Optical methods in chemistry
or
Photon tools for chemical sciences

Session 12

Course layout – contents overview and general structure

- Introduction and ray optics
- Wave optics
- Beams and cavities
- Principles of Lasers
- More Lasers and a Specific Application: Optical Tweezers
- From diffraction and Fourier optics
- Application: Microscopy
- Application: Manipulation
- Application: Spectroscopy
- Electrodynamic optics
- Materials properties, linear and non-linear
- Ultrafast lasers
- Introduction to X-rays
- Summary and review

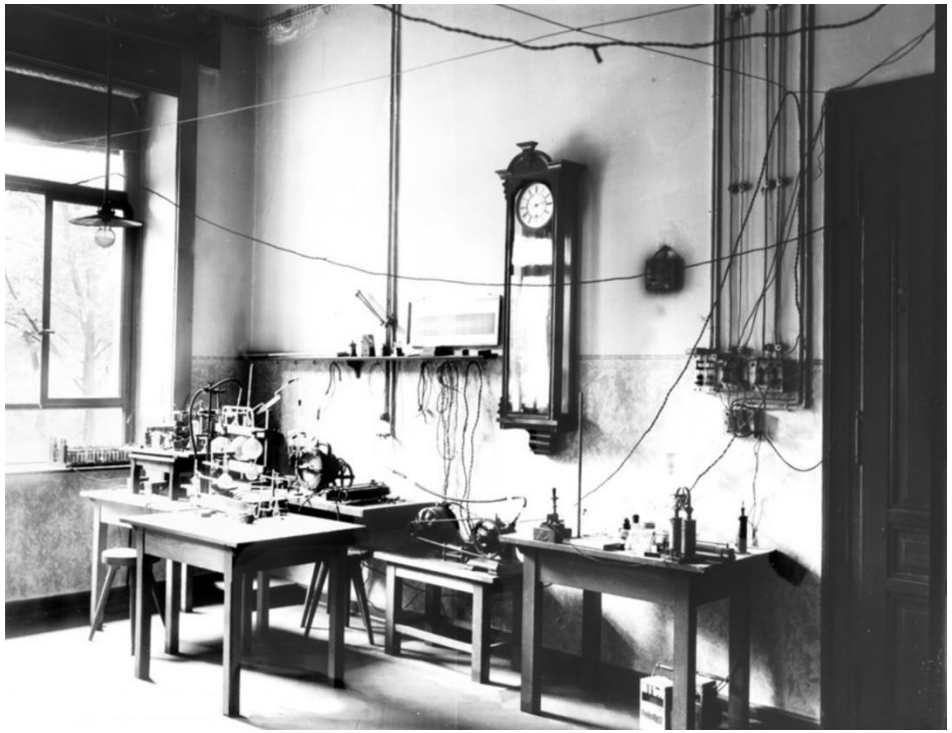
Today:

Lets get going with x-rays

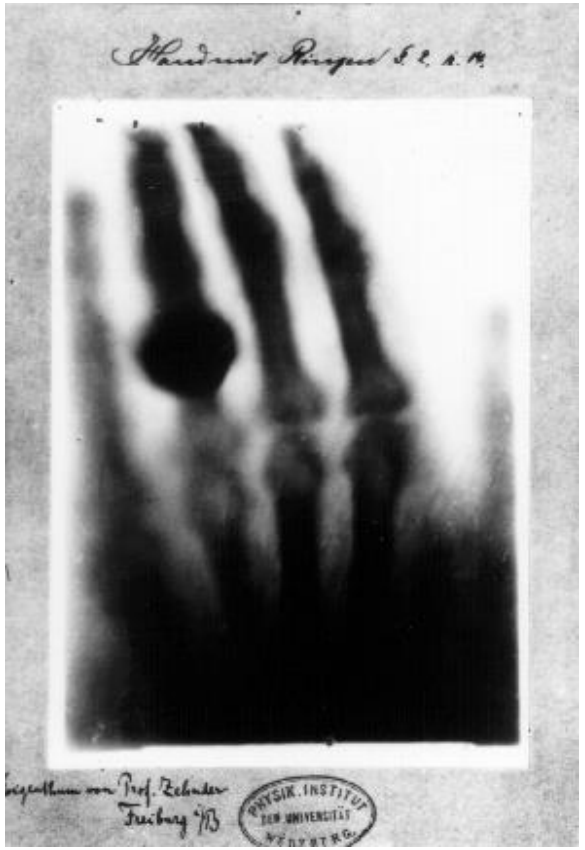
Some new ideas and many applications of previous material

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-ray diffraction / Scattering

↓

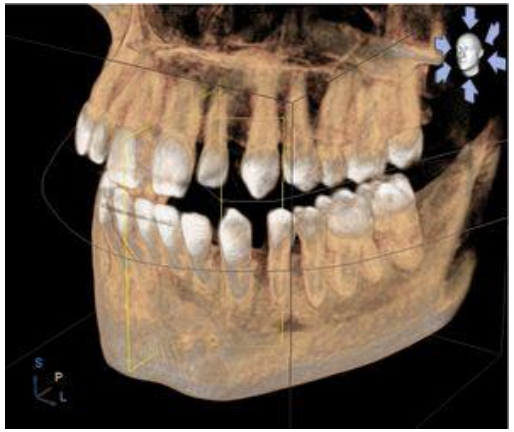
atomic resolution

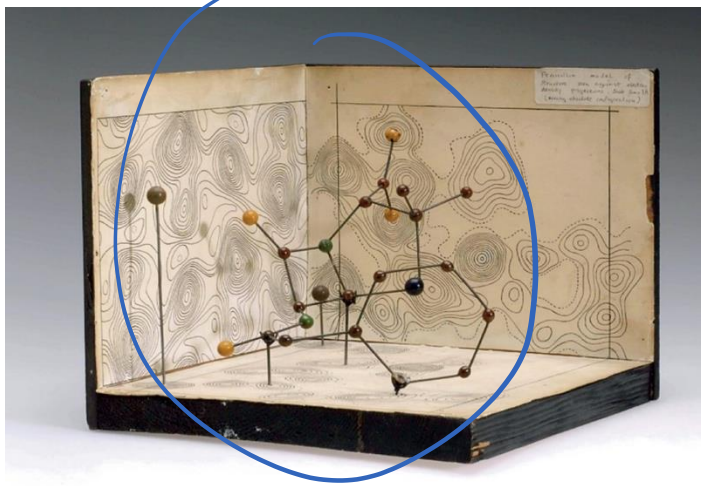
↓

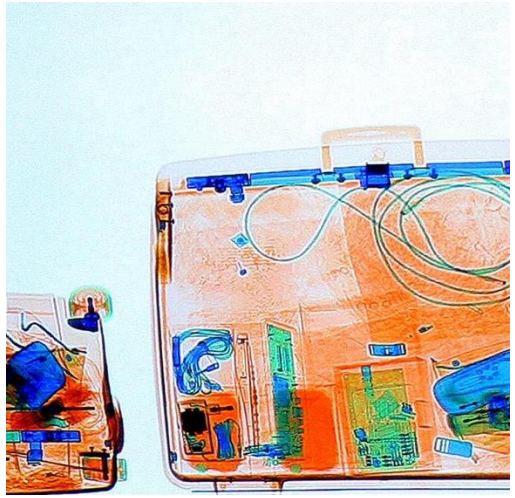
Nobel price Dorothy Crowfoot

↓

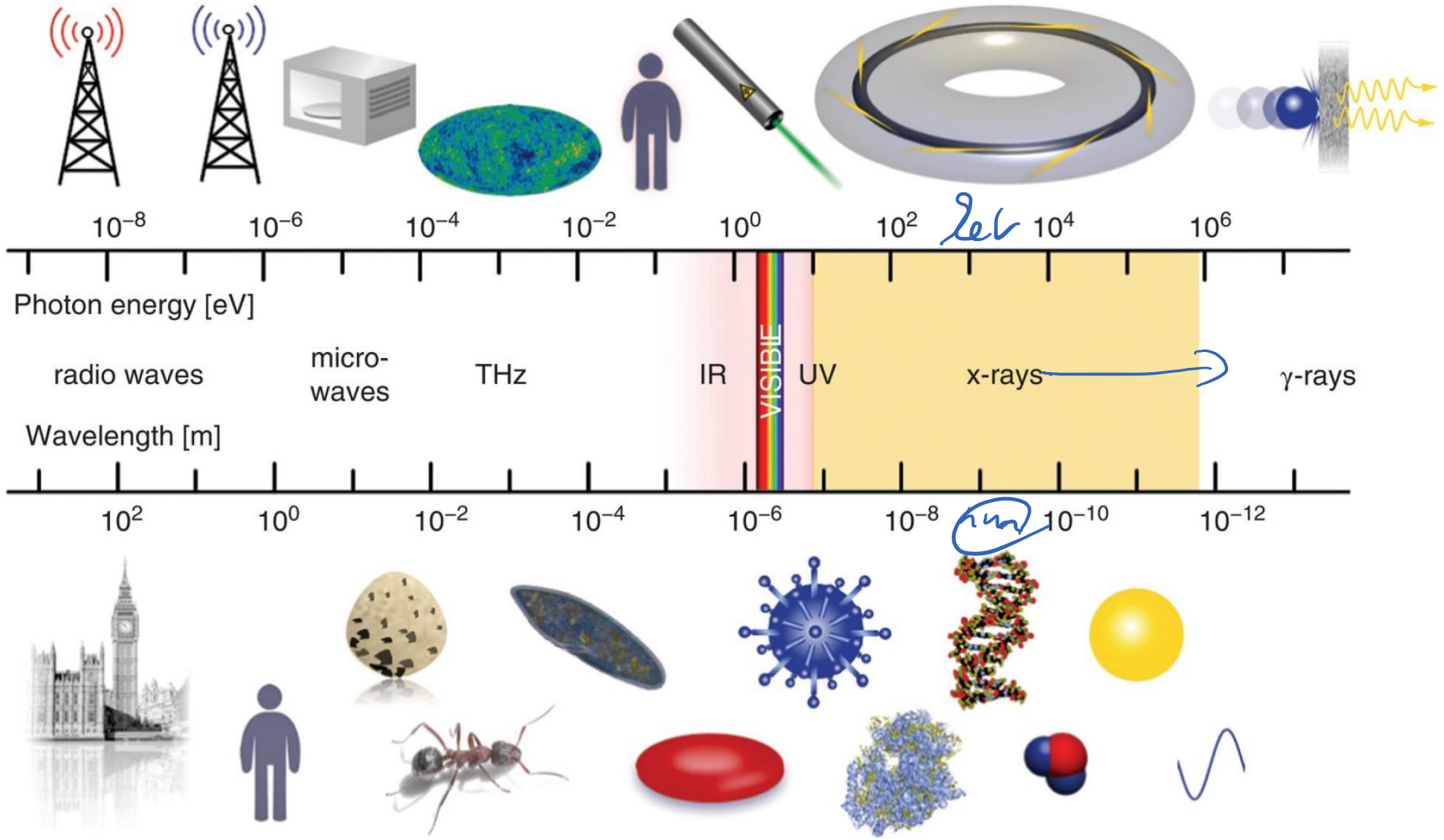
Structure of penicillin







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

Why care about x-ray diffraction of crystals?

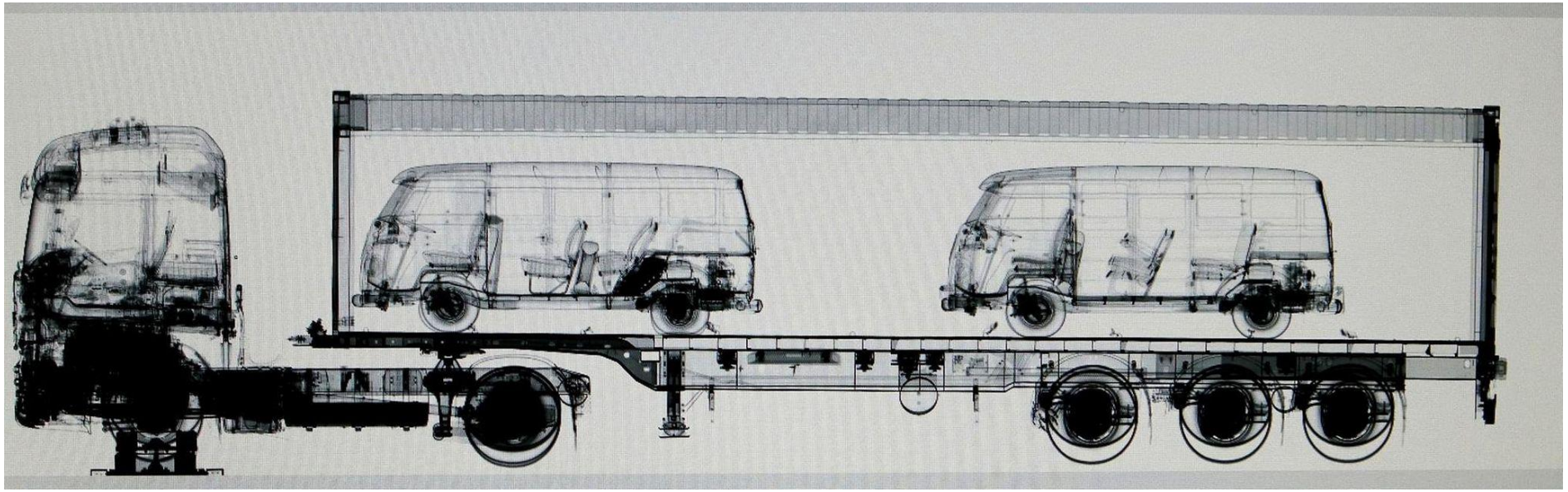
From: https://www.nobelprize.org/prizes/chemistry/1964/perspectives/

Chemists were still struggling to isolate penicillin in a pure and active form. It was not until July 1943 that they knew the composition of the active ingredient. After systematically breaking down penicillin into smaller pieces, chemists knew it consisted of 27 atoms: 11 hydrogen, 9 carbon, 4 oxygen, 2 nitrogen atoms and 1 sulphur atom. The trouble was that this combination of atoms could form two very different structures, and chemists couldn't decide which structure was more likely. Some chemists were convinced the structure contained two five-membered rings connected by a single bond, known as a thiazolidine-oxazolone. Others were equally sure it was a four-membered ring fused to a five-membered ring, known as a beta lactam.

"No absolutely unequivocal conclusion could be derived from it," Ernst Chain explained in his Nobel Lecture. "The final solution of the problem of the structure of penicillin came from crystallographic X-ray studies."

The power of x-rays

X-rays – Penetration depth



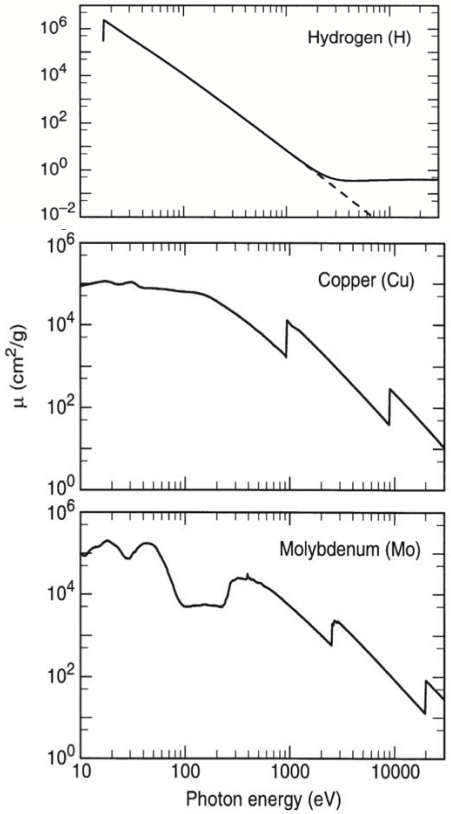
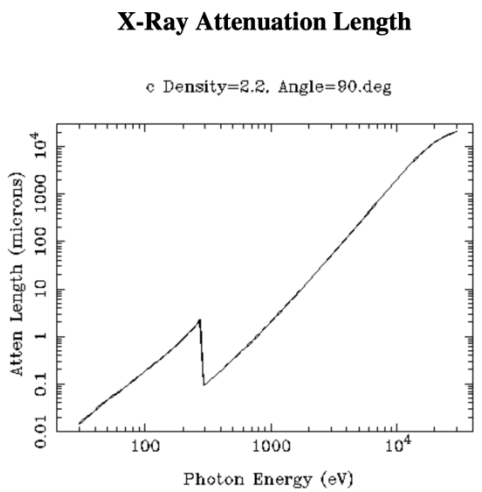


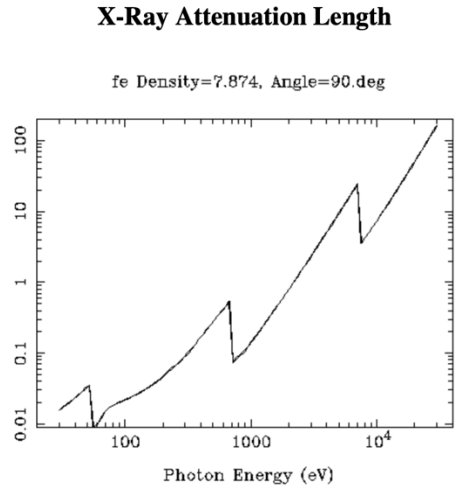
Fig. 1-5. Mass absorption coefficients (continued).

Lambert-Beer absorption

→ interactions of x-rays with matter weaker

→ larger penetration depth





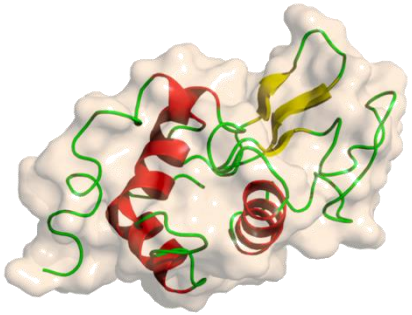
Scattering with atomic resolution

Lysozym (Protein, Immunsystem)

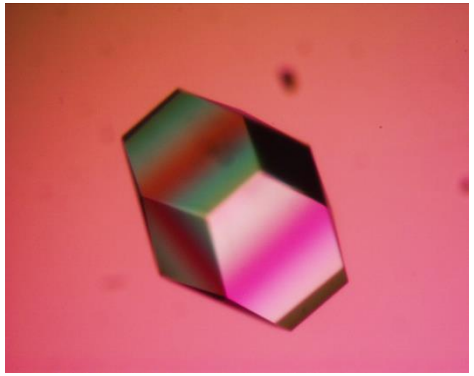
Stochiometric formula

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

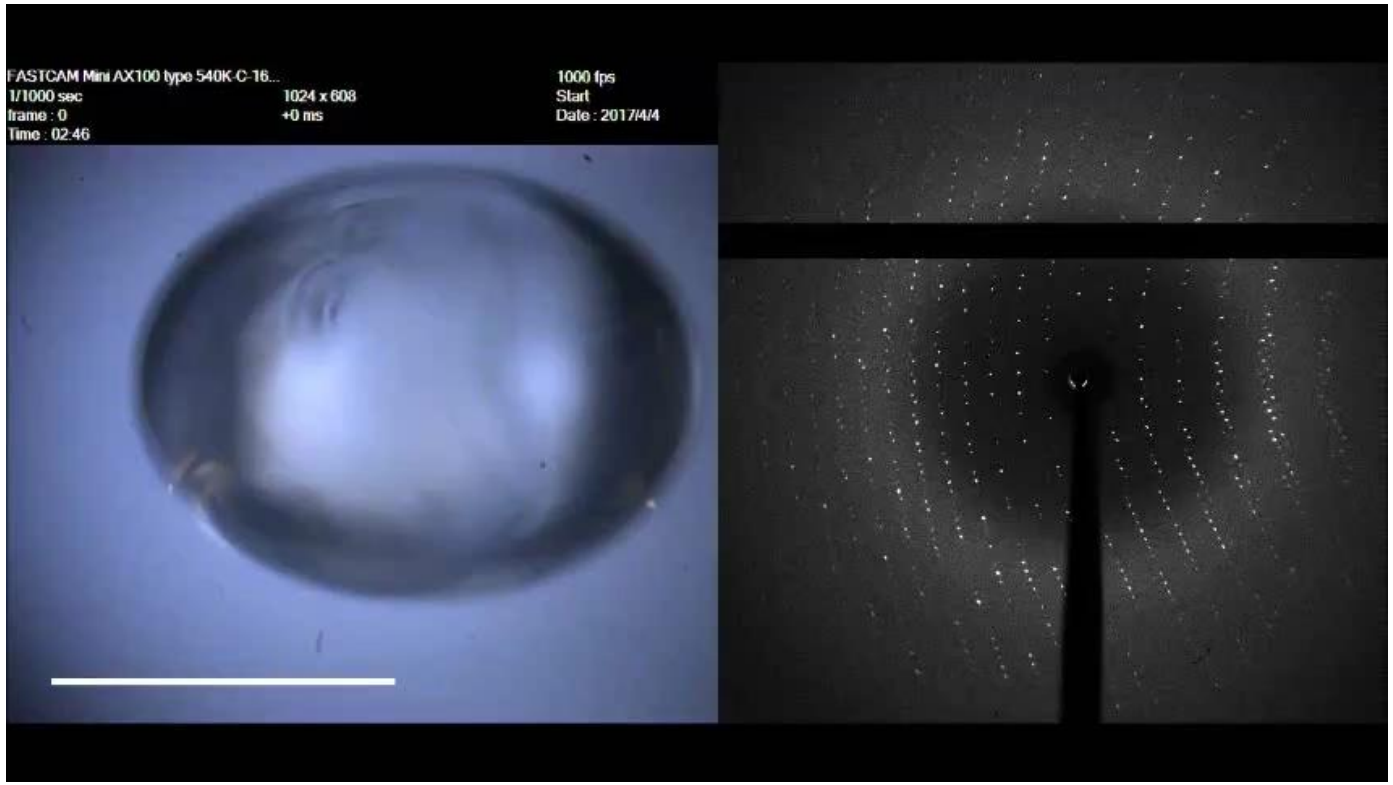
Structure



Crystal



Experiment at the Swiss Light Source



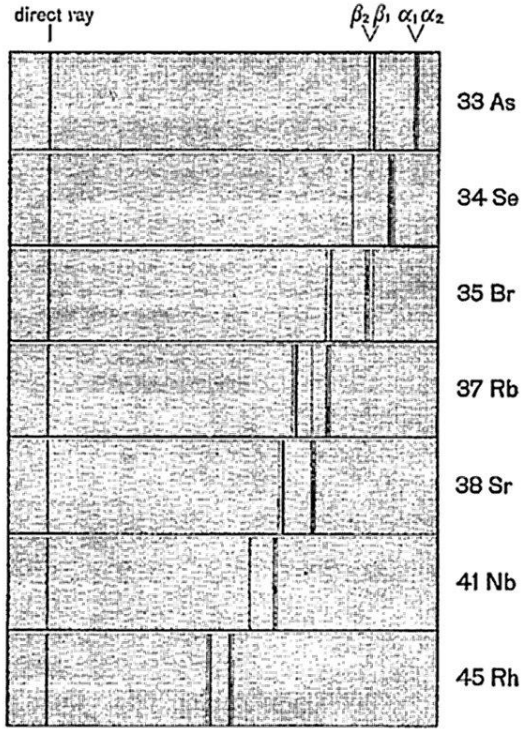
Elements possess specific colors – also in X-ray spectral regime

Barkla, Nobel Prize in 1917

Rose of Lausanne:
Characteristic visible colors

↳ valence transitions
→ visible to eye

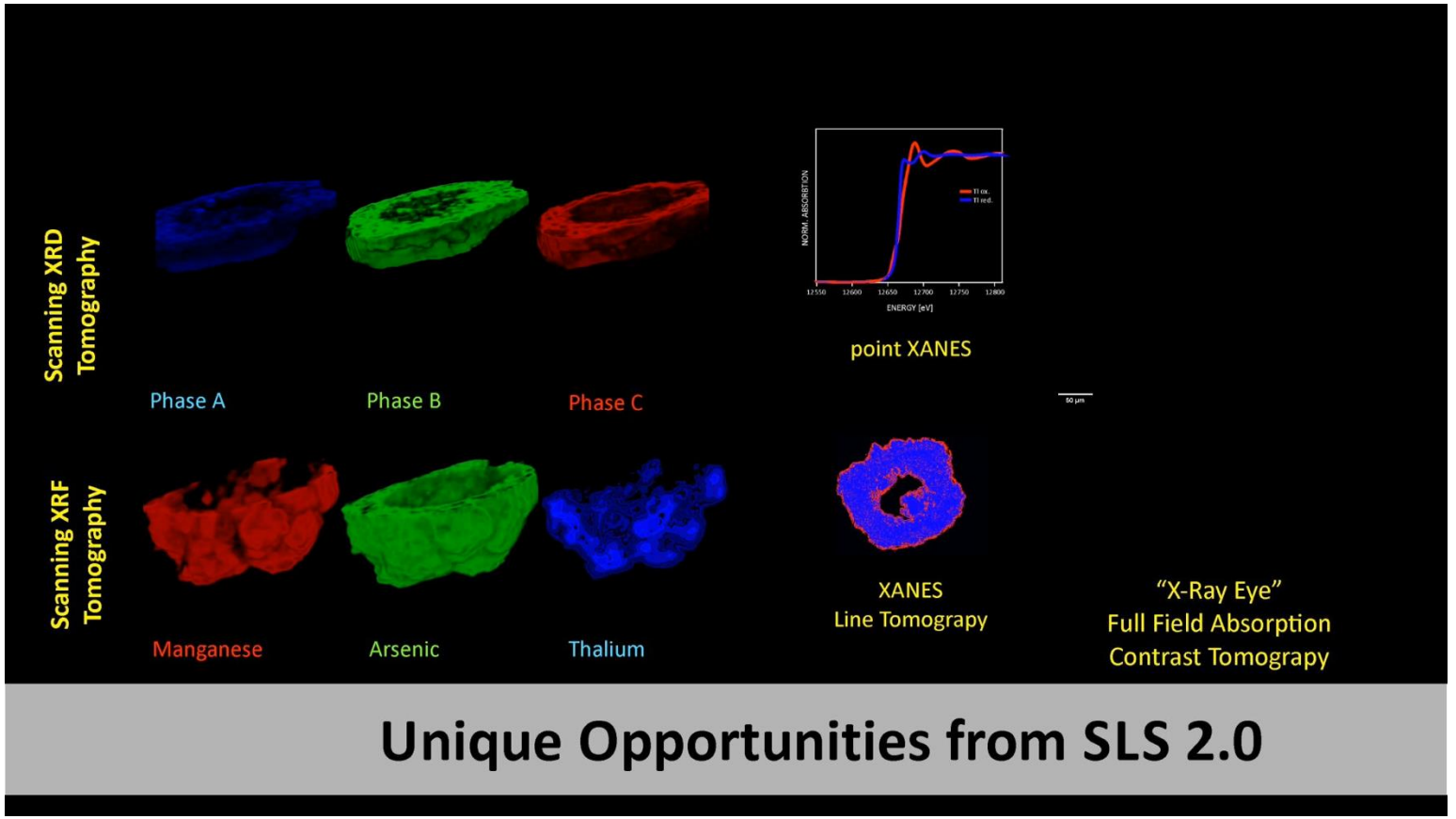
Barkla:
Characteristic emission lines of elements in x-ray regime



↳ core electrons / transitions
↳ visible to x-ray detection

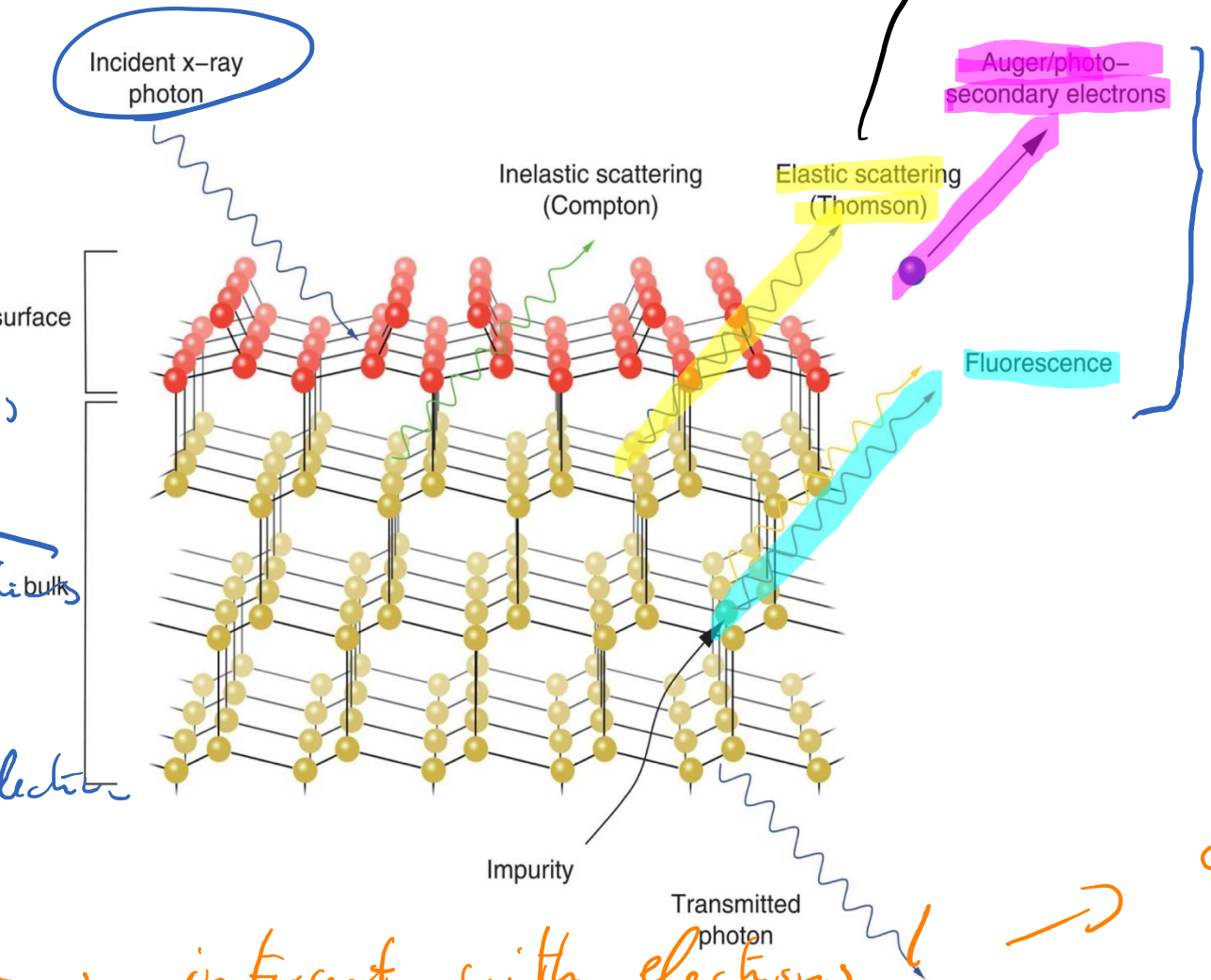
Combination of large penetration depth, elemental information, and high resolution

Example: Geological Thalium sample (Geochemistry)

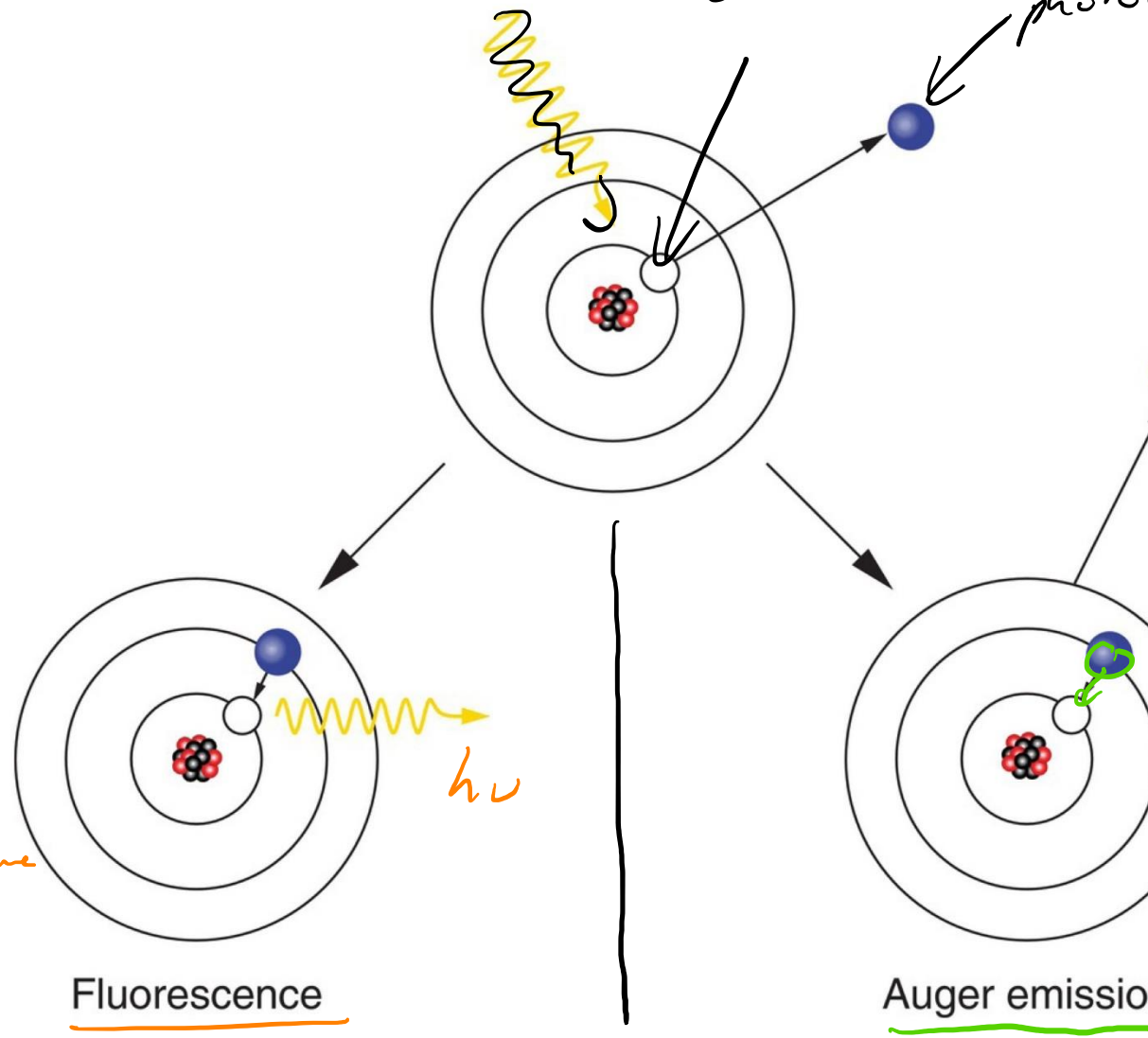


X-ray interactions with matter

X-ray interactions with matter

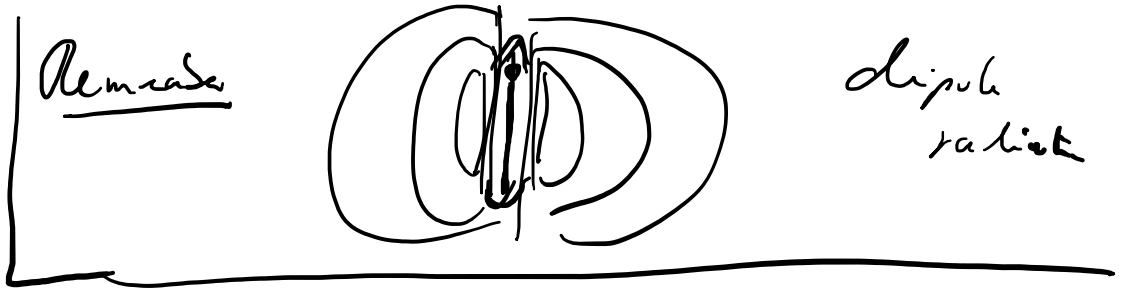


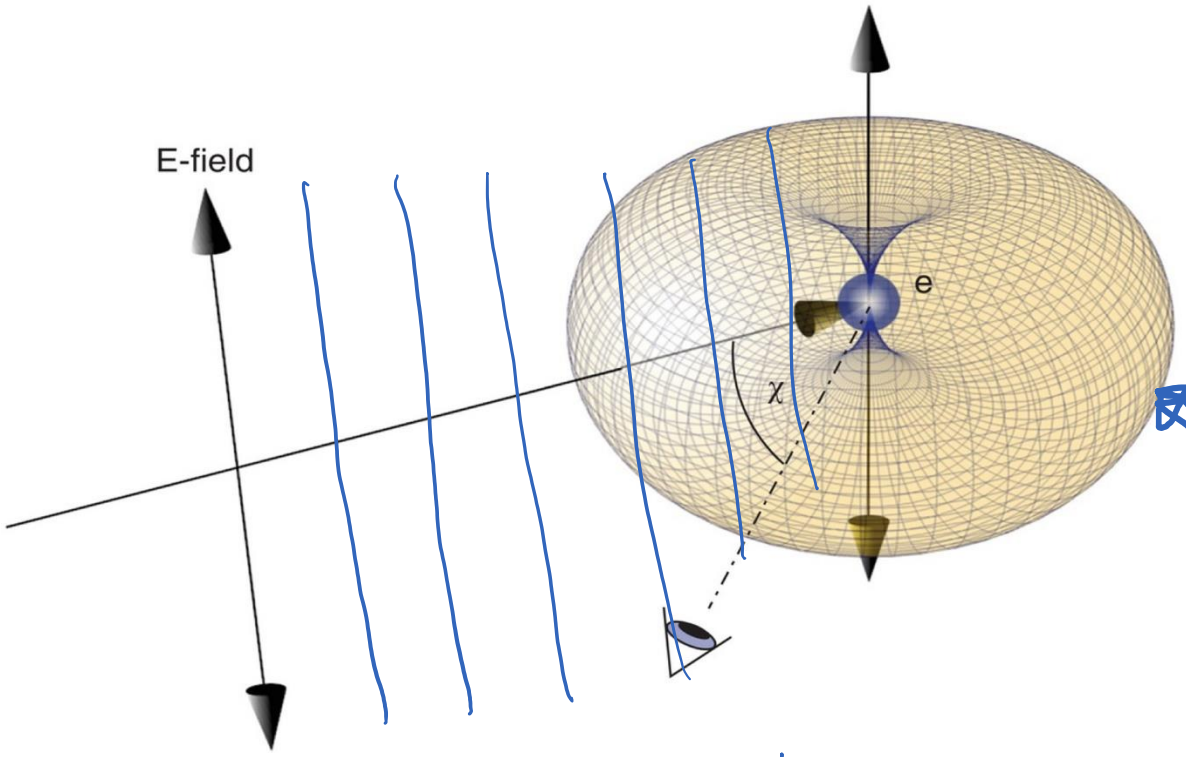
Photoionization / absorption



Thomson scattering

↳ elastic process



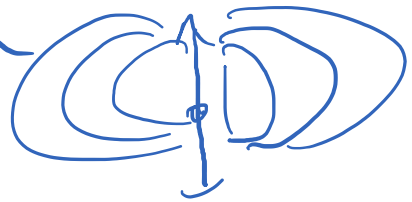


→ Semiclassical description

→ X-rays approx. plane wave

→ X-ray scattering process is described by dipole radiation

emission in 3D like figure

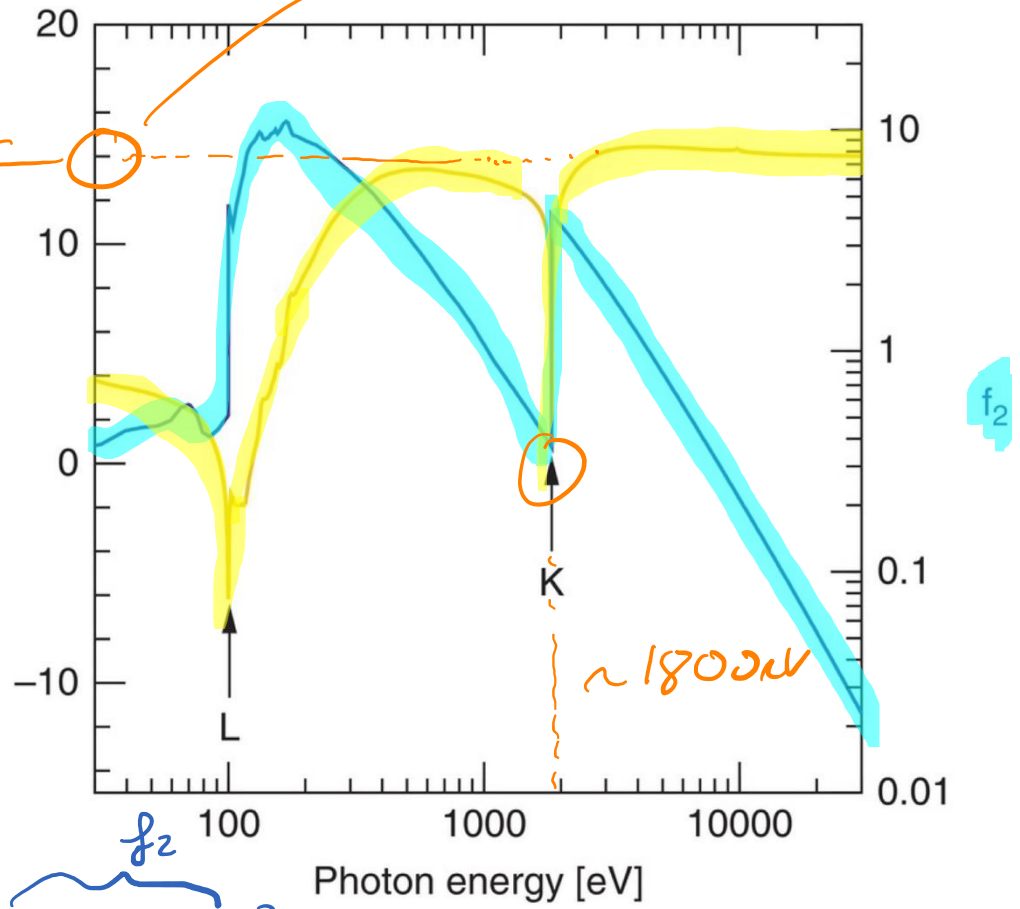


Scattering process

- transforms incoming plane wave into dipole wave
- no frequency shift → full elastic
- phase shift

1 Spherical wave emerges

Atomic scattering factors and refractive index



Si

proportional to #e⁻

~1800eV

importance

absorption ⇒ electronic levels

Scattering ⇒ electronic structure

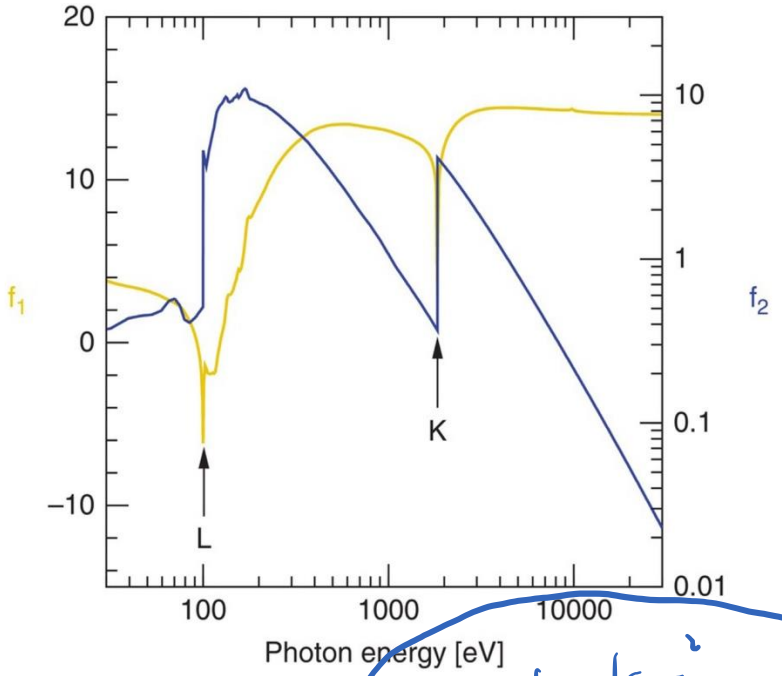
$$f(h\nu) = \underbrace{f_0 + f'(h\nu)}_{f_1} + i\underbrace{f''(h\nu)}_{f_2}$$

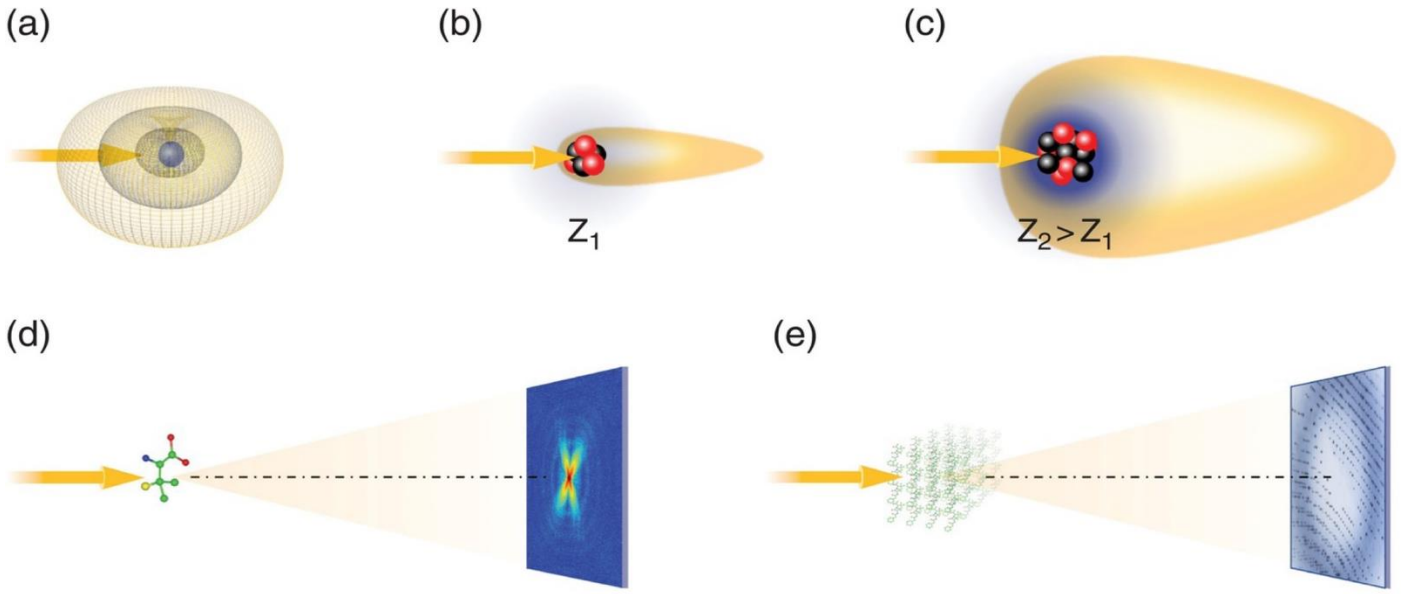
$f_0 + f'(h\nu)$: scattering / refraction

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

→ analogue of "refractive index"

Atomic scattering factors again





"form factor" for Q → 0 FT (electron density)

Note: atomic scattering factors also function of Q

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

X-ray cross sections

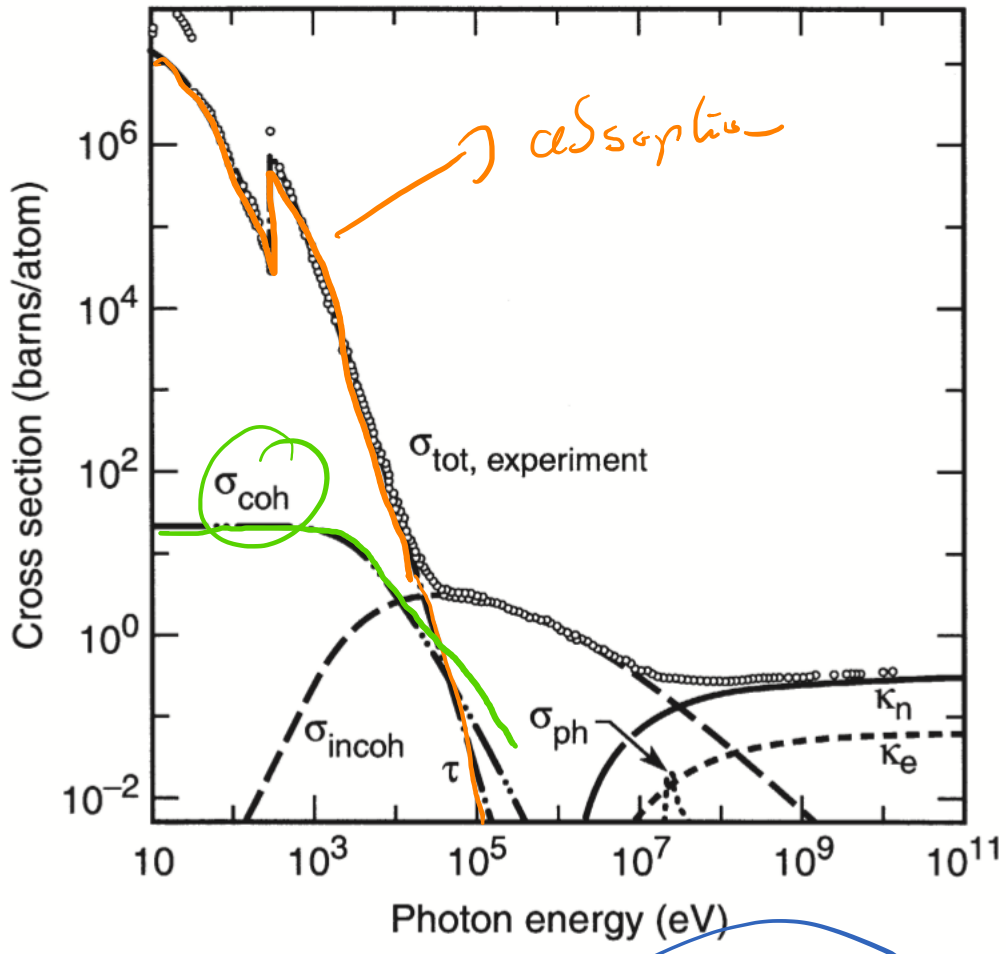


Fig. 3-1. *Total photon cross section σ_{tot} in carbon, as a*

Diffraction by crystals

Why should we care about x-rays, crystals, lattices, etc?

Source:
The Cambridge Structural Database (CSD)

Organic
43%

Metal-Organic
57%
At least one transition metal, lanthanide, actinide or any of Al, Ga, In, Tl, Ge, Sn, Pb, Sb, Bi, Po

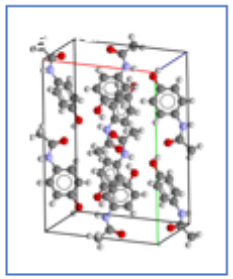
Not Polymeric
89%

Polymeric: 11%

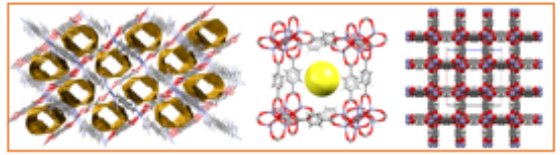
Single Component
56%

Multi Component
44%

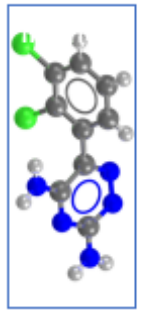
Organic
- Drugs
- Agrochemicals
- Pigments
- Explosives
- Protein ligands



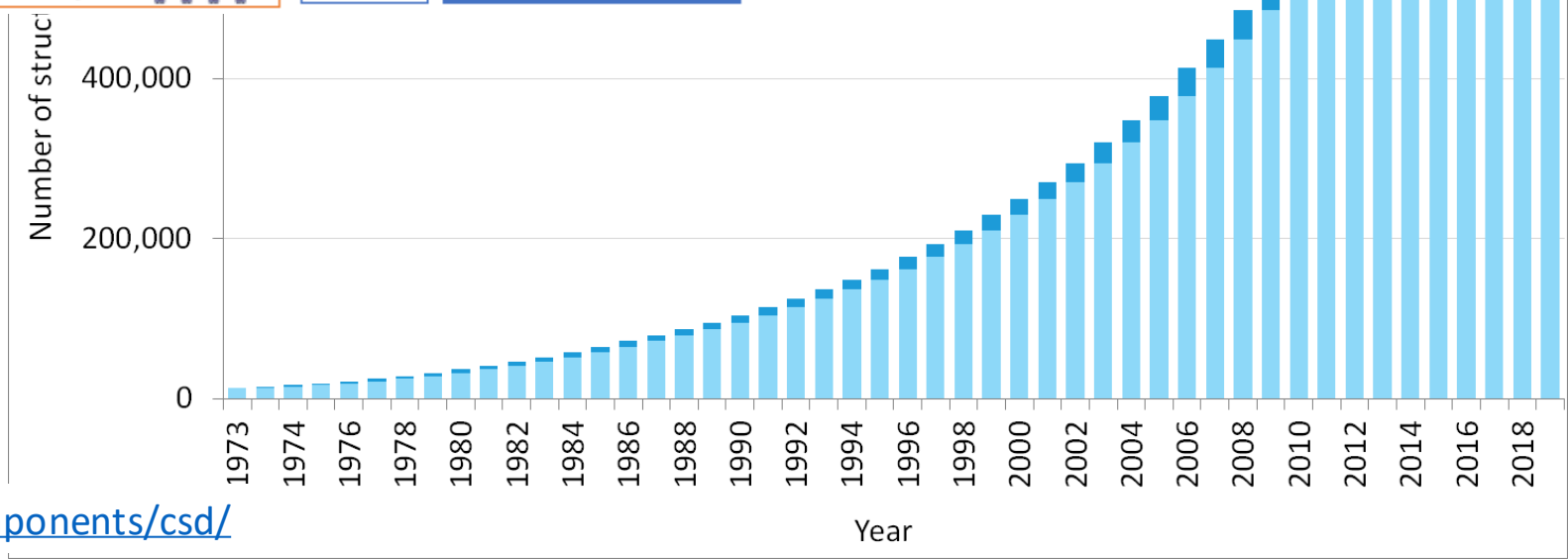
Metal-Organic
- Metal Organic Frameworks
- Models for new catalysts
- Porous frameworks for gas storage
- Fundamental chemical bonding



Additional data
- >10,000 polymorph families
- >160,000 melting points
- >700,000 crystal colours
- >600,000 crystal shapes
- >23,000 bioactivity details
- >9,000 natural source data
- > 250,000 oxidation states



Links and subsets
- Drugbank
- Druglike
- MOFs
- PDB ligands
- PubChem
- ChemSpider



https://www.ccdc.cam.ac.uk/solutions/csd-system/components/csd/

The Huygens-Fresnel Principle

- Hugens: every point a wave (a luminous disturbance) reaches becomes a source of a spherical wave; the sum of these secondary waves determines the form of the wave at any subsequent time.
- Huygens-Fresnel: every unobstructed point of a wavefront serves as a source of spherical secondary wavelets. The amplitude of the wave beyond is the superposition of all these wavelets. (includes amplitude and relative phase)

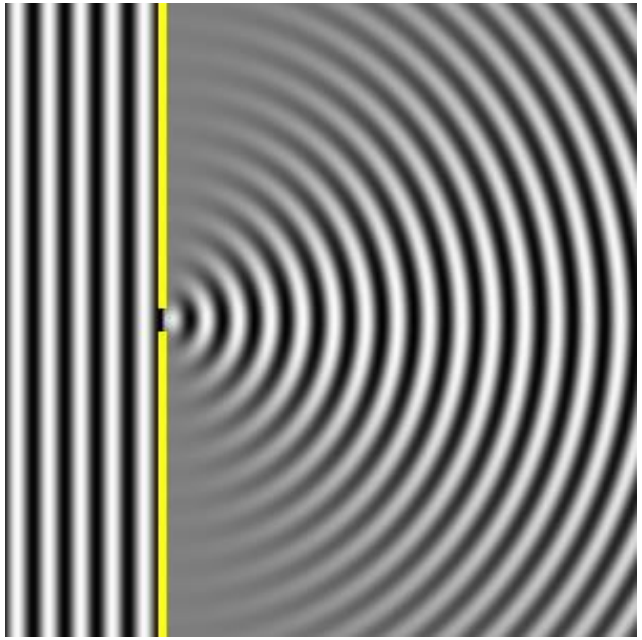
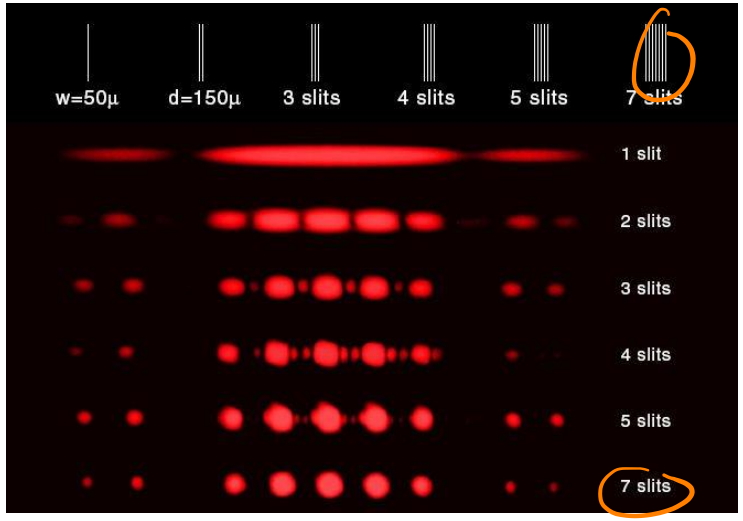
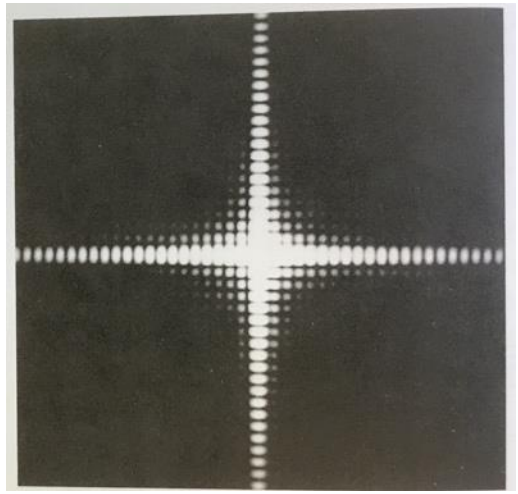
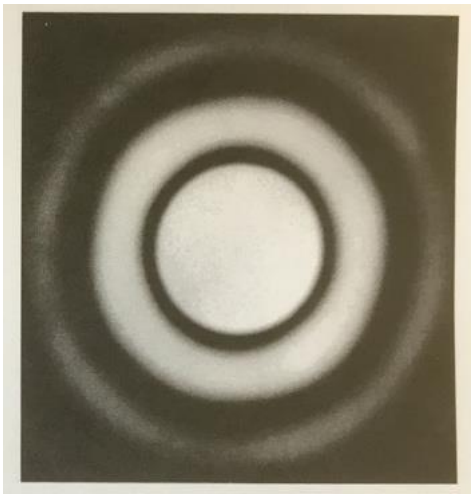


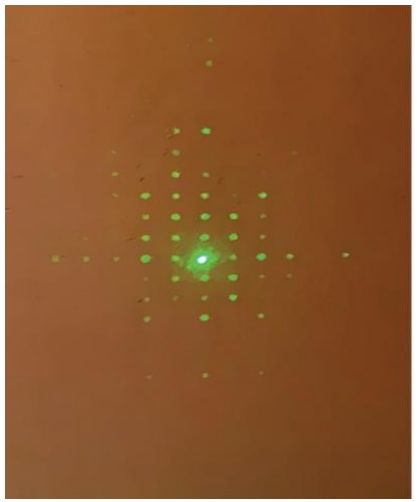
Image credits: By Lookangmany thanks to Fu-Kwun Hwang and author of Easy Java Simulation = Francisco Esquembre - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=16981632

Diffraction examples





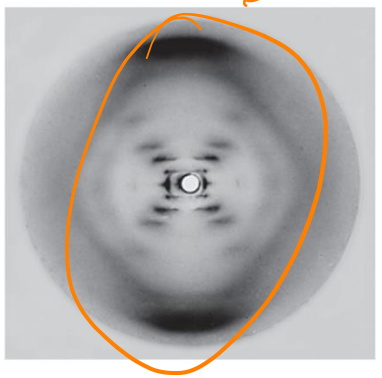




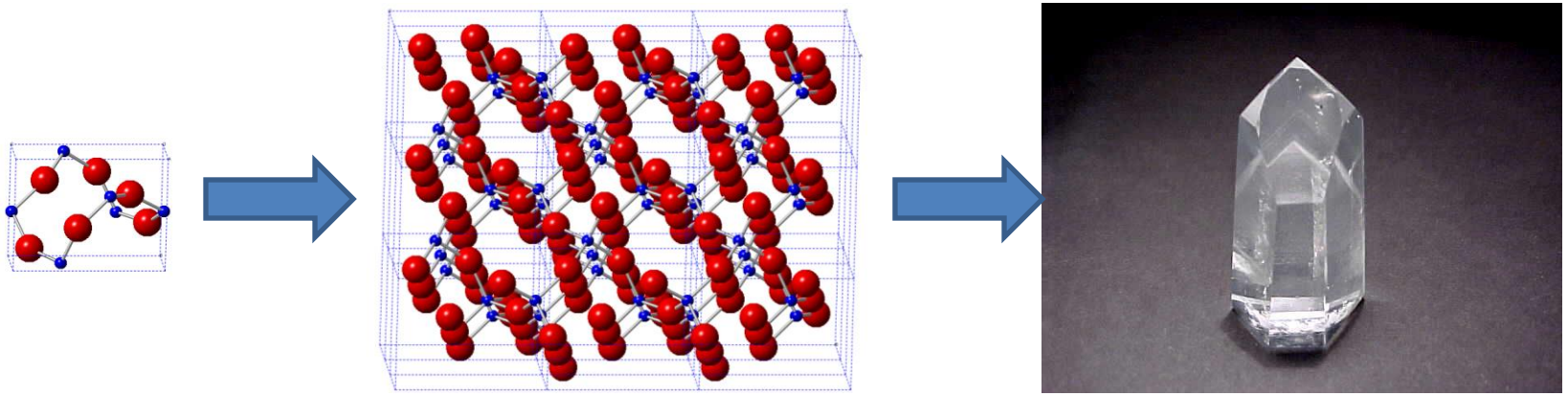
Watson-Crick

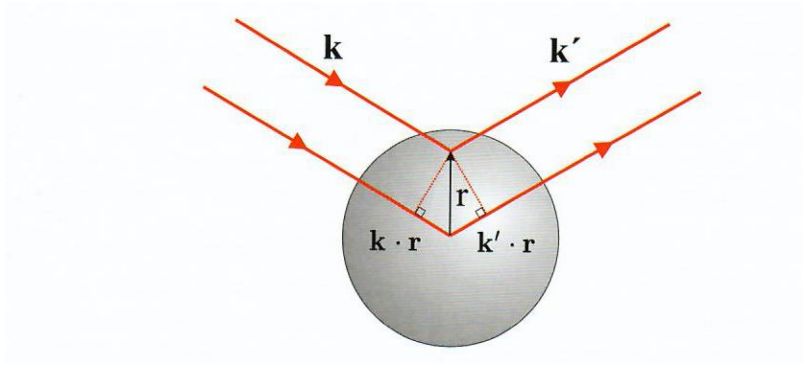
Rosalind Franklin

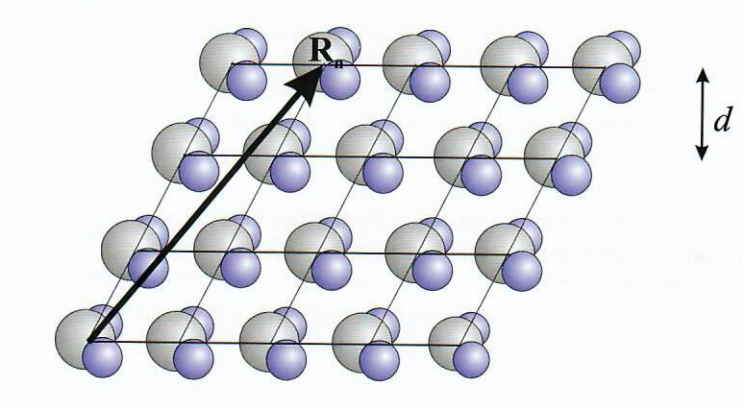
X-ray diffraction of DNA



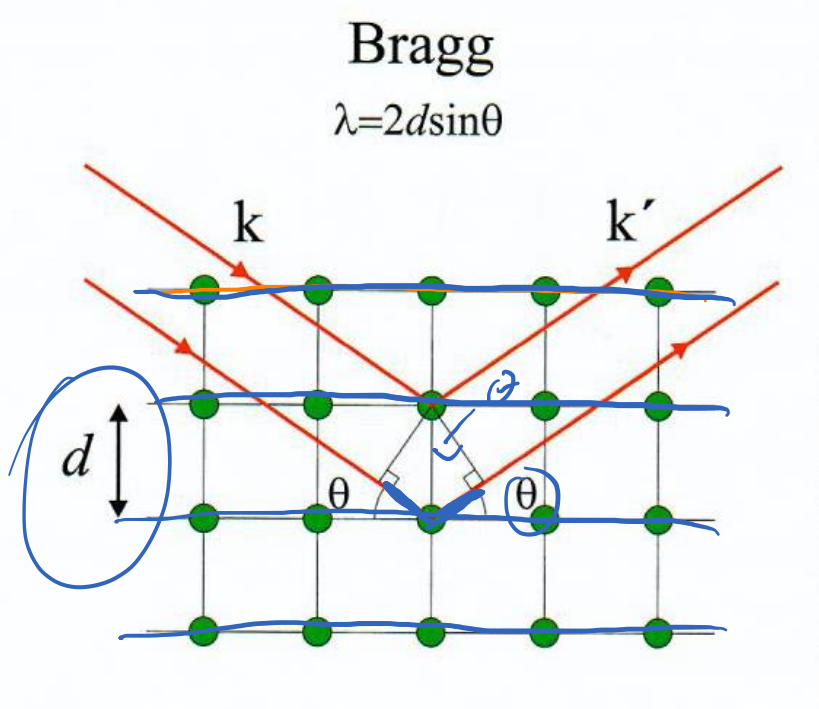
Crystaline materials are characterized by the long-range order

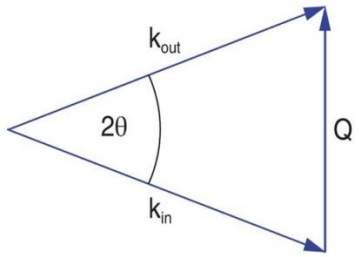






Bragg scattering





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

Bragg law

The Nobel Prize in Physics 1915

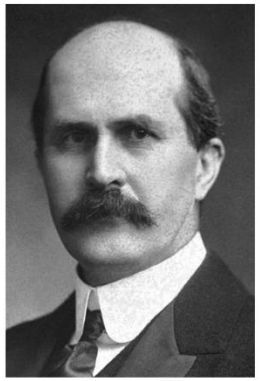


Photo from the Nobel Foundation archive.

Sir William Henry Bragg

Prize share: 1/2

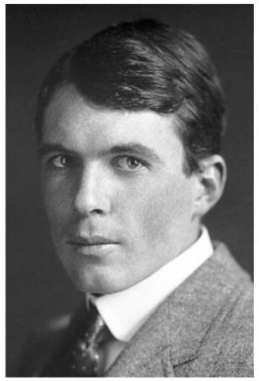
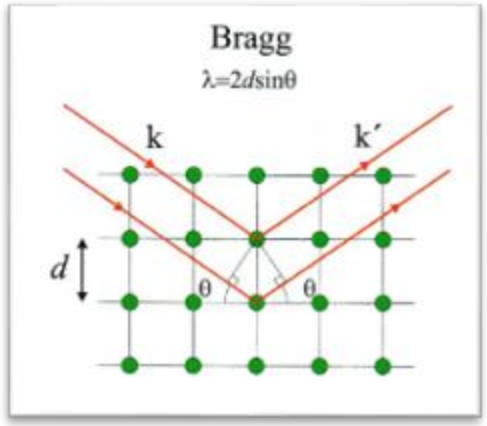


Photo from the Nobel Foundation archive.

William Lawrence Bragg

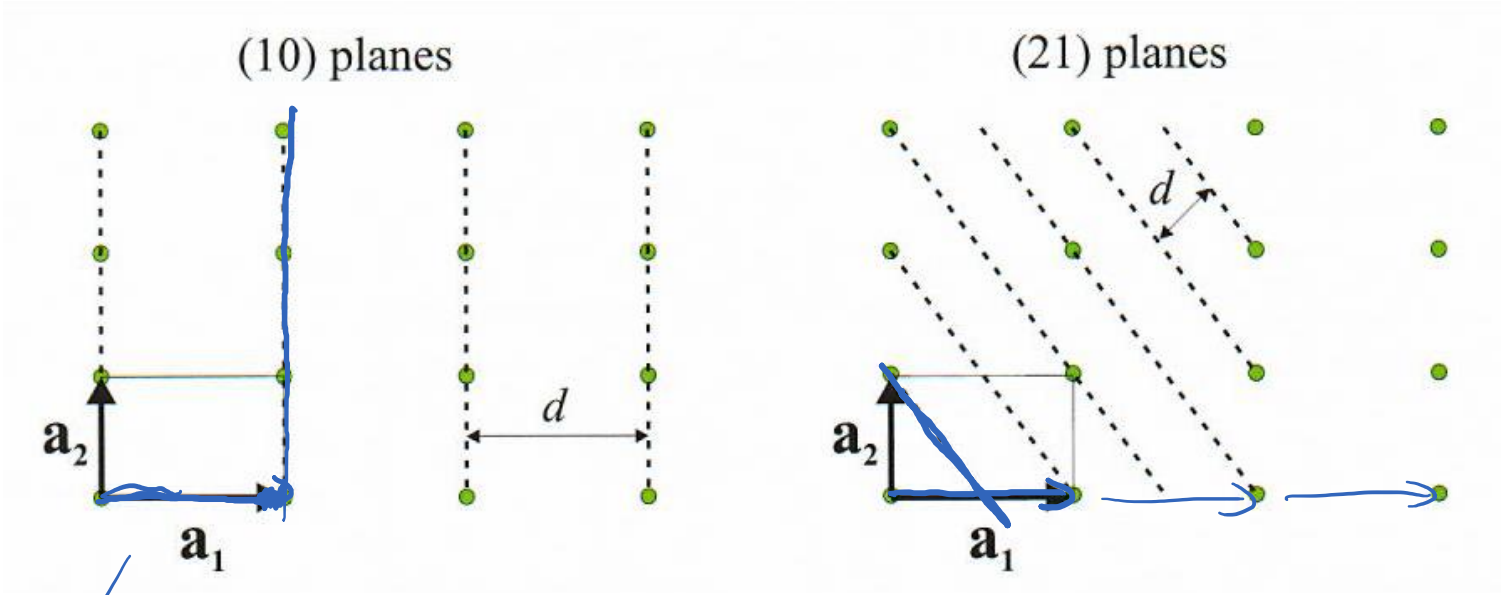
Prize share: 1/2

Lattice planes



1) Look when plane intersects axis

2) Take inverse & reduce to smallest numbers



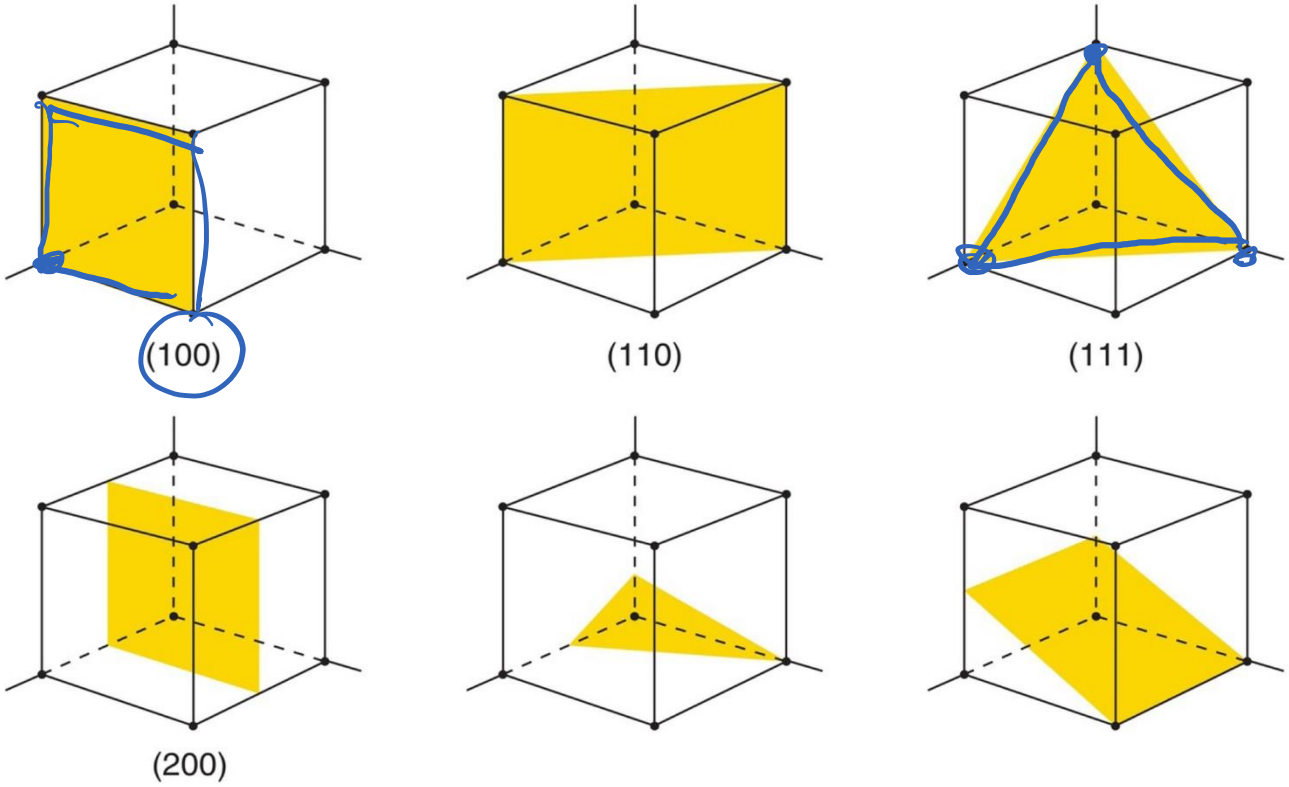
(1) intersects at 1, ∞

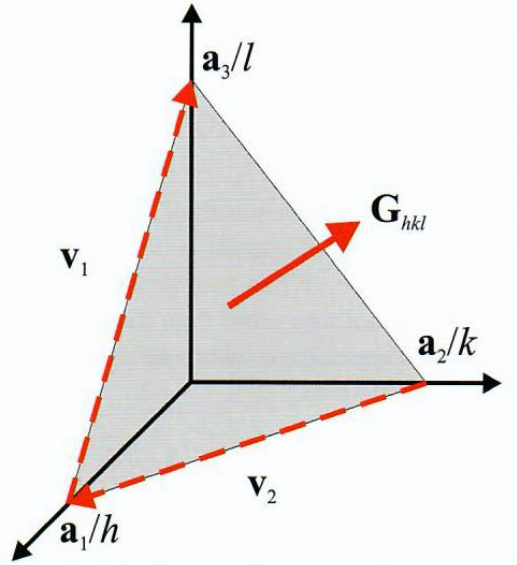
(2) inverse (1,0) → 10 plane

(1) intersects at ½, 1

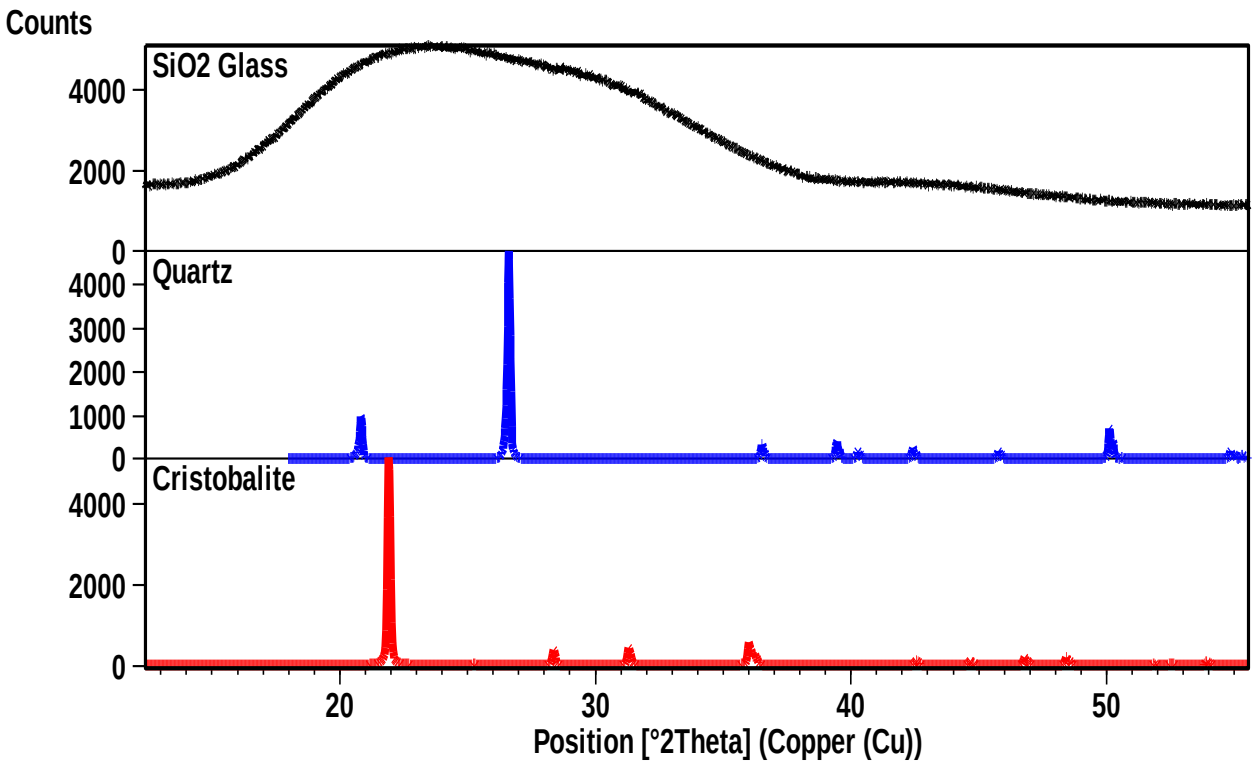
(2) inverse (21) plane

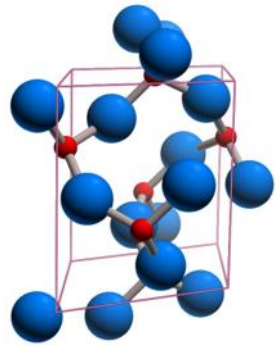
Miller indices

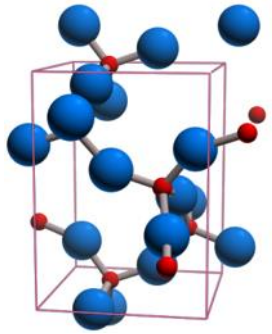




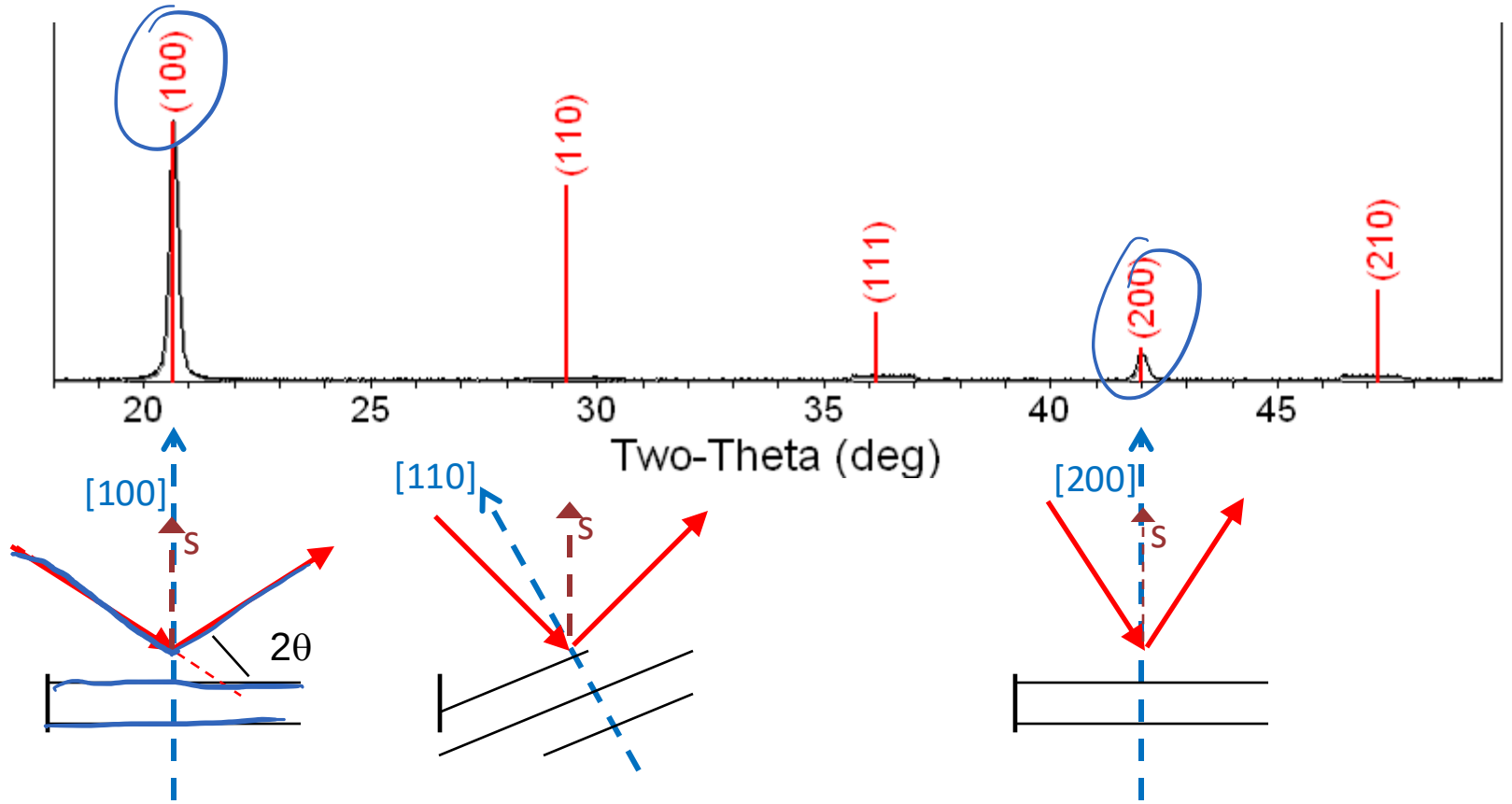
Characteristic signals from different – chemically identical – samples





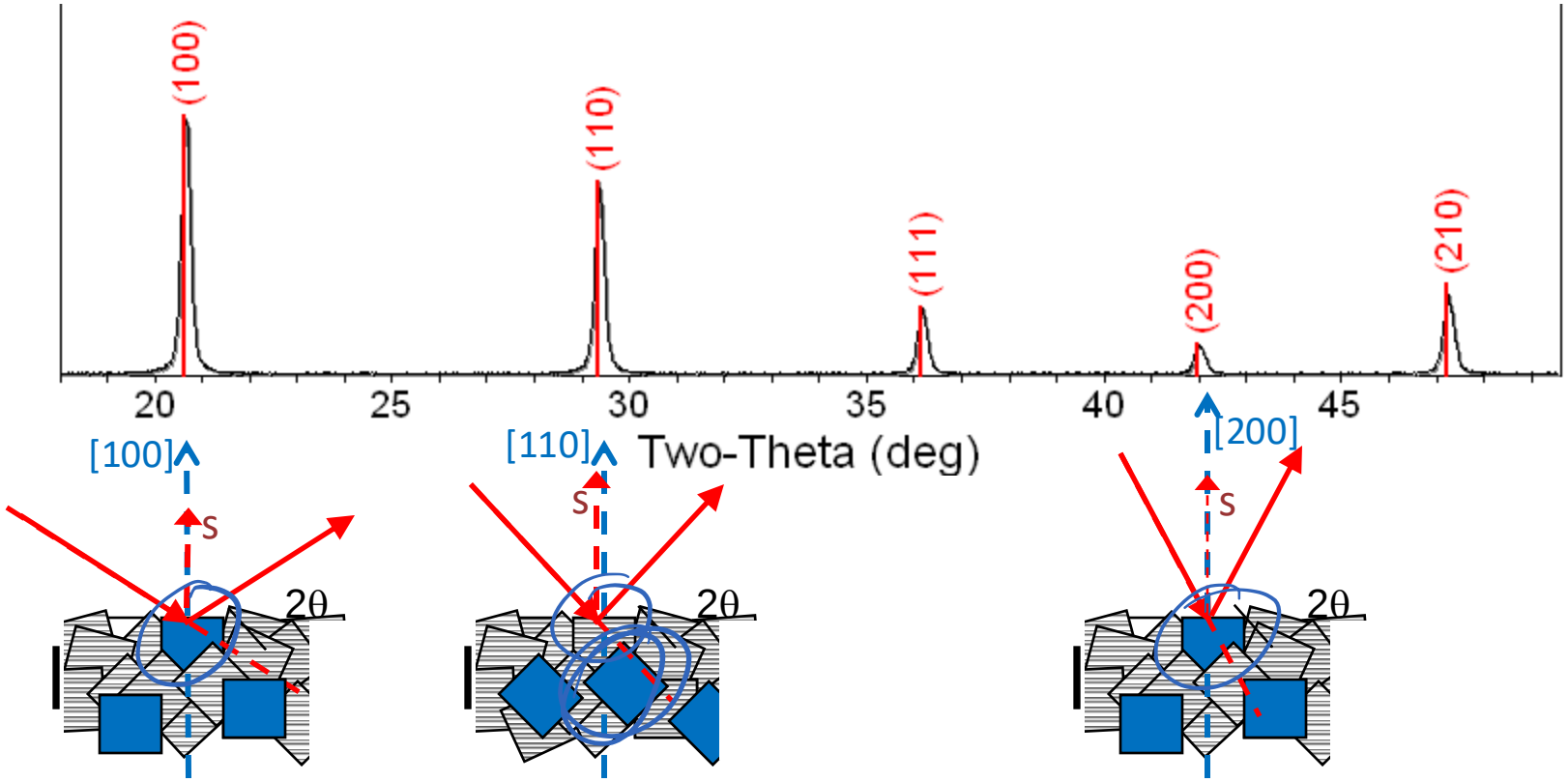


A single crystal (typically) produces one family of Bragg peaks for fixed geometry and λ

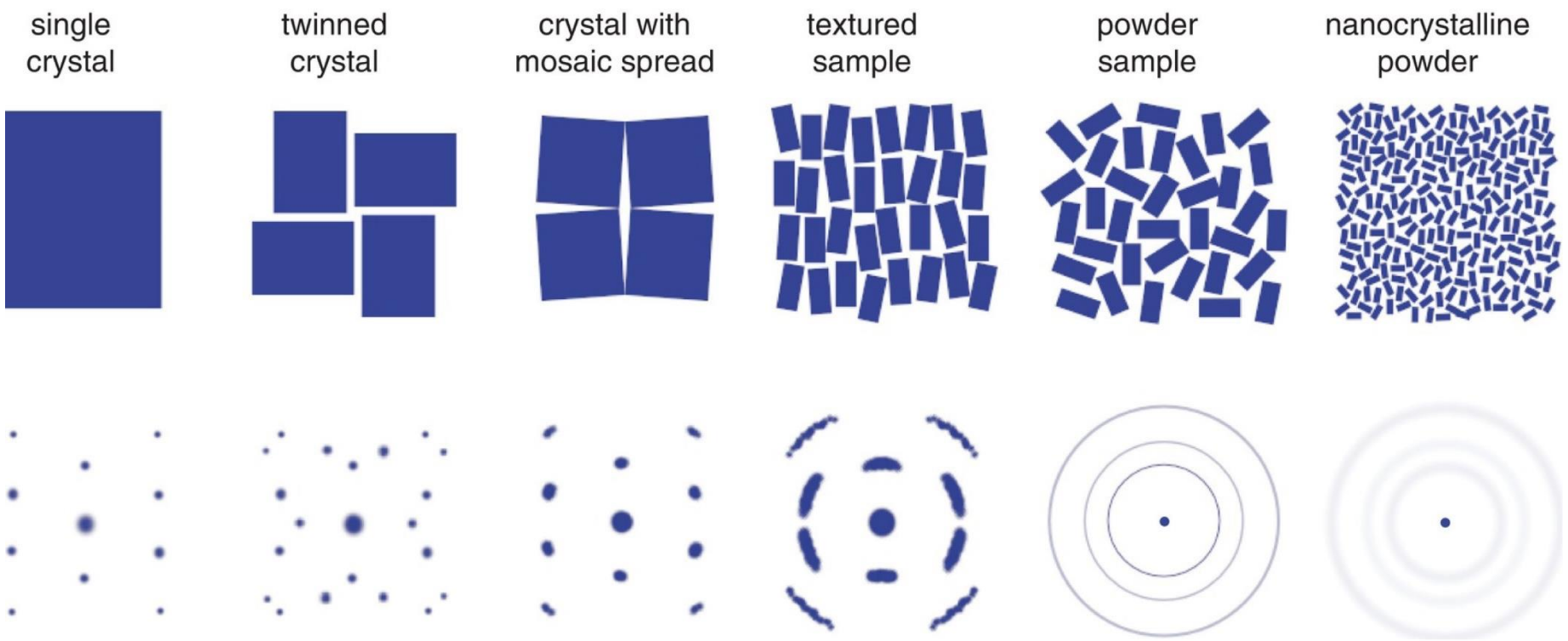


Powder diffraction

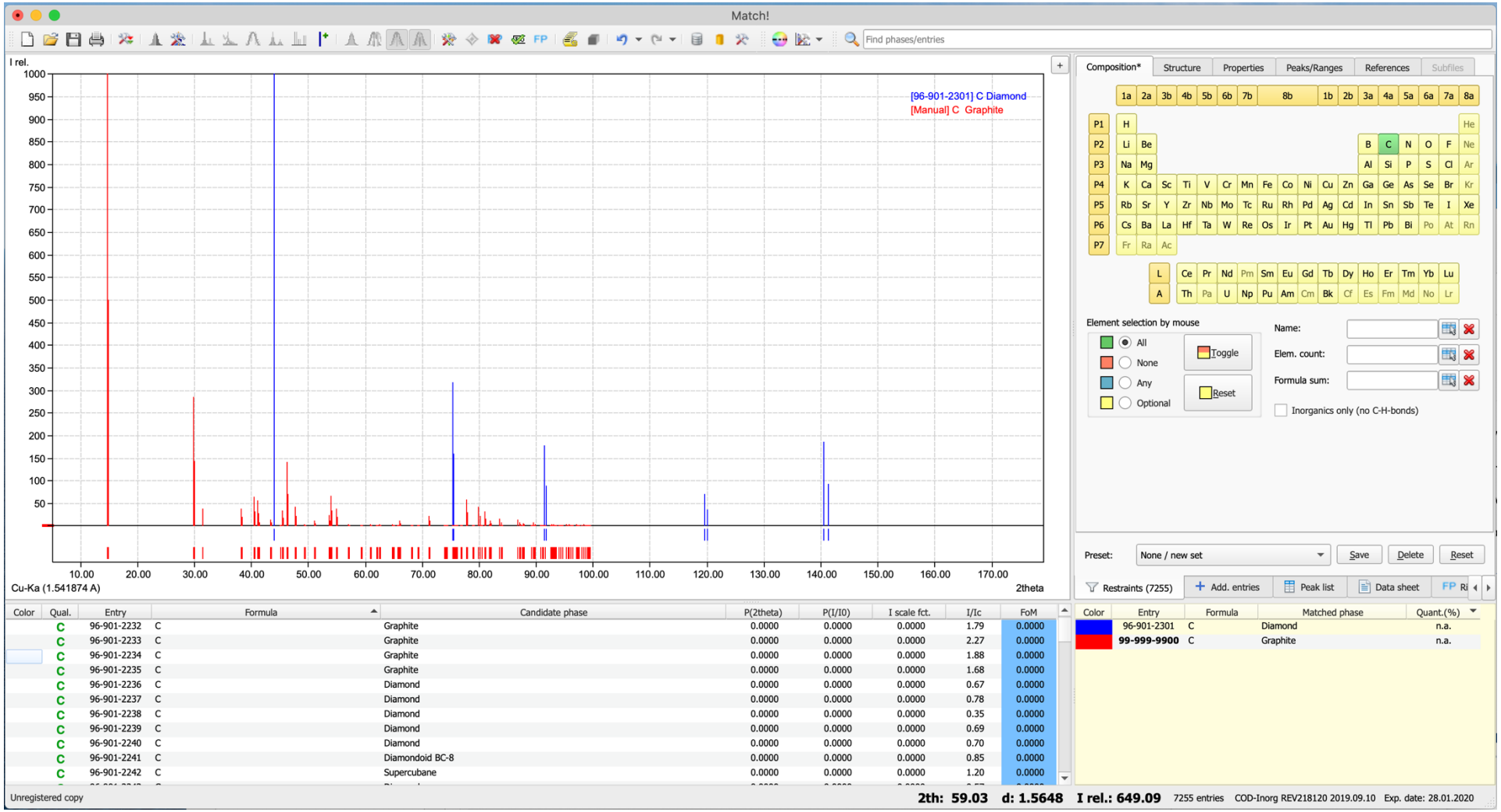
Diffraction of a polycrystalline sample



Diffraction signal of different sample types

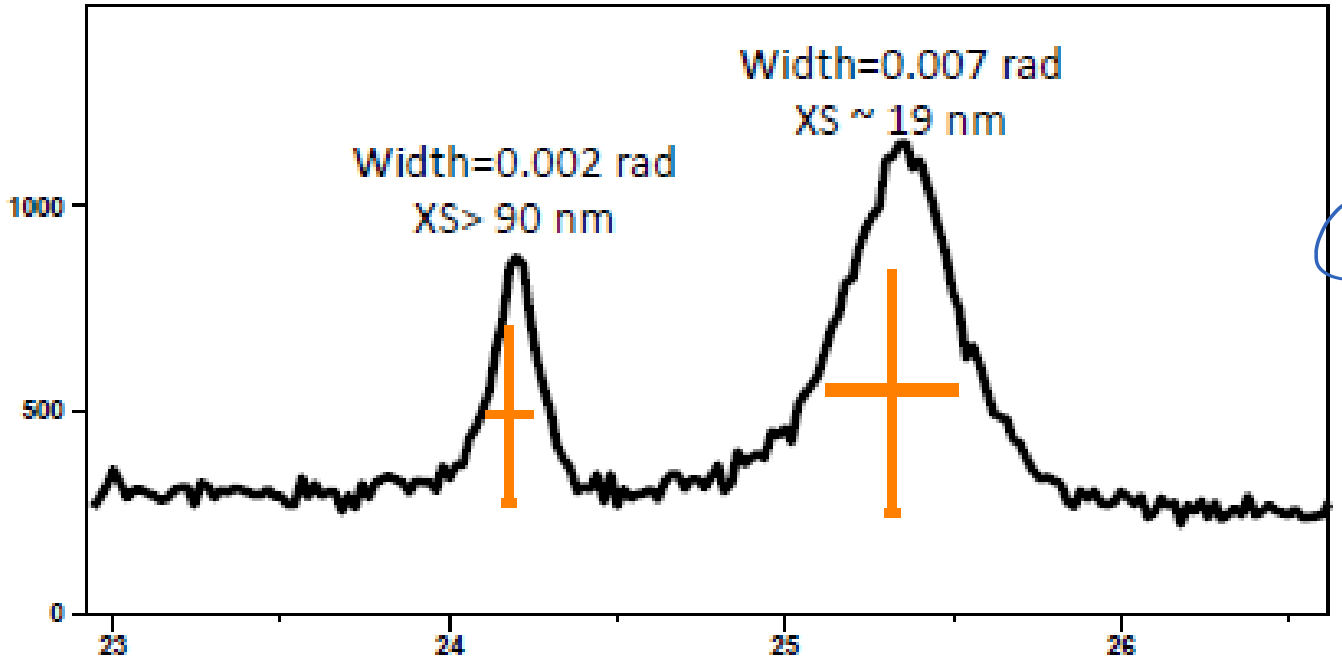


Powder diffraction data bases for elemental analysis



Debye-Scherrer Formula

The diffraction peak width may contain microstructural information

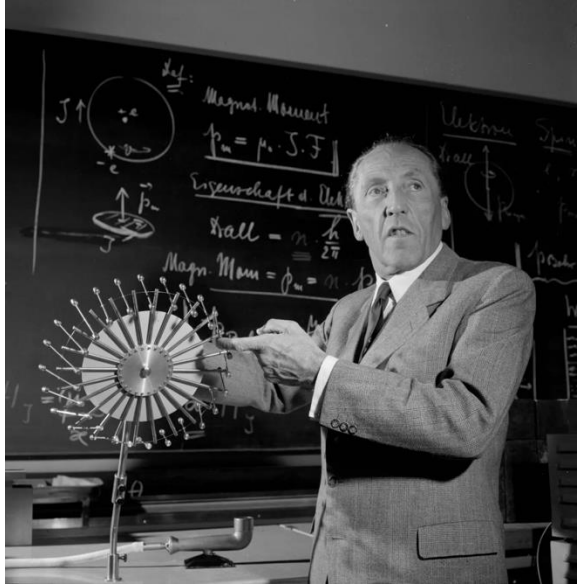


$$\text{Size} = \frac{K\lambda}{Width \cdot \cos\theta}$$

$K \sim 0.9$

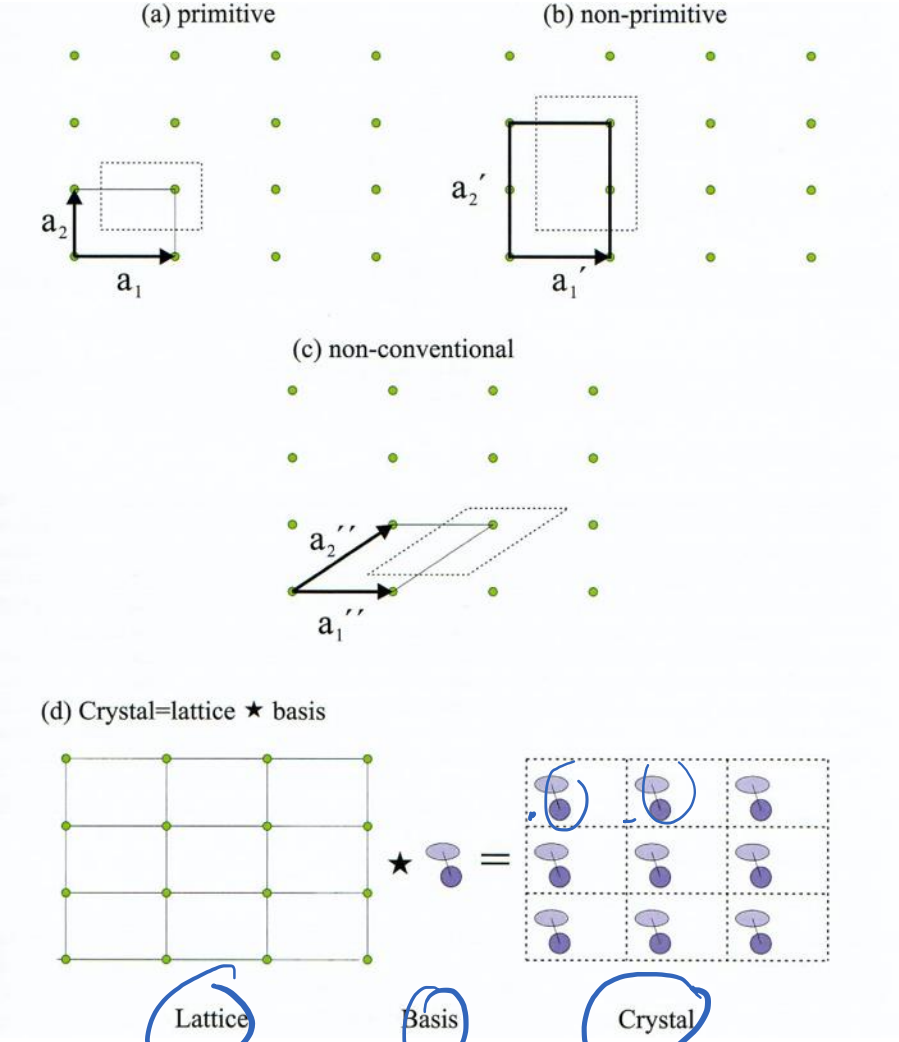
Relates width of the diffraction peak → particle size

for small samples without inhomogeneous broadening of symmetry



Paul Scherrer
Swiss Physicist (1890-1969)

A crystal is defined by ist lattice and basis



Convolution Lattice ⊗ Base

Remark diffraction ⟺ Fourier transform

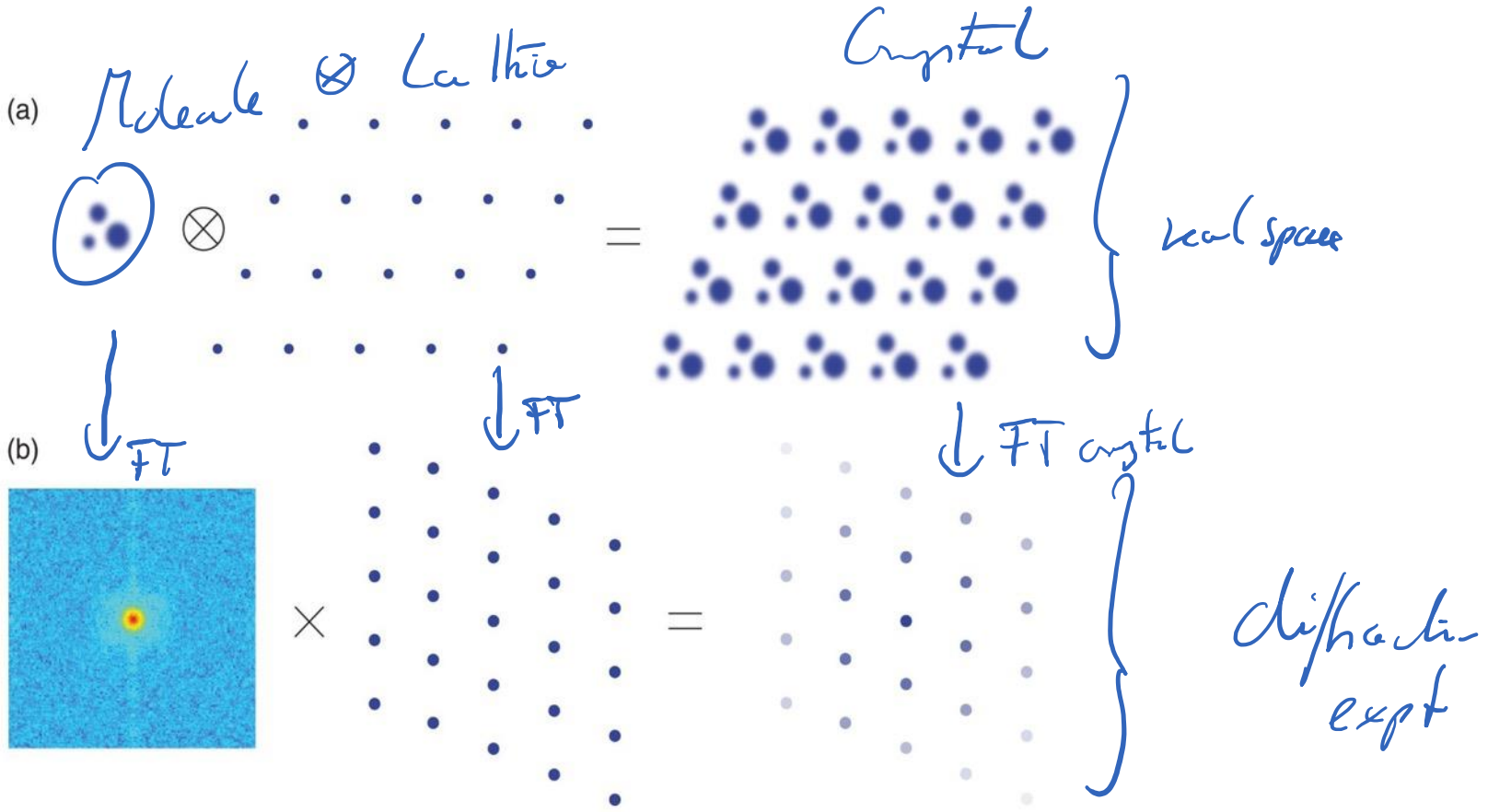
Diffraction FT

$FT(g \otimes g) = FT_{(g)} \cdot FT_{(g)}$

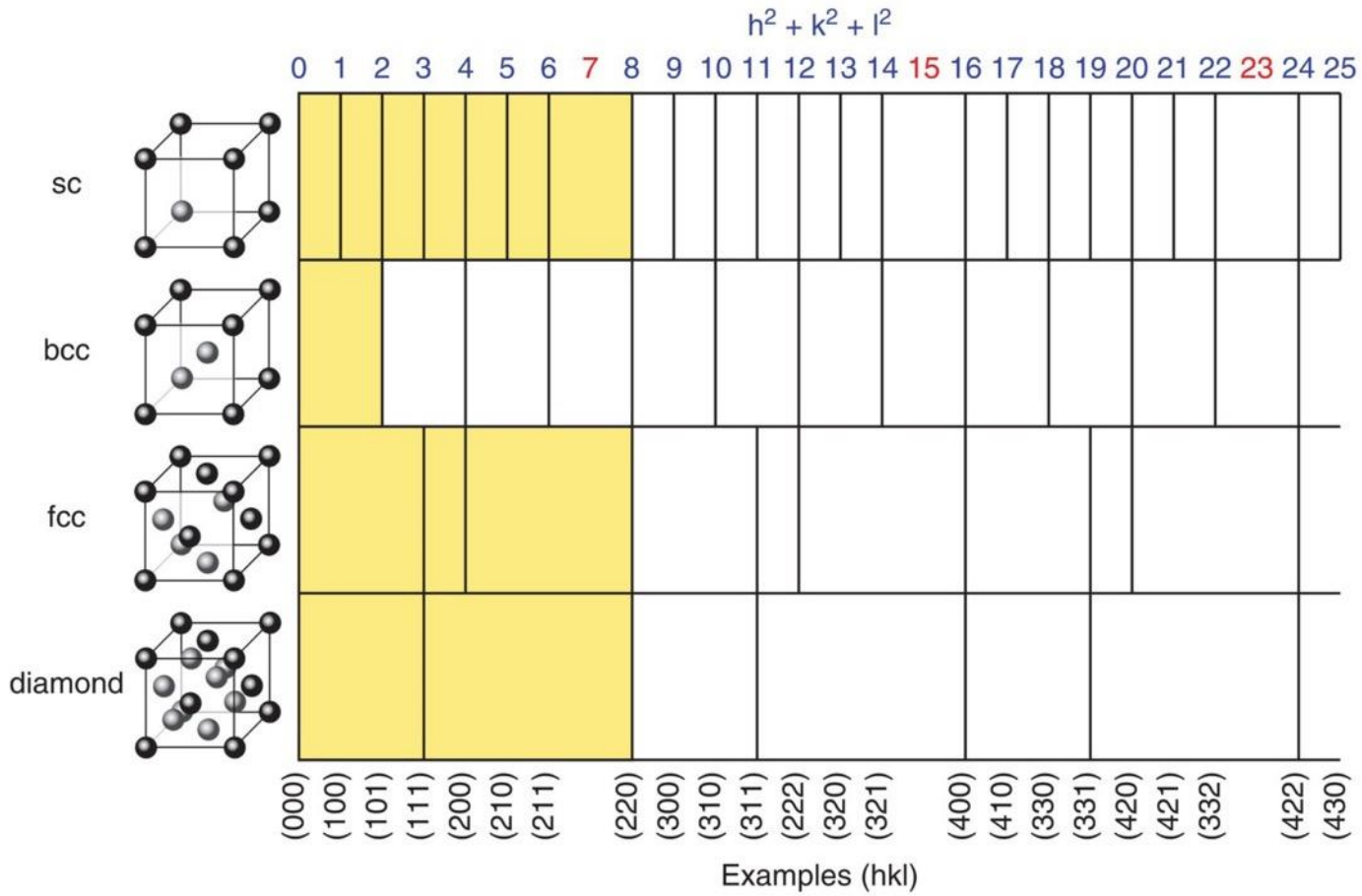
Lattice → FT → physics

Why and how does it work?

Remember last week:

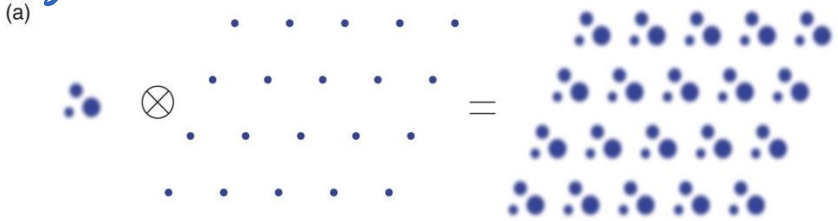


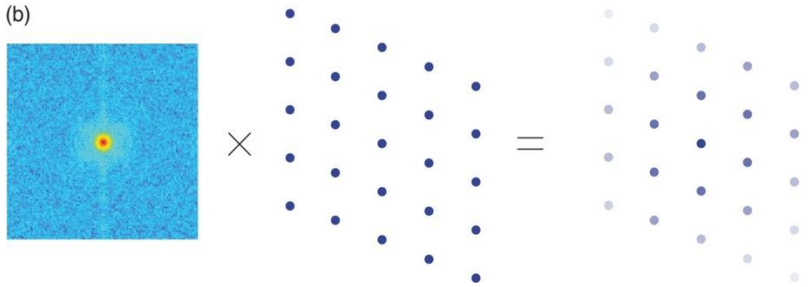
Allowed and forbidden reflections



Solving a crystal structure

Box ⊗ Lattice = Crystal





Molecule ⊗ Bragg = diffraction
path ⊗ path = path

↓

"electrons"

Envelope ⊗ Peaks = diffraction data

Phase

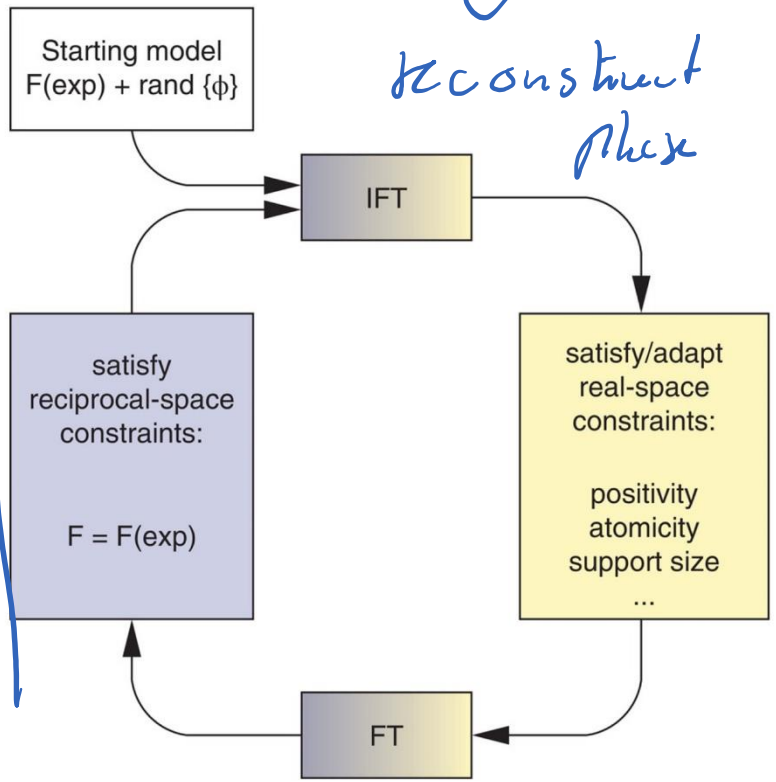
$A = A_0 \exp[-\dots\phi]$

$I = |A|^2$

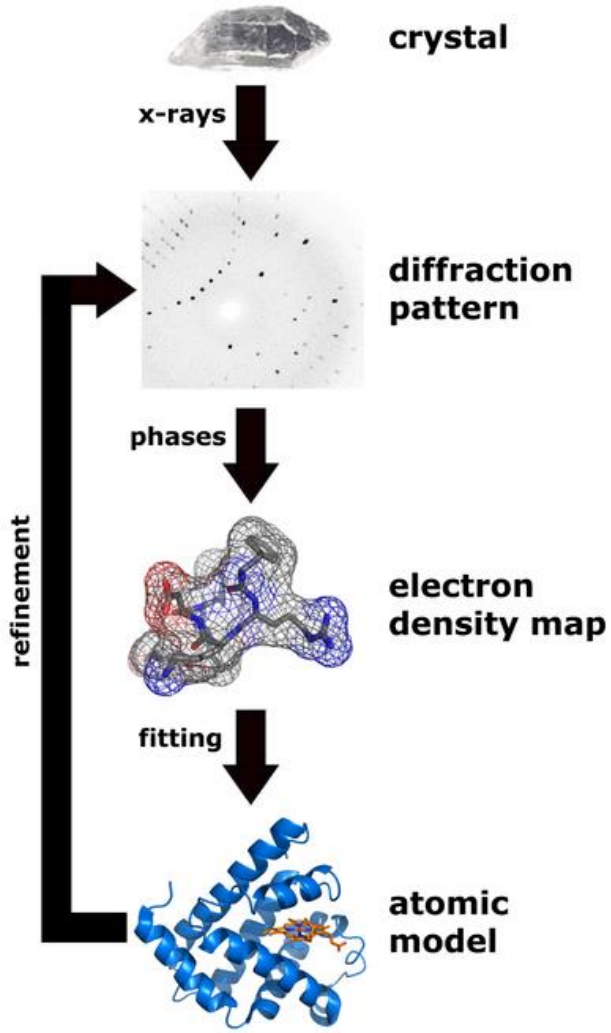
phase lost

↓

reconstruct phase



← iterative



The end