periodically laterally deflect ('wiggle') a beam of charged particles
- the oscillations are of relatively large amplitude (broad) and these add together incoherently
- increase the flux proportional to the number of magnetic periods
- shift critical wavelength (λ_c) (which the total power spectrum reaches 50%) to a shorter wavelength → often referred to as a ***wavelength shifter***

Clearly wiggler magnets are very important for short wavelength powder diffraction experiments.

Undulator : narrow and coherent emission



undulator

- consists of many (typically 20-30) alternating low field magnetic poles
- produces an alternating series of inward and outward electron accelerations (undulations) each with its individual radiation emission from each pole

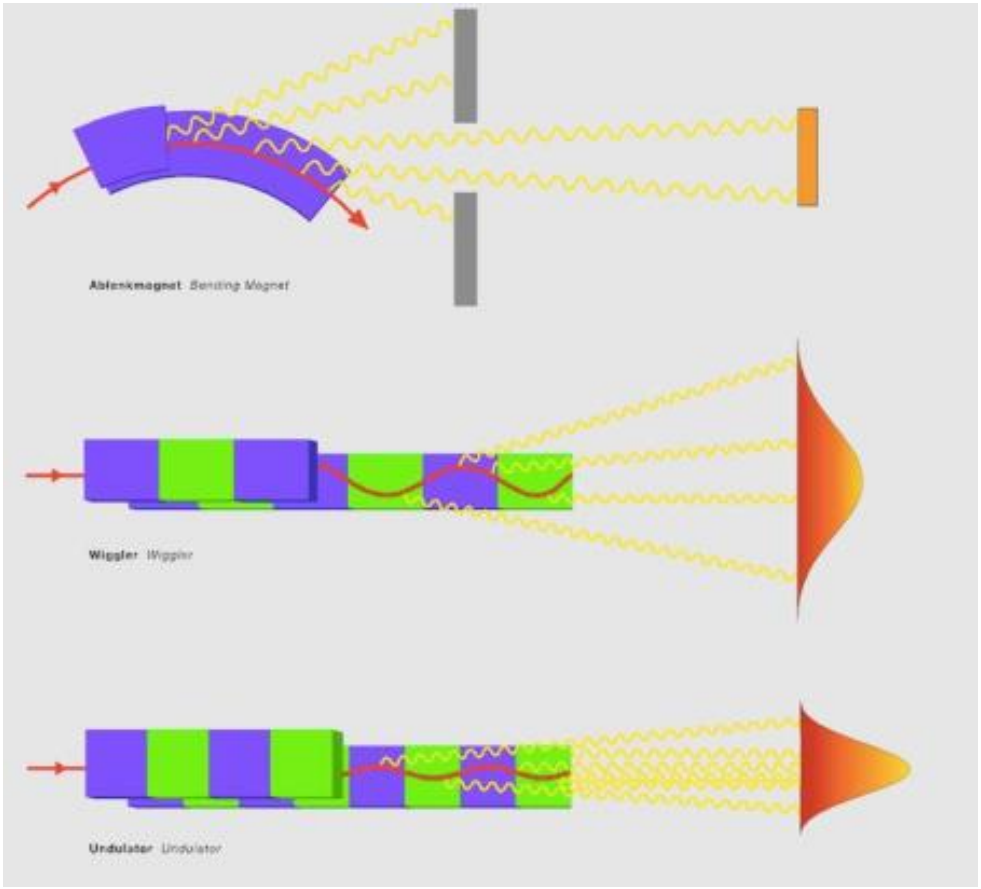
- Deflection of the electrons is relatively small and comparable to the natural opening angle of the emitted radiation $1/\gamma$.
- Radiation from different oscillations interferes, and the beam becomes collimated in the horizontal plane.
- Thus rather than being spread out in a horizontal fan, as for a bending magnet or a wiggler, the radiation is concentrated into a central on-axis cone surrounded by additional weaker rings.
- The flux density arriving on a small sample from this central cone is therefore very high.

Bending magnet / Wiggler / Undulator

B

W

U



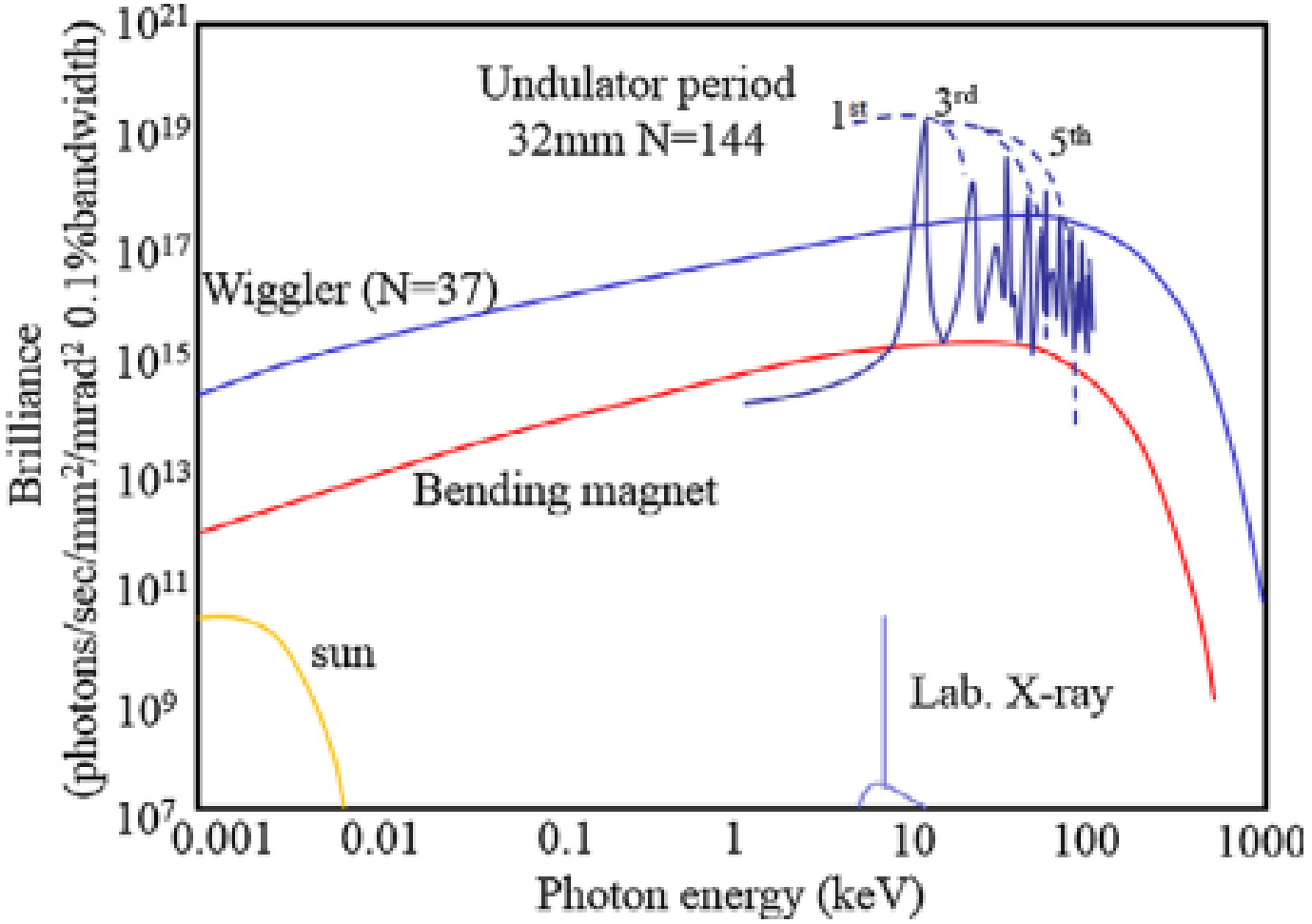
B & W

- The tighter the curvature (the higher the magnetic field), the higher energy of X-ray
- Continuous spectra

U

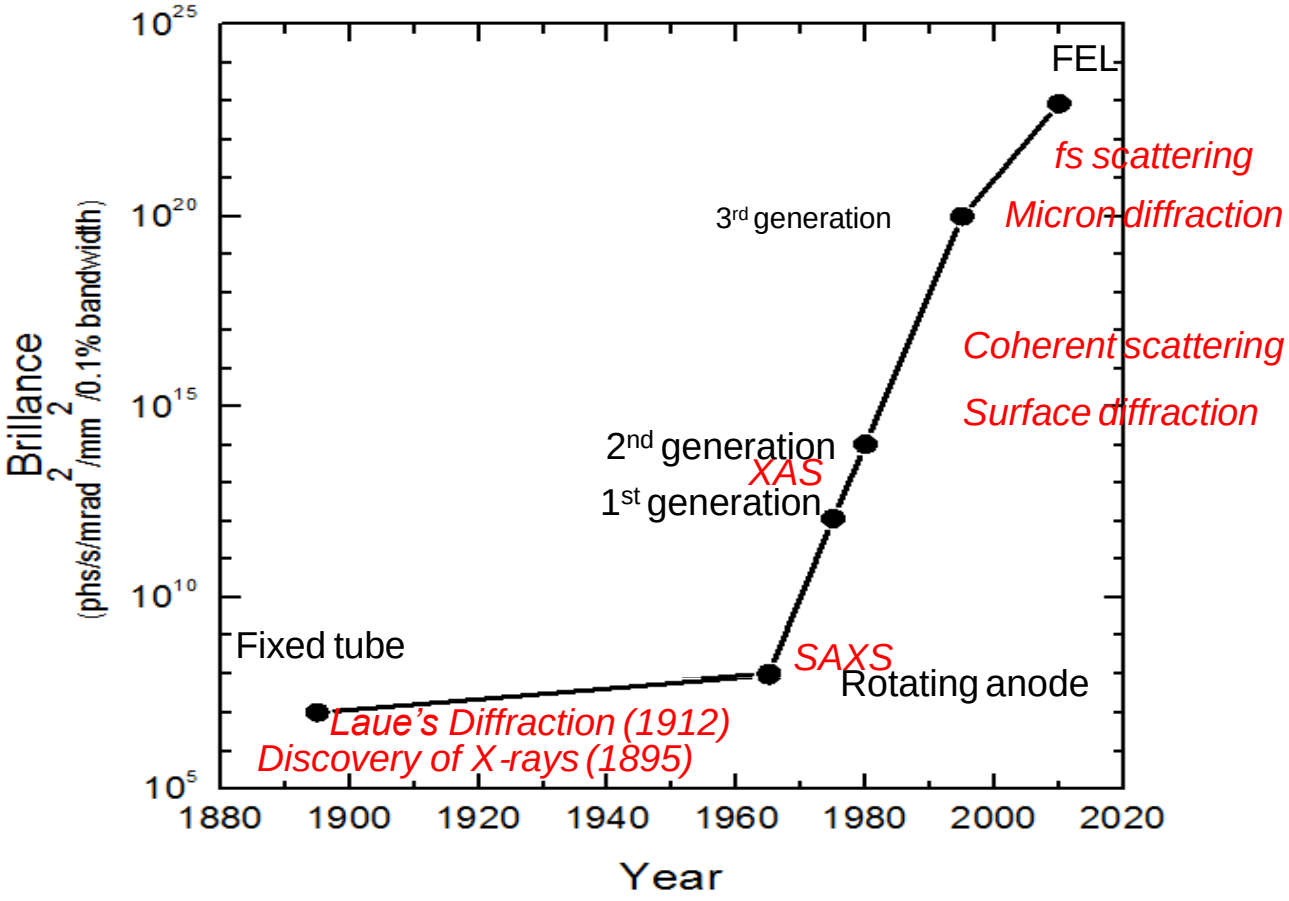
- series of peaks at integer multiples of fundamental energy, depending on the strength of magnetic field
- a high flux at a particular wavelength

Spectral brilliance of bending magnet, wiggler and undulator



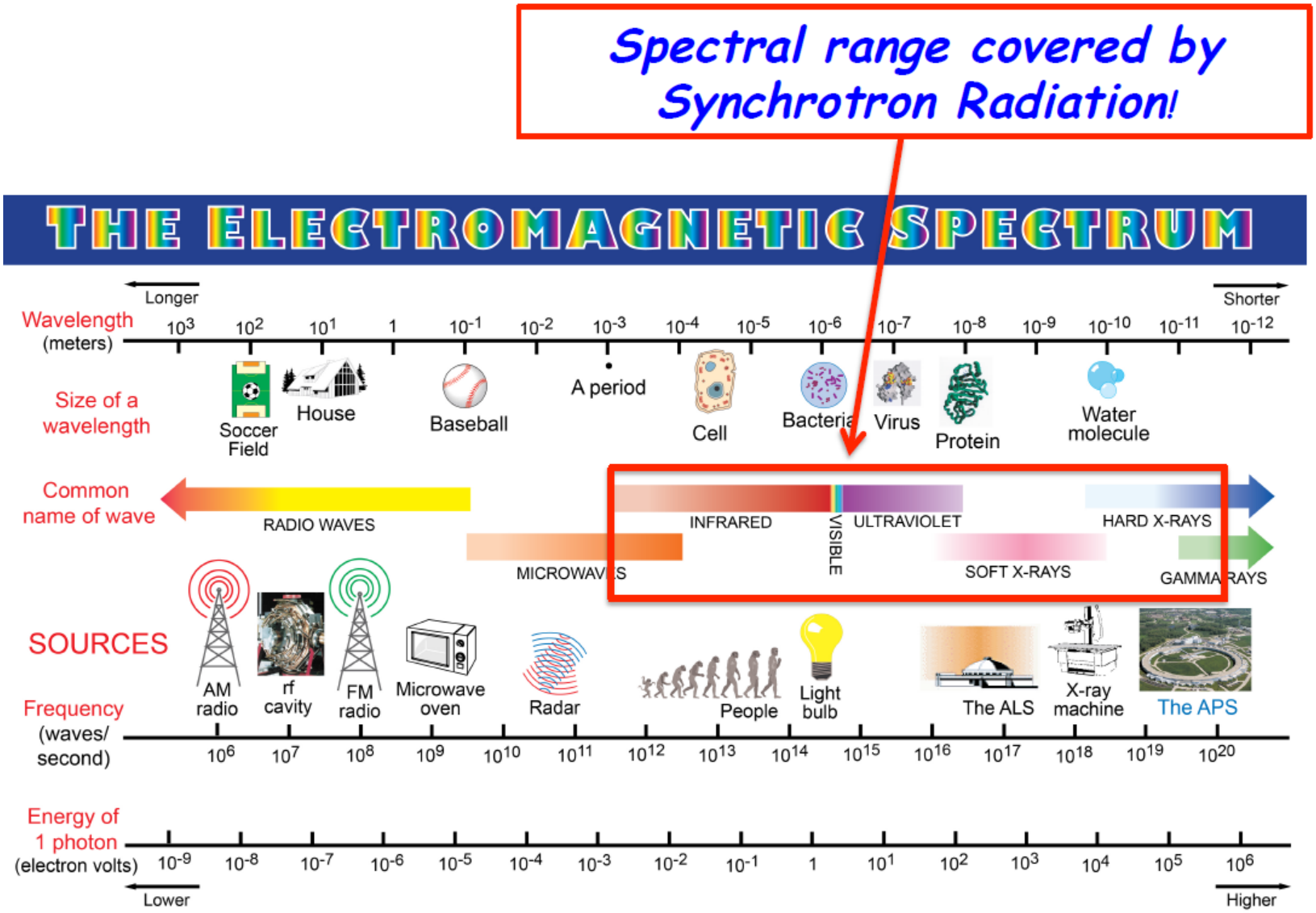
S. C. Wu, T. Q. Xiao, P. J. Withers, Engineering Fracture Mechanics 182 (2017) 127–156.

Superior properties of synchrotron light

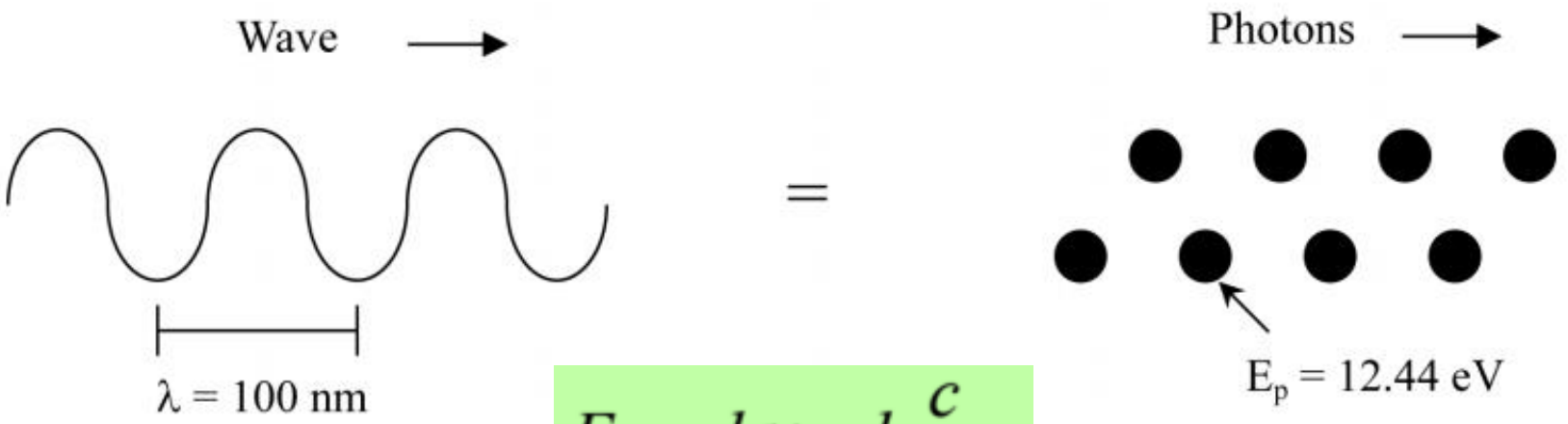


High brightness; small & dilute samples
High collimation; diffraction, imaging
Continuum of photon energies; broad applications
Temporal structure; pump-probe experiments

Spectral range



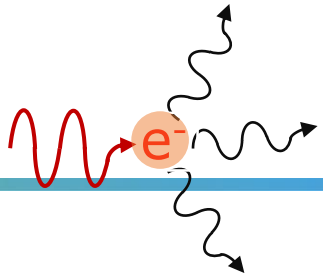
Wave-Particle duality



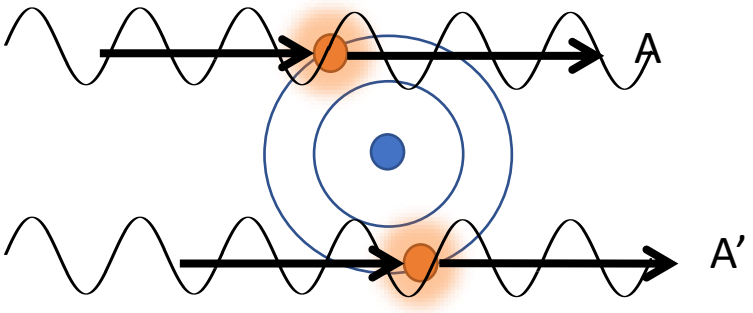
$$E_p = h\nu = h\frac{c}{\lambda}$$

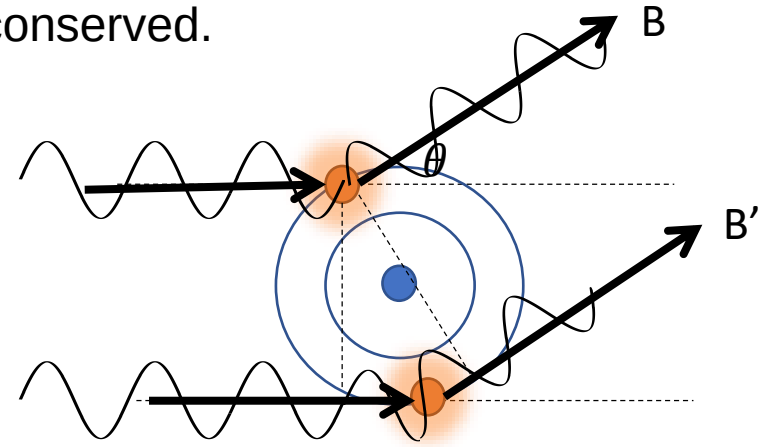
- All forms of electromagnetic radiation exhibit both wave-like and particle-like properties at the same time.
- The propagation of an electromagnetic wave can be described as a stream of light particles (called photons, which have discreate amount of energy E = hc / λ).

Elastic scattering



- Incoming X-rays exert a force on atomic electrons
  → electrons begin to oscillate at the same frequency
  → emit radiation with the same energy in any direction
- Total kinetic energy of the system is conserved.





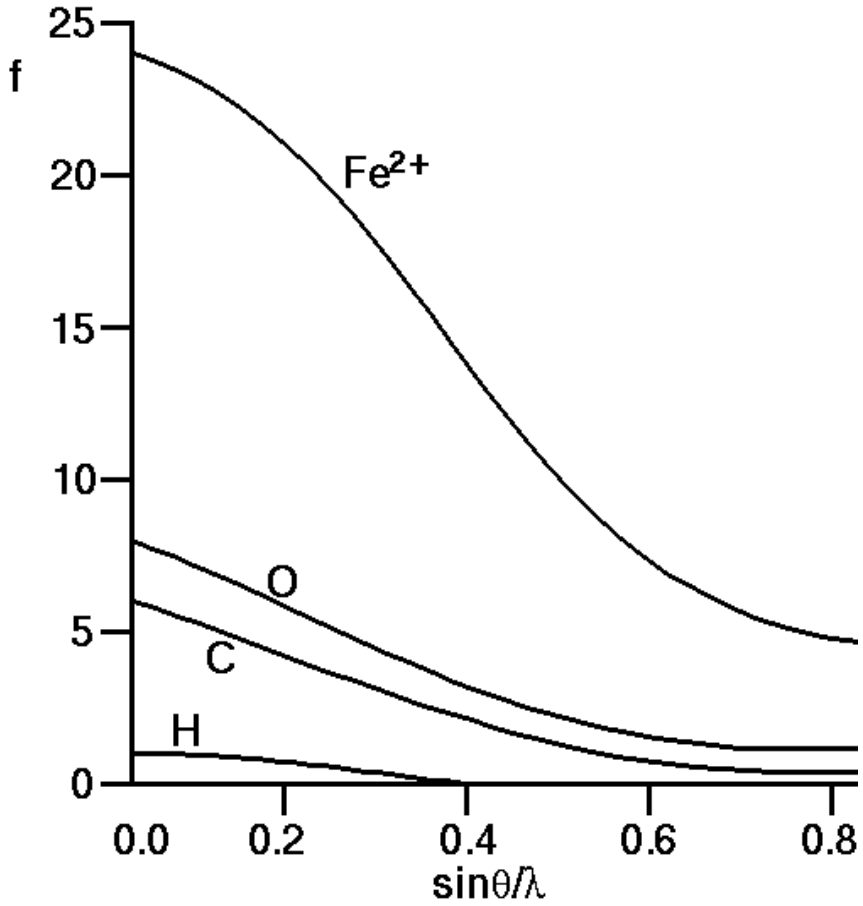
Forward scattering: viewed at 0°, waves A and A' are exactly in phase (coherent)

Other directions: path length difference, phase shift and **destructive interference** total intensity < forward scattered beam

X-ray diffraction : elastic coherent scattering

Elastic Scattering by atom

Atomic scattering factor (f(s))



- Sum of scattering by all electrons in atom (different positions in space, phase shift, partial destructive interferences)
- At higher scattering angles, the sum of the elastic scattering is less.
- Scattering factor is used to indicate strength of atomic scattering in particular direction.
- Denser atom scatters with greater intensity (with some variation related to oxidation state)

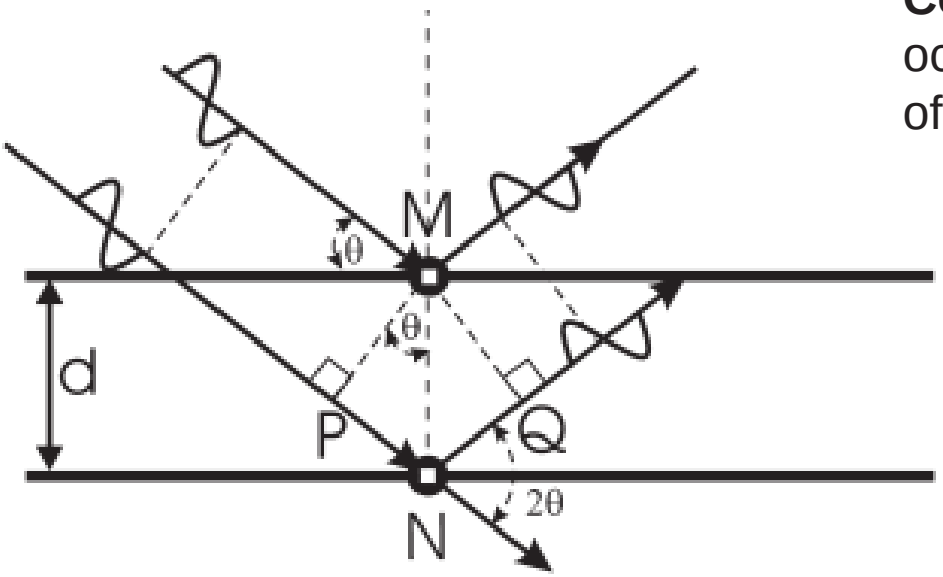
$$f(S) = \int \rho(r) e^{2\pi i S \cdot r} \delta V$$

($\rho(\boldsymbol{r})\delta V$) :sum of scattering from each elementary region

($e^{2\pi\, i\, S.r}$) : taking phase difference into account.

Crystals: Derivation of the Bragg equation

- **describes XRD for crystal** → a reflection of X-rays by sets of lattice planes
- In contrast to visible light, X-rays penetrate deep inside the material where additional reflections occur at thousands of consecutive parallel planes.
- Since all X-rays are reflected in the same direction, superposition of the scattered rays occurs.



Constructive interference (coherent) occurs only if $\Delta = PN + NQ$ is a multiple of $n = 0, \pm1, \pm2, \ldots$ of the wavelength λ.

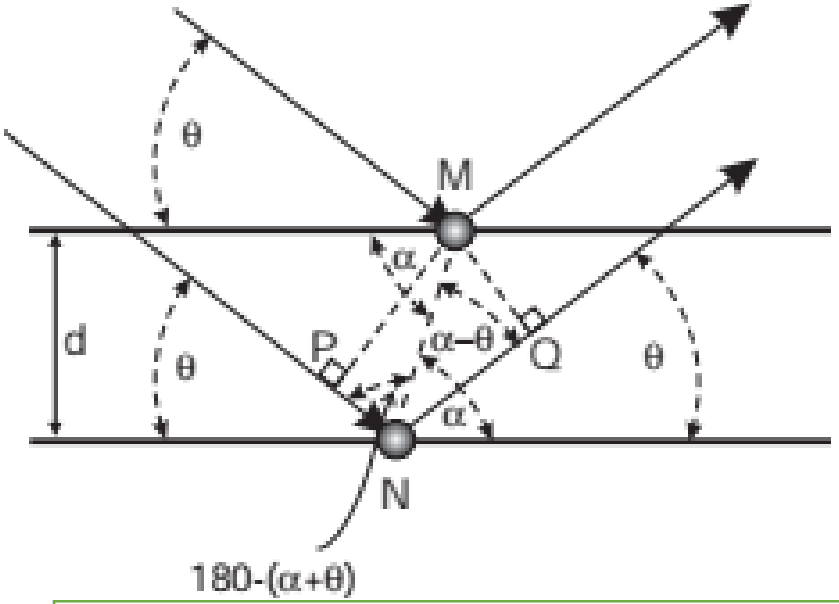
$$\Delta = n\lambda$$
$$PN + NQ = n\lambda$$
$$d\sin\theta + d\sin\theta = n\lambda$$

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

Ref. R.E. Dinnebier & S.J.L. Billinge, Powder diffraction theory and practice 2008.

Is Bragg equation still valid in reality?

- In reality the X-rays are not reflected by planes but are **scattered by electrons bound to the atoms**.
- Crystal planes are not like shiny optical mirrors, but **contain discrete atoms separated by regions of much lower electron intensity**.
- In general, atoms in one plane will **not lie exactly above atoms** in the plane below.



$$PN + NQ = n\lambda$$
$$MN\cos(180°-(\alpha+\theta)) + MN\cos(\alpha-\theta) = n\lambda$$
$$MN[-\cos(\alpha+\theta) + \cos(\alpha-\theta)] = n\lambda$$
$$MN(2\sin\alpha\sin\theta) = n\lambda$$
$$d = MN\sin\alpha$$
$$2d\sin\theta = n\lambda$$

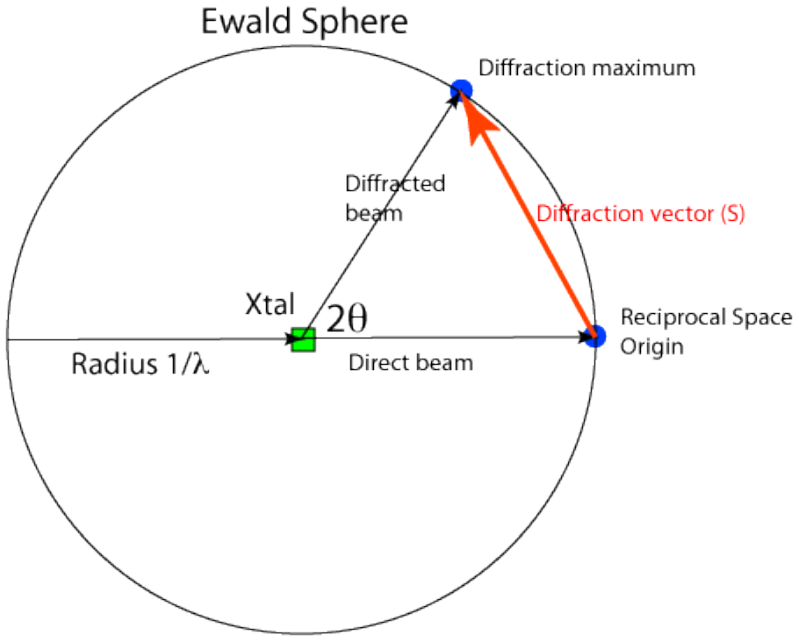
Valid!!! → if the atom of the lower lattice plane is shifted by an arbitrary amount parallel to the plane.

crystalline materials: destructive interference completely destroys
disordered materials: diffracted intensity can be observed in all directions away from reciprocal lattice points, known as **diffuse scattering**

Ref. R.E. Dinnebier & S.J.L. Billinge, Powder diffraction theory and practice 2008.

Ewald sphere construction

- Bragg's Law describes the requirement for diffraction in algebraic form.
- The diffraction vector translates Bragg's Law into a 3D vector whose direction is linked to real space unit cell axes.
- The Ewald construction shows this equation in graphical form, integrating the ***scalar (Bragg)*** and ***vector (Miller index)*** description of the diffraction process, and allows us to visualize diffraction.

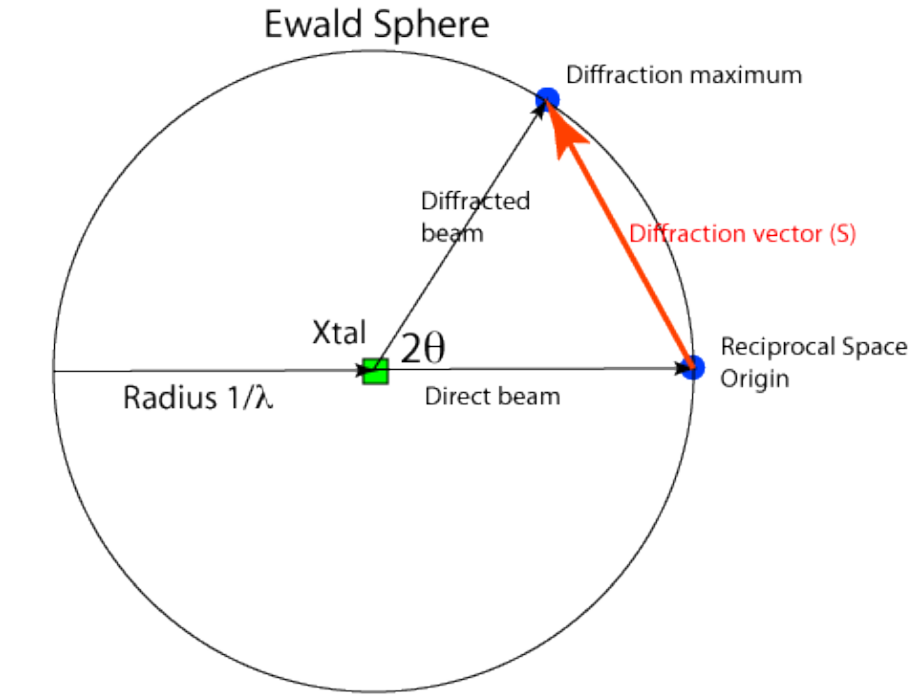


Graphical Representation of Geometry of Bragg's Law

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

Ref. Adapted from Solid State 2018/1 Lecture, VISTEC from Dr. Sareeya Bureekaew

Ewald sphere construction



Graphical Representation of Geometry of Bragg's Law

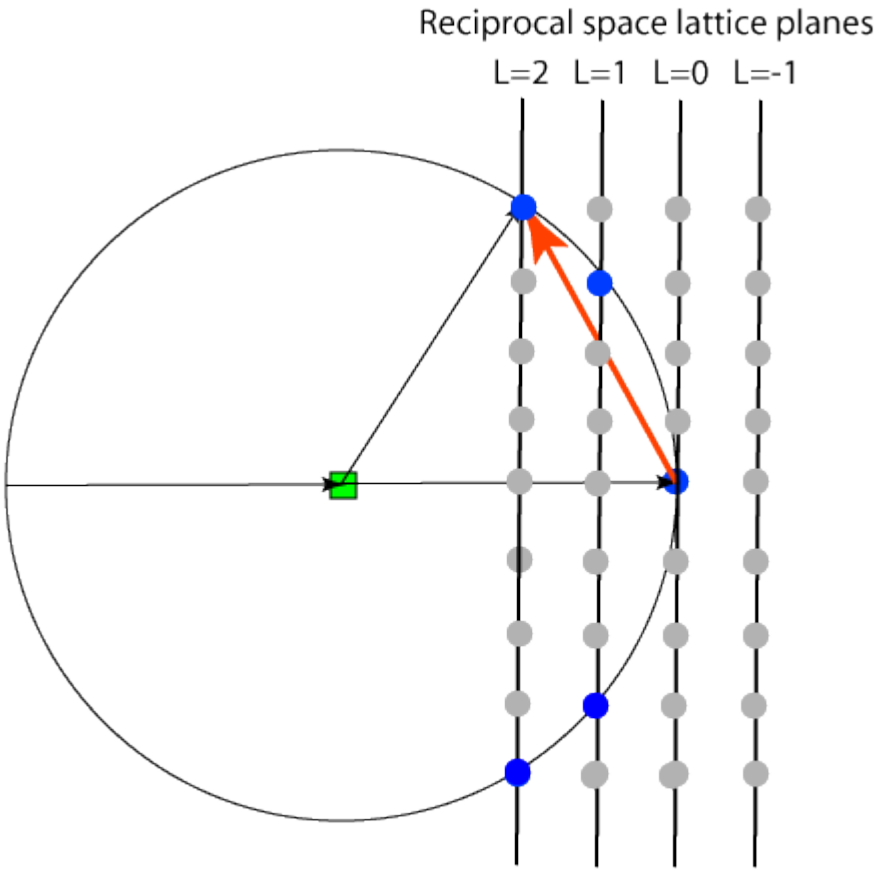
$n\lambda = 2d\sin\theta$

- There sphere has a **radius of 1/λ**.
- The crystal sits at the center of the sphere.
- In the diagram X-ray beam comes from the left.
- The un-scattered (direct) beam passes through the crystal and the point where it reaches the sphere surface is the **origin of reciprocal space**.

- For a diffraction point in reciprocal space to be in diffraction condition, it must **lie on the surface of the Ewald sphere**.
- The angle between the incident and diffracted beams is **2θ** and the vector connecting the reciprocal space origin and the diffraction point is the **diffraction vector (S or q)**.

Ref. Adapted from Solid State 2018/1 Lecture, VISTEC from Dr. Sareeya Bureekaew

Ewald sphere construction



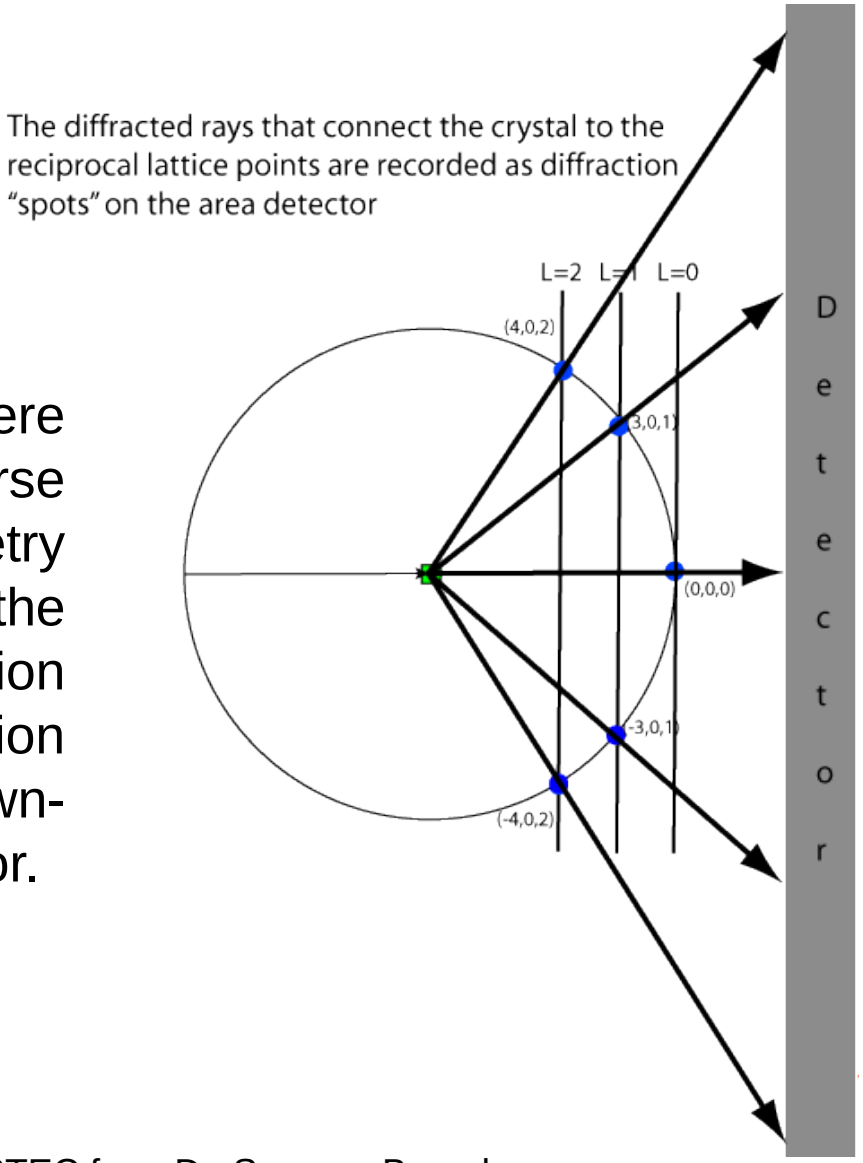
A perfectly-aligned crystal shooting down the C* axis
Only spots lying on the Ewald sphere are diffracting

- Visualization of the Ewald sphere construction is useful in data collection because it gives a way to understand **which points are in diffraction condition**.
- In the diagram a "perfectly aligned crystal" is arranged such that the reciprocal lattice planes are perpendicular to the beam.
- Lattice points are shown in gray, and those in diffraction condition are shown in blue.

Ref. Adapted from Solid State 2018/1 Lecture, VISTEC from Dr. Sareeya Bureekaew

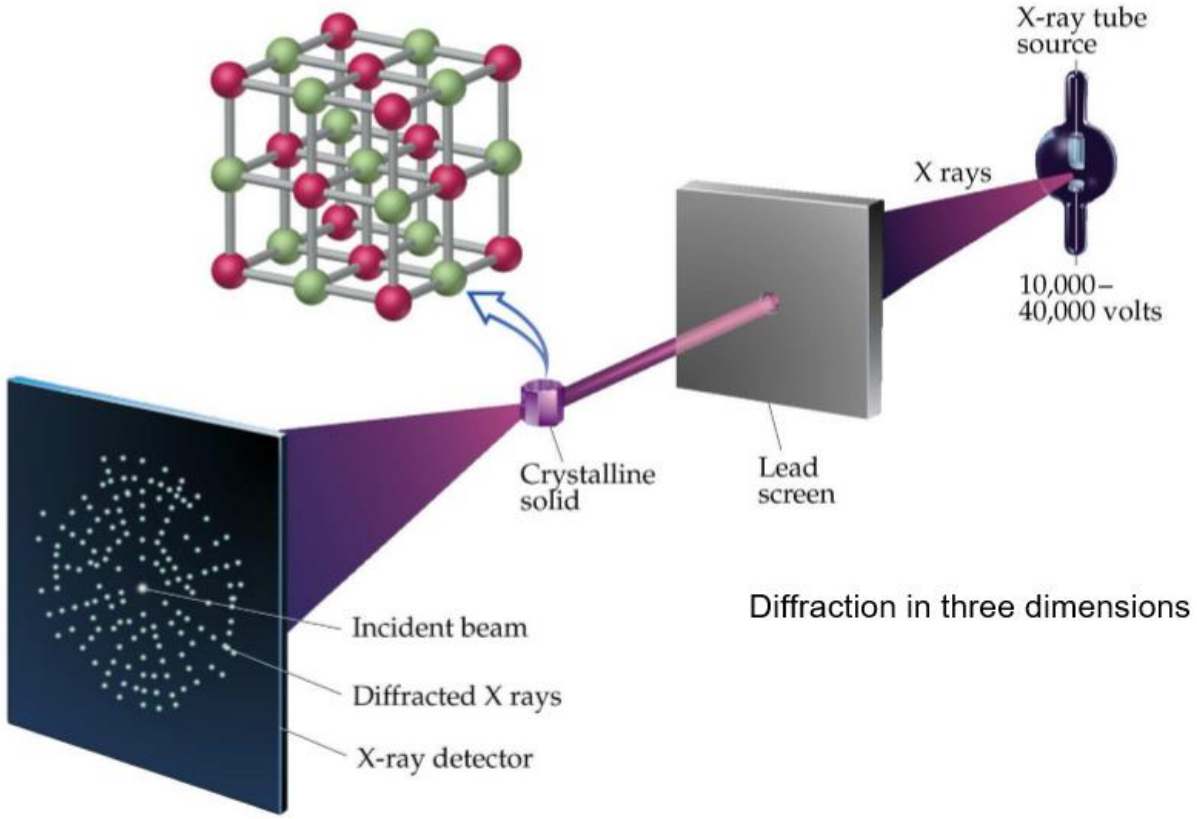
Ewald sphere construction

Even though the Ewald sphere is in reciprocal space (inverse distance) and detector geometry is in real space, we can use the predicted angles of diffraction (2θ) to predict the diffraction pattern measured by a known-instrumental geometry detector.



Ref. Adapted from Solid State 2018/1 Lecture, VISTEC from Dr. Sareeya Bureekaew

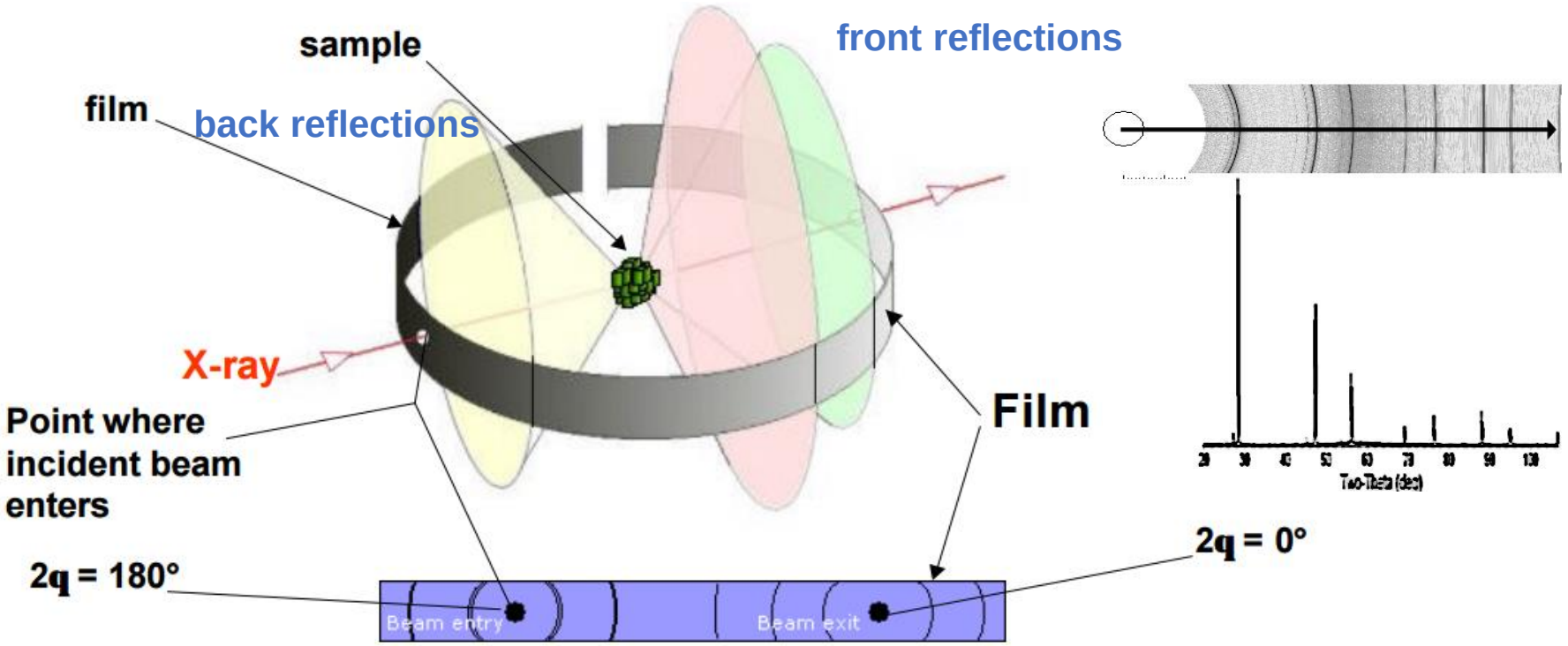
Single crystal X-ray diffraction



- **Position (pattern):** relates to the lattice and unit cell geometry
  → the repeat distances in the crystal
- **Intensity (size of spots):** gives internal symmetry of cell and electron density
  → information about the contents

Ref. for figure: https://slideplayer.com/slide/12047455/

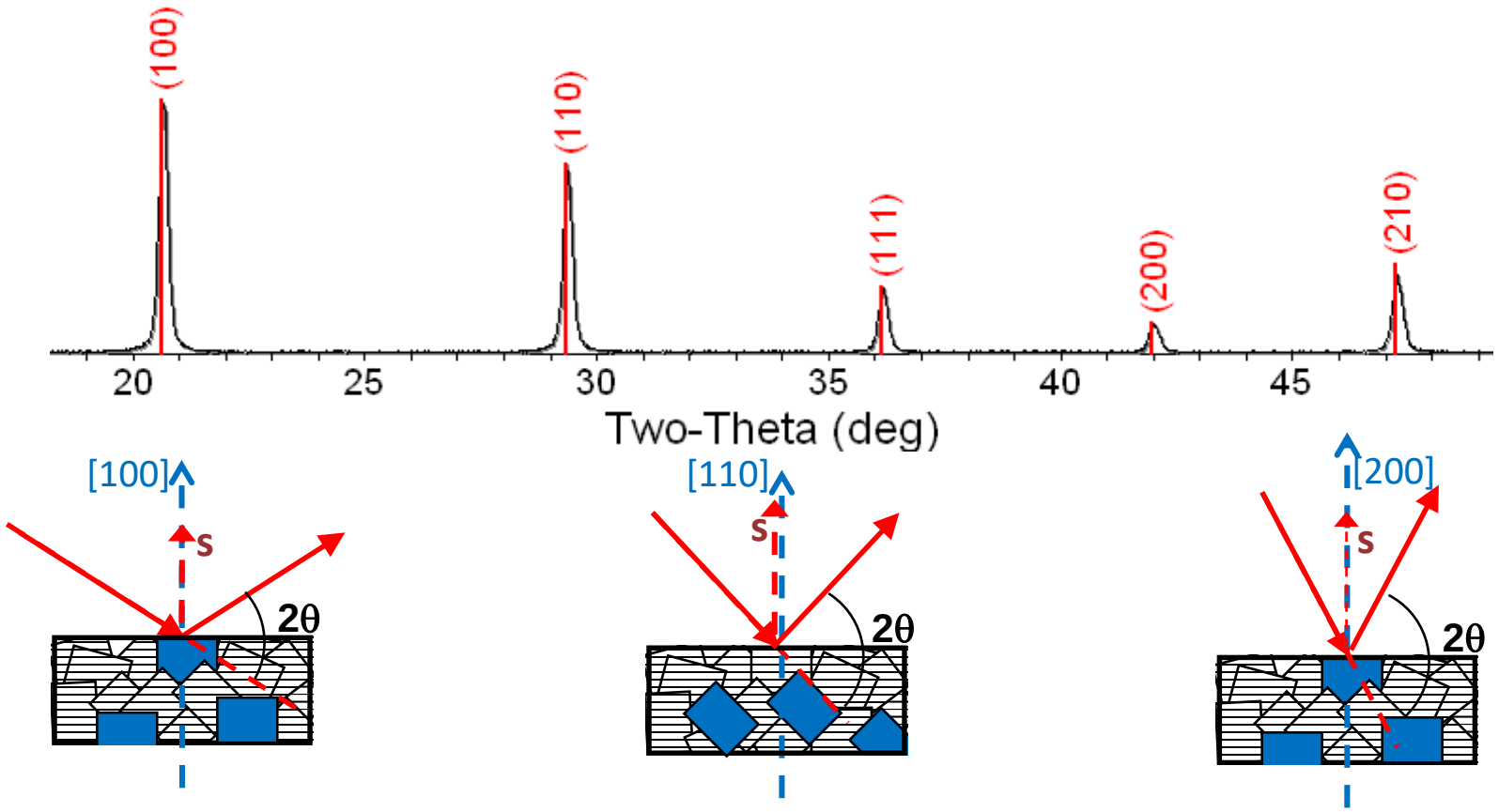
XRD for polycrystalline powders



Powder sample consists of hundreds of randomly-orientated single crystals:

- A large number of diffracted spots forms continuous “Debye diffraction cones”.
- Cones emerge in all directions (forwards and backwards) ↔ Bragg’s equation.
- Circle film (or detector) is used to record the diffraction pattern.
- Linear diffraction pattern is formed as the detector scans along an arc that intersects each Debye cone at a single point.

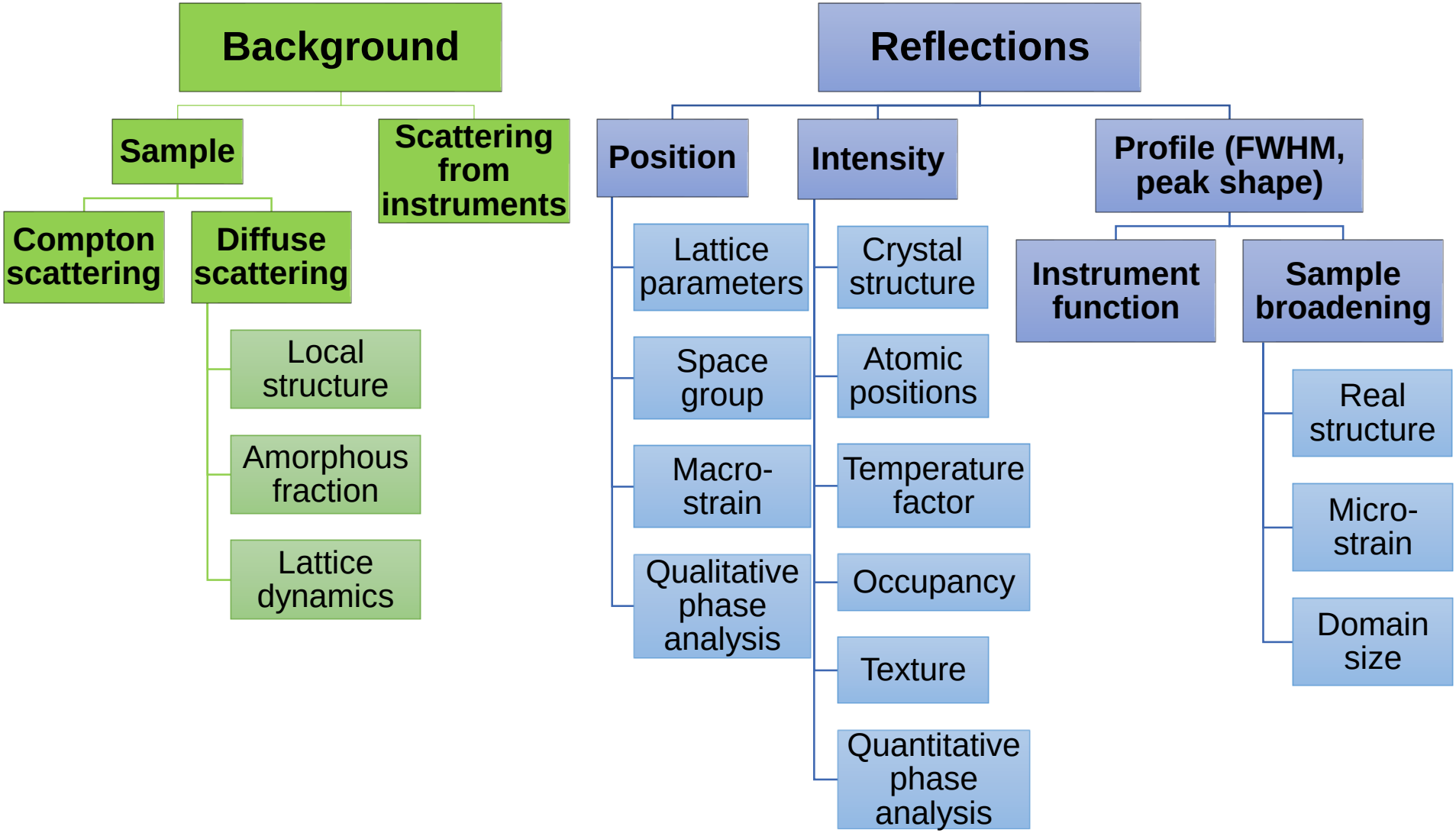
Powder X-ray diffraction (PXRD)



Basic assumptions

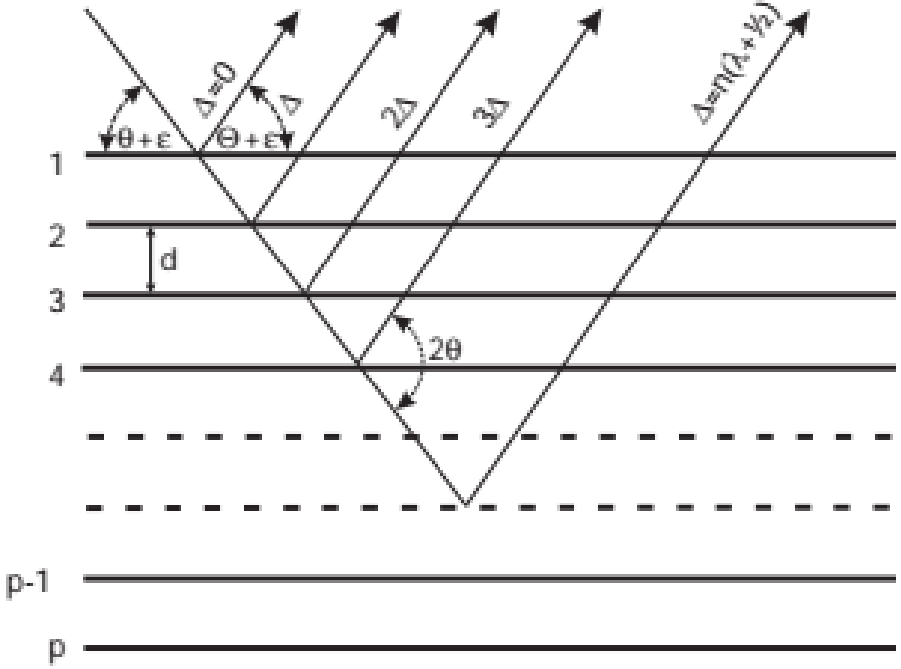
For every set of planes, there will be a statistically-relevant number of crystallites that are properly oriented to diffract the incident X-ray (i.e. the plane perpendicular bisects the incident and diffracted beams).

General information content of PXRD data



Ref. R.E. Dinnebier & S.J.L. Billinge, Powder diffraction theory and practice 2008.

Scherrer equation for finite size crystallites



Crystal with finite dimensions

- no perfect cancellation of the intensity away from the Bragg's condition
- intensity distribution over some small angular range
- broadening of a Bragg reflection due to size effects

$$\beta_{hkl} = \frac{K\,\lambda}{L_{hkl}\cos\theta}$$

β_{hkl} = FWHM or line broadening ,
L_{hkl} = crystallite size,
K = scale factor (0.89 perfect sphere, 0.94 cubic)

Use it with care!!

Large crystallites → the peak width is governed by the coherence of the incident beam and not by particle size.

Nano-scale crystallites → Bragg's law fails (replaced by the Debye equation)

Ref. R.E. Dinnebier & S.J.L. Billinge, Powder diffraction theory and practice 2008.