Structural Analysis
Part III - X-ray tools

Session 1

Introduction and motivation

Contact:

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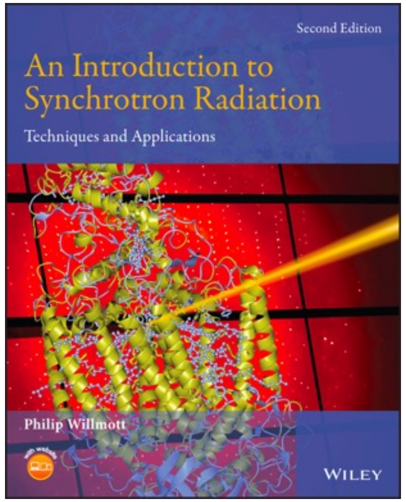
Course layout

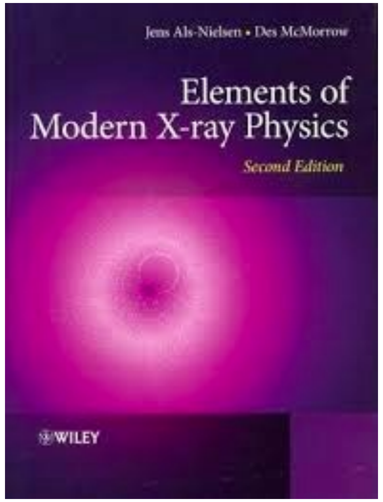
Session 1:
- Introduction to x-rays
- Very basic x-ray – matter interactions
- Sources and transport

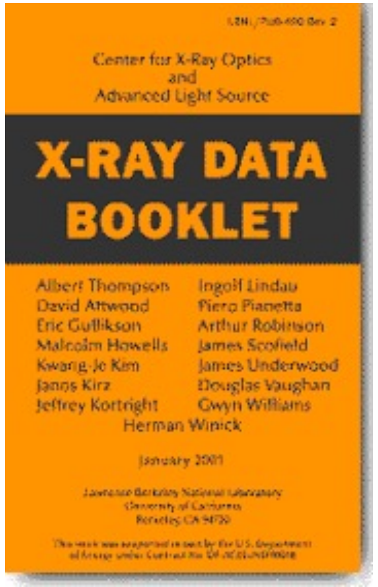
Session 2:
- X-ray diffraction in chemistry
- Diffraction, the basics
- Bragg diffcations
- Small angle scattering

Session 3:
- Crystal lattice and reciprocal lattice
- Laue diffraction
- The structure factor

Session 4:
- Solving crystal structures
- X-ray diffraction examples and case studies
- X-ray spectroscopy

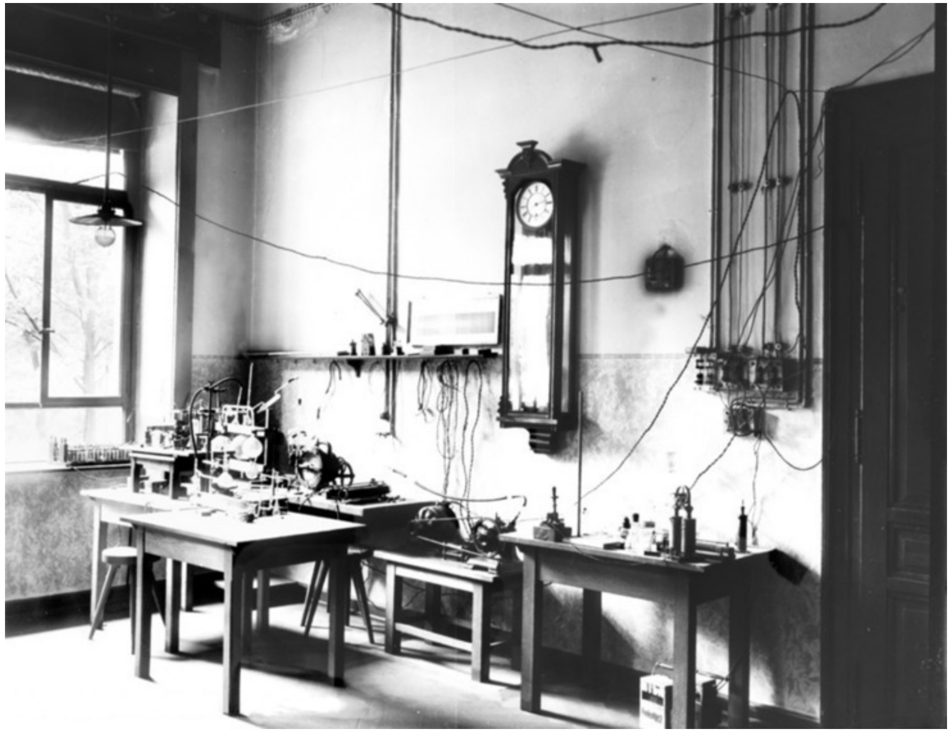






Introduction and historical perspective

The discovery of x-rays in 1895

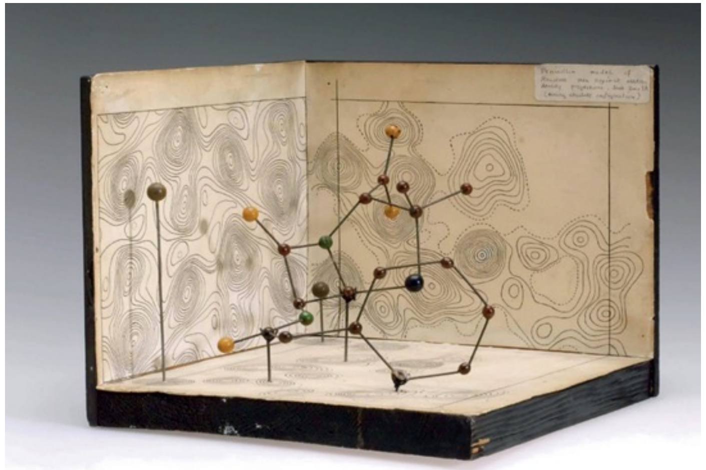


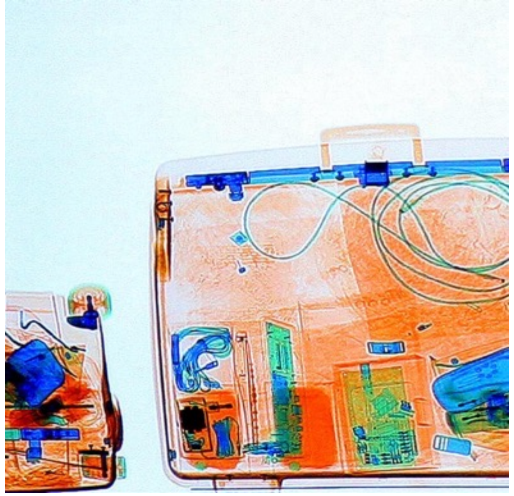
- Röntgens lab in Würzburg
- Experiments with vacuum tube
- Noticed fluorescence on a screen despite light-tight packaging of tube
- Postulated mysterios x-rays

- During experiments illuminated his hand and saw bone structure
- Took first “medical” x-ray on his wifes hand
- Denied patenting request to fully exploit potential of x-rays

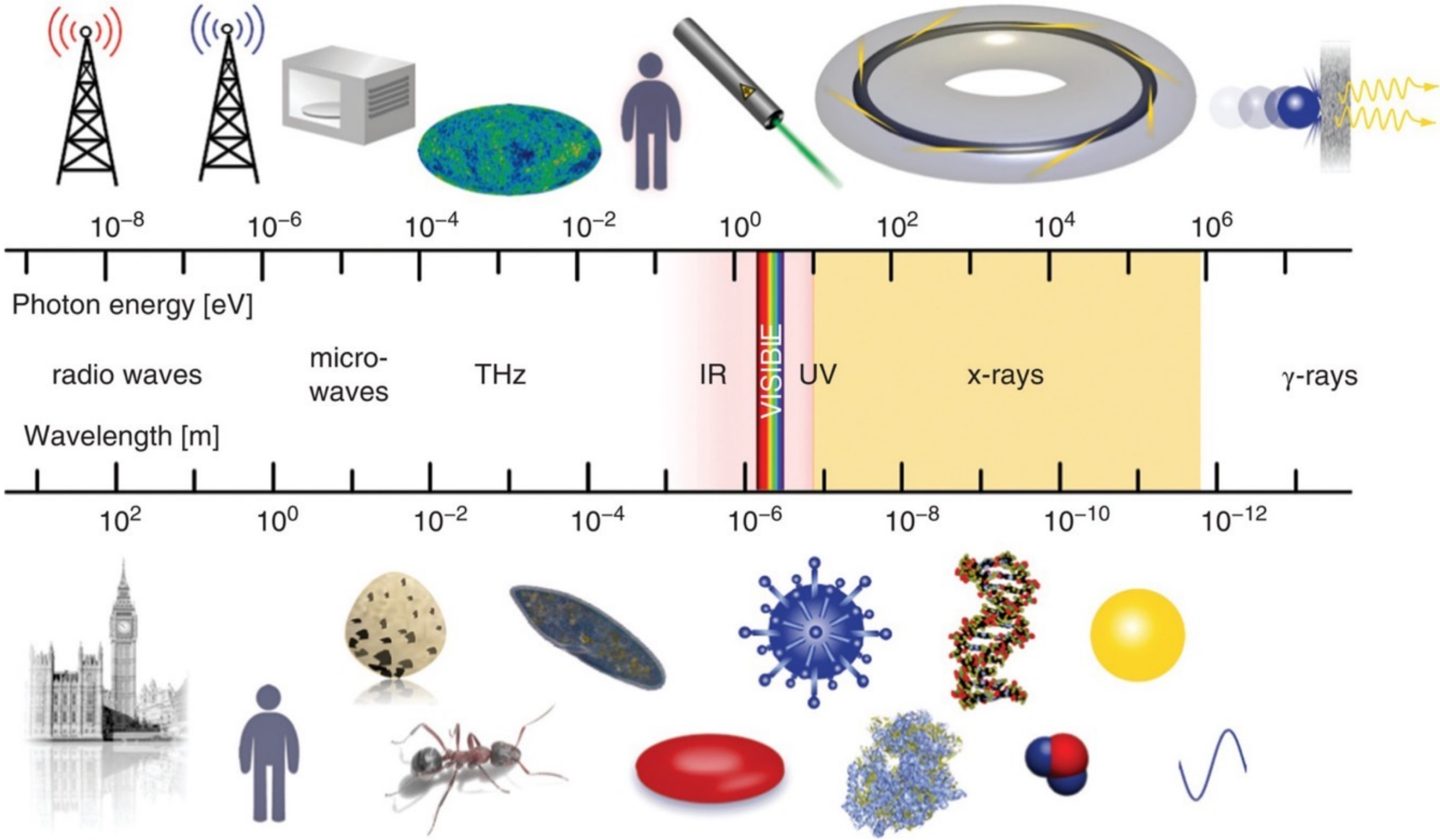
Discovery of X-rays triggered many technological and scientific developments

First Nobel Prize in 1901





X-rays are high-energy electromagnetic (em) waves



X-rays: Physics? Chemistry? Biology? Medicine?

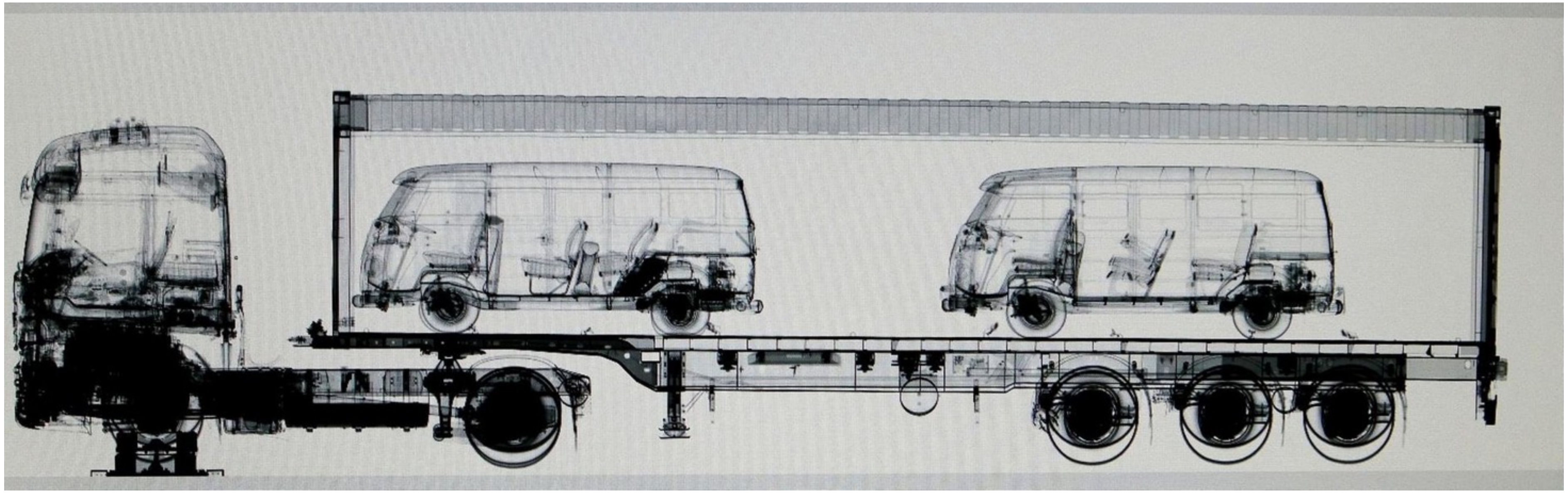
Table 1.1 Nobel Prizes awarded in the field of x-ray research.

Year	Recipient(s)	Research discipline
1901	W. C. Röntgen	Physics; discovery of x-rays
1914	M. von Laue	Physics; x-ray diffraction from crystals
1915	W. H. Bragg and W. L. Bragg	Physics; crystal structure derived from x-ray diffraction
1917	C. G. Barkla	Physics; characteristic radiation of elements
1924	K. M. G. Siegbahn	Physics; x-ray spectroscopy
1927	A. H. Compton	Physics; scattering of x-rays by electrons
1936	P. Debye	Chemistry; diffraction of x-rays and electrons in gases
1946	H. J. Muller	Medicine; discovery of x-ray-induced mutations
1962	M. Perutz and J. Kendrew	Chemistry; structures of myoglobin and haemoglobin
1962	J. Watson, M. Wilkins, and F. Crick	Medicine; structure of DNA
1964	D. Crowfoot-Hodgkin	Chemistry; structure of penicillin
1976	W. N. Lipscomb	Chemistry; x-ray studies on the structure of boranes
1979	A. McLeod Cormack and G. Newbold Hounsfield	Medicine; computed axial tomography
1981	K. M. Siegbahn	Physics; high-resolution electron spectroscopy
1985	H. Hauptman and J. Karle	Chemistry; direct methods to determine x-ray structures
1988	J. Deisenhofer, R. Huber, and H. Michel	Chemistry; determining the structure of proteins crucial to photosynthesis
1997	P. D. Boyer and J. E. Walker	Chemistry; mechanism of adenosine triphosphate synthesis†
2003	R. MacKinnon and P. Agre	Chemistry; structure and operation of ion channels†
2006	R. D. Kornberg	Chemistry; atomic description of DNA transcription†
2009	V. Ramakrishnan, T. A. Steitz, and A. E. Yonath	Chemistry; structure and function of the ribosome†
2012	R. J. Lefkowitz and B. K. Kobilka	Chemistry; studies of G-protein-coupled receptors†
2018	F. H. Arnold	Chemistry; the directed evolution of enzymes†

†Work using synchrotron radiation as a primary tool.

The power of x-rays

X-rays – Penetration depth



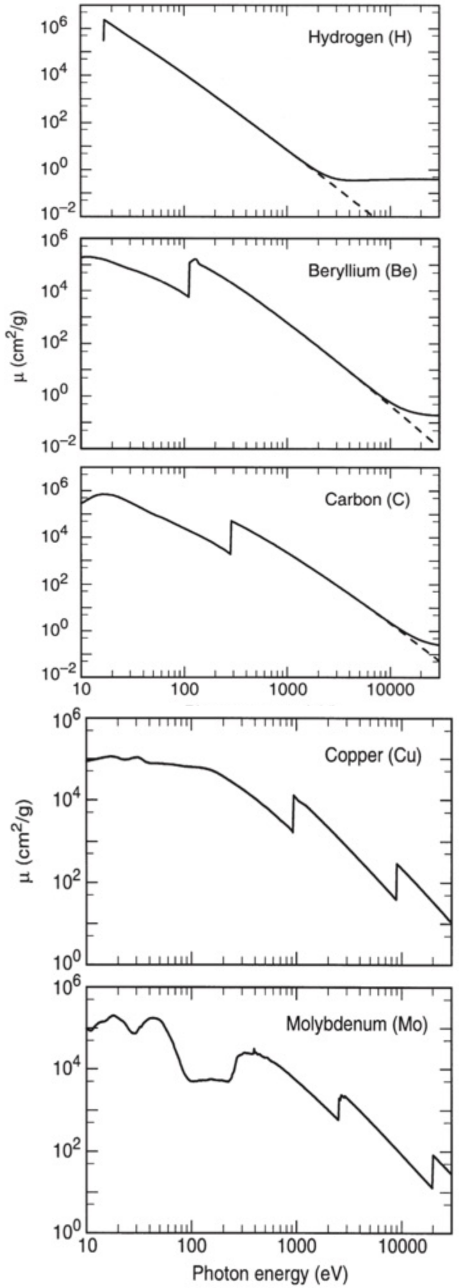


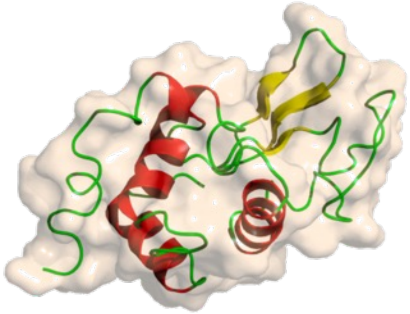
Fig. 1-5. Mass absorption coefficients (continued).

Scattering with atomic resolution

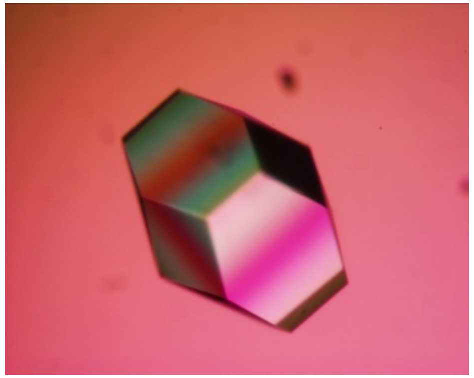
Lysozym (Protein, Immunsystem)

Stochiometric formula
$C_{125}H_{196}N_{40}O_{36}S_2$

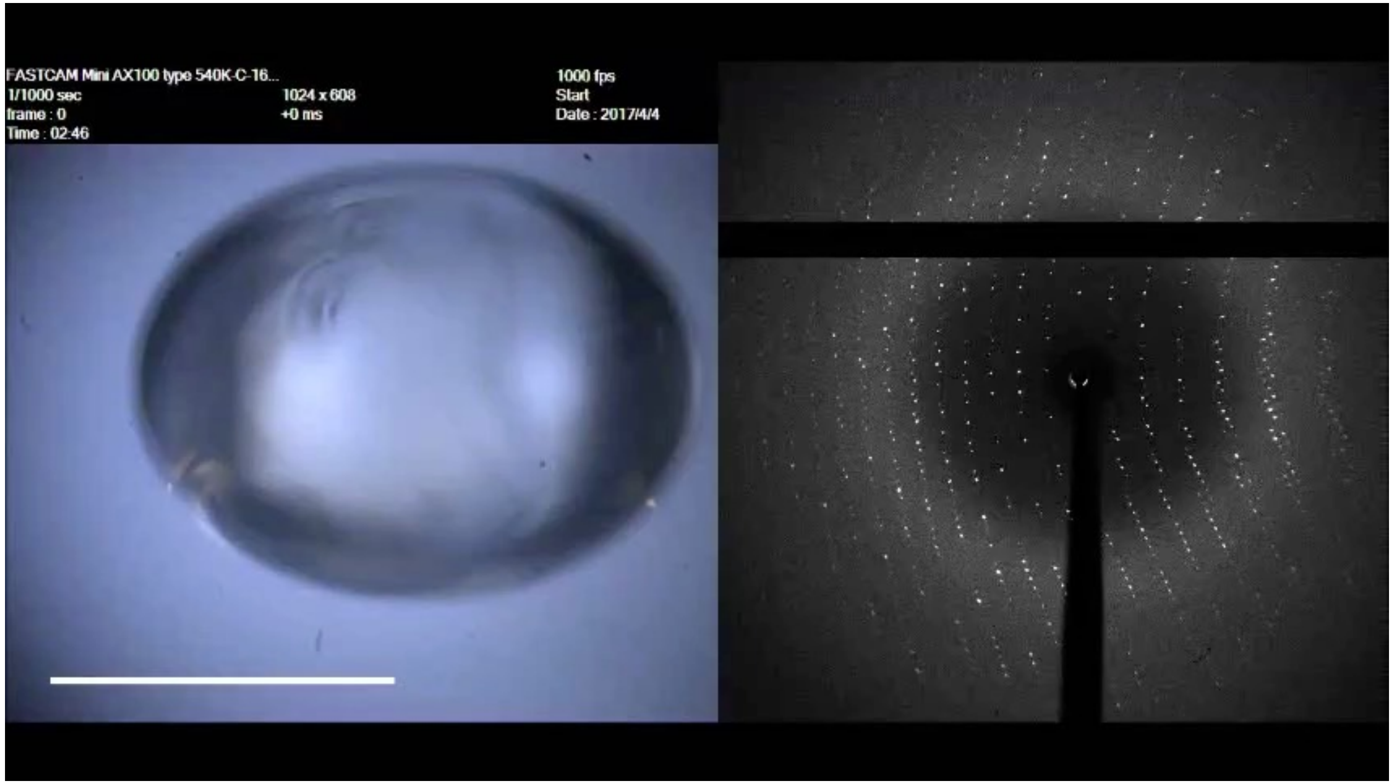
Structure



Crystal



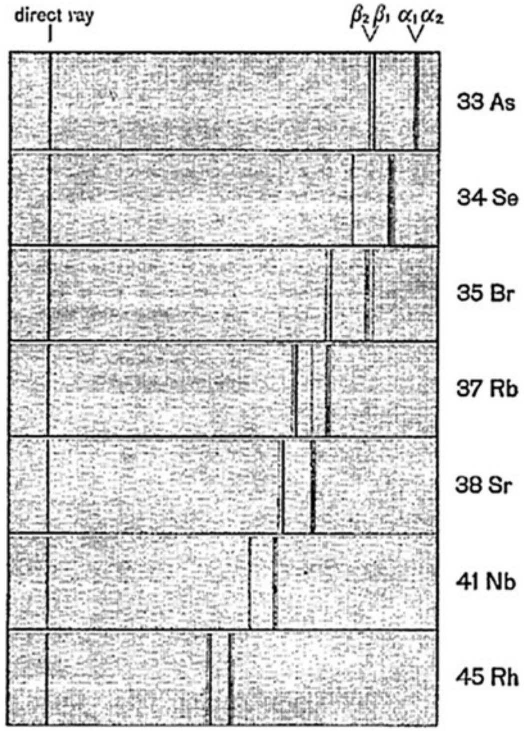
Experiment at the Swiss Light Source



Elements possess specific colors – also in X-ray spectral regime

Rose of Lausanne:
Characteristic visible colors

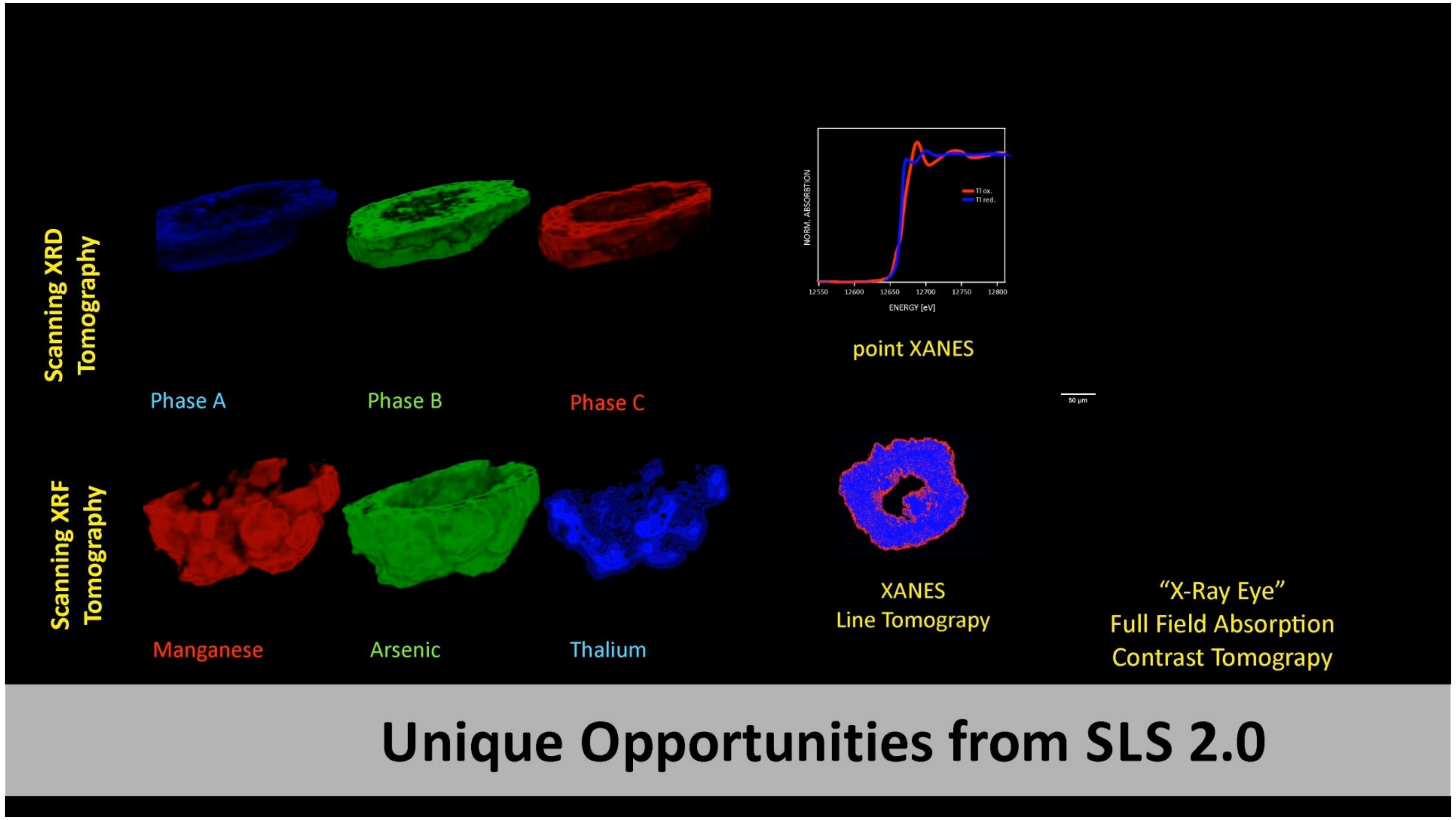
Barkla:
Characteristic emission lines of elements in x-ray regime



Barkla, Nobel Prize in 1917

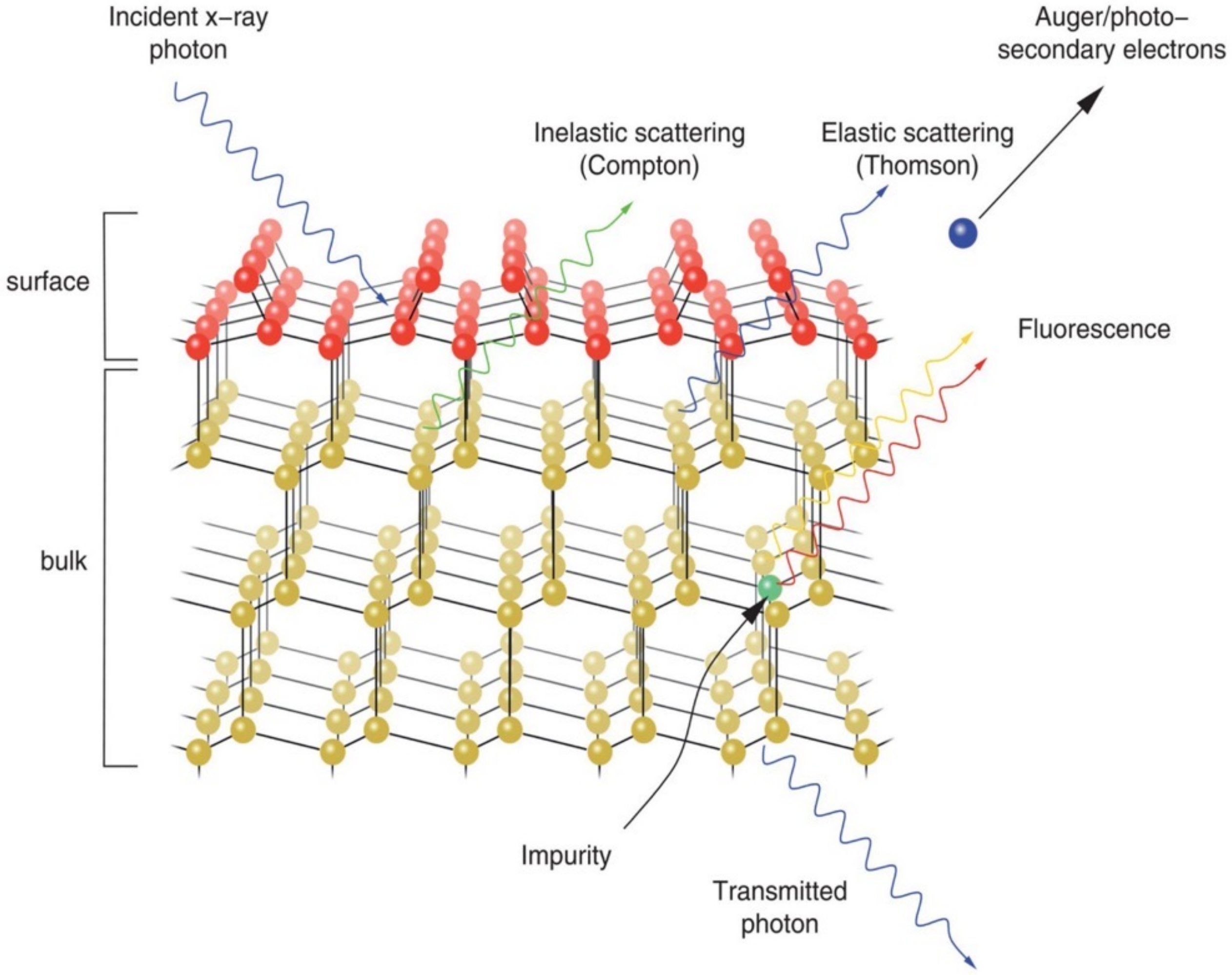
Combination of large penetration depth, elemental information, and high resolution

Example: Geological Thalium sample (Geochemistry)



X-ray interactions with matter

X-ray interactions with matter



X-ray cross sections

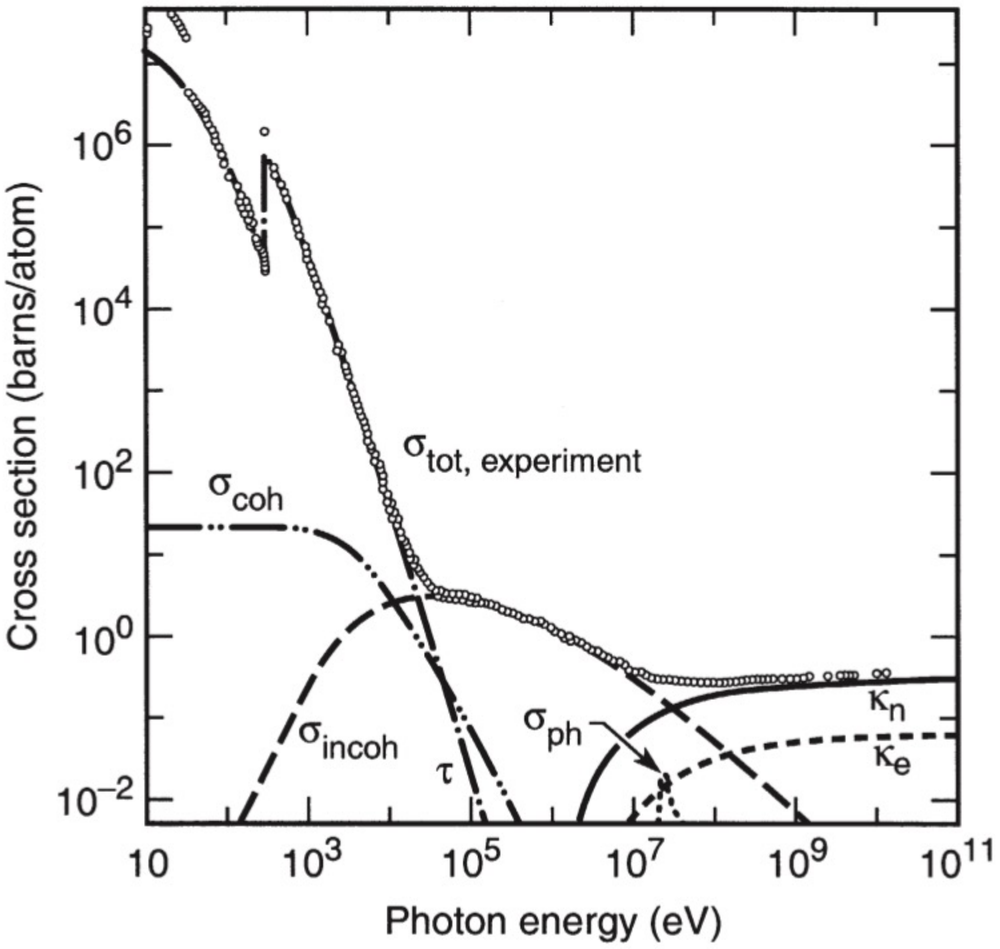
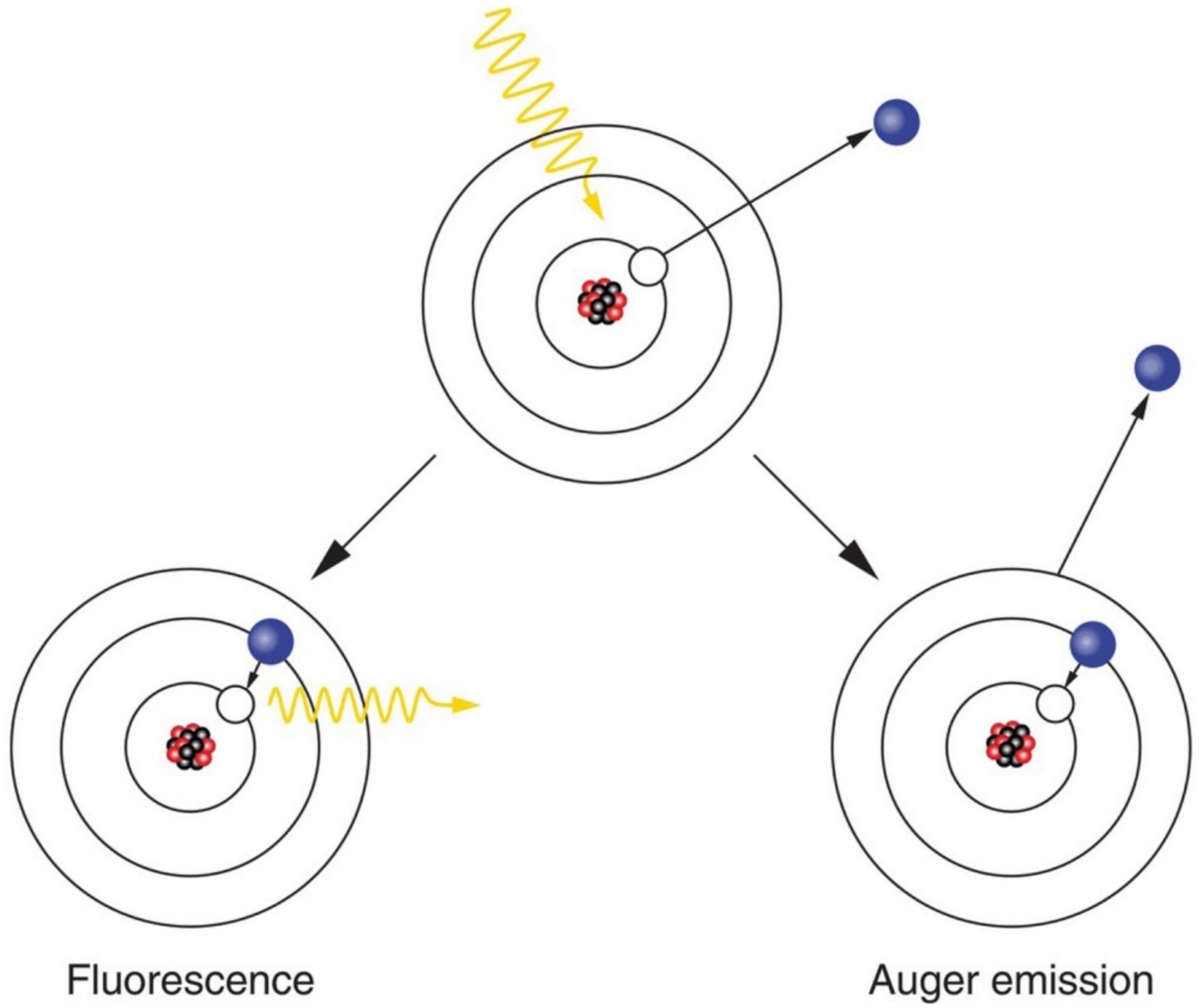


Fig. 3-1. *Total photon cross section σ_{tot} in carbon, as a*

Photoionization / absorption



Ionization energies of elements

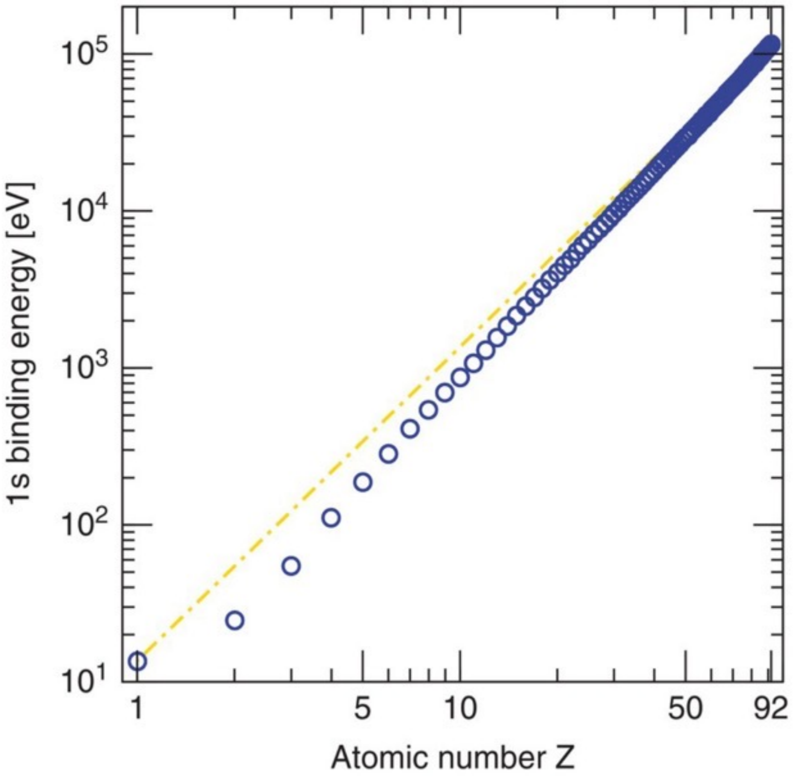
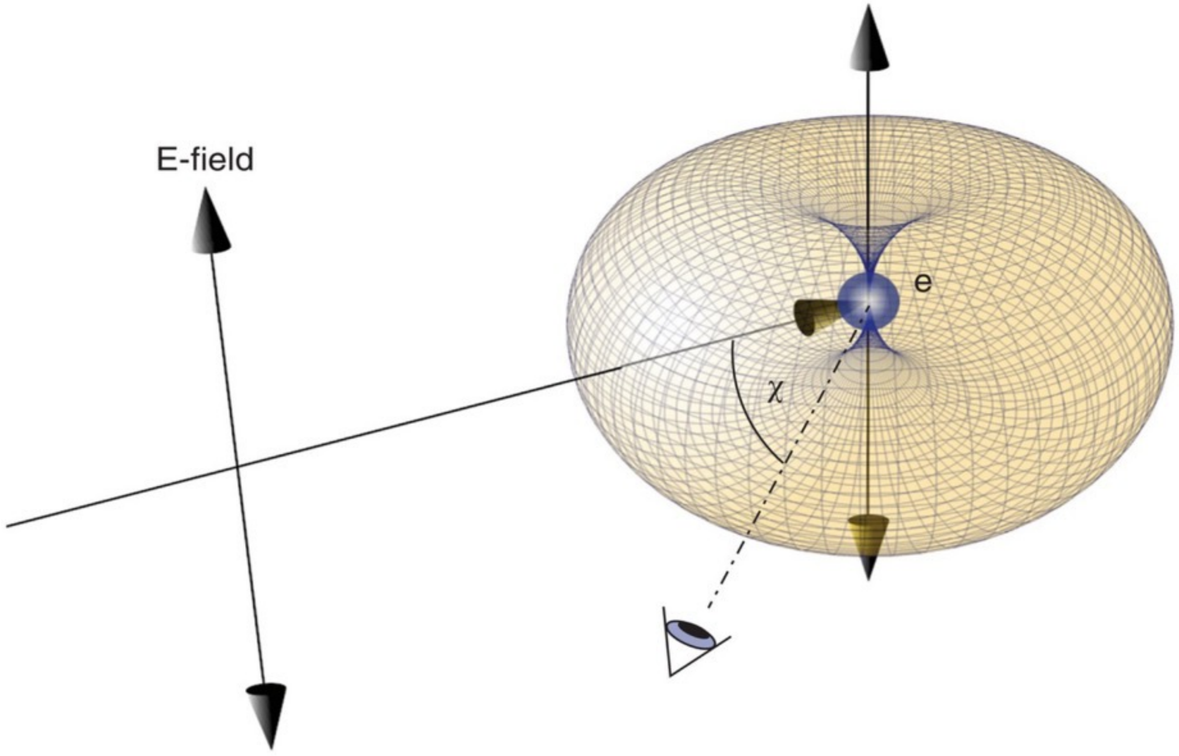


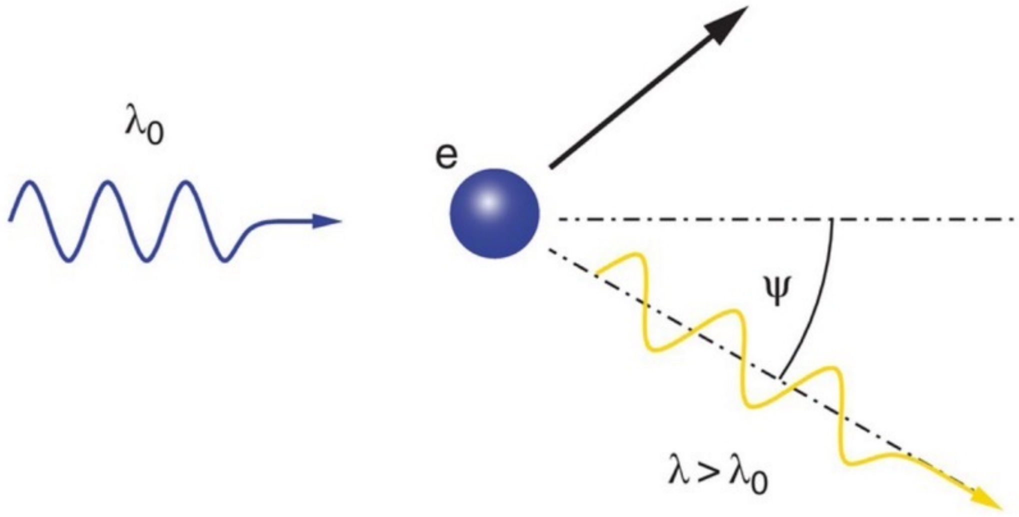
Table 1-1. Electron binding energies, in electron volts, for the elements in their natural forms.

Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$	M_4 $3d_{3/2}$	M_5 $3d_{5/2}$	N_1 4s	N_2 $4p_{1/2}$
1 H	13.6										
2 He	24.6*										
3 Li	54.7*										
4 Be	111.5*										
5 B	188*										
6 C	284.2*										
7 N	409.9*	37.3*									
8 O	543.1*	41.6*									
9 F	696.7*										
10 Ne	870.2*	48.5*	21.7*	21.6*							
11 Na	1070.8†	63.5†	30.65	30.81							
12 Mg	1303.0†	88.7	49.78	49.50							
13 Al	1559.6	117.8	72.95	72.55							
14 Si	1839	149.7*b	99.82	99.42							
15 P	2145.5	189*	136*	135*							
16 S	2472	230.9	163.6*	162.5*							
17 Cl	2822.4	270*	202*	200*							
18 Ar	3205.9*	326.3*	250.6†	248.4*	29.3*	15.9*	15.7*				
19 K	3608.4*	378.6*	297.3*	294.6*	34.8*	18.3*	18.3*				
20 Ca	4038.5*	438.4†	349.7†	346.2†	44.3 †	25.4†	25.4†				
21 Sc	4492	498.0*	403.6*	398.7*	51.1*	28.3*	28.3*				
22 Ti	4966	560.9†	460.2†	453.8†	58.7†	32.6†	32.6†				

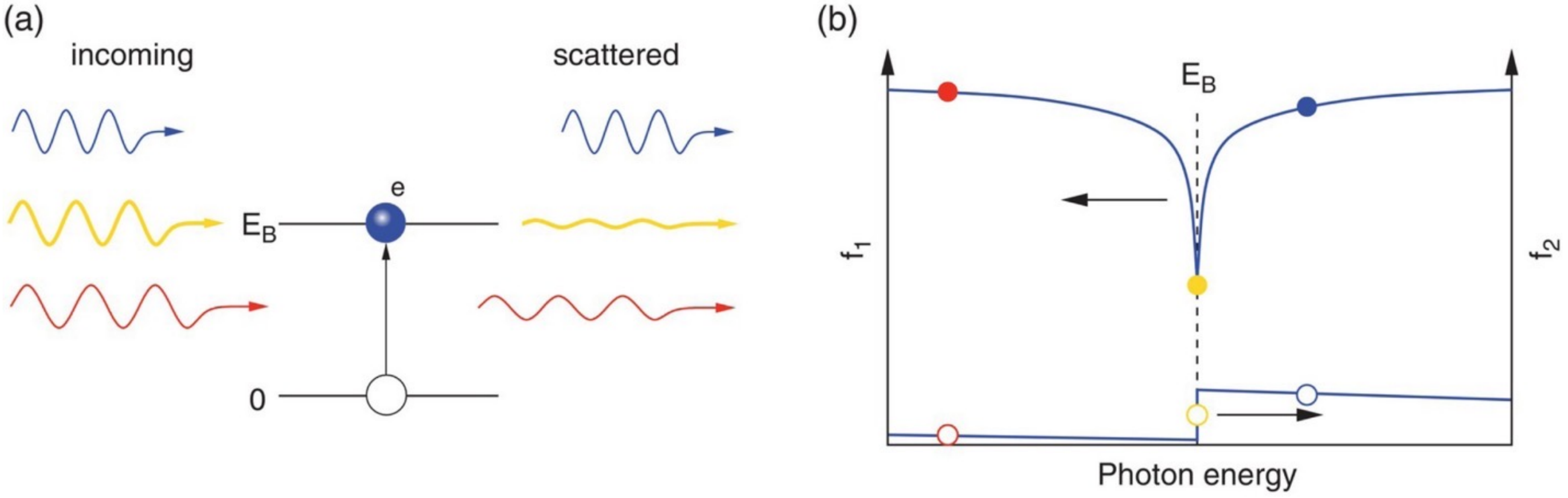
Thomson scattering



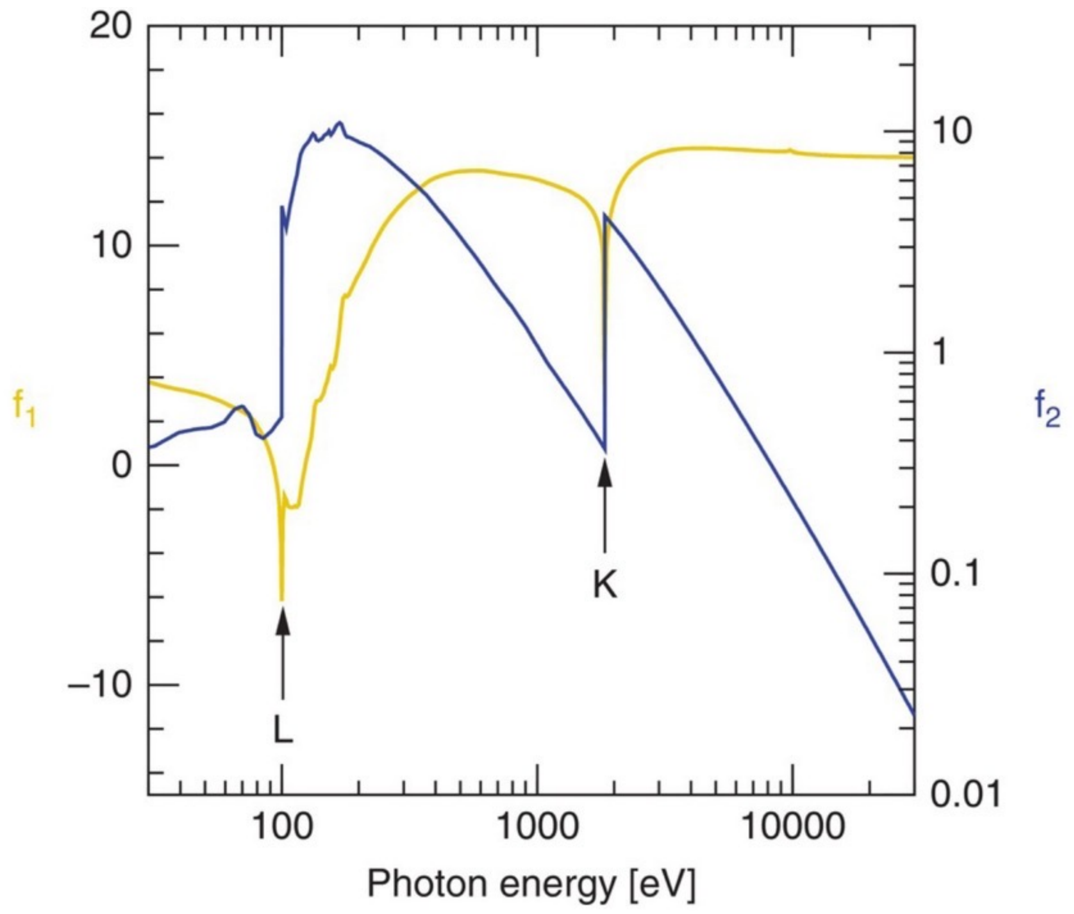
Compton scattering



Atomic scattering factors

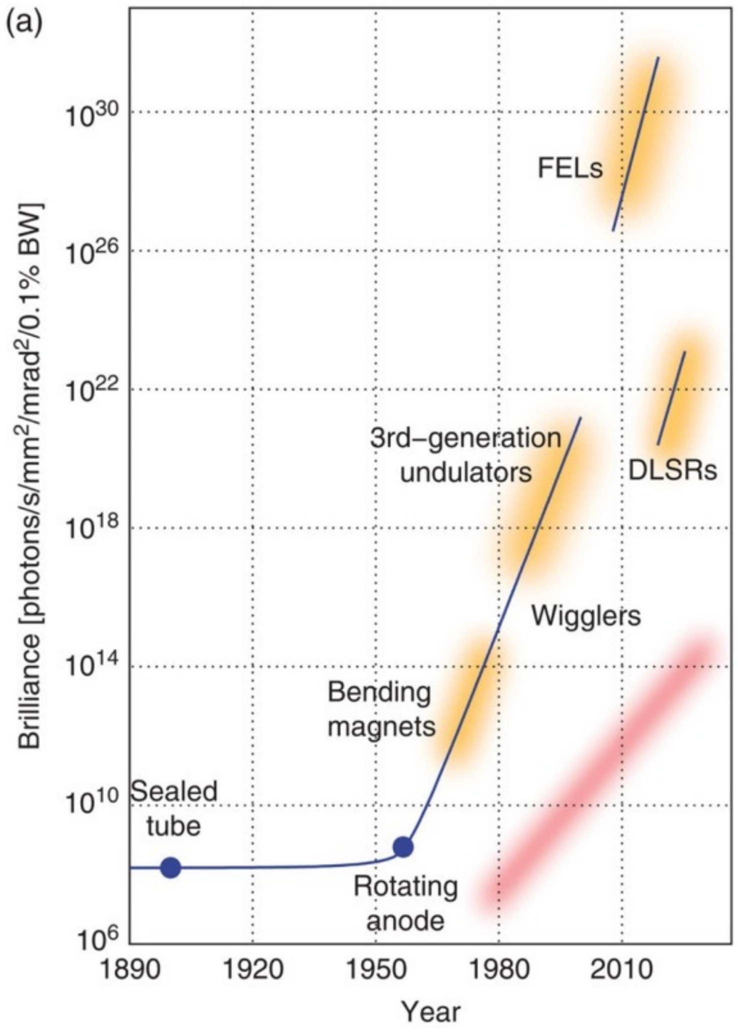


Atomic scattering factors and refractive index

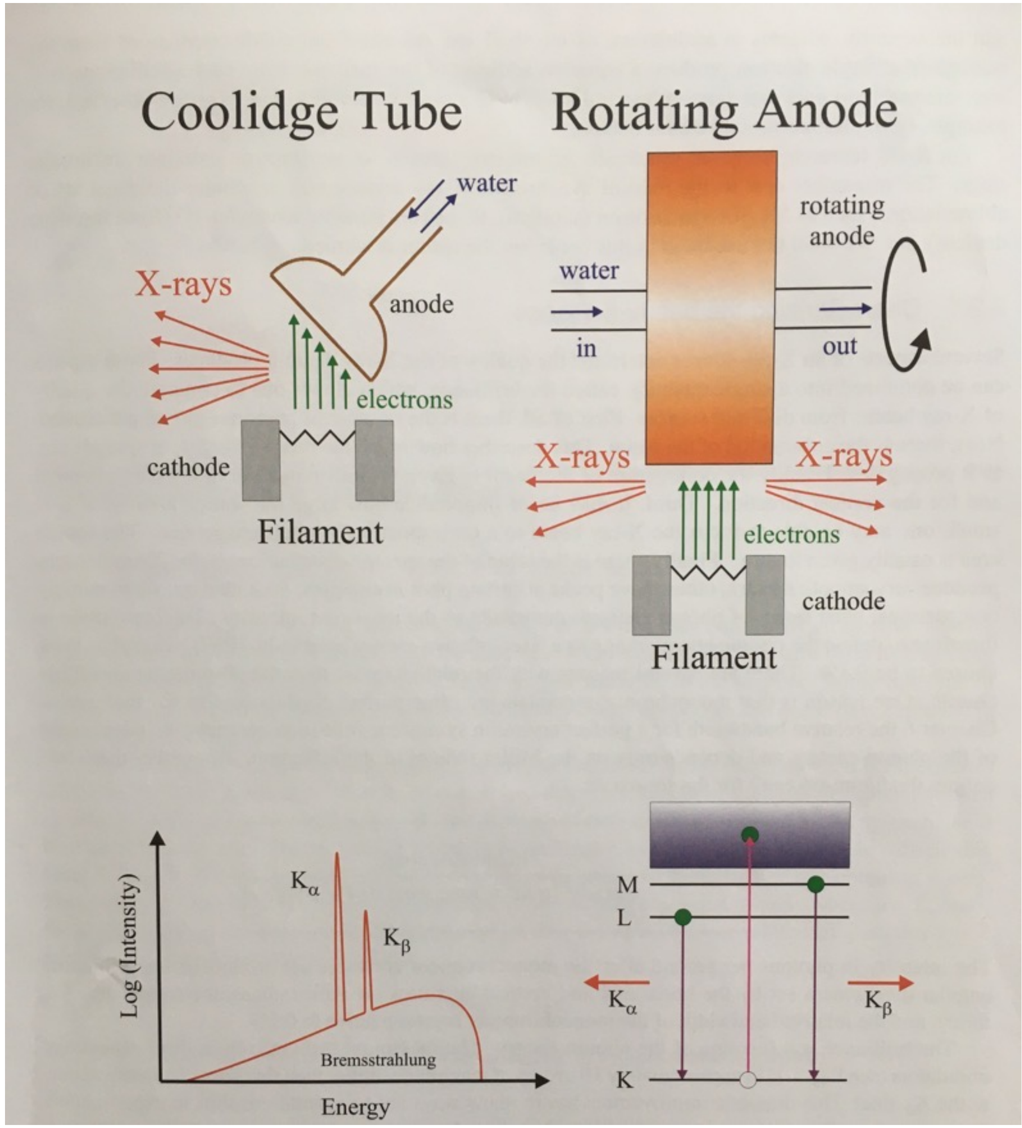


X-ray sources

X-ray source development has gone through exponential improvements since the 1950s



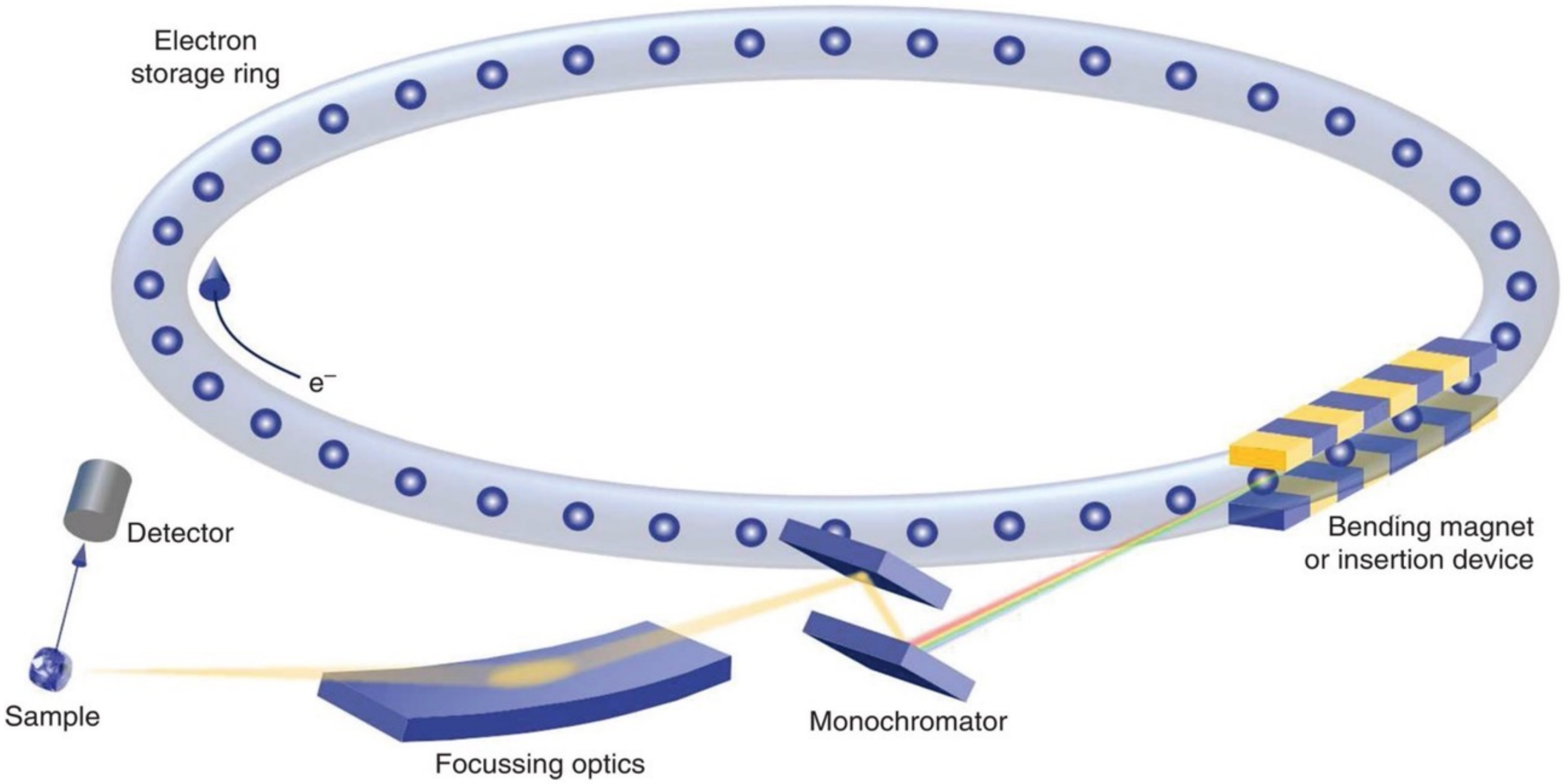
(Rotating) anode sources



X-ray laboratory sources at EPFL

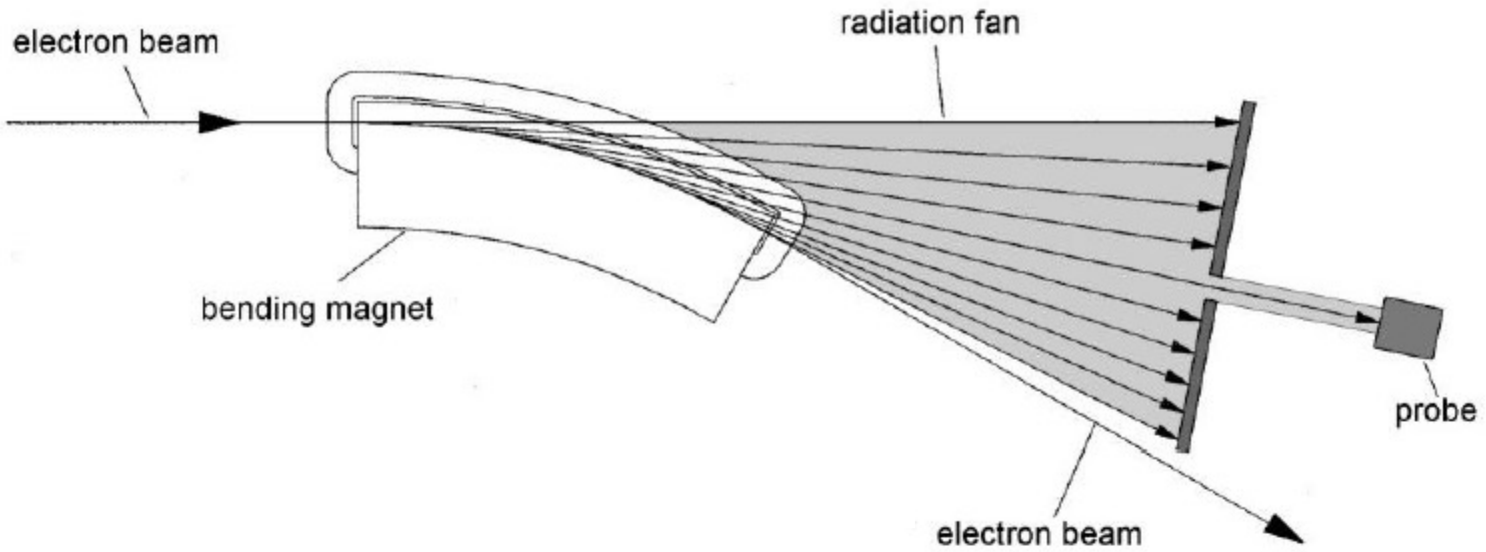
https://www.epfl.ch/schools/sb/research/isic/platforms/x-ray_diffraction/

Synchrotron radiation source

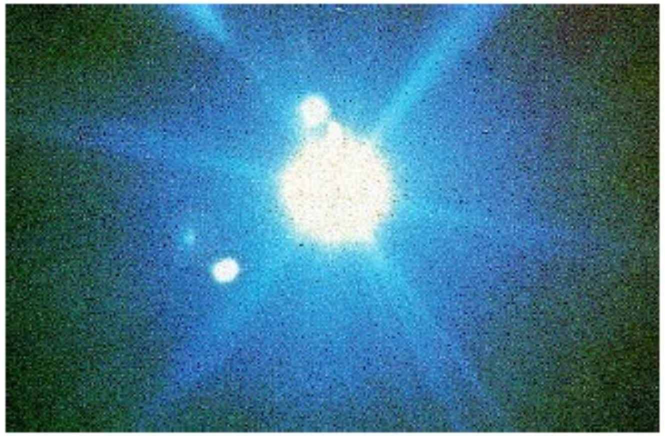


Aerial view of Paul-Scherrer-Institute

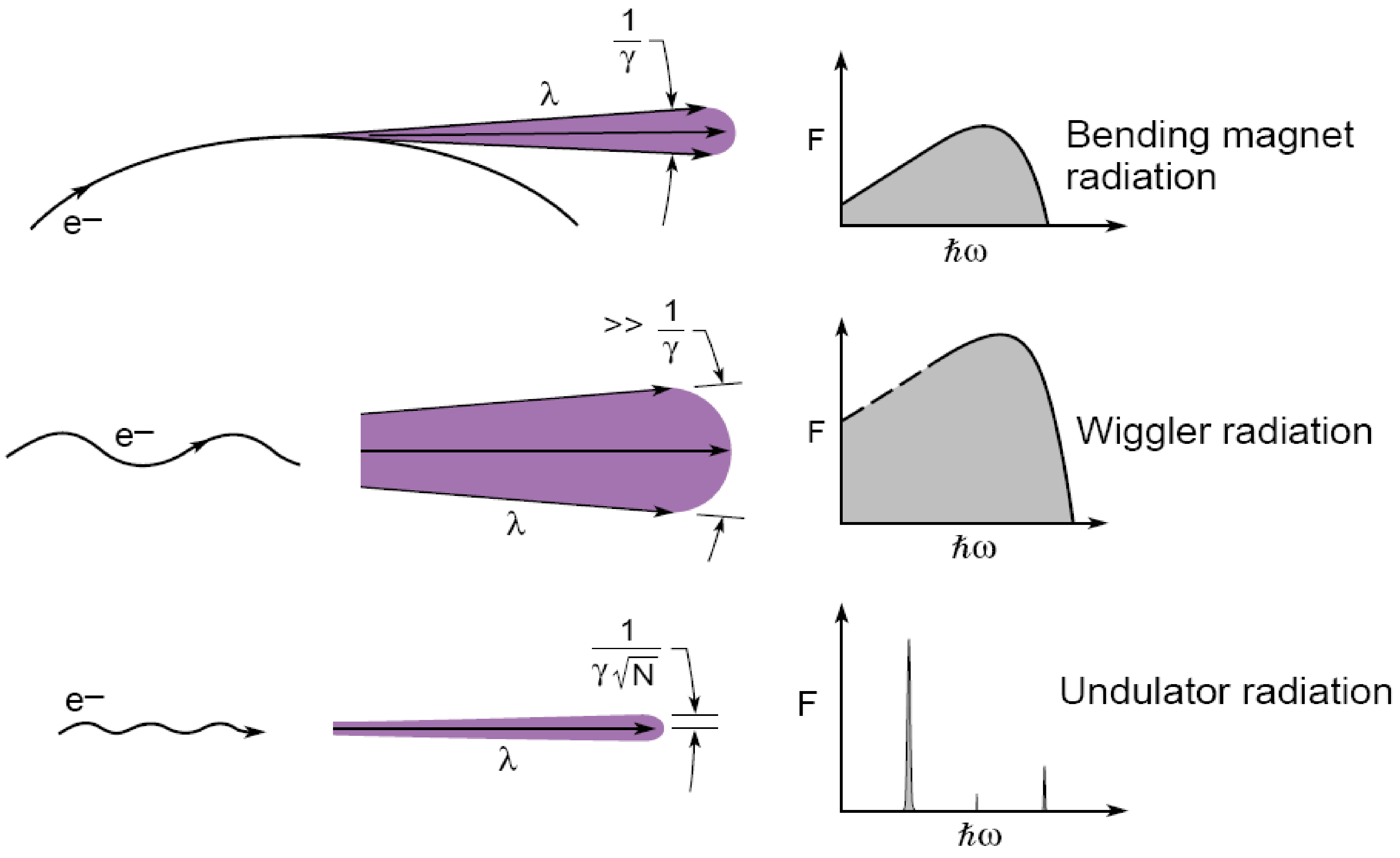
Synchrotron radiation: The idea



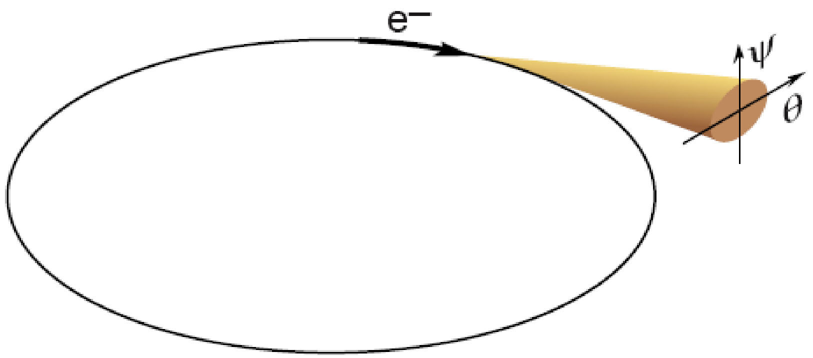
Light point of synchrotron radiation (close to white light)



Three type of sources in synchrotron radiation storage ring:



Bending magnet source



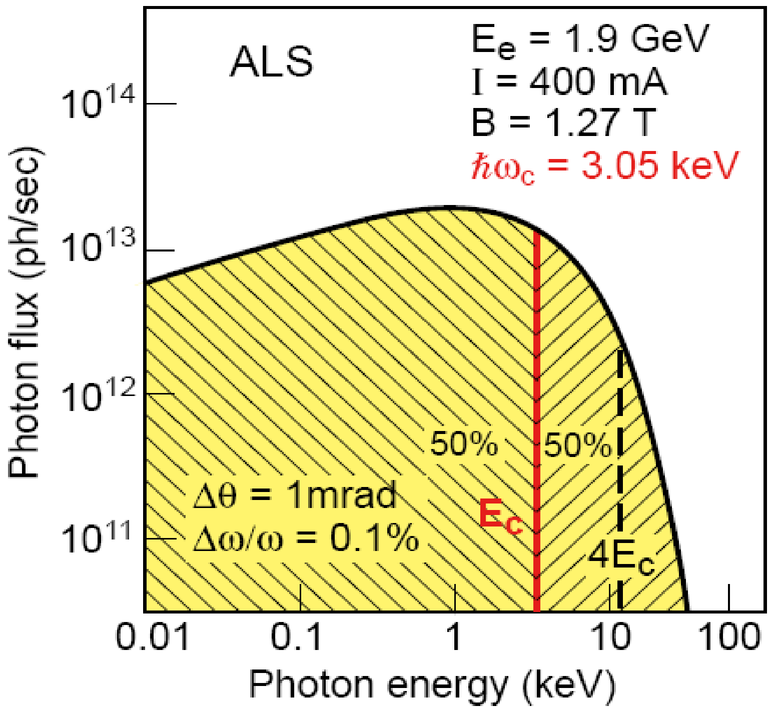
$$E_c = \hbar\omega_c = \frac{3e\hbar B\gamma^2}{2m} \quad (5.7a)$$

$$E_c(\mathrm{keV}) = 0.6650 E_e^2(\mathrm{GeV}) B(\mathrm{T}) \quad (5.7b)$$

$$\frac{d^2F_B}{d\theta\, d\omega/\omega} = 2.46\times 10^{13} E_e(\mathrm{GeV}) I(\mathrm{A}) G_1(E/E_c) \frac{\mathrm{photons/s}}{\mathrm{mrad}\cdot(0.1\%\mathrm{BW})} \quad (5.8)$$

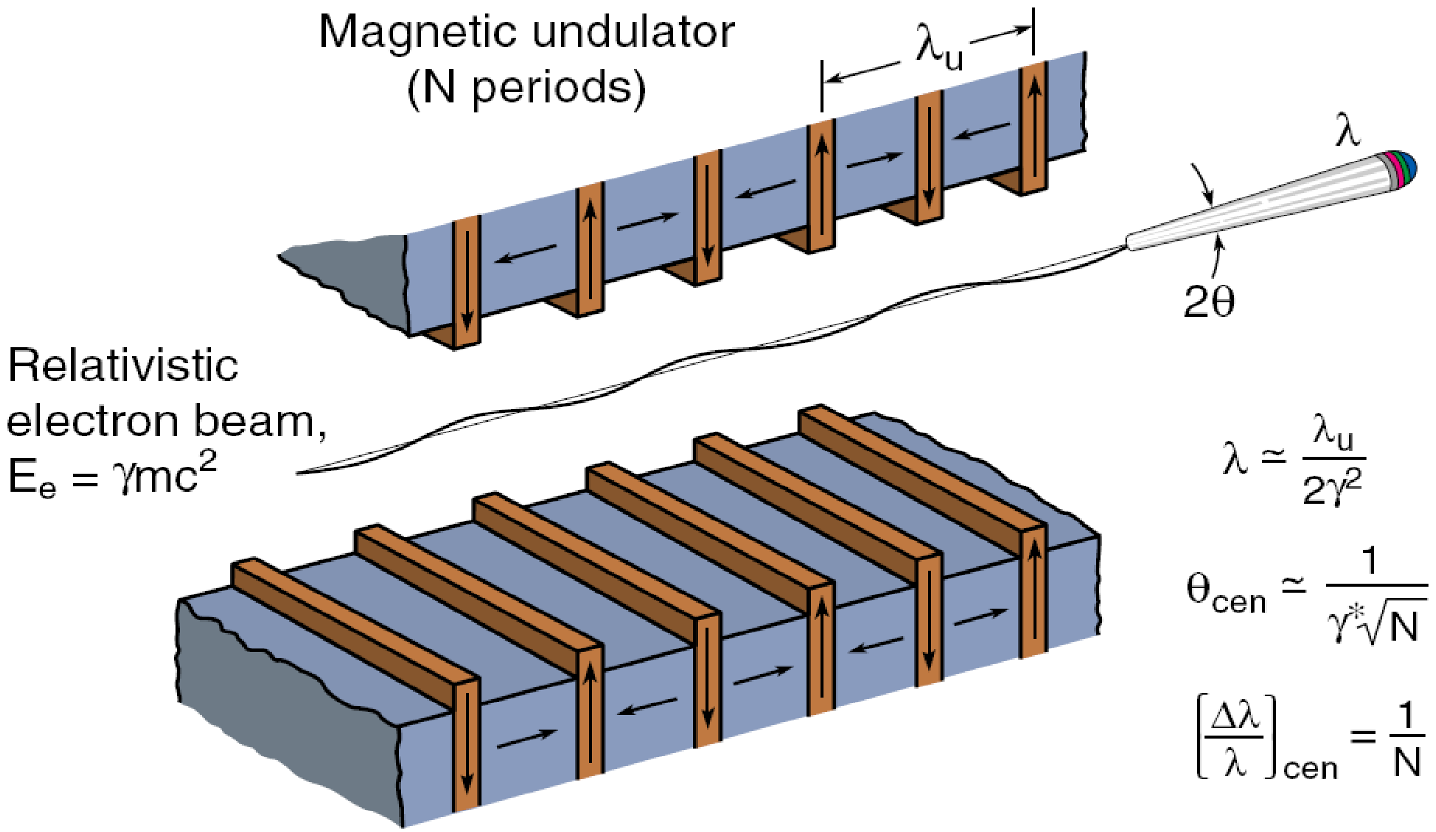
Advantages:
- covers broad spectral range
- least expensive
- most accessable

Disadvantages:
- limited coverage of hard x-rays
- not as bright as undulator



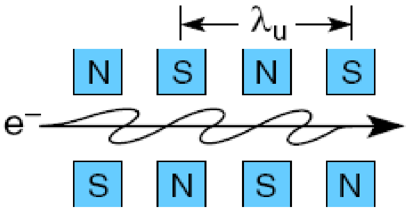
ω_c divides spectrum into two parts of equal power

Undulator source



Undulator source – explained in a nutshell

Laboratory Frame of Reference

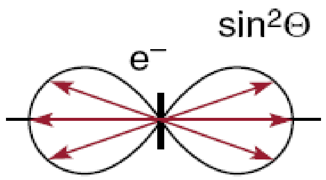


$E = \gamma mc^2$

$$\gamma = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}$$

N = # periods

Frame of Moving e⁻



e^- radiates at the Lorentz contracted wavelength:

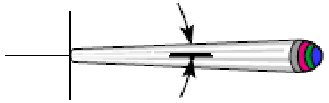
$$\lambda' = \frac{\lambda_u}{\gamma}$$

Bandwidth:

$$\frac{\lambda'}{\Delta\lambda'} \simeq N$$

Frame of Observer

$\theta \simeq \frac{1}{2\gamma}$



Doppler shortened wavelength on axis:

$$\lambda = \lambda'\gamma(1 - \beta\cos\theta)$$

$$\lambda = \frac{\lambda_u}{2\gamma^2}(1 + \gamma^2\theta^2)$$

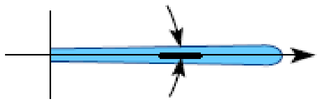
Accounting for transverse motion due to the periodic magnetic field:

$$\boxed{\lambda = \frac{\lambda_u}{2\gamma^2}\left(1 + \frac{K^2}{2} + \gamma^2\theta^2\right)}$$

where $K = eB_0\lambda_u/2\pi mc$

Following Monochromator

θ_{cen}



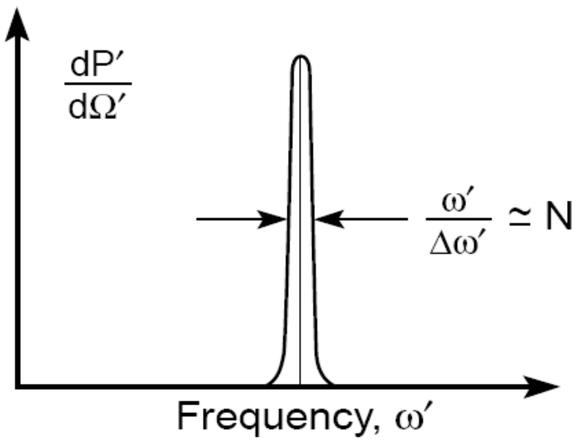
For $\frac{\Delta\lambda}{\lambda} \simeq \frac{1}{N}$

$$\theta_{cen} \simeq \frac{1}{\gamma\sqrt{N}}$$

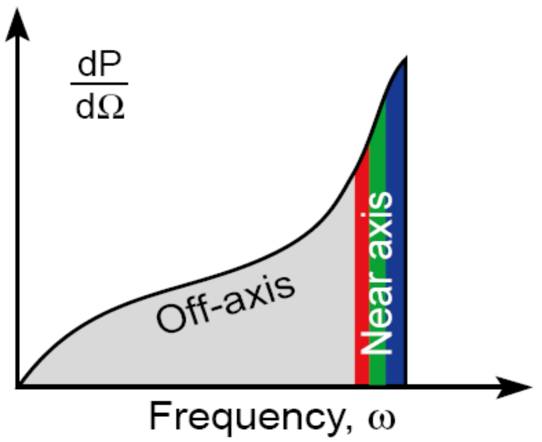
typically

$$\theta_{cen} \simeq 40 \text{ rad}$$

Undulator source – a final note

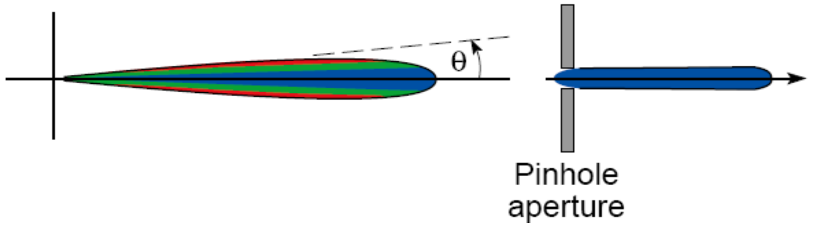


Execution of N electron oscillations produces a transform-limited spectral bandwidth, $\Delta\omega'/\omega' = 1/N$.

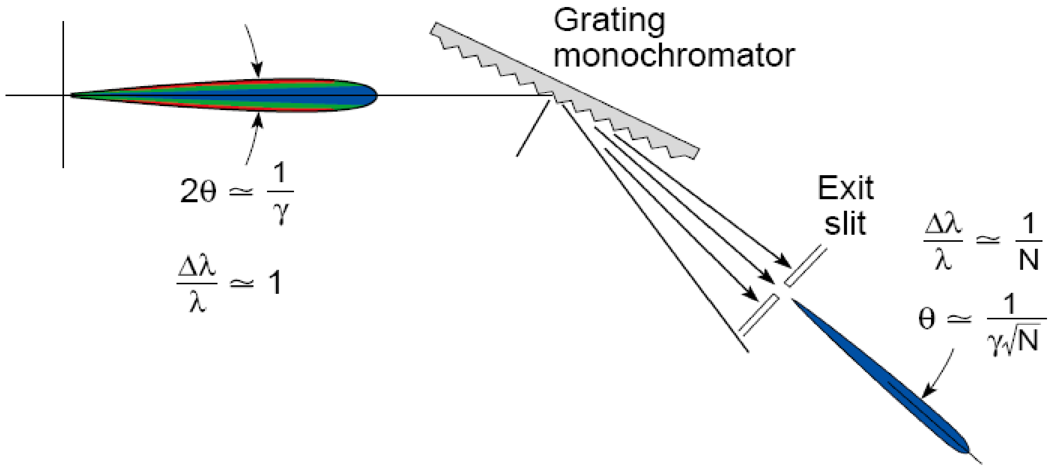


The Doppler frequency shift has a strong angle dependence, leading to lower photon energies off-axis.

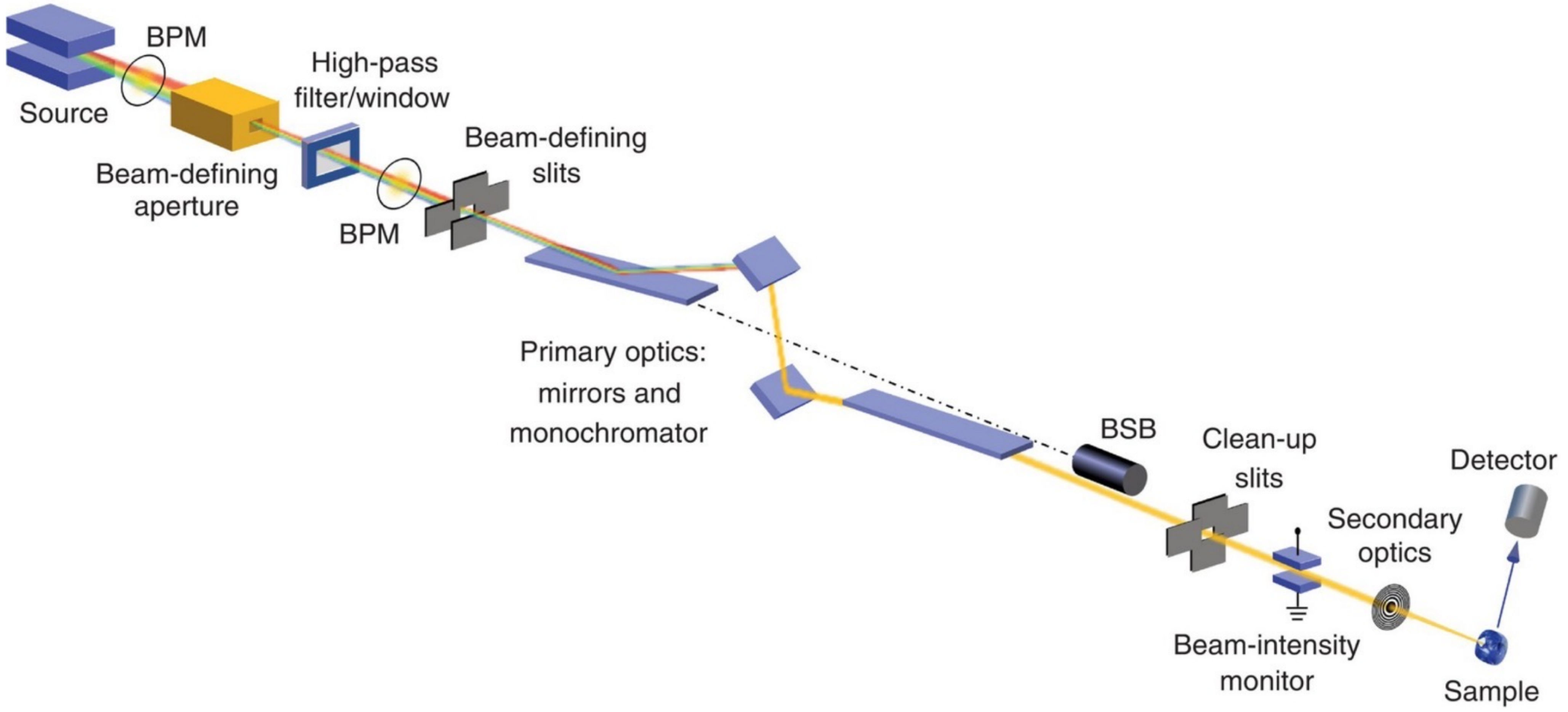
With a pinhole aperture



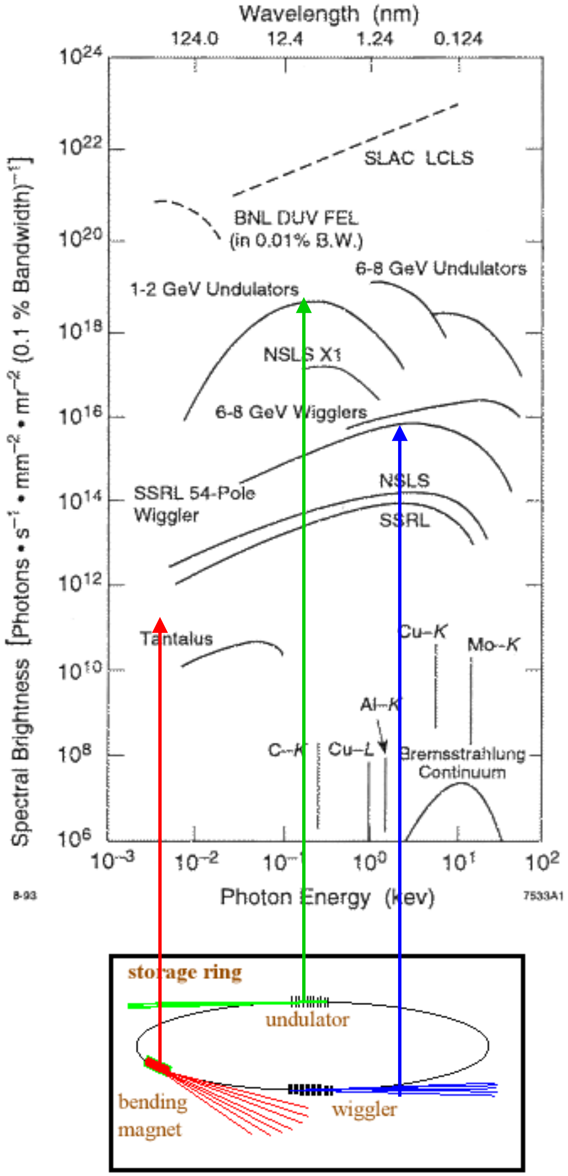
With a monochromator

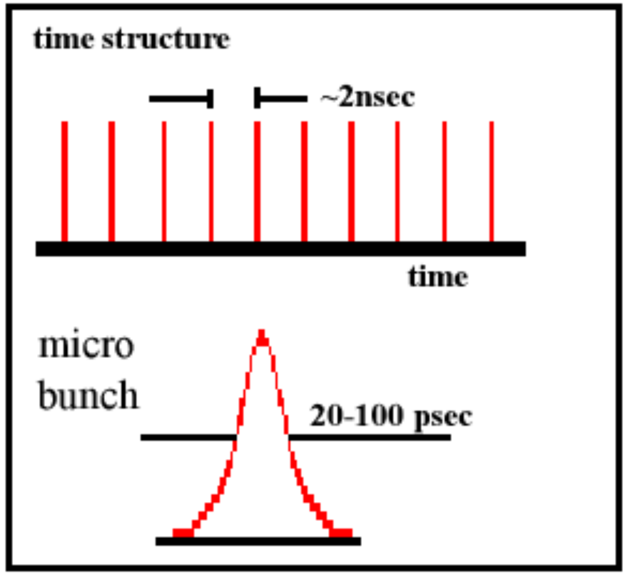


Layout of a synchrotron beamline



Properties of synchrotron radiation





Typical numbers:

~ 10^{11}-10^{13} Photonen/s
Total power10W- 30 kW

X-ray free-electron lasers (XFELs) – the latest and brightest x-ray source

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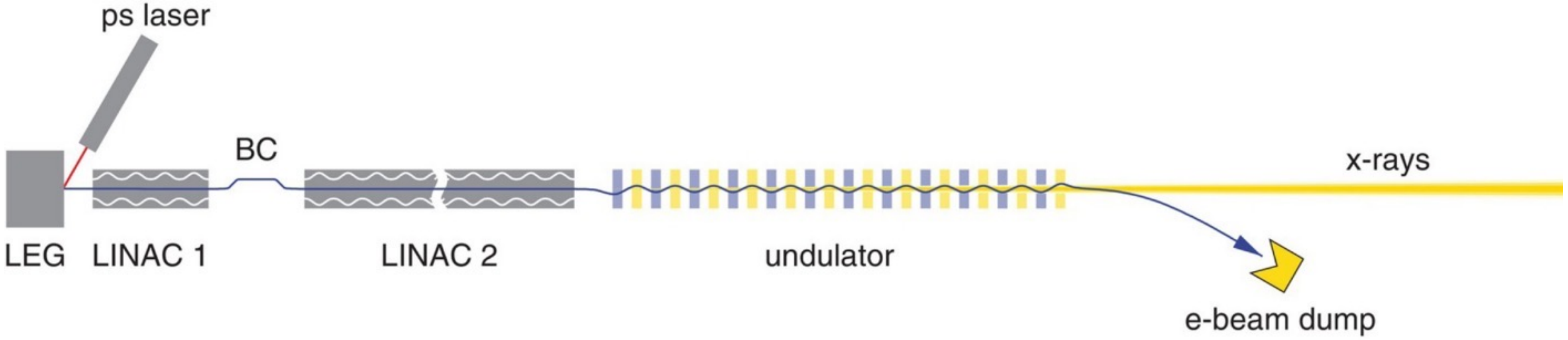
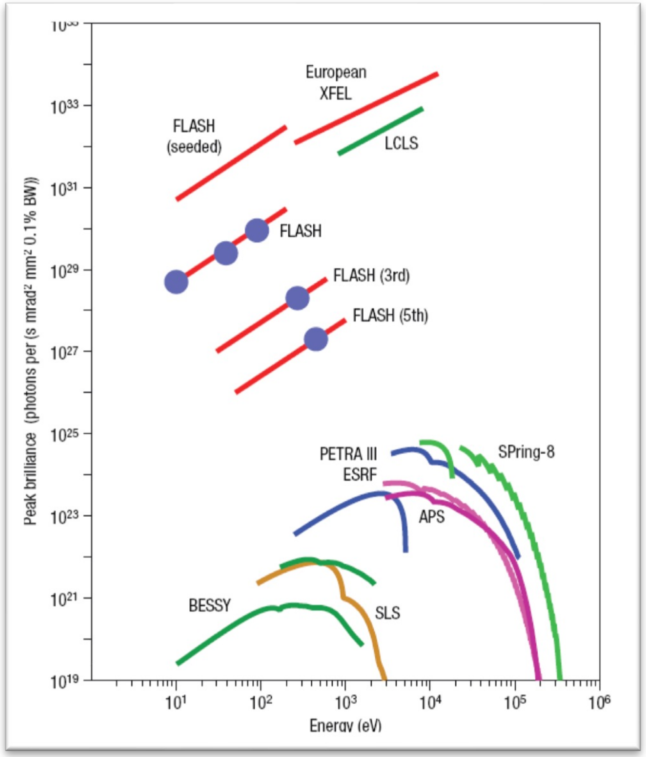
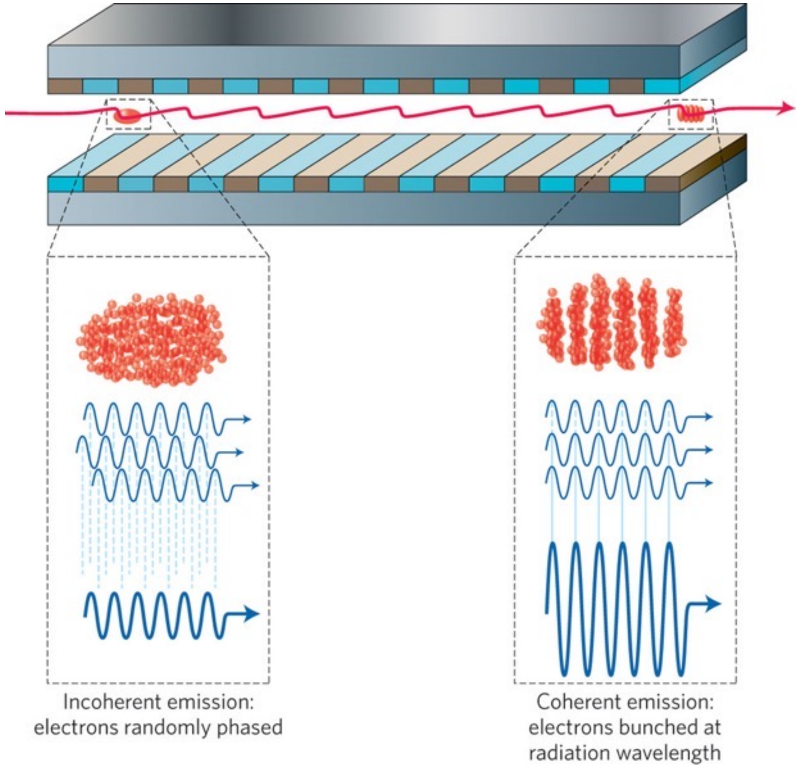
Layout and working principle of XFEL





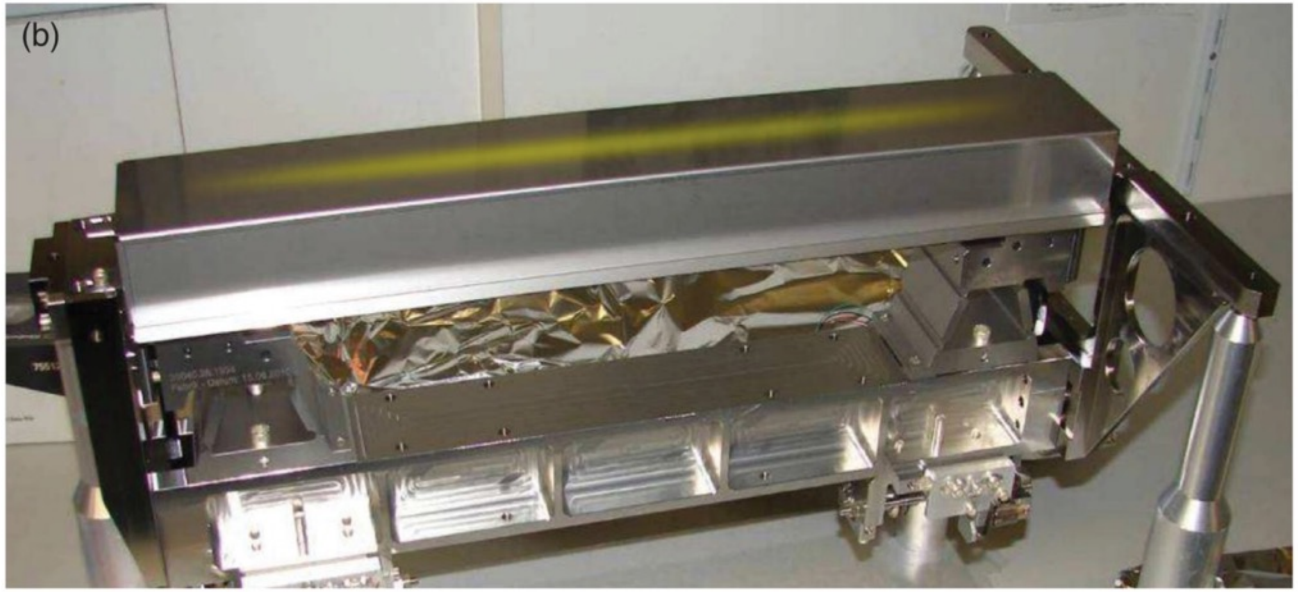


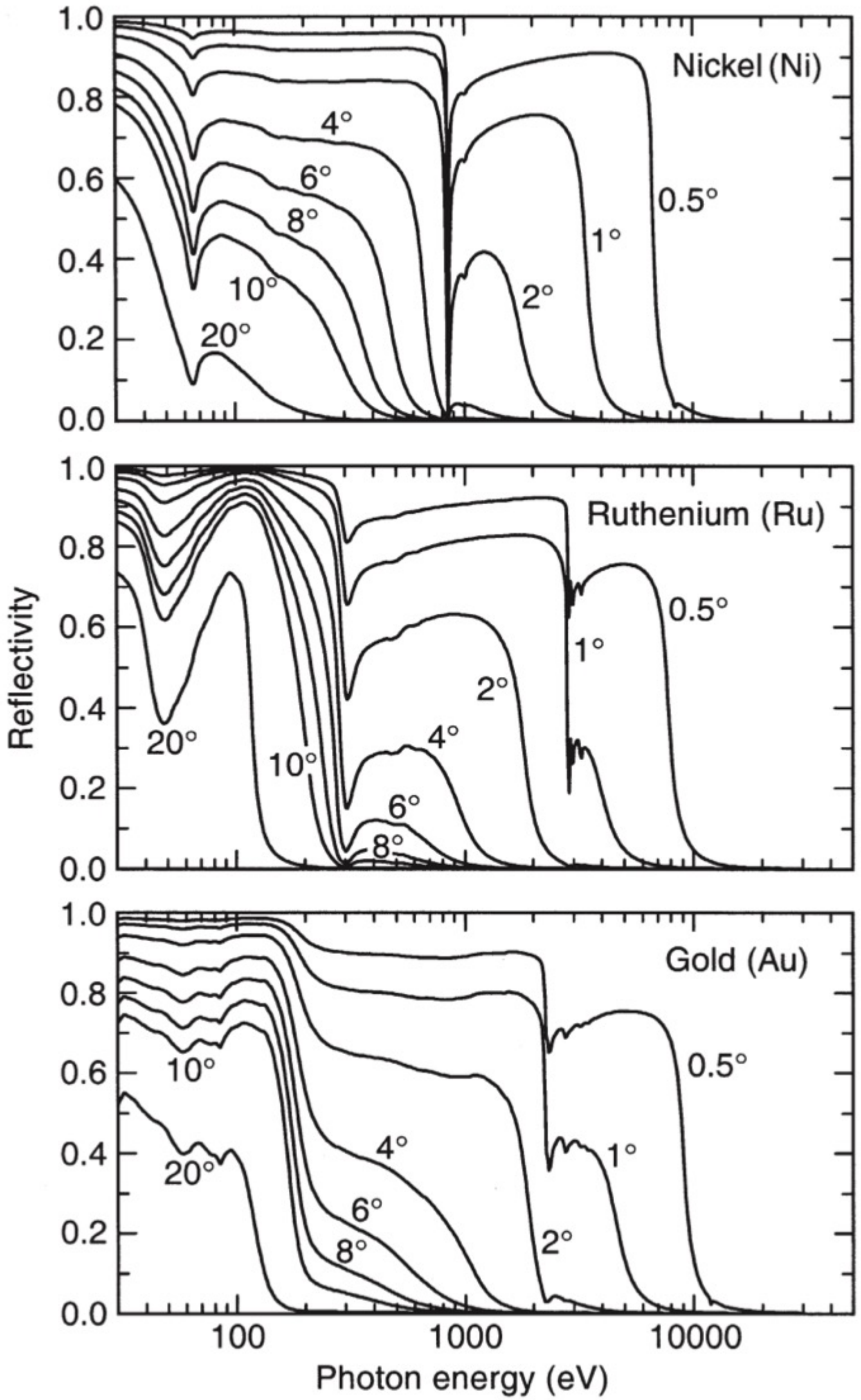
- Intensity ~ N^2
- N - # of coherently emitting electrons ~ 10^9

10^{12} X-ray photons / 100 fsec pulse

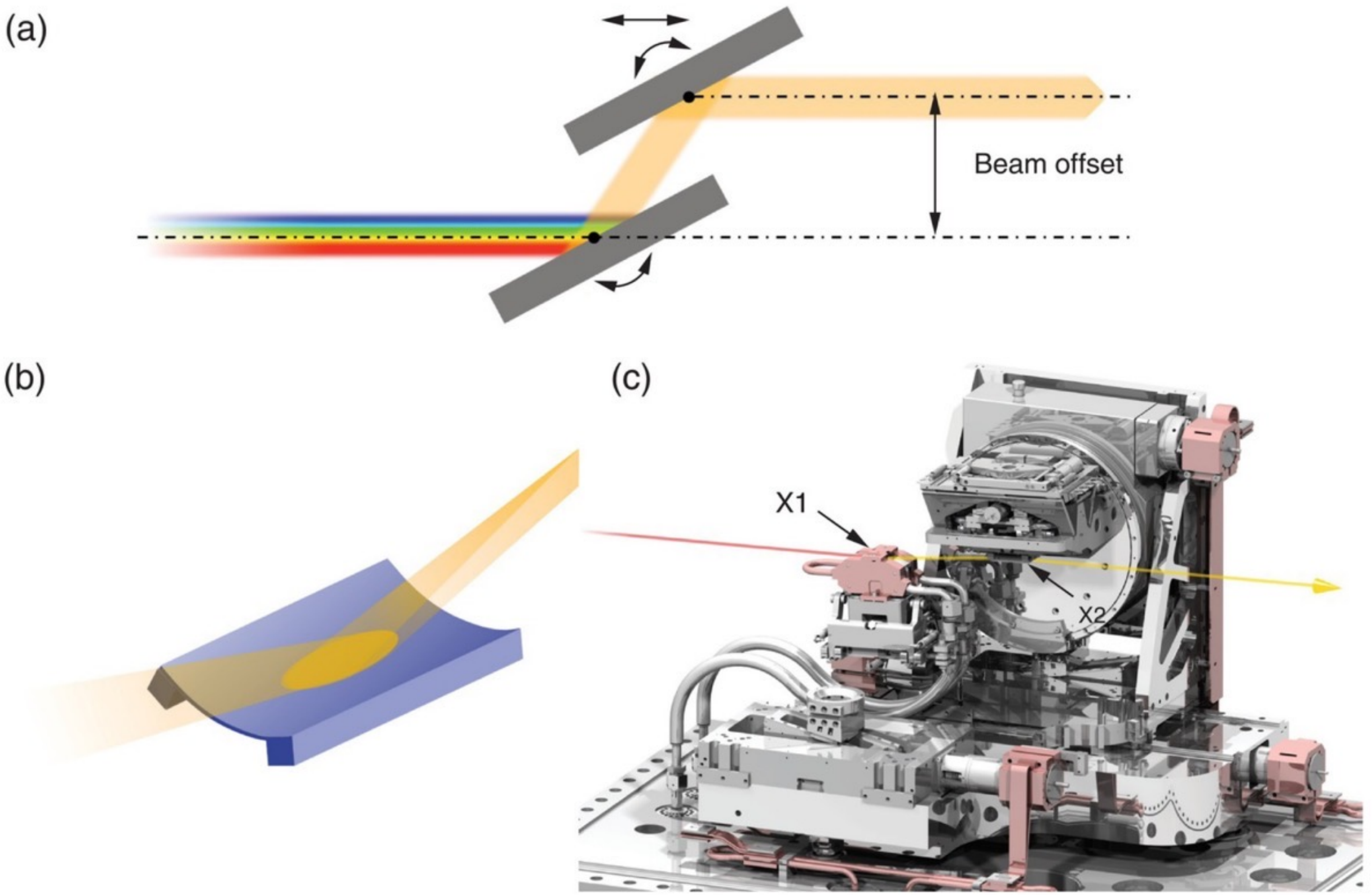
X-ray transport

Mirrors

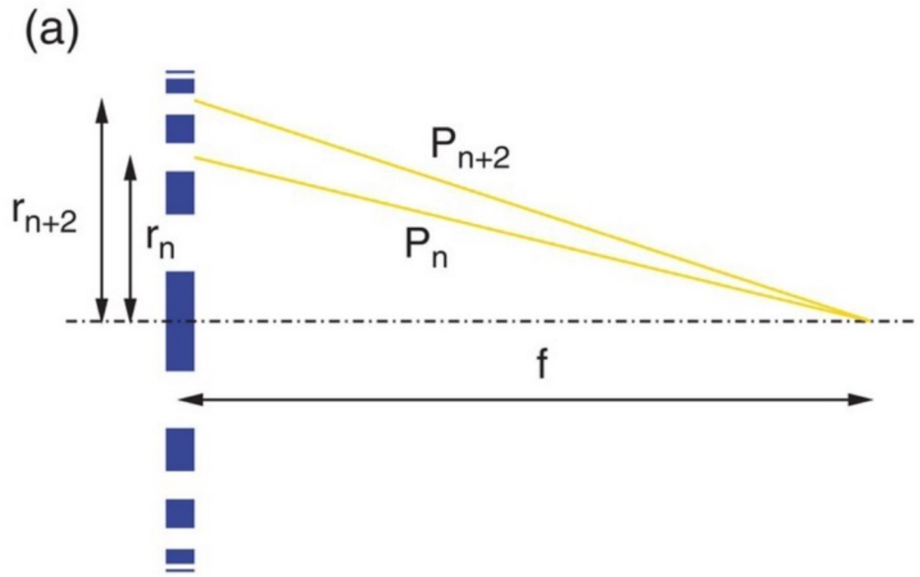

(b)

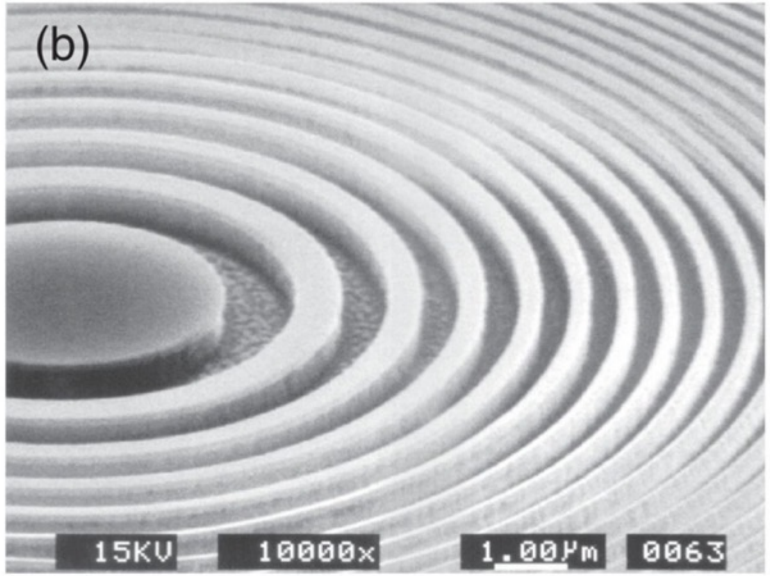

Nickel (Ni)
Ruthenium (Ru)
Gold (Au)
Reflectivity
Photon energy (eV)
0.5°
1°
2°
4°
6°
8°
10°
20°
1.0
0.8
0.6
0.4
0.2
0.0
100
1000
10000

Crystals

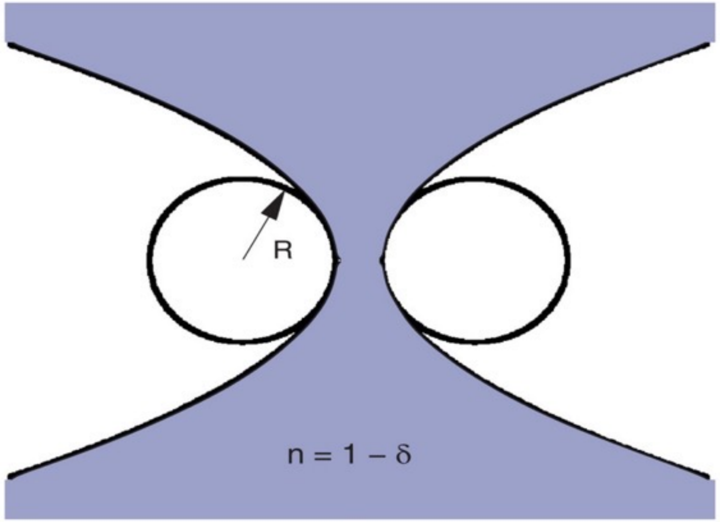


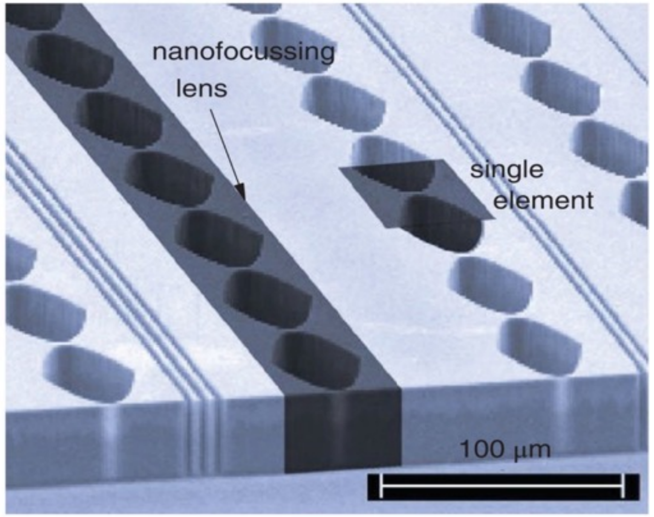
Zone plates

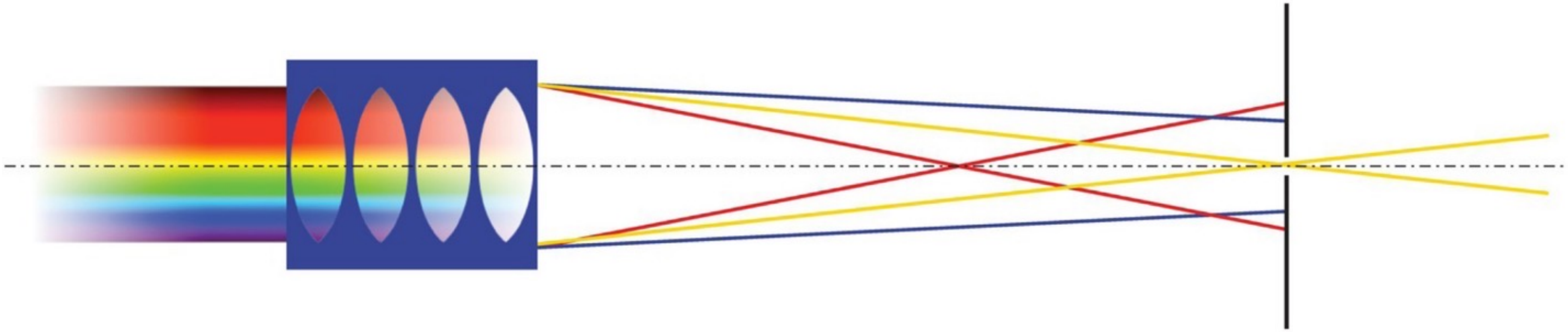




Compound refractive lenses







The end