Structural Analysis
Part III - X-ray tools

Session 1

Introduction and motivation

Contact:

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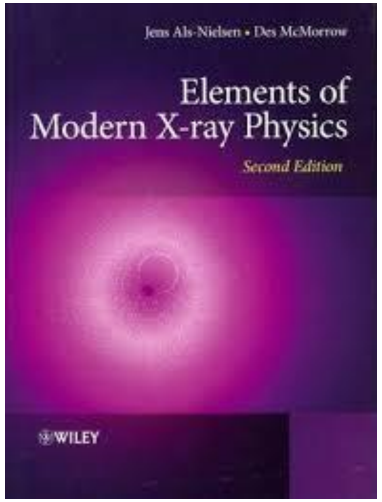
Course layout

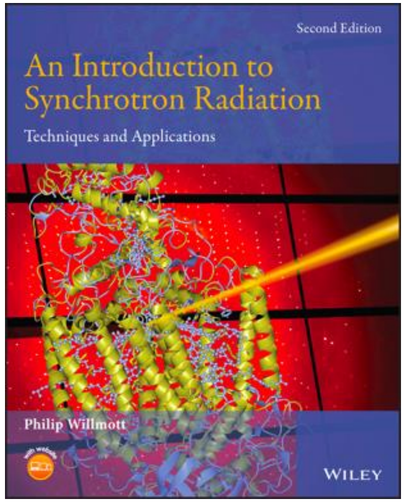
Session 1:
- Introduction to x-rays
- Very basic x-ray – matter interactions
- Sources and transport

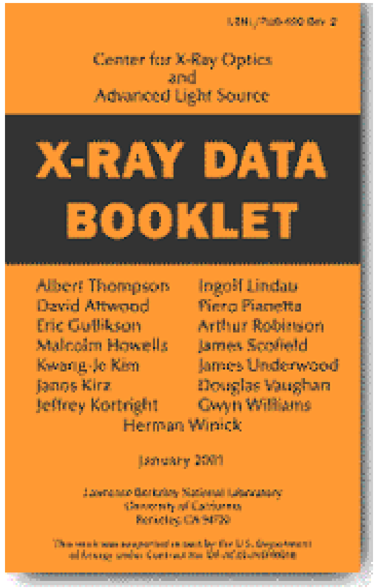
Session 2:
- X-ray diffraction in chemistry
- Diffraction, the basics
- Bragg diffcations
- Small angle scattering

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

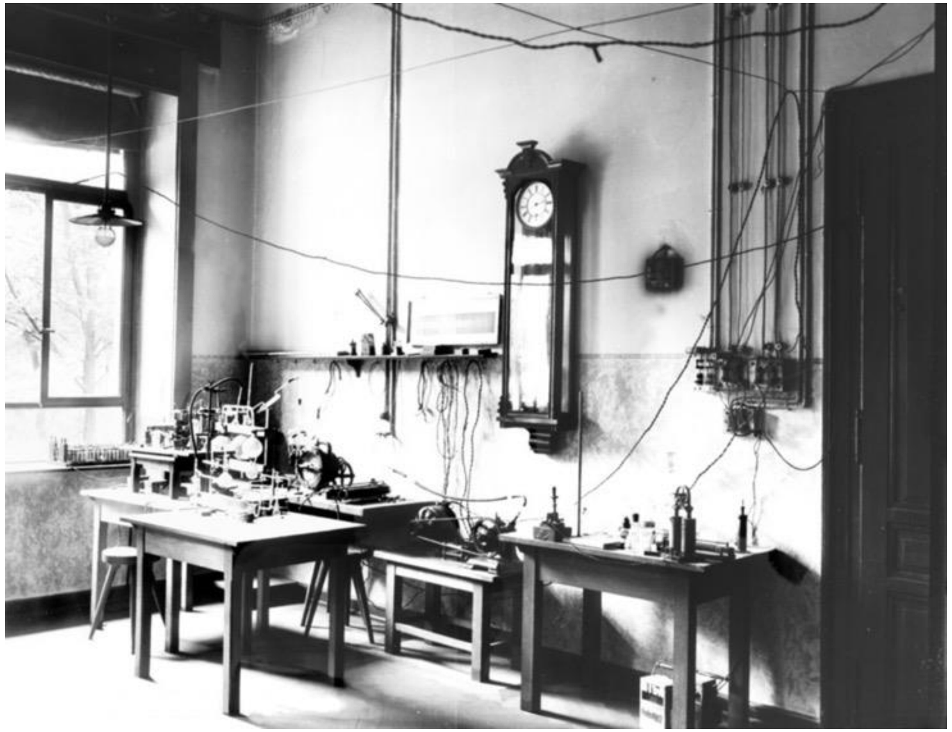






Introduction and historical perspective

The discovery of x-rays in 1895



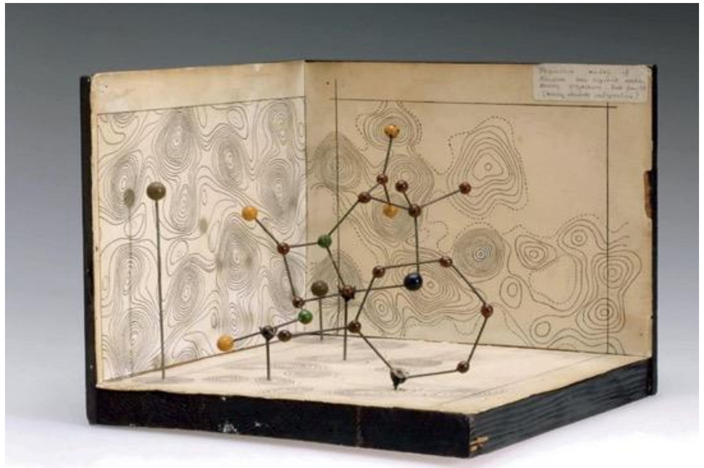
- Röntgens lab in Würzburg
- Experiments with vacuum tube
- Noticed fluorescence on a screen despite light-tight packaging of tube
- Postulated mysterios x-rays

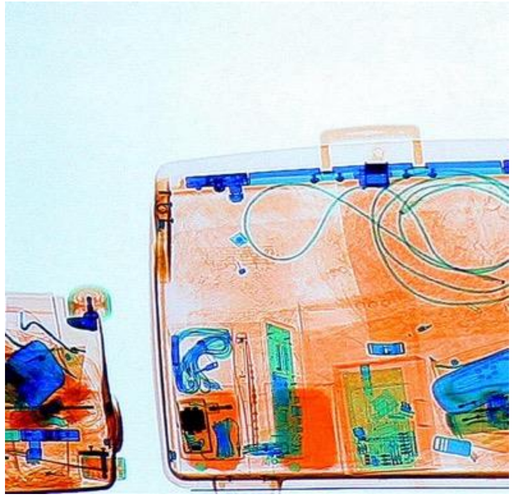
- During experiments illuminated his hand and saw bone structure
- Took first “medical” x-ray on his wifes hand
- Denied patenting request to fully exploit potential of x-rays

Discovery of X-rays triggered many technological and scientific developments

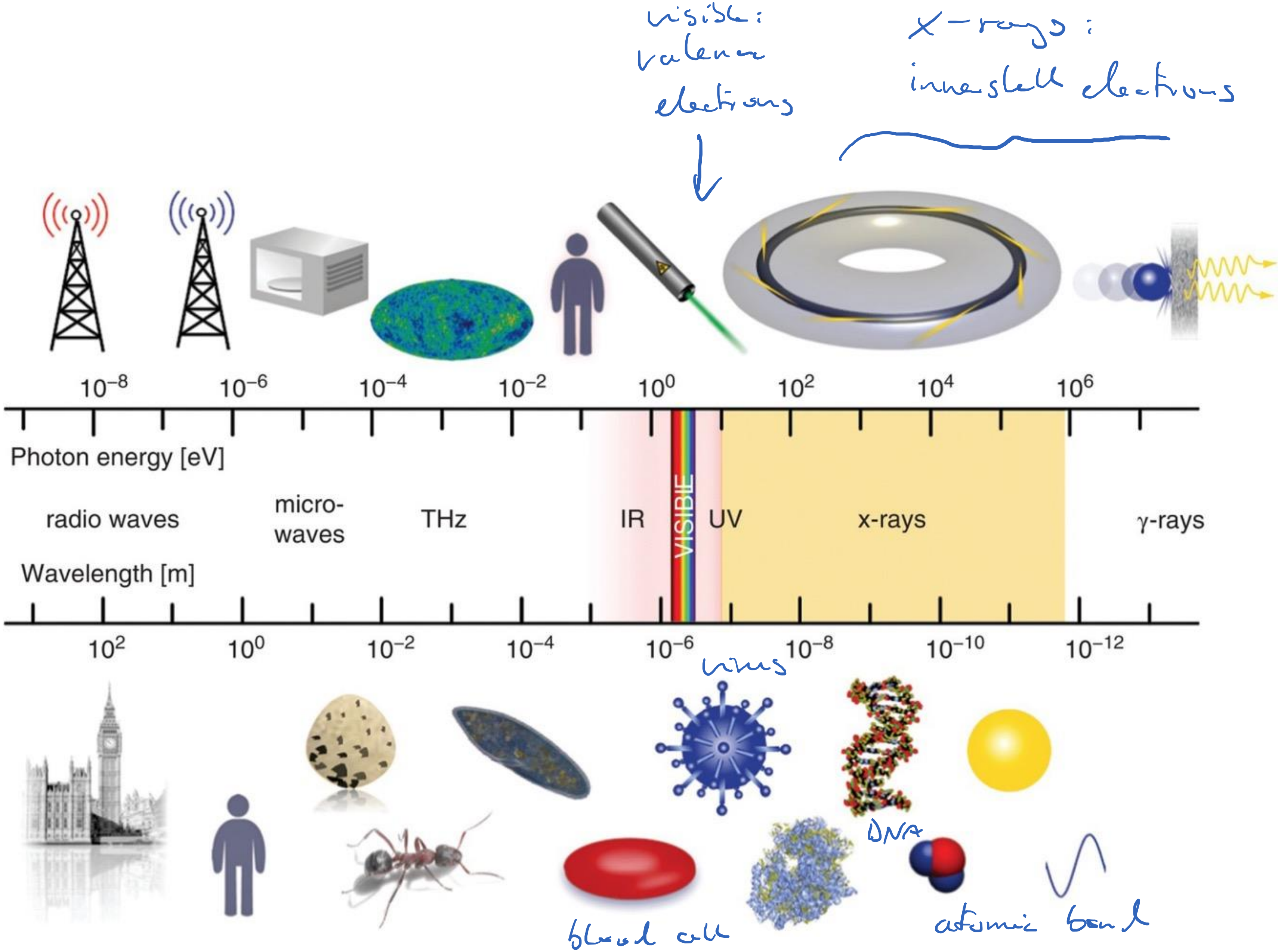
Dorothy Crowfoot
Nobel price:
Structure of penicillin
from x-ray diffraction

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.

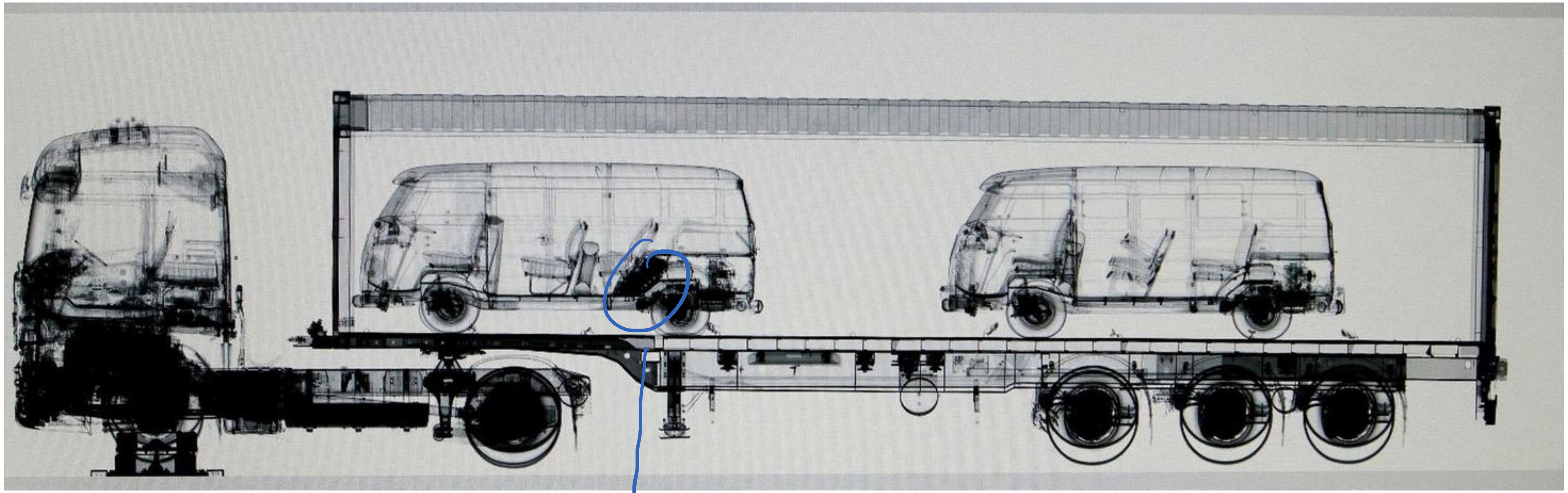
mostly physics

dominantly chemistry

The power of x-rays

X-rays – Penetration depth

(chemistry: in situ / in operando)



illegal substances

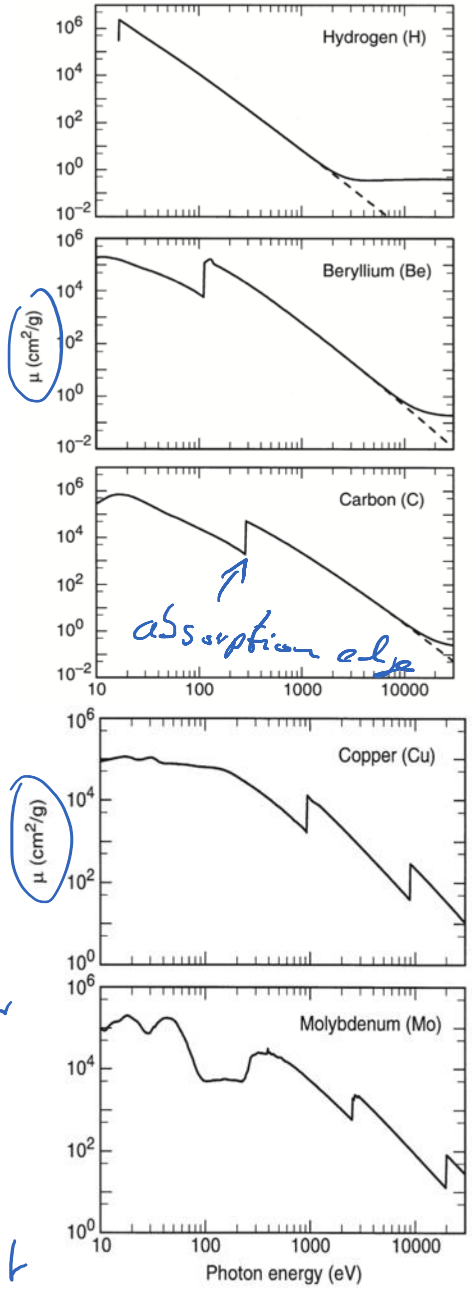


Fig. 1-5. Mass absorption coefficients (continued).

Lambert–Beer absorption law ⟺ Intensity decreases equally over unit distance

$$dI = -I \varepsilon c \, dl$$

↑ extinction factor (ε)

Extinction $\log \frac{I_0}{I} = \varepsilon c d \Rightarrow I = I_0 e^{-\mu \delta d}$

absorption coefficient (μ)

Scattering with atomic resolution

$\lambda \leq$ atomic distances

Note: $E = h\nu = \frac{hc}{\lambda} \Longleftrightarrow \lambda = \frac{12.4}{E[keV]}$ Å

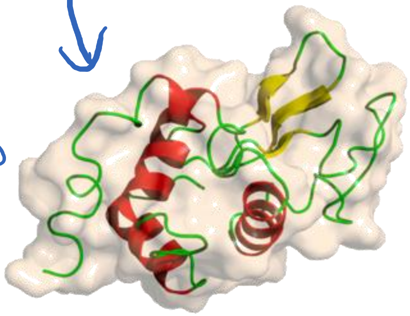
Lysozym (Protein, Immunsystem)

Stochiometric formula

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

MS

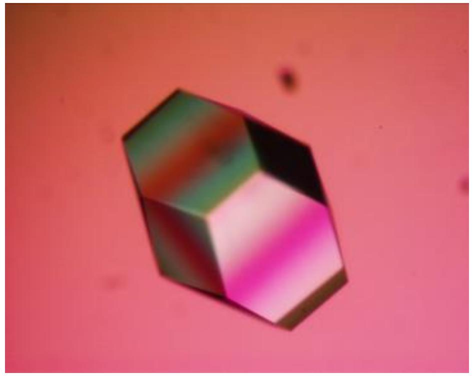
Structure



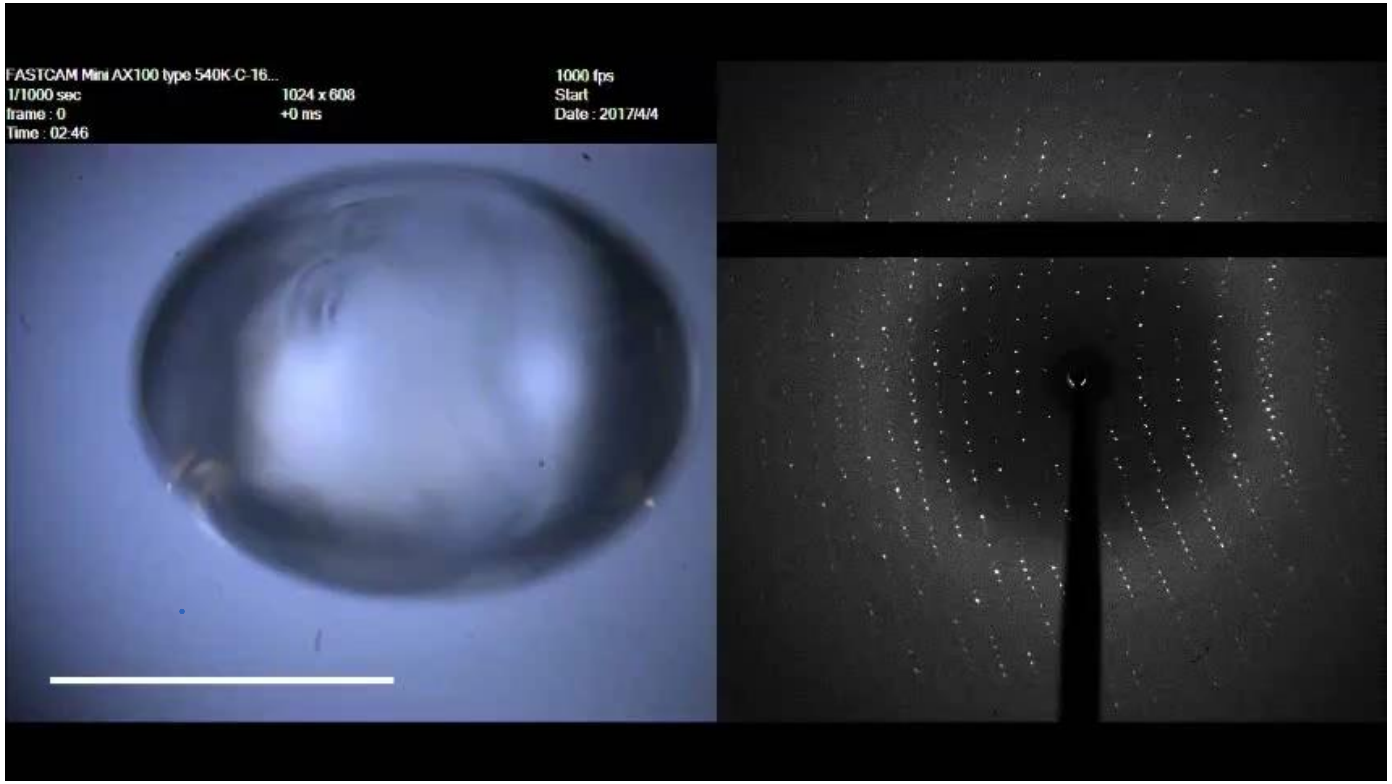
NMR

x-rays

Crystal



Experiment at the Swiss Light Source



Lysozym crystal

Bragg reflections

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

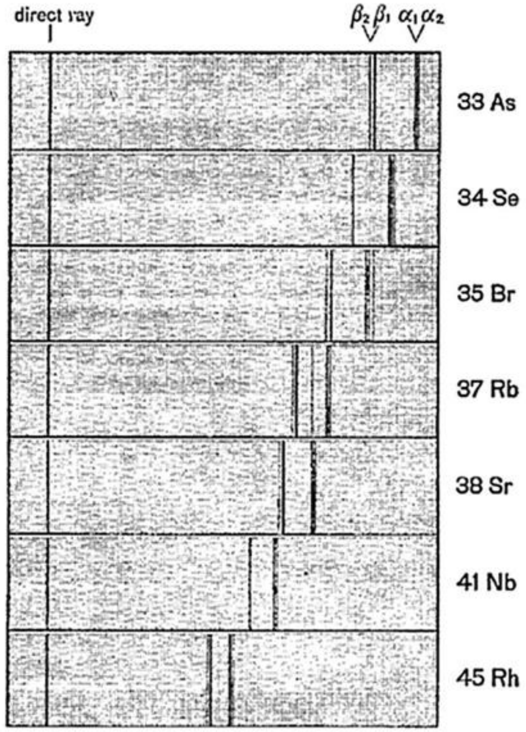
Barkla, Nobel Prize in 1917

Rose of Lausanne:
Characteristic visible colors

valence transitions

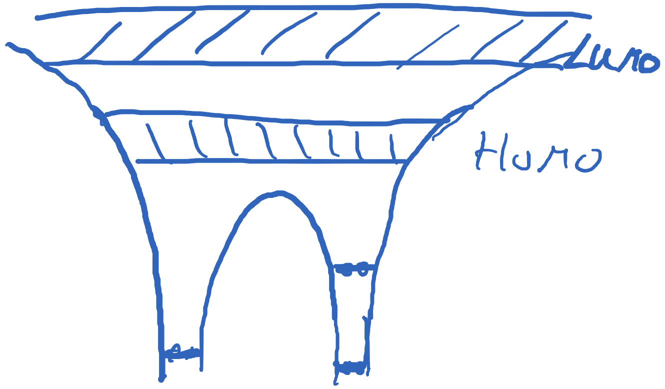
→ visible to eye

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



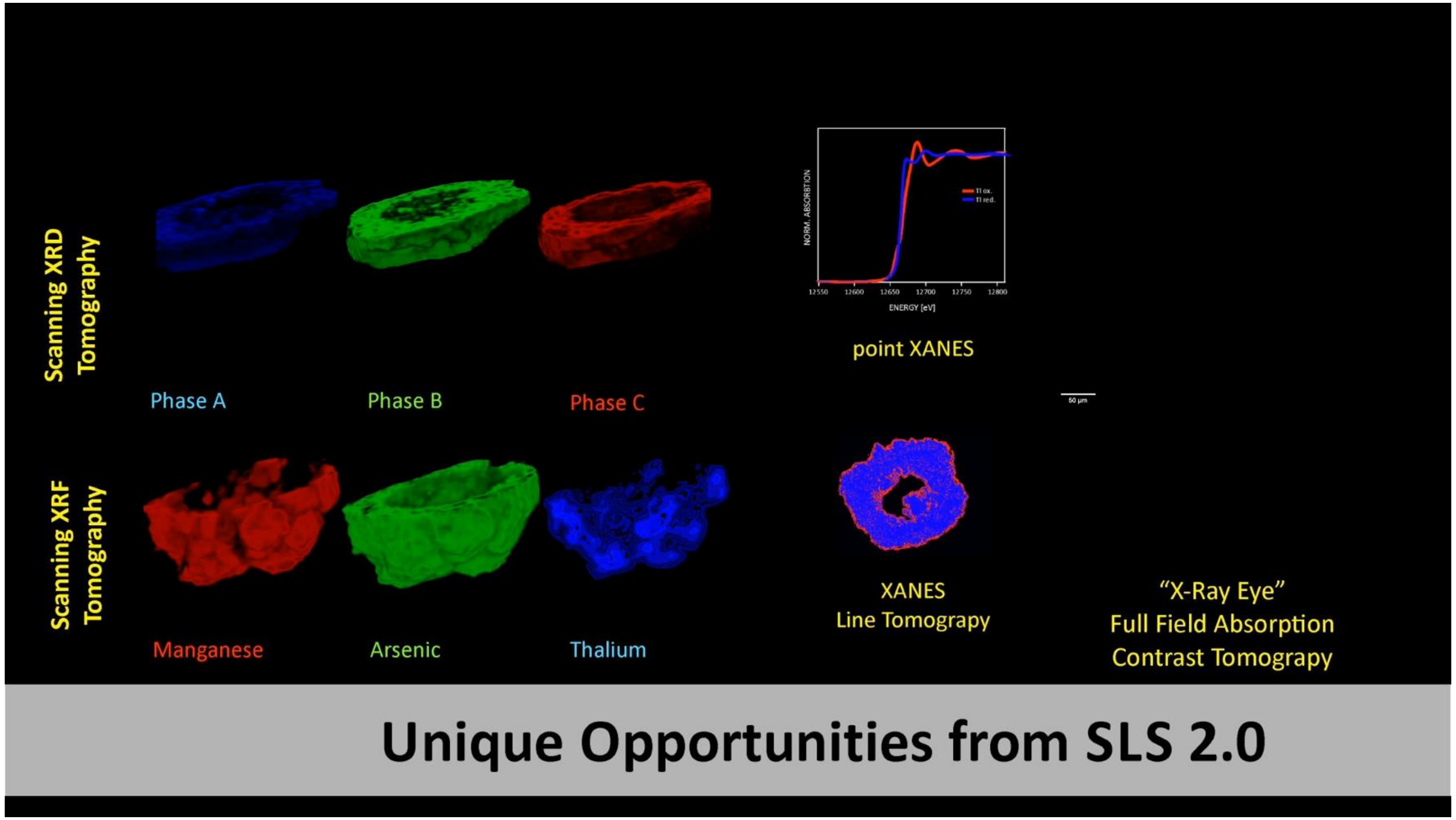
innershell transitions

→ visible to x-ray detectors



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

non-resonant

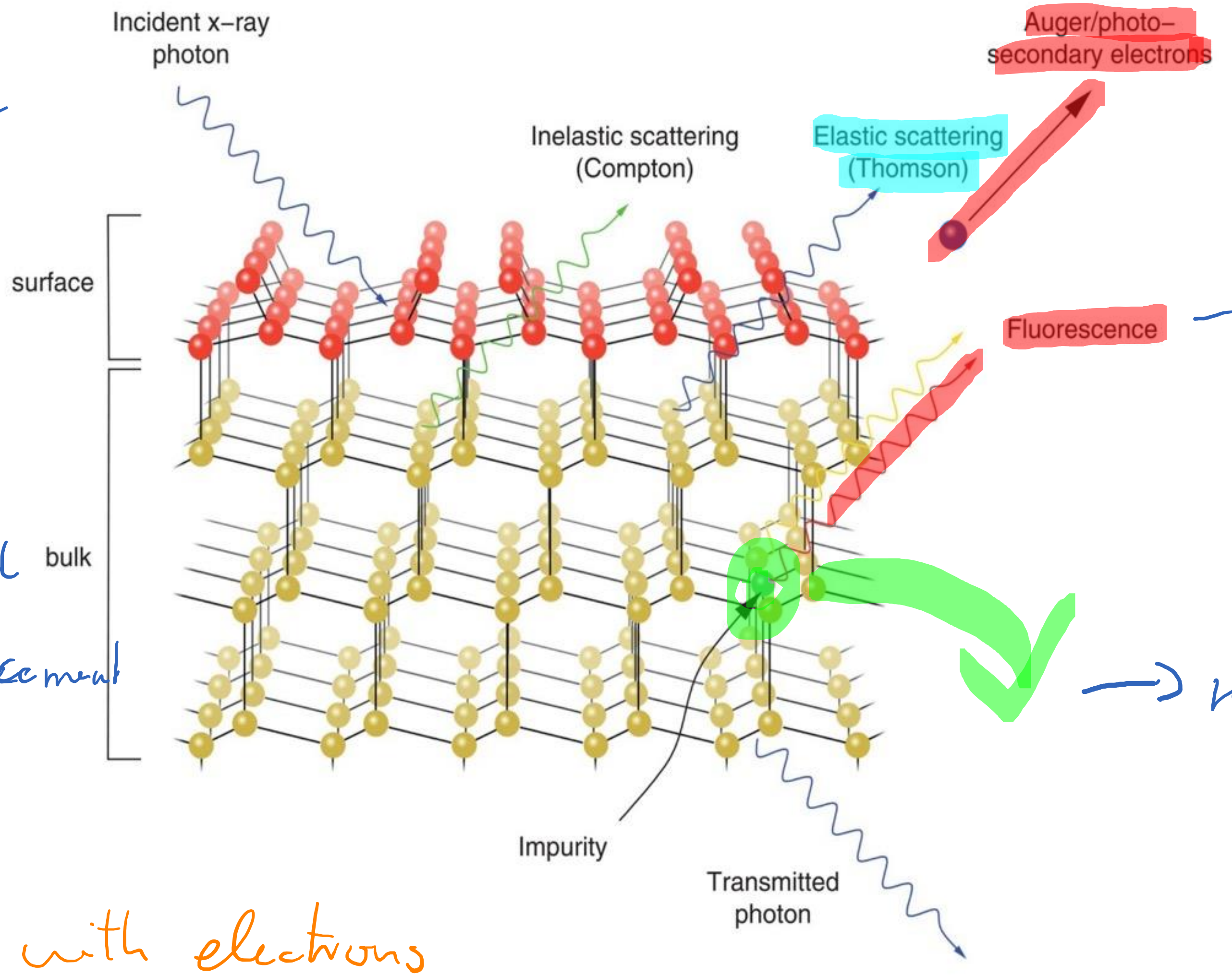
general case

cross section σ

resonant

interaction with specific core level

↳ large σ enhancement



electronic structure

↓

binding energy info

↓

local chem environment

→ resonant conditions

⇕

layer contrast

Remember:

x-rays interact with electrons (not nuclei) → dominantly innershell electrons

X-ray cross sections

→ measures probability that a specific process will take place

Barn $= 10^{-24}\ cm^2$

MBarn $= 10^{-18}\ cm^2$

Coherent Scattering (elastic scattering)

much smaller σ

⇓

starts dropping around 3 keV

$\lambda \leq$ atom

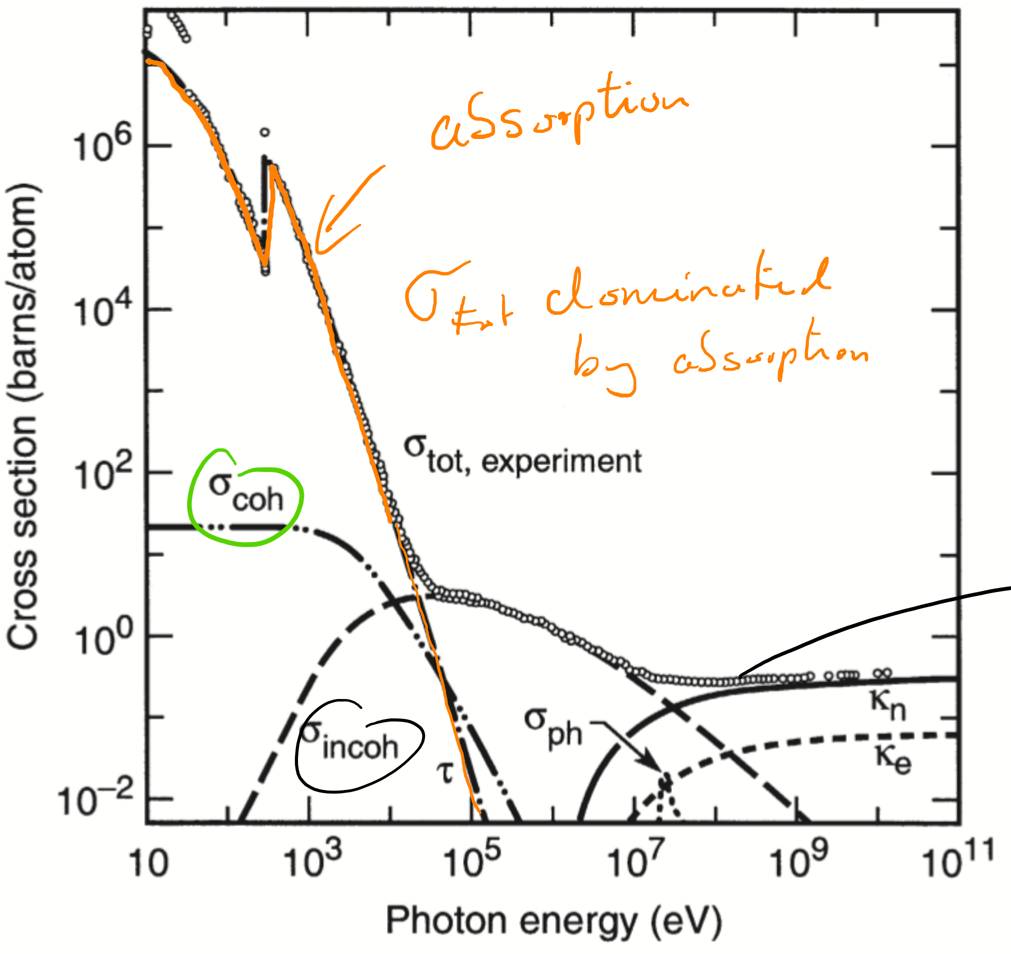
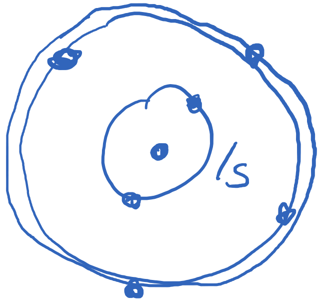


Fig. 3-1. Total photon cross section σ_{tot} in carbon, as a

Carbon: $1s^2\ 2p^2 2s^2$



valence shells

Compton scattering

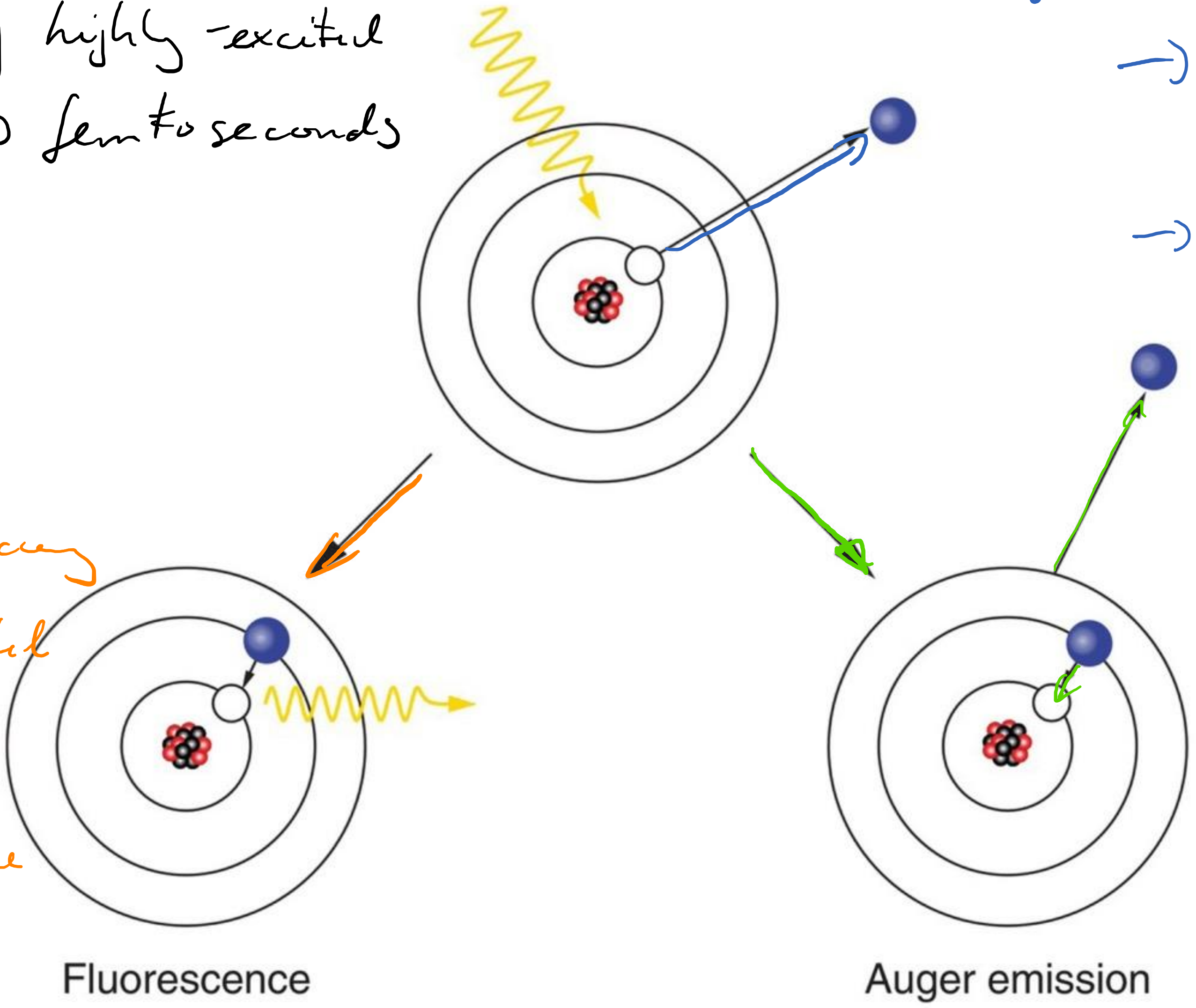
Pair production

(Physics)

Photoionization / absorption

Note: decay of highly-excited atoms → femtoseconds

Photoelectron
→ core-electron spectroscopy
$E_{kin} = h\nu - E_B$
→ electronic structure info



fluorescence decay
→ photon emitted

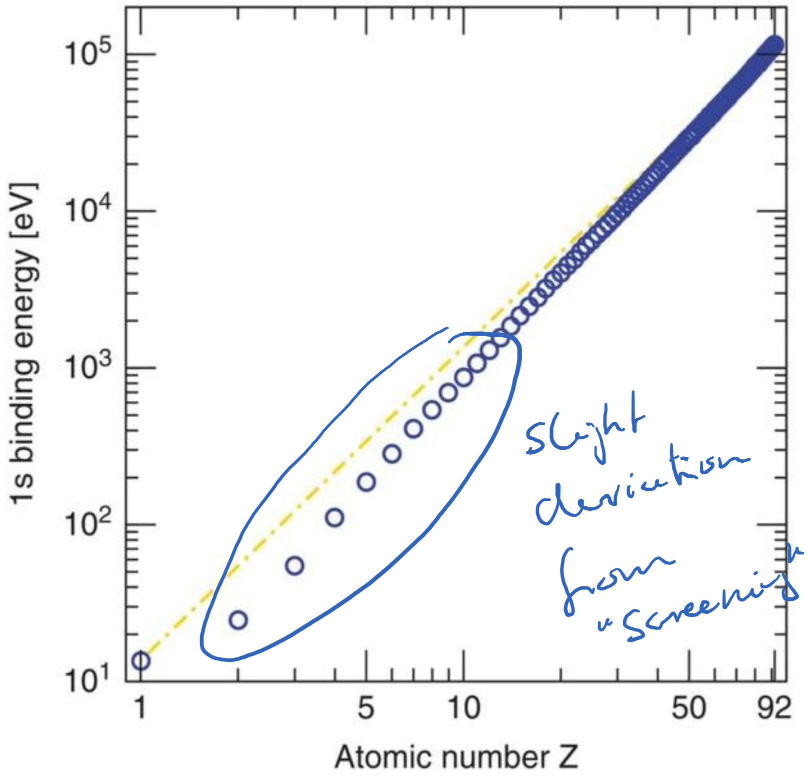
dominant in hard x-ray regime

Auger decay
→ Auger electron

⇒ Auger spectroscopy
powerful tool for elemental analysis
(element specific)

Ionization energies of elements

from X-ray data booklet



↳ 1s electrons

$\sim Z^2 \cdot 13.6\,eV$

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

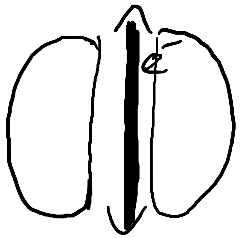
Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$	M_4 $3d_{3/2}$	M_5 $3d_{5/2}$	N_1 4s	N_2 $4p_{1/2}$
1 H	13.6										
2 He	24.6*										
3 Li	54.7*										
4 Be	111.5*										
5 B	188*										
6 C	284.2*										
7 N	409.9*	37.3*									
8 O	543.1*	41.6*									
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†				

in X-ray regime

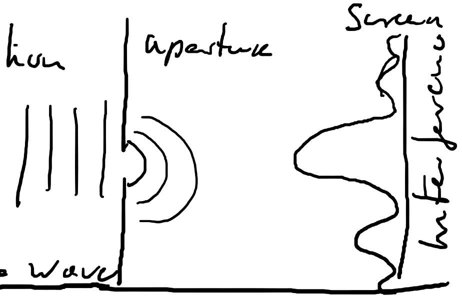
→ outer shells

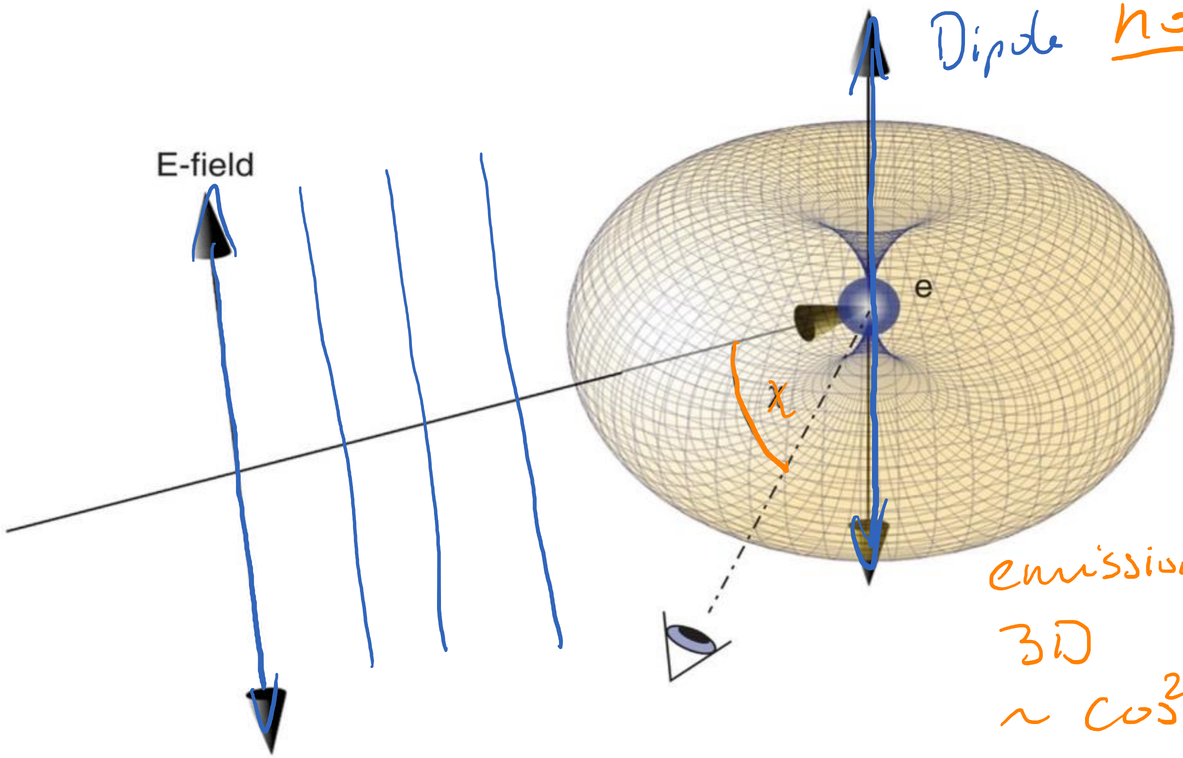
Thomson scattering

Remember from Physics: Dipole radiation



Diffraction





Dipole **no** intensity along axis

emission in 3D $\sim \cos^2\chi$

→ semi-classical description

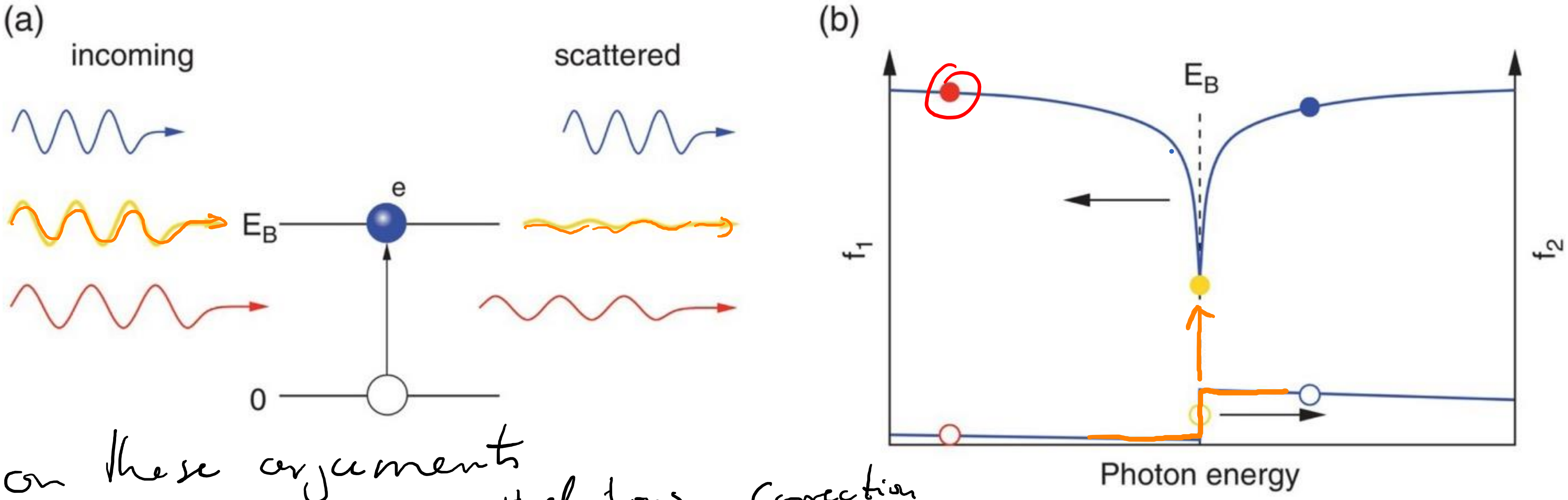
→ x-rays well approximated by planar wave

→ x-ray scattering process described by dipole radiation

Scattering process:
- transfer incoming plane wave to dipole wave
- no frequency shift → elastic
- phase shift

Atomic scattering factors → Absorption & scattering of x-rays by atoms

- Consider forced oscillator model → resonance frequency E_B
- At resonance → transfer energy into system
- Below resonance → system follows with damping



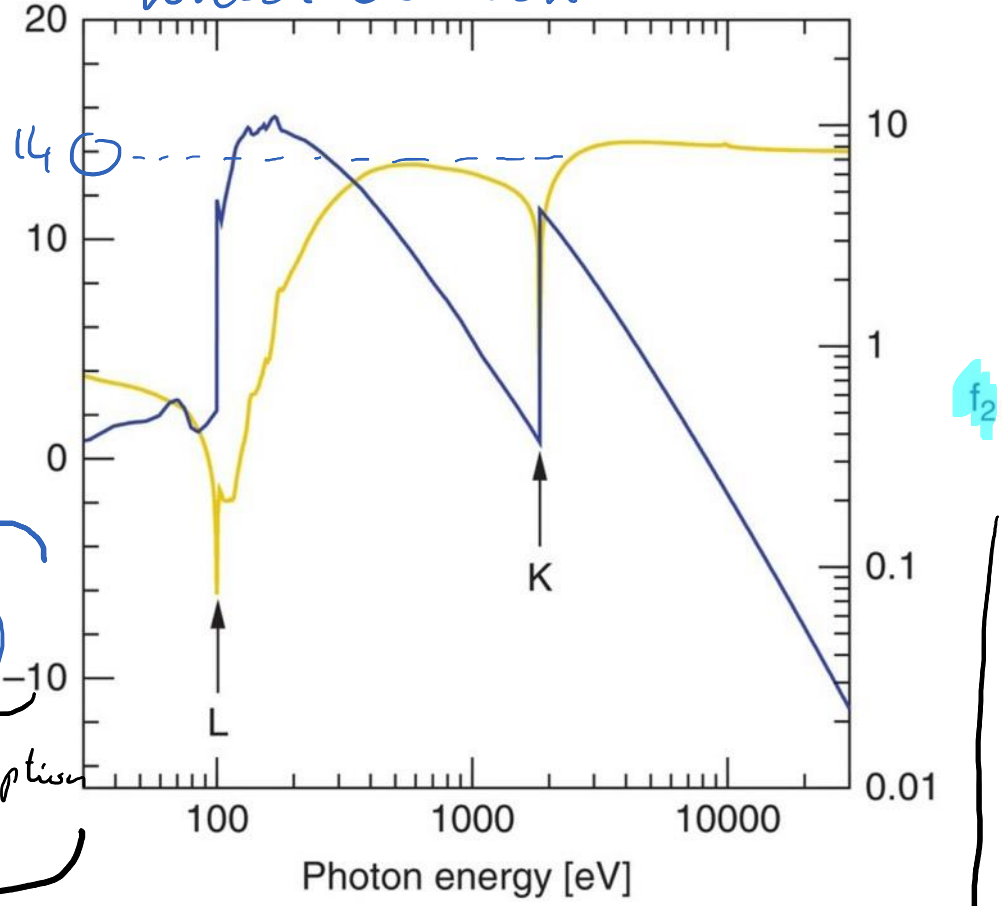
Based on these arguments

$$f(h\nu) = \underbrace{\overbrace{f^0}^{\#\text{ electrons}} + \overbrace{f'(h\nu)}^{\text{correction}}}_{\text{scattering}} + \underbrace{i f''(h\nu)}_{\text{absorption}}$$

Note:
Real story more complicated but ok for now

Atomic scattering factors and refractive index

which element?



$\Rightarrow f_1 \sim$ # electrons

$\Rightarrow 14$

$\Rightarrow 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^2$

$\Rightarrow$ Si

$\Rightarrow$ double check with absorption edge / f_2

$$f(h\nu) = \underbrace{f_0 + f'(h\nu)}_{f_1} + i\,\underbrace{f''(h\nu)}_{f_2}$$

$f_0 + f'(h\nu)$: # electrons

$f''(h\nu)$: absorption

x-ray analogue to "refraction index"

Relevance

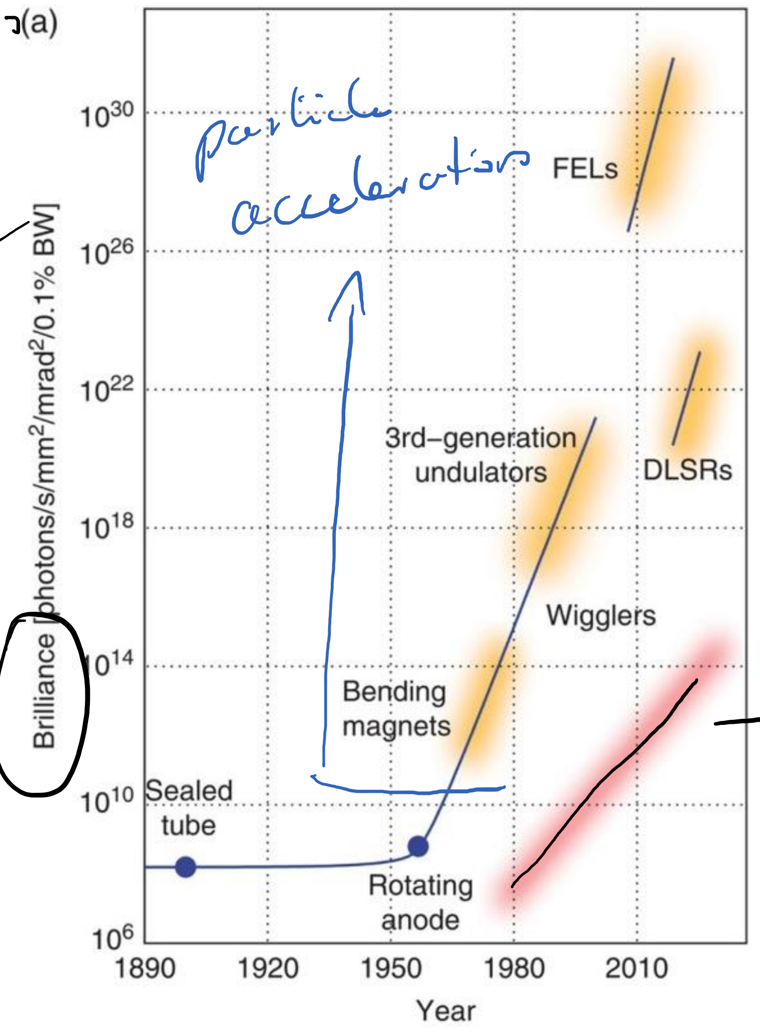
absorption → electronic levels

scattering → electronic information

X-ray sources

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

Note gain of 20 orders of magnitude since 1950s



~ # photons that arrive in your experiment

→ free electron lasers

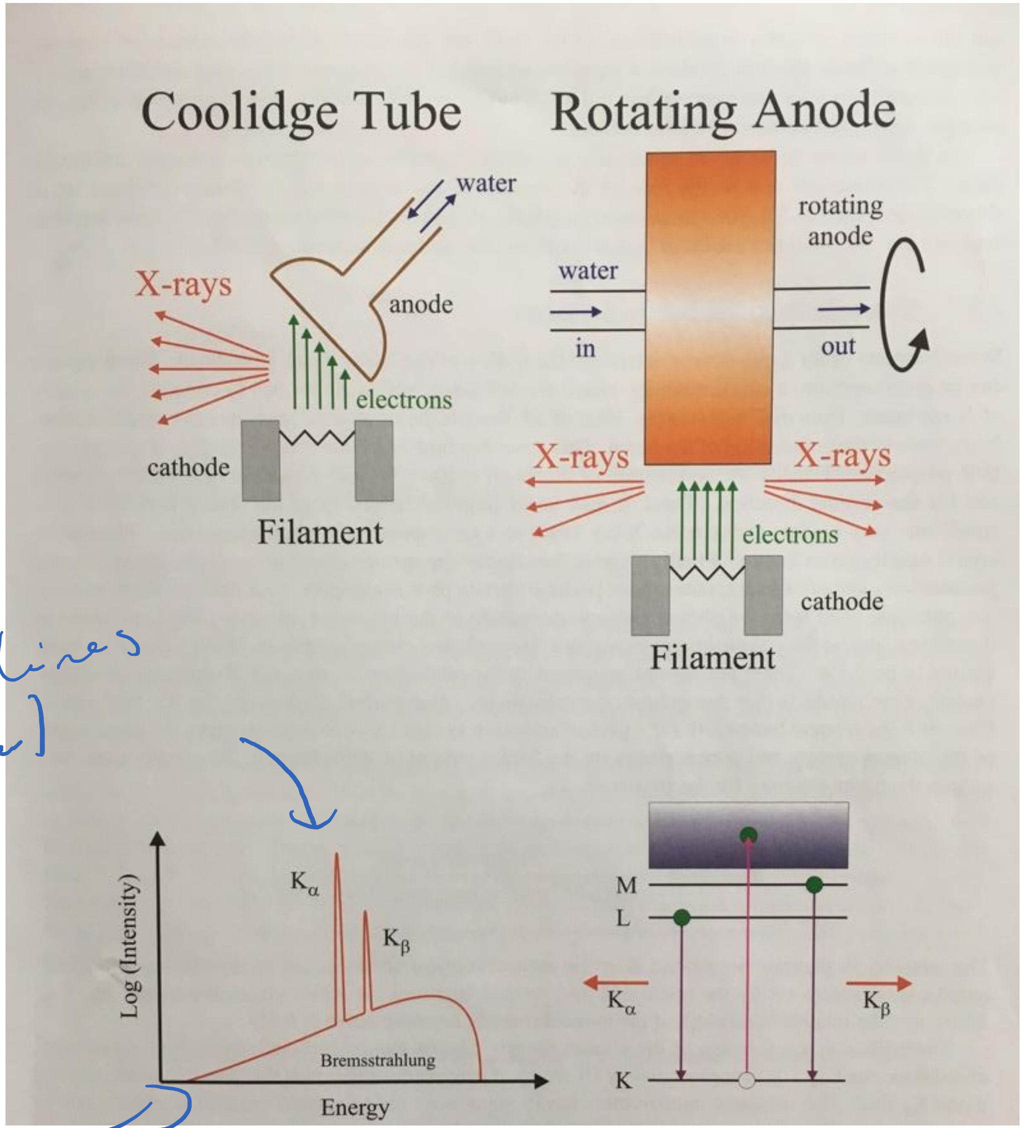
↑ shift in technology

→ synchrotron radiation sources

→ Moore's Law for reference

(Rotating) anode sources

→ Lab source , shoot electrons in materials



emission lines (Barkla)

continuous background

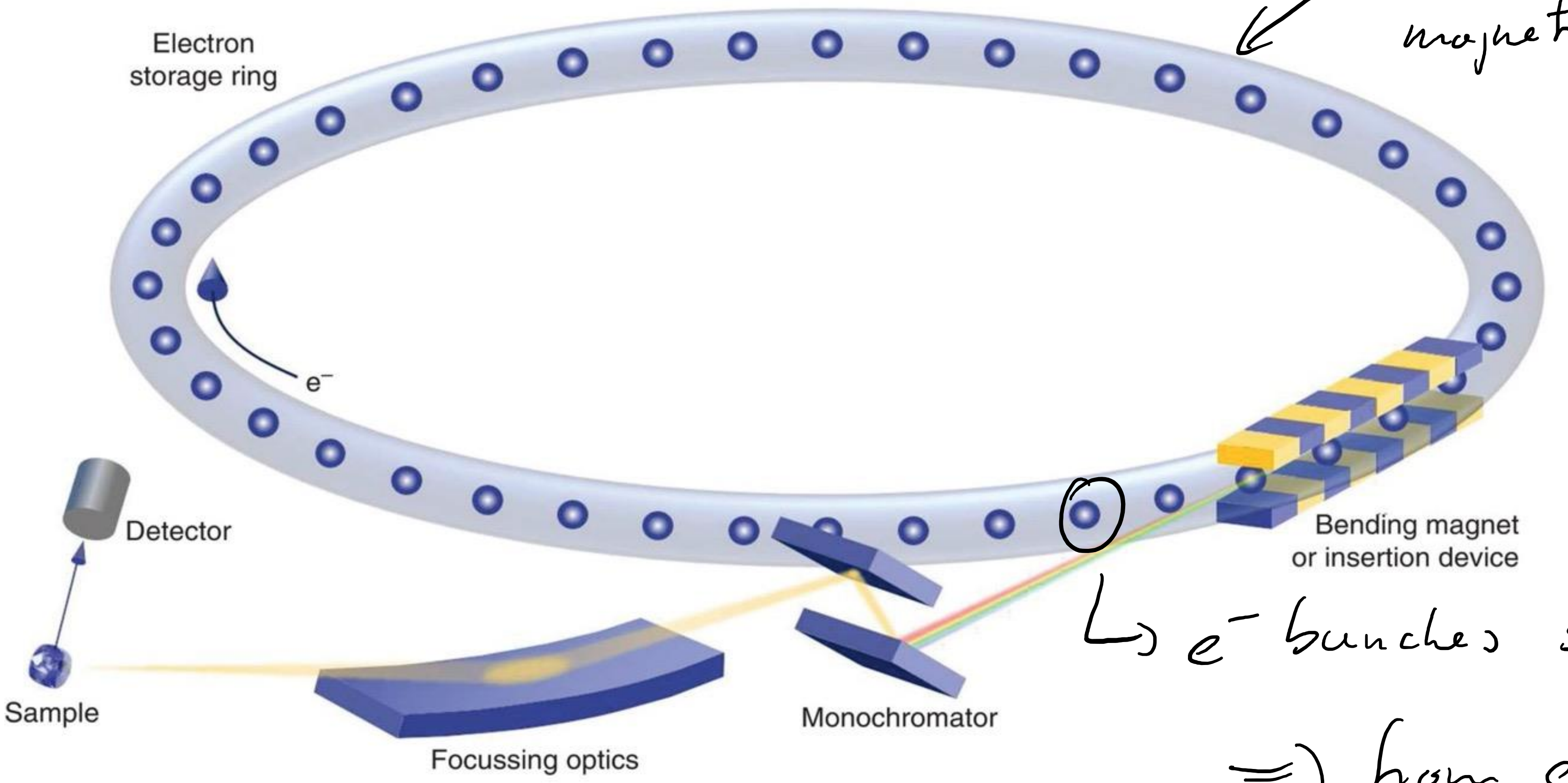
X-ray laboratory sources at EPFL

Note
elective course in Master's programme

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

Synchrotron radiation source

↓
storage ring



bend magnets

↳ e^- bunches stored in synchrotron

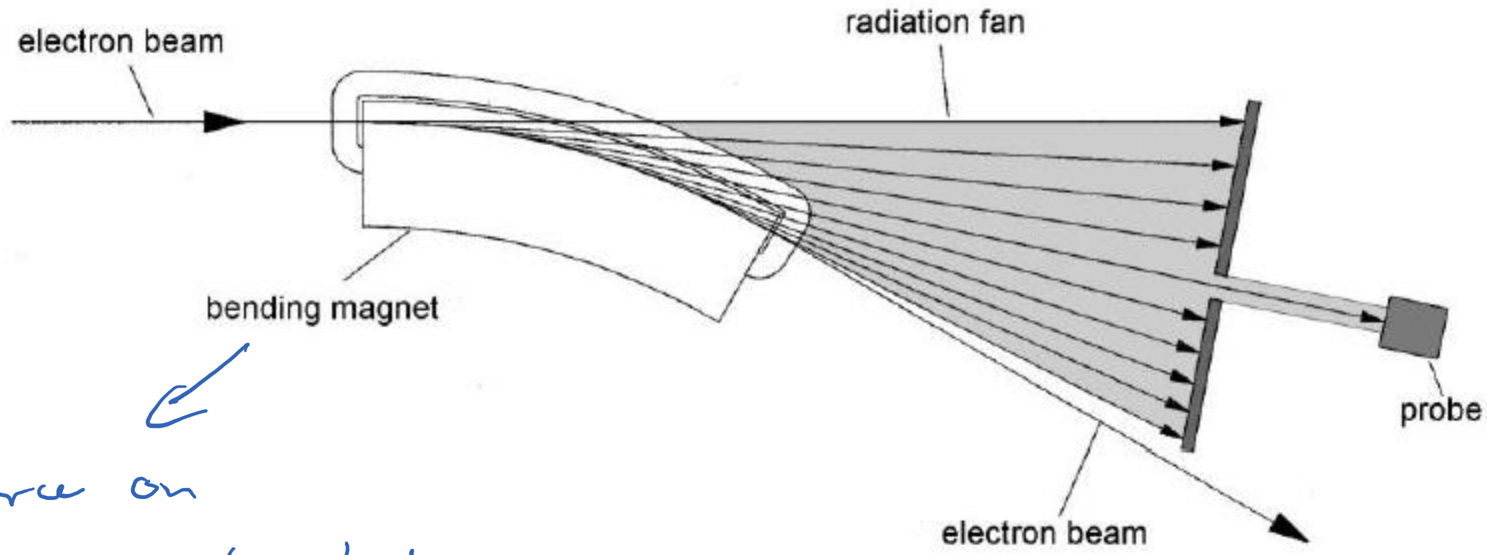
⇒ from electro-dynamics: accelerated charges radiate

Aerial view of Paul-Scherrer-Institute

SLS: Swiss Light Source

SLS: 5 exps fully focussed on chem research

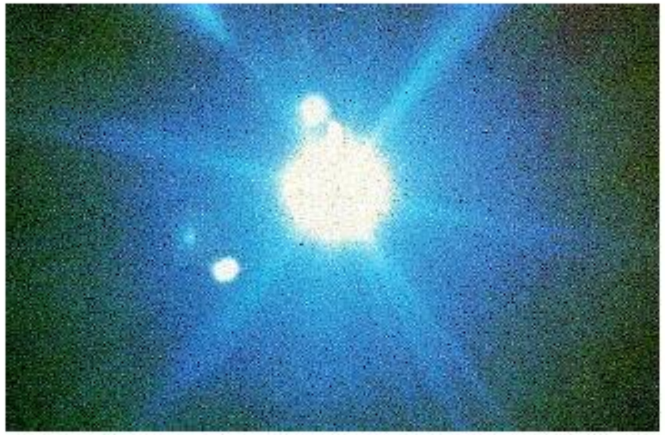
Synchrotron radiation: The idea



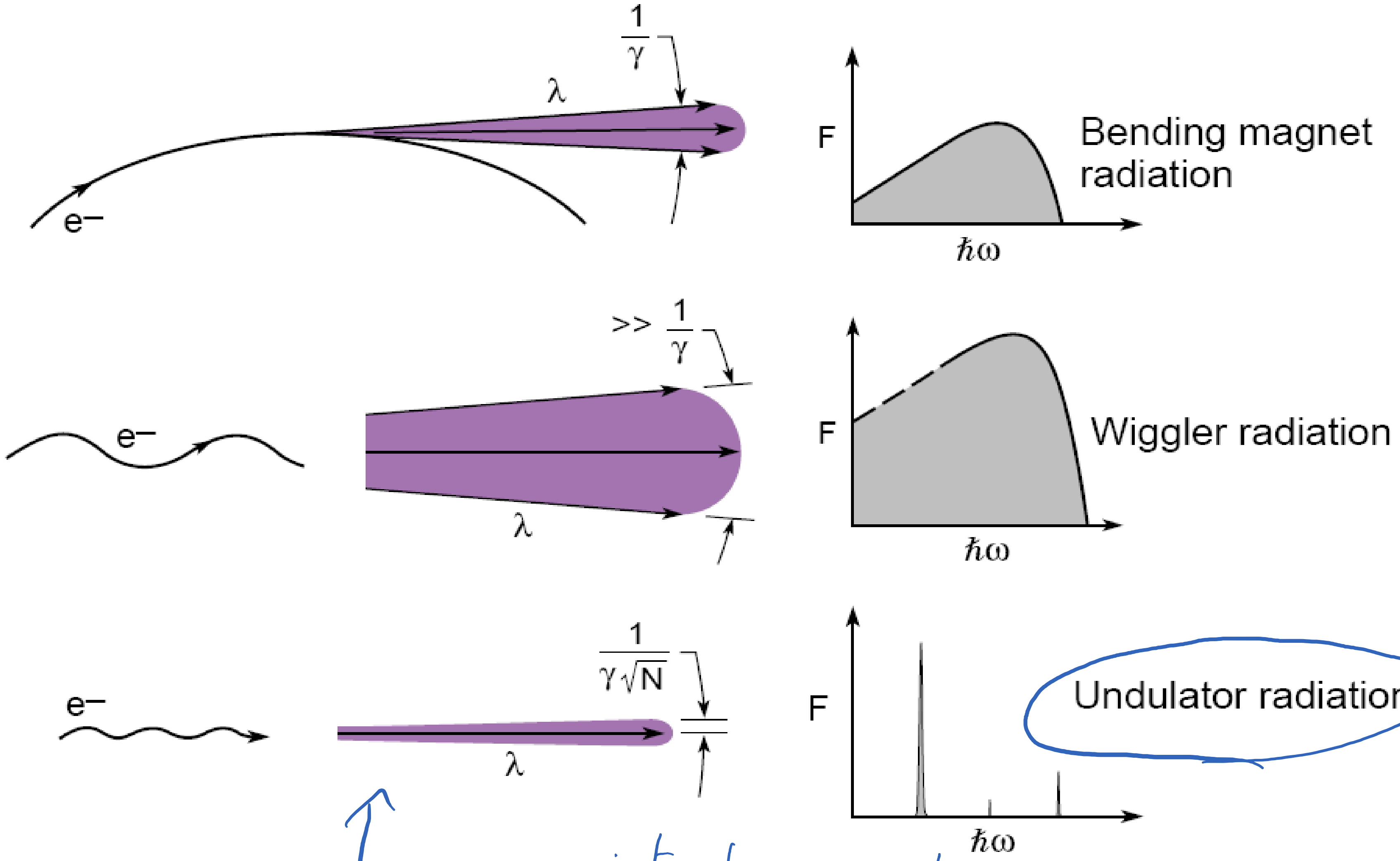
Lorentz force on electrons → accelerated

S.r.: visible to hard x-rays

Light point of synchrotron radiation (close to white light)



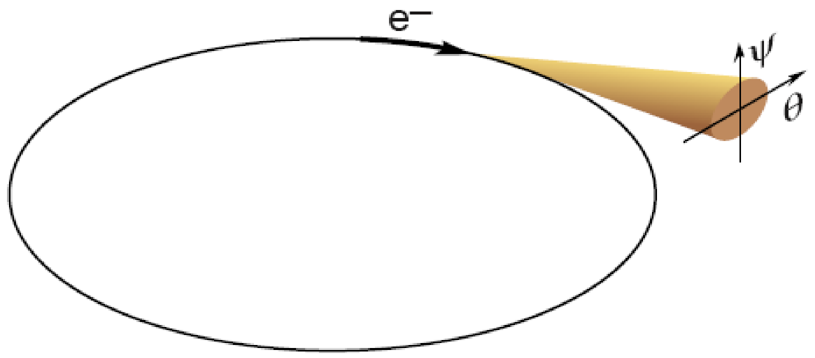
Three type of sources in synchrotron radiation storage ring:



intense, with sharp max

use interference phenomena → constructive interference

Bending magnet source



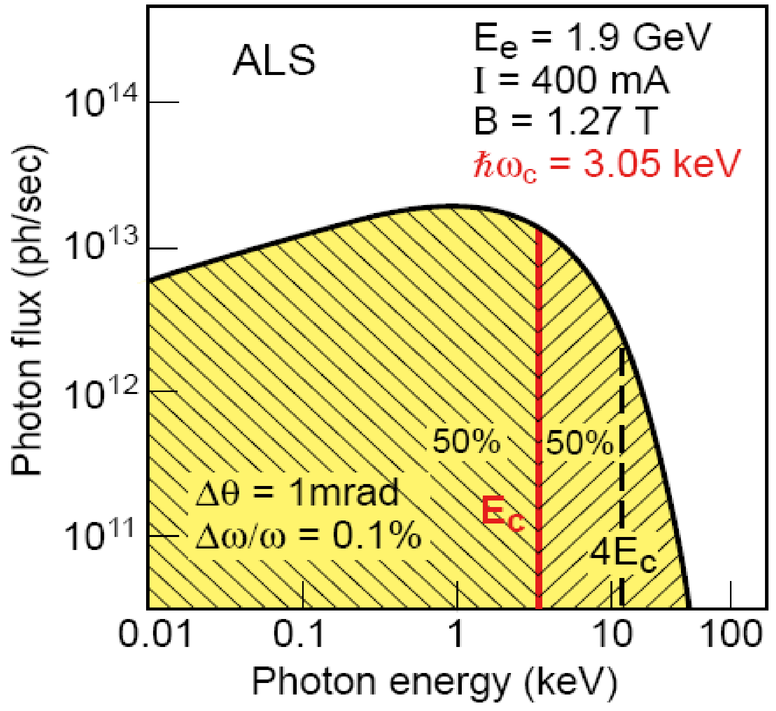
$$E_c = \hbar\omega_c = \frac{3e\hbar B\gamma^2}{2m} \qquad (5.7a)$$

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

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

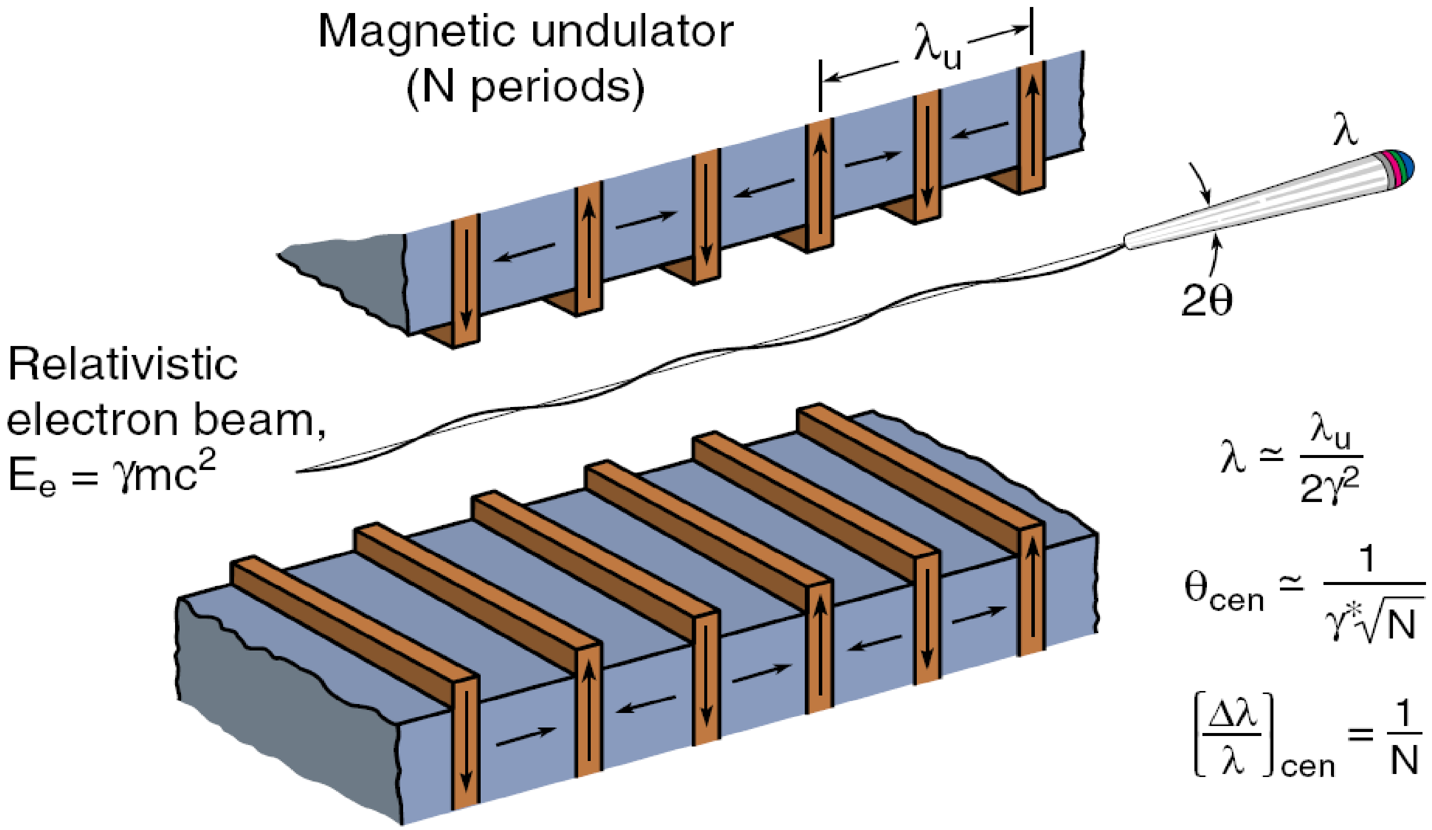
Advantages:
- covers broad spectral range
- least expensive
- most accessable

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



ω_c divides spectrum into two parts of equal power

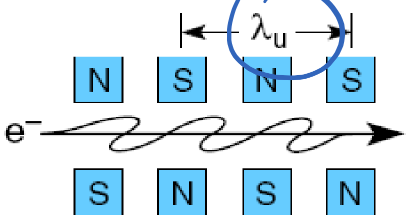
Undulator source



Undulator source – explained in a nutshell

keV x-rays

Laboratory Frame of Reference



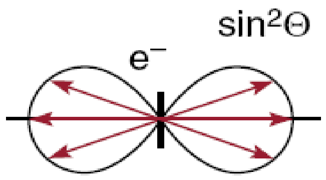
$E = \gamma mc^2$

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

N = # periods

relativistic conditions

Frame of Moving e⁻



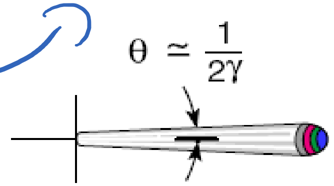
e^- radiates at the Lorentz contracted wavelength:

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

Bandwidth:

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

Frame of Observer



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:

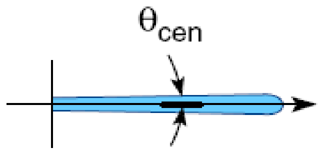
$$\lambda = \frac{\lambda_u}{2\gamma^2}\left(1 + \frac{K^2}{2} + \gamma^2\theta^2\right)$$

λ_u *magnetic field*

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

energy

Following Monochromator



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

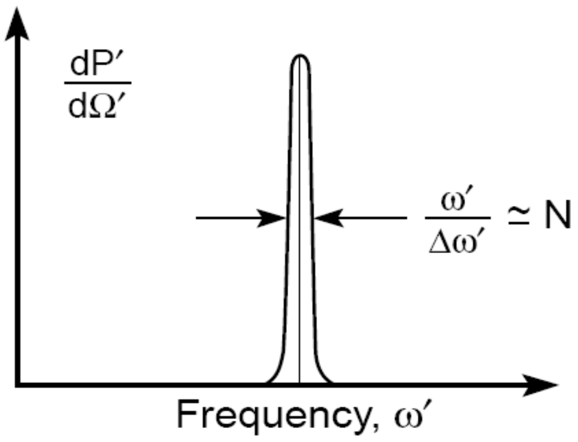
$$\theta_{cen} \simeq \frac{1}{\gamma\sqrt{N}}$$

typically

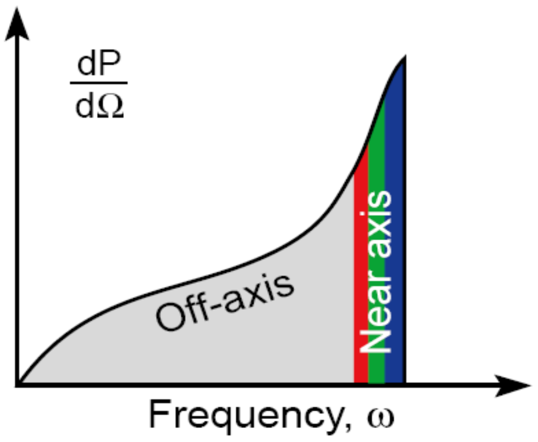
$\theta_{cen} \simeq$ 40 rad

Note: two Lorentz transformations

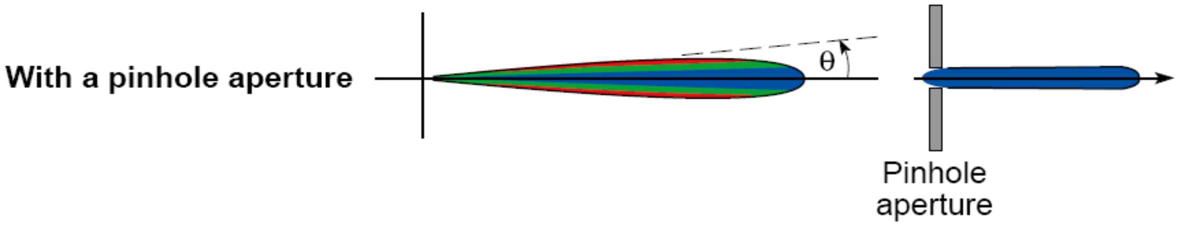
Undulator source – a final note

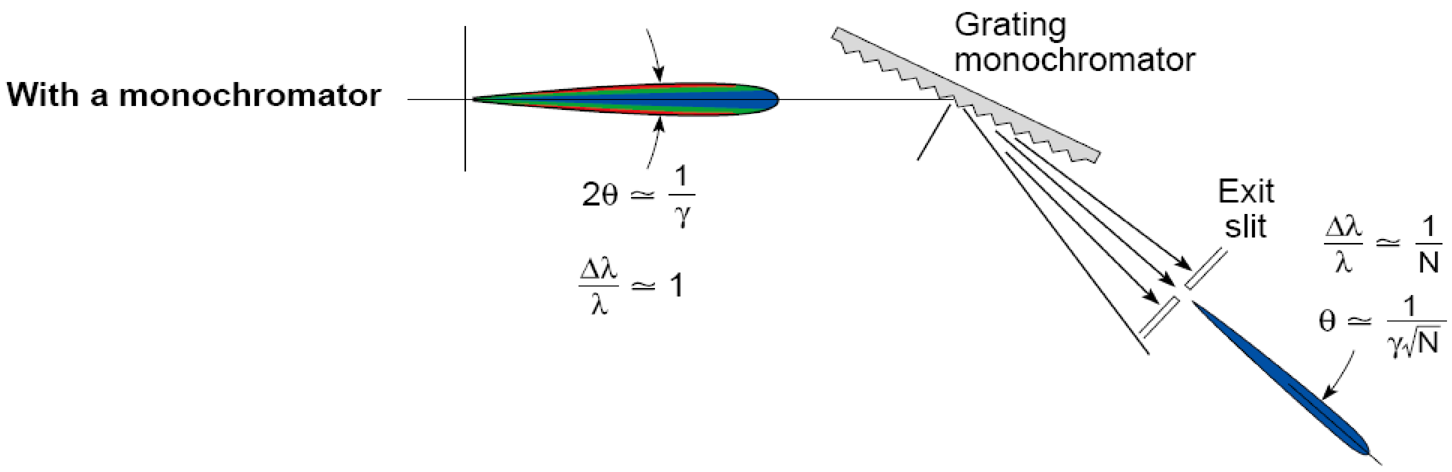


Execution of N electron oscillations produces a transform-limited spectral bandwidth, $\Delta\omega'/\omega' = 1/N$.

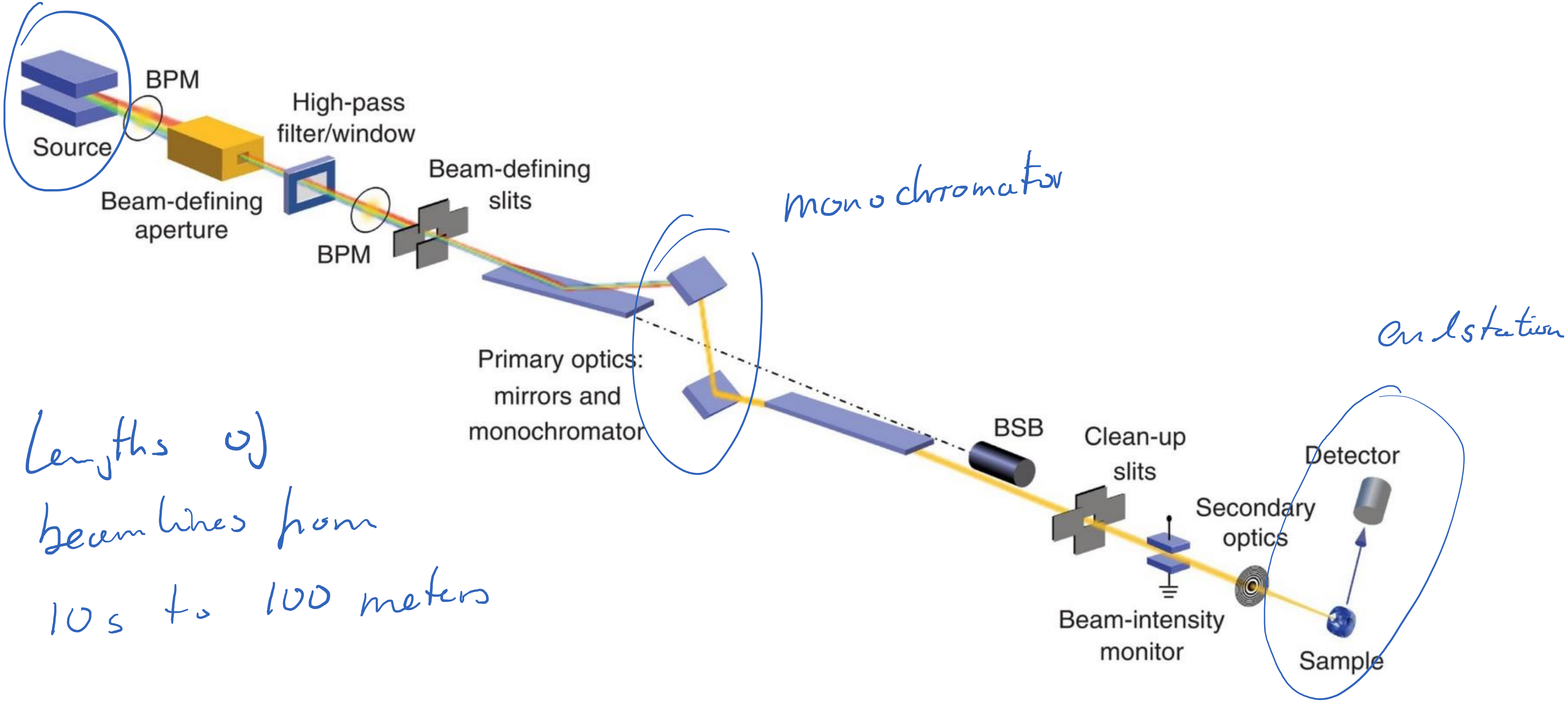


The Doppler frequency shift has a strong angle dependence, leading to lower photon energies off-axis.



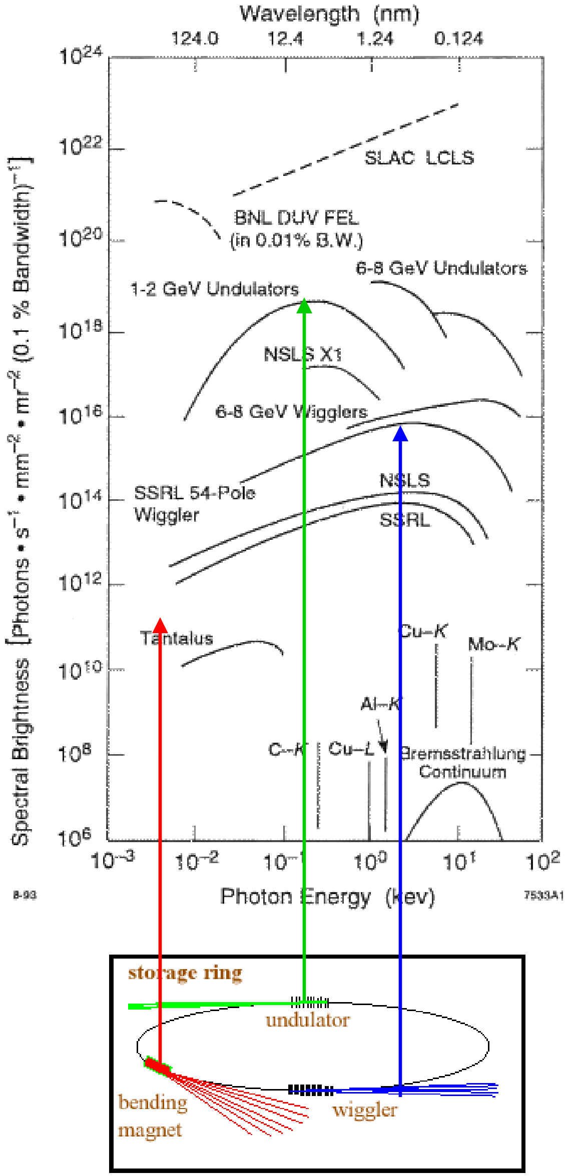


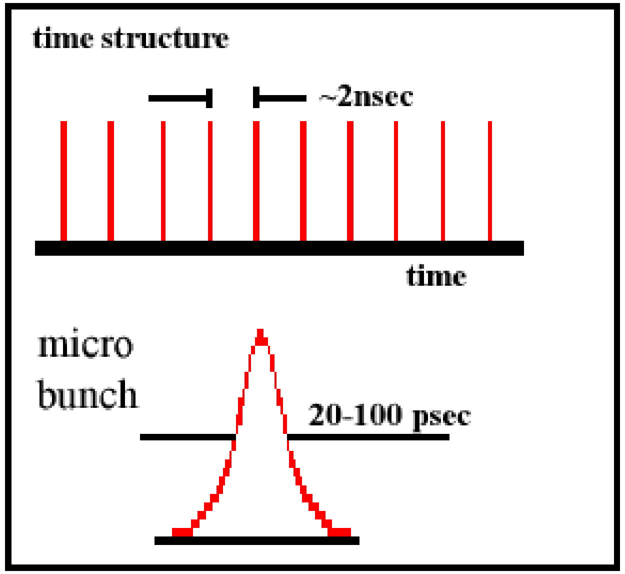
Layout of a synchrotron beamline



Lengths of beamlines from 10s to 100 meters

Properties of synchrotron radiation





Typical numbers:

~ 10^{11}-10^{13} Photonen/s

Total power10W- 30 kW

↳ pulsed source

→ time resolved exps

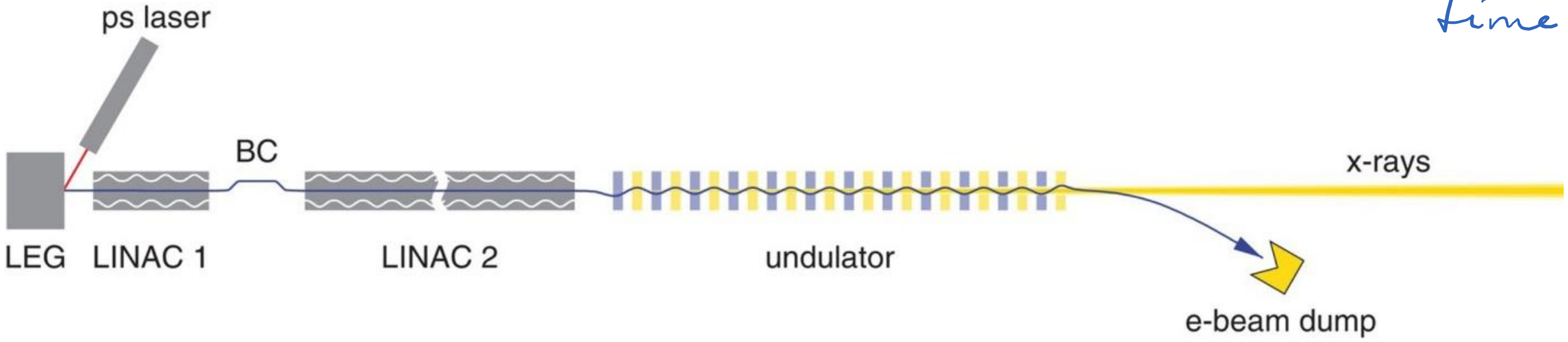
X-ray free-electron lasers (XFELs) – the latest and brightest x-ray source

PAUL SCHERRER INSTITUT
PSI

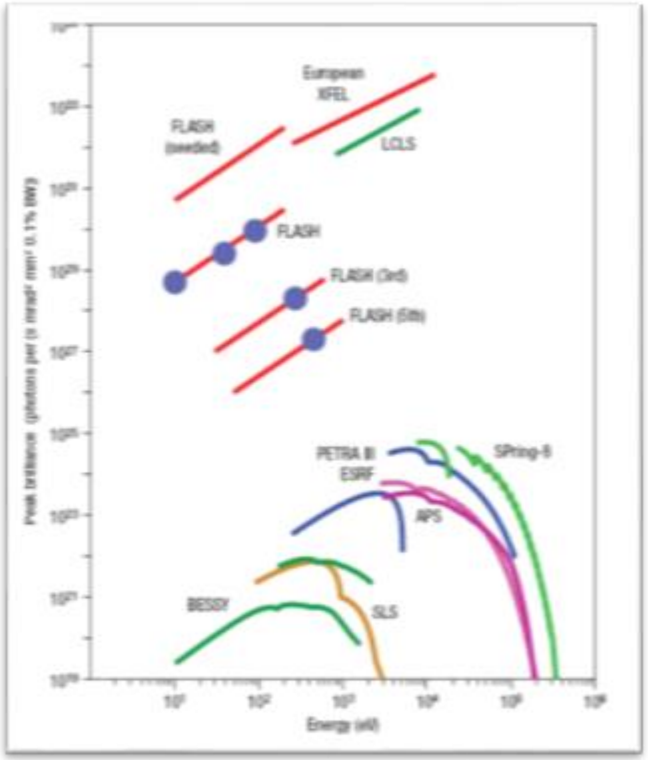
Swiss FEL

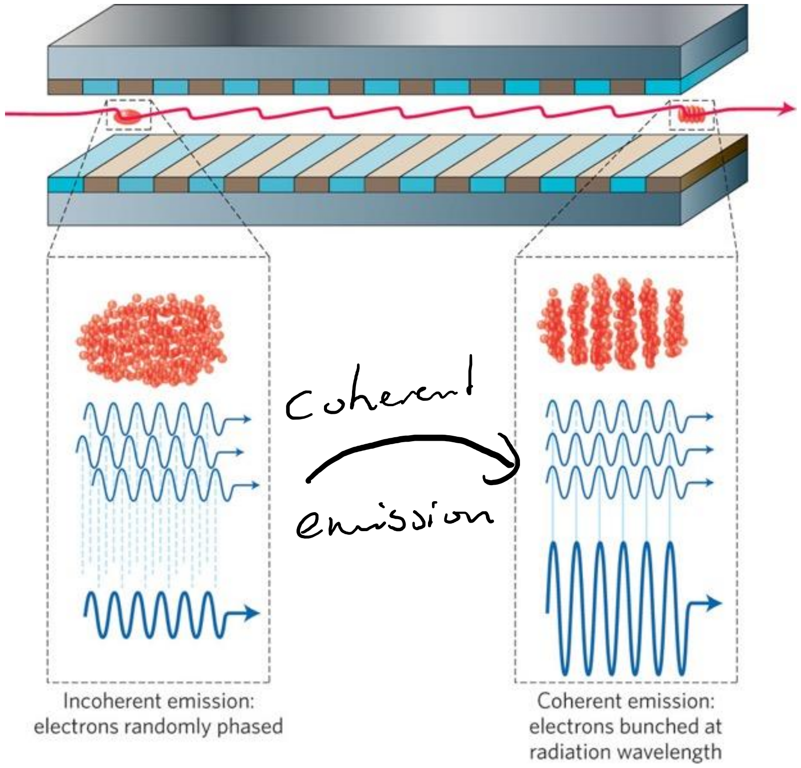
Layout and working principle of XFEL

→ ideal for dilute samples & time-resolved exps



fsec: relevant time scale for electron motion (→ chemistry)





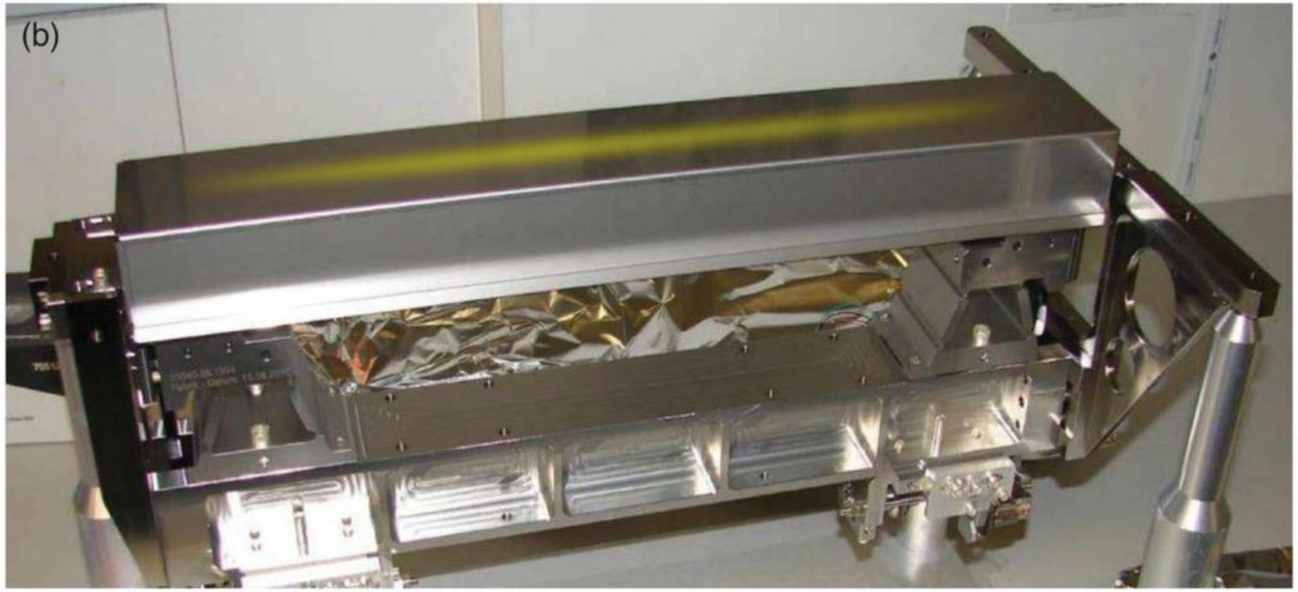
↳ coherent!

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

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

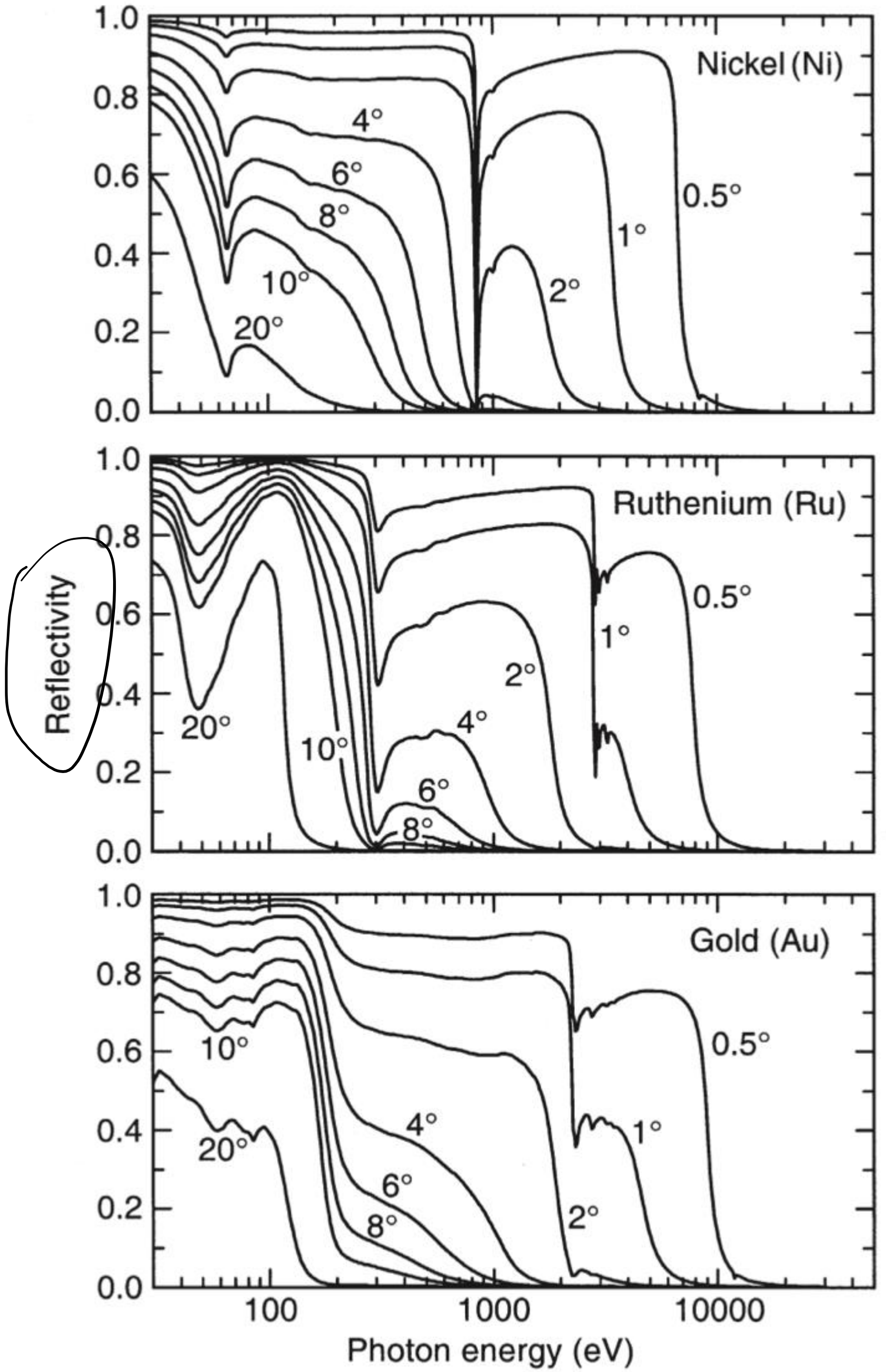
X-ray transport

Mirrors

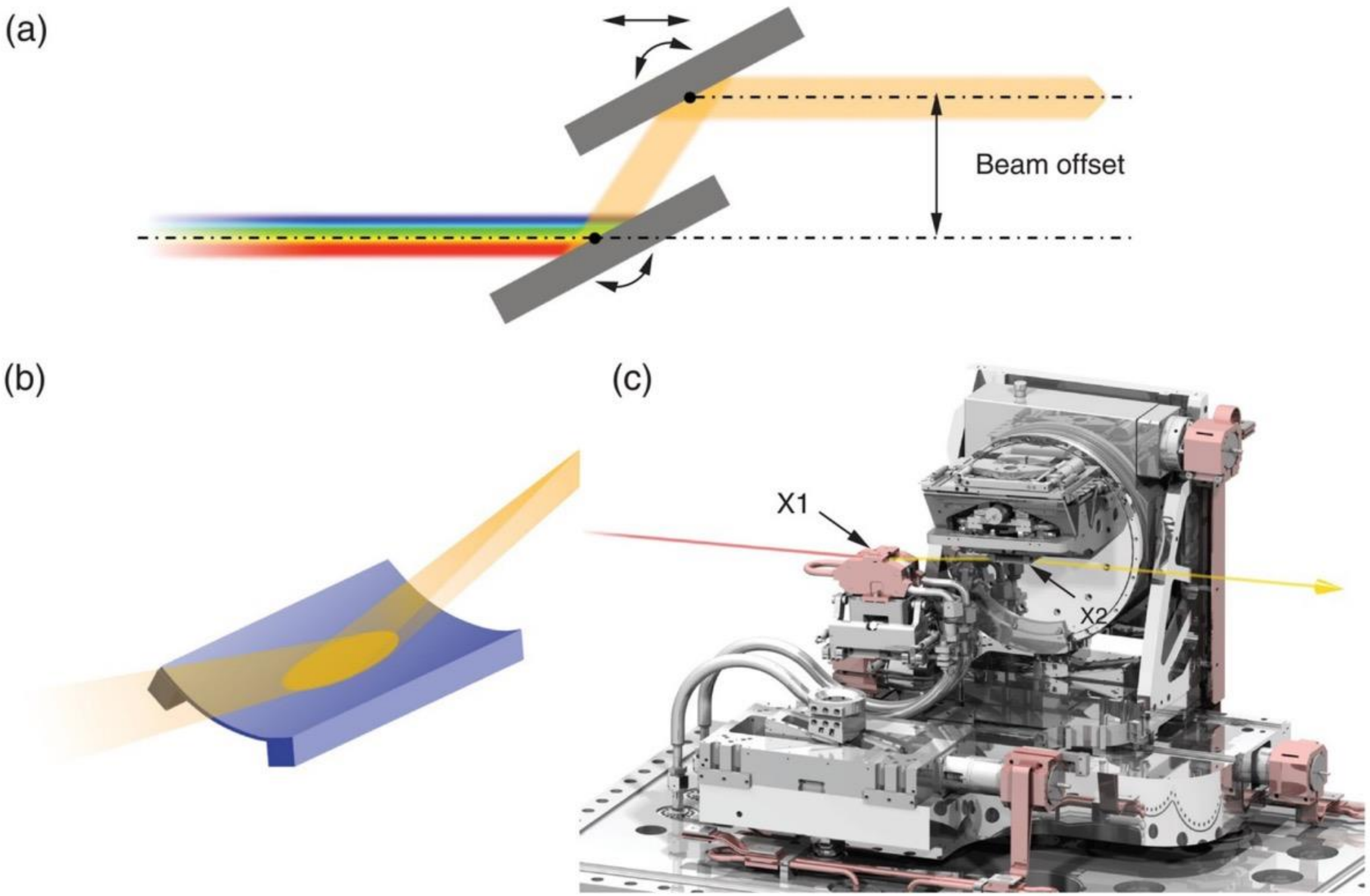


→ works only in grazing incidence

→ long mirrors and beamlines

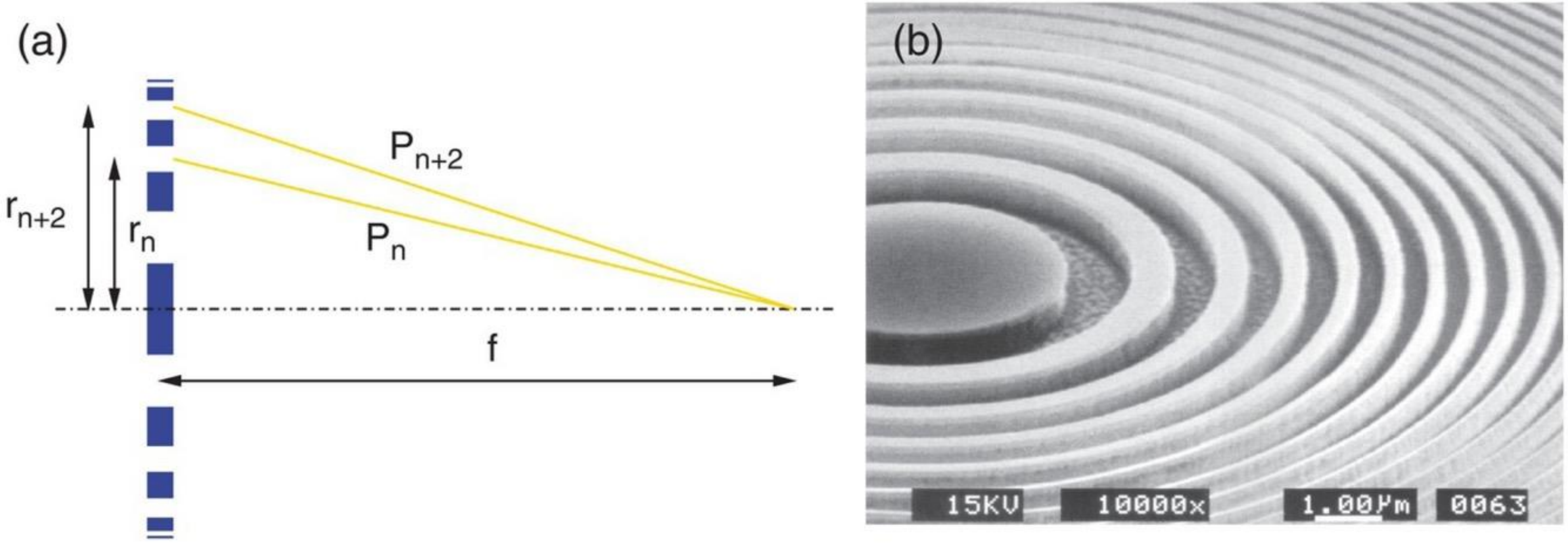


Crystals



good solution for hard X-rays with Bragg reflections

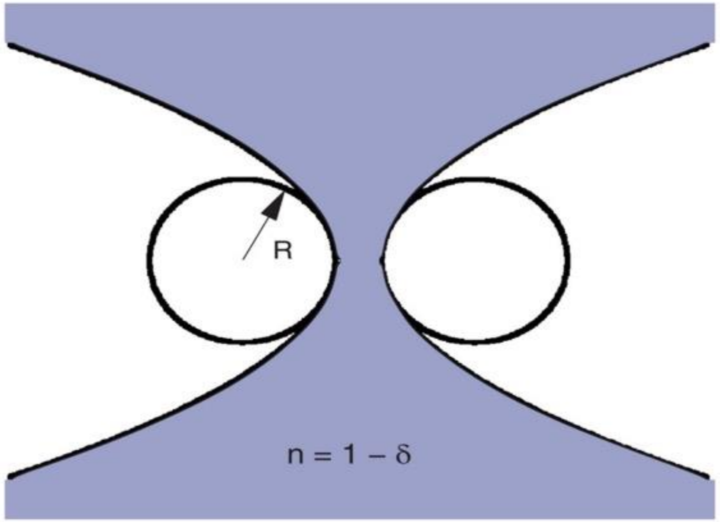
Zone plates

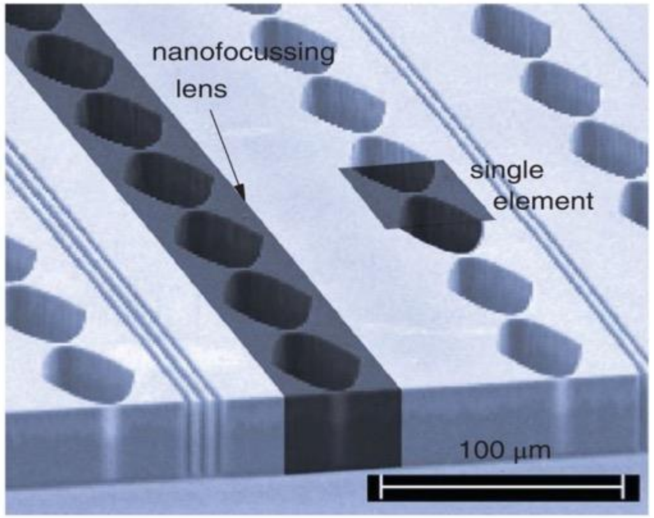


good solution for soft X-rays

can produce small foci but chromatic

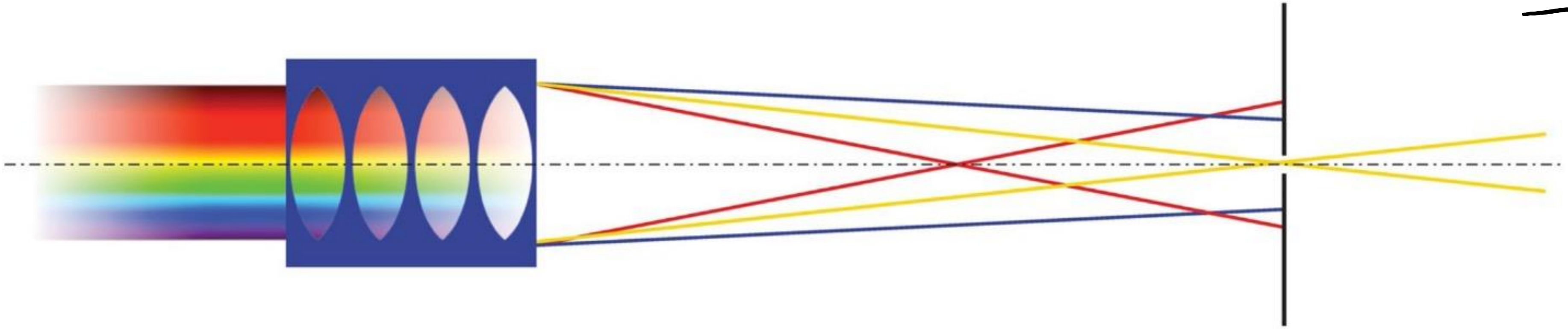
Compound refractive lenses





→ Note refractive index in X-ray regime < 1

→ now concave lense focuses



→ this technology has recently become more popular

The end