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

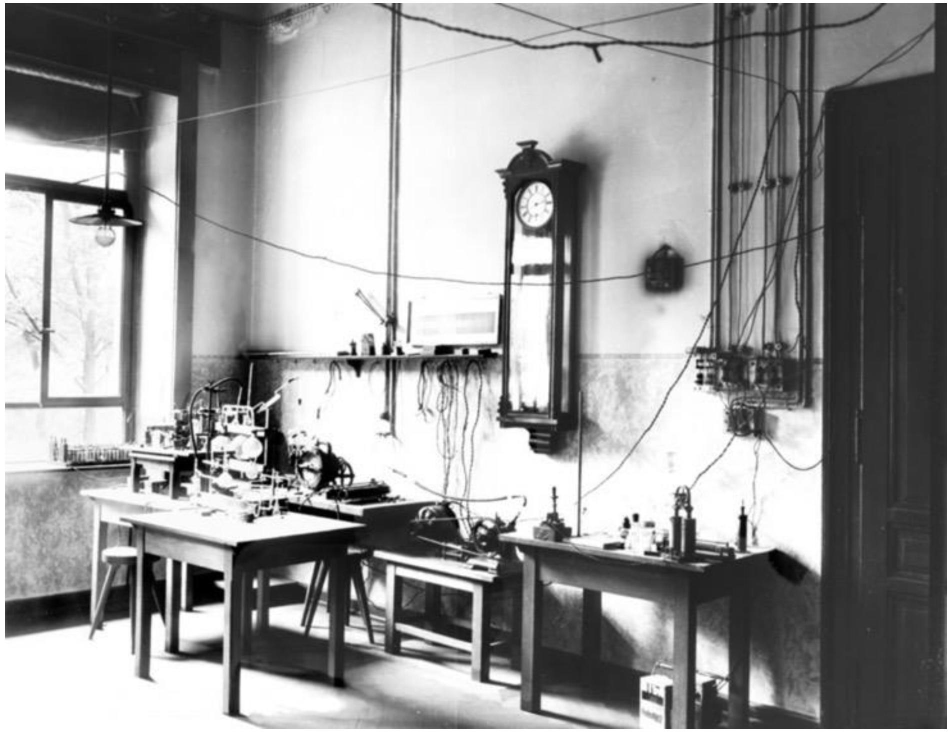
Today:

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



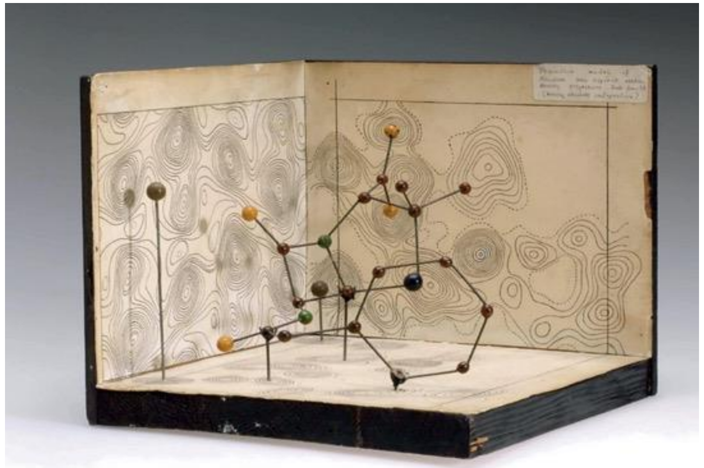
- Röntgens lab in Würzburg
- Experiments with vacuum tube
- Noticed fluorescence on a screen despite light-tight packaging of tube
- Postulated mysterios x-rays

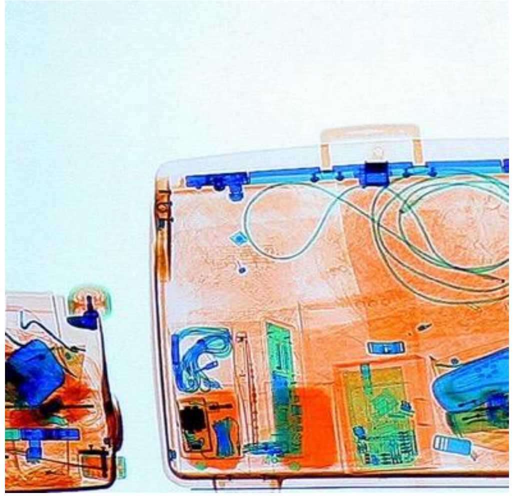
- During experiments illuminated his hand and saw bone structure
- Took first "medical" x-ray on his wifes hand
- Denied patenting request to fully exploit potential of x-rays

Discovery of X-rays triggered many technological and scientific developments

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

First Nobel Prize in 1901

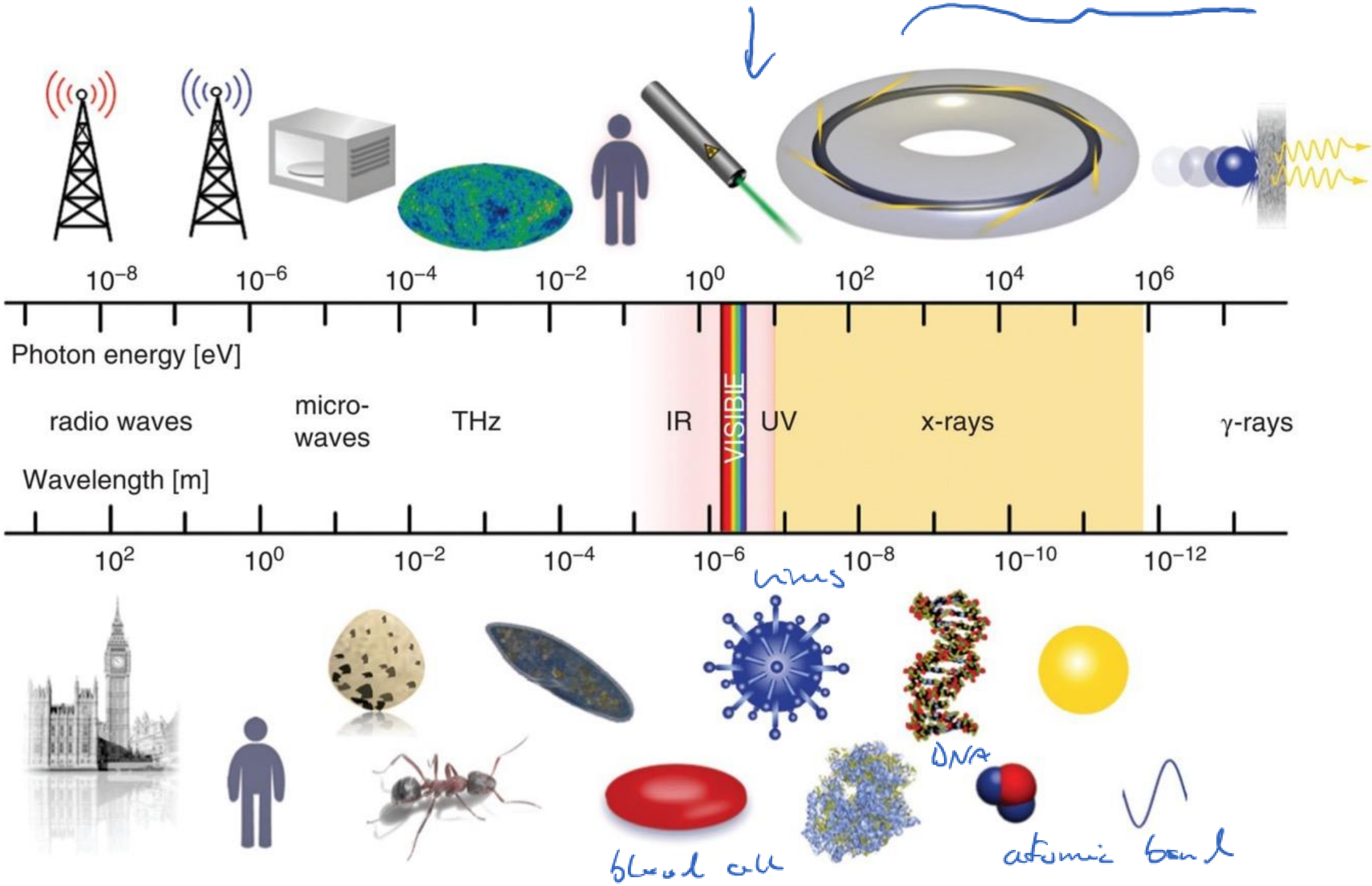




X-rays are high-energy electromagnetic (em) waves

visible: valence electrons

x-rays: innershell electrons



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

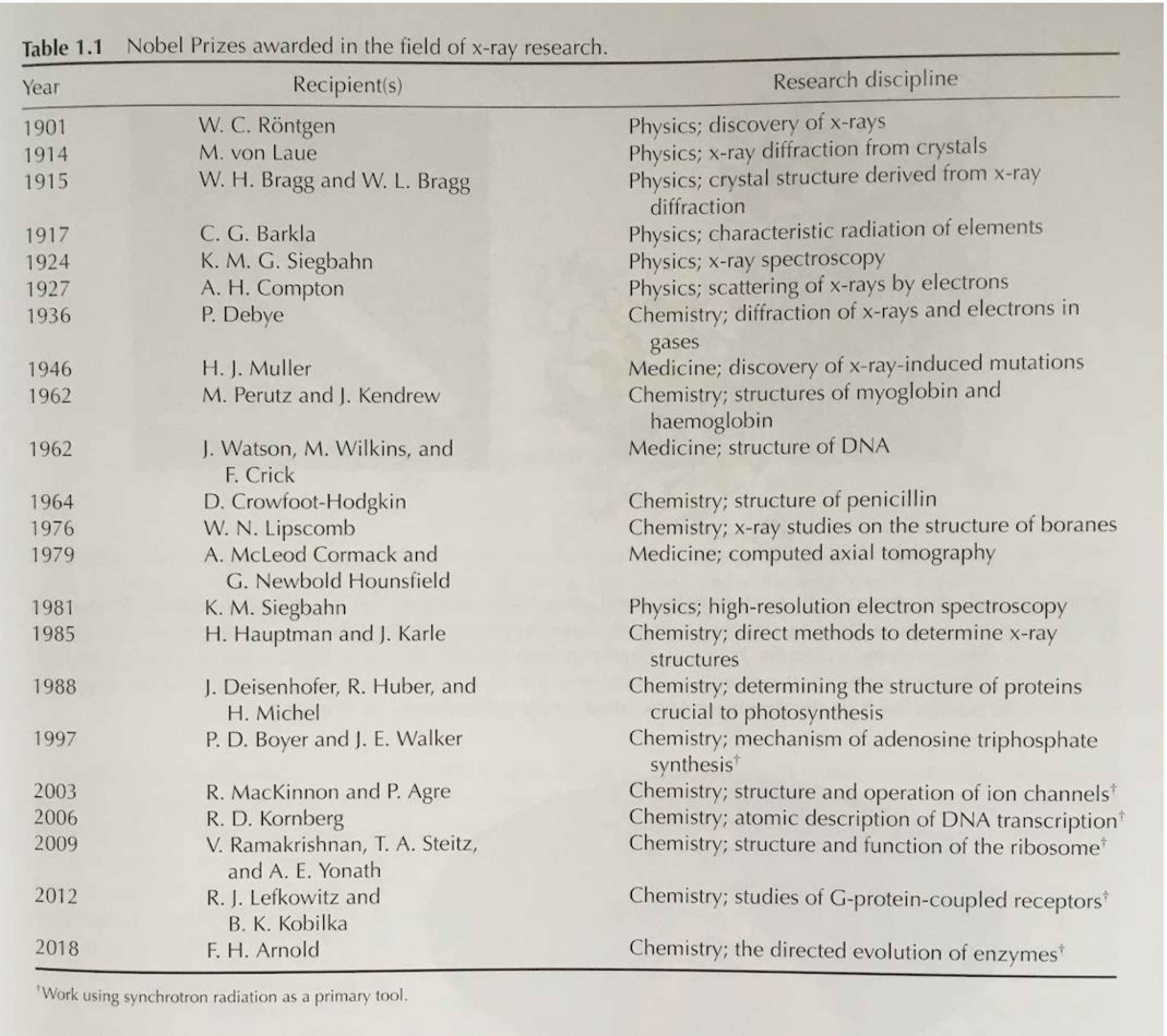


Table 1.1 Nobel Prizes awarded in the field of x-ray research.

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†

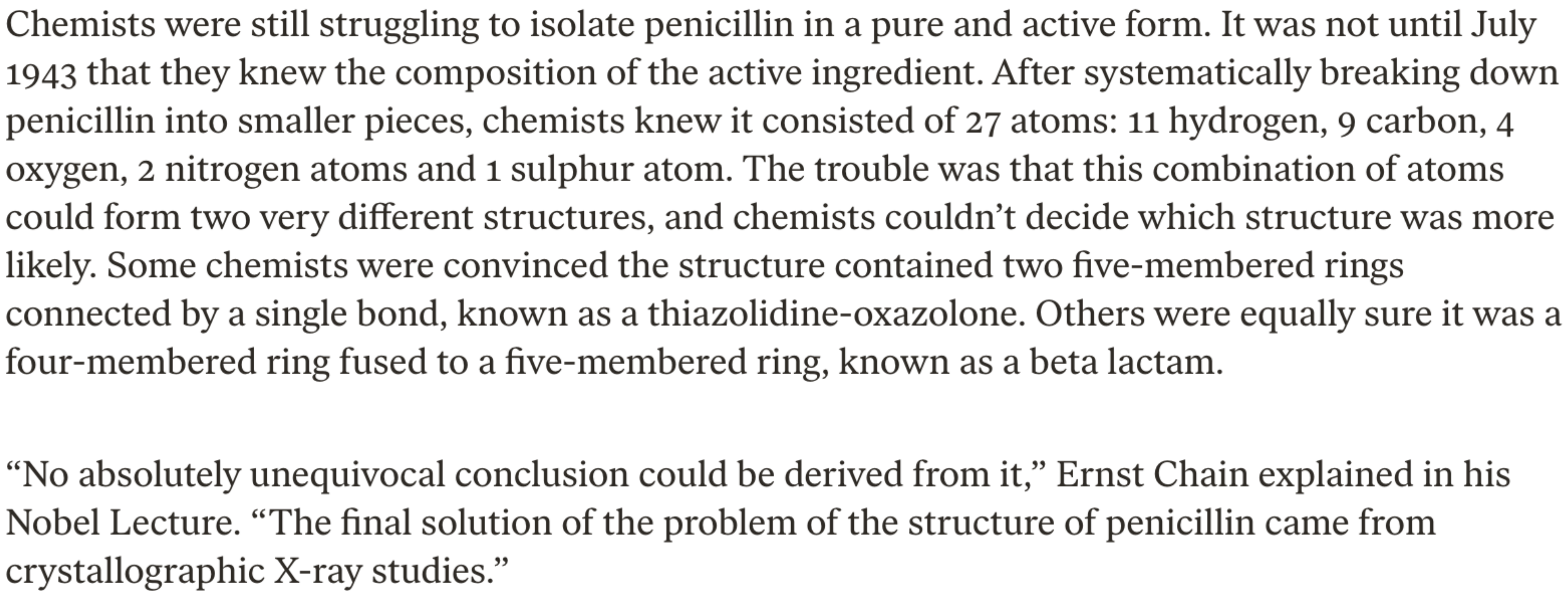
†Work using synchrotron radiation as a primary tool.

mostly physics

dominantly chemistry

Why care about x-ray diffraction of crystals?

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



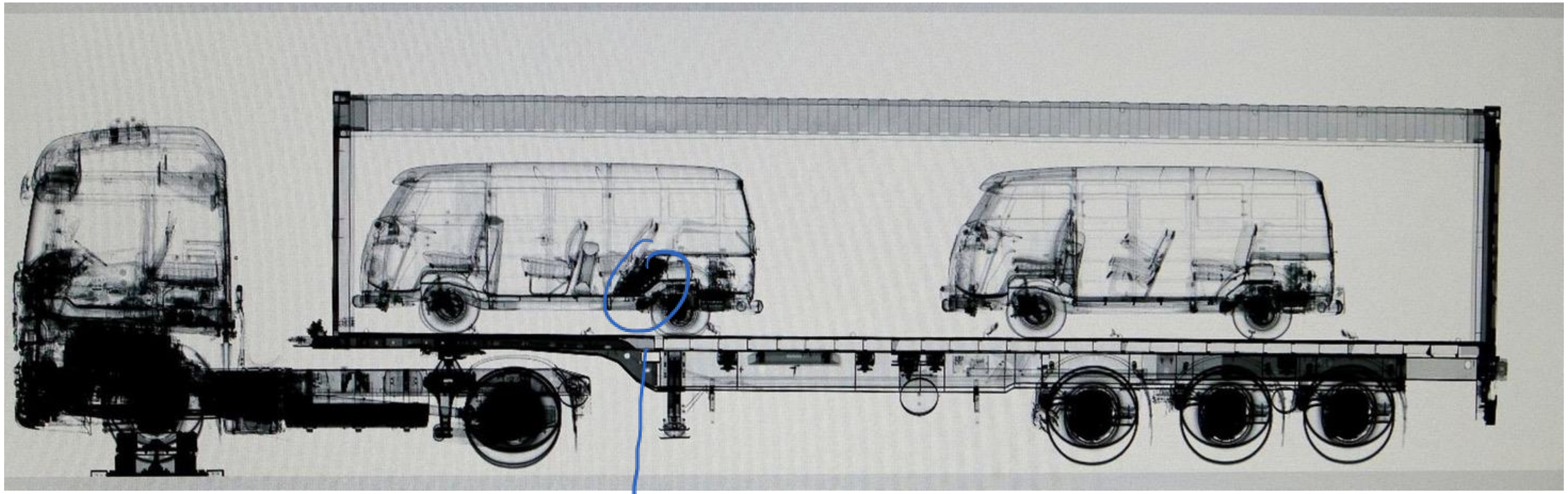
Chemists were still struggling to isolate penicillin in a pure and active form. It was not until July 1943 that they knew the composition of the active ingredient. After systematically breaking down penicillin into smaller pieces, chemists knew it consisted of 27 atoms: 11 hydrogen, 9 carbon, 4 oxygen, 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

(chemistry: in situ / in operando)



illegal substances

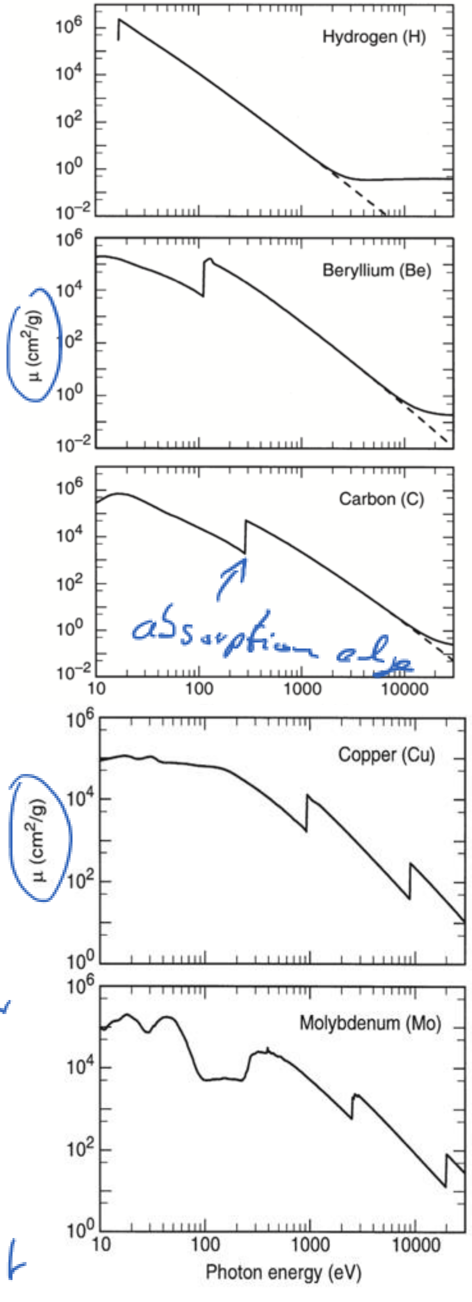


Fig. 1-5. *Mass absorption coefficients (continued).*

Lambert - Beer absorption law ⟷ Intensity decreases equally over unit distance

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

ε extinction factor

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

μ absorption coefficient

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

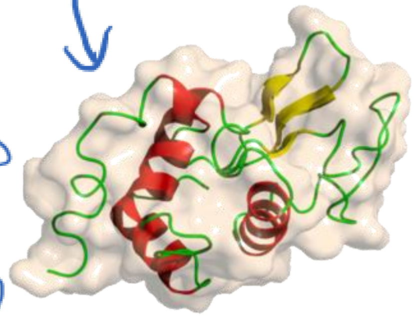
$C_{125}H_{196}N_{40}O_{36}S_2$

Structure

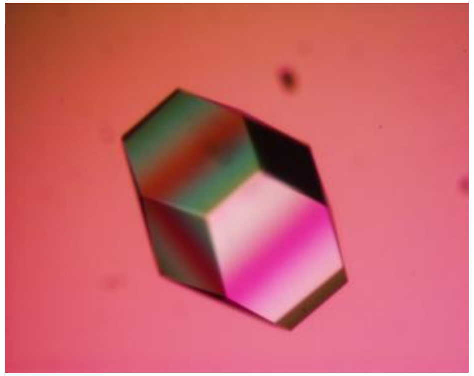
MS

NMR →

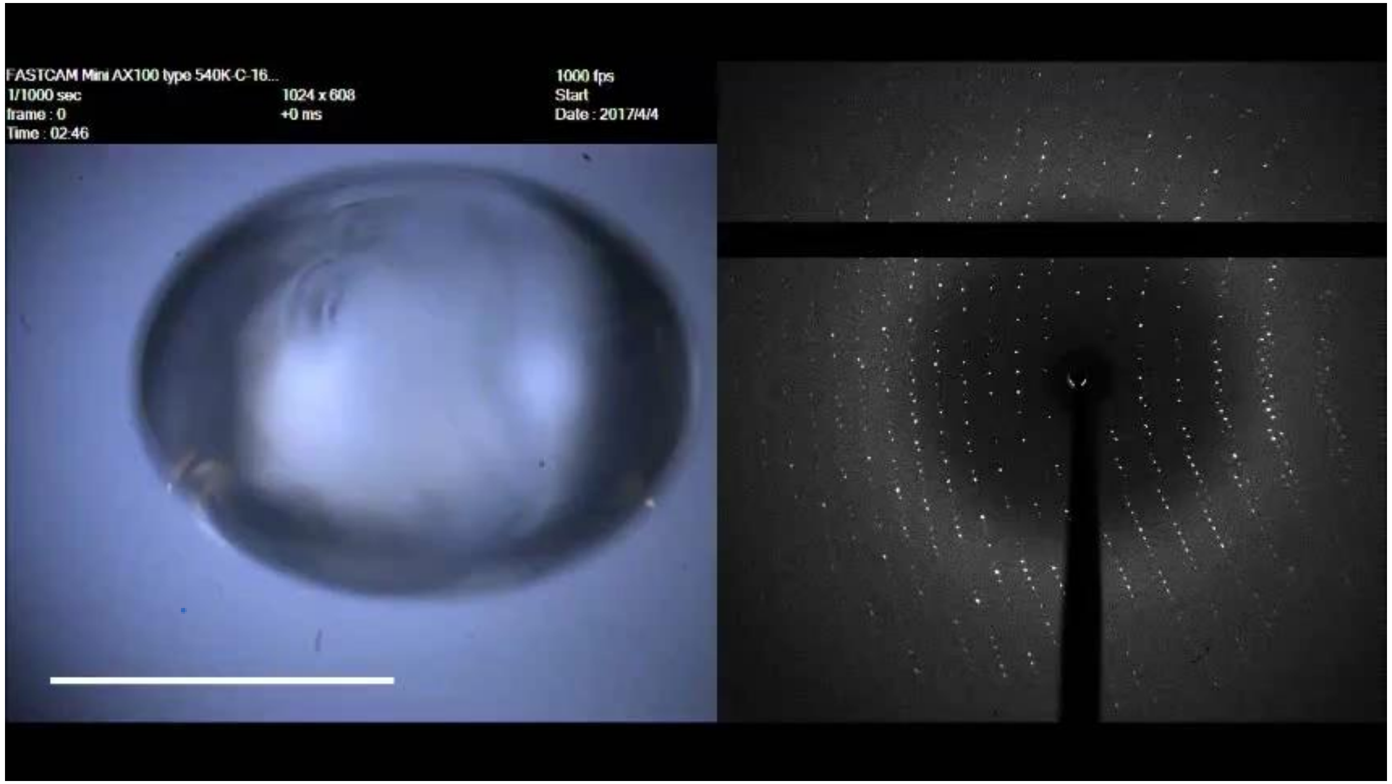
x-rays



Crystal



Experiment at the Swiss Light Source



Lysozym crystal

Bragg reflections

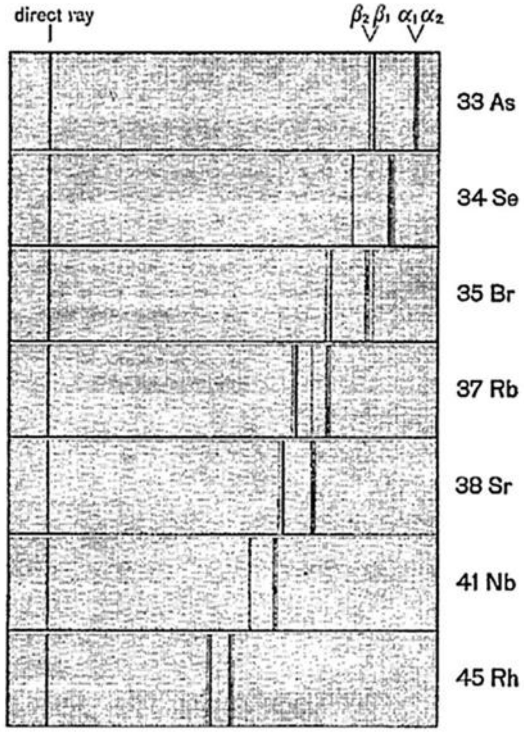
Elements possess specific colors – also in X-ray spectral regime

Barkla, Nobel Prize in 1917

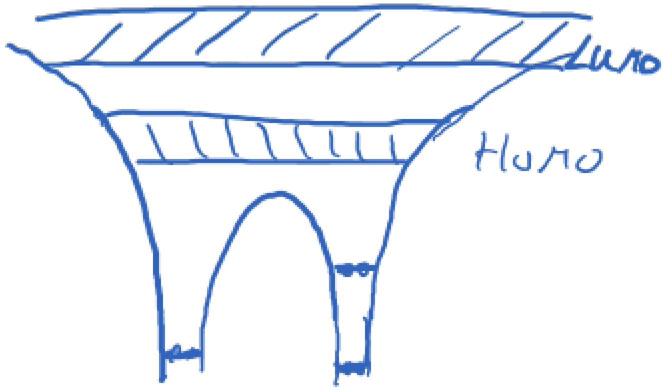
Rose of Lausanne:
Characteristic visible colors

valence transitions
→ visible to eye

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

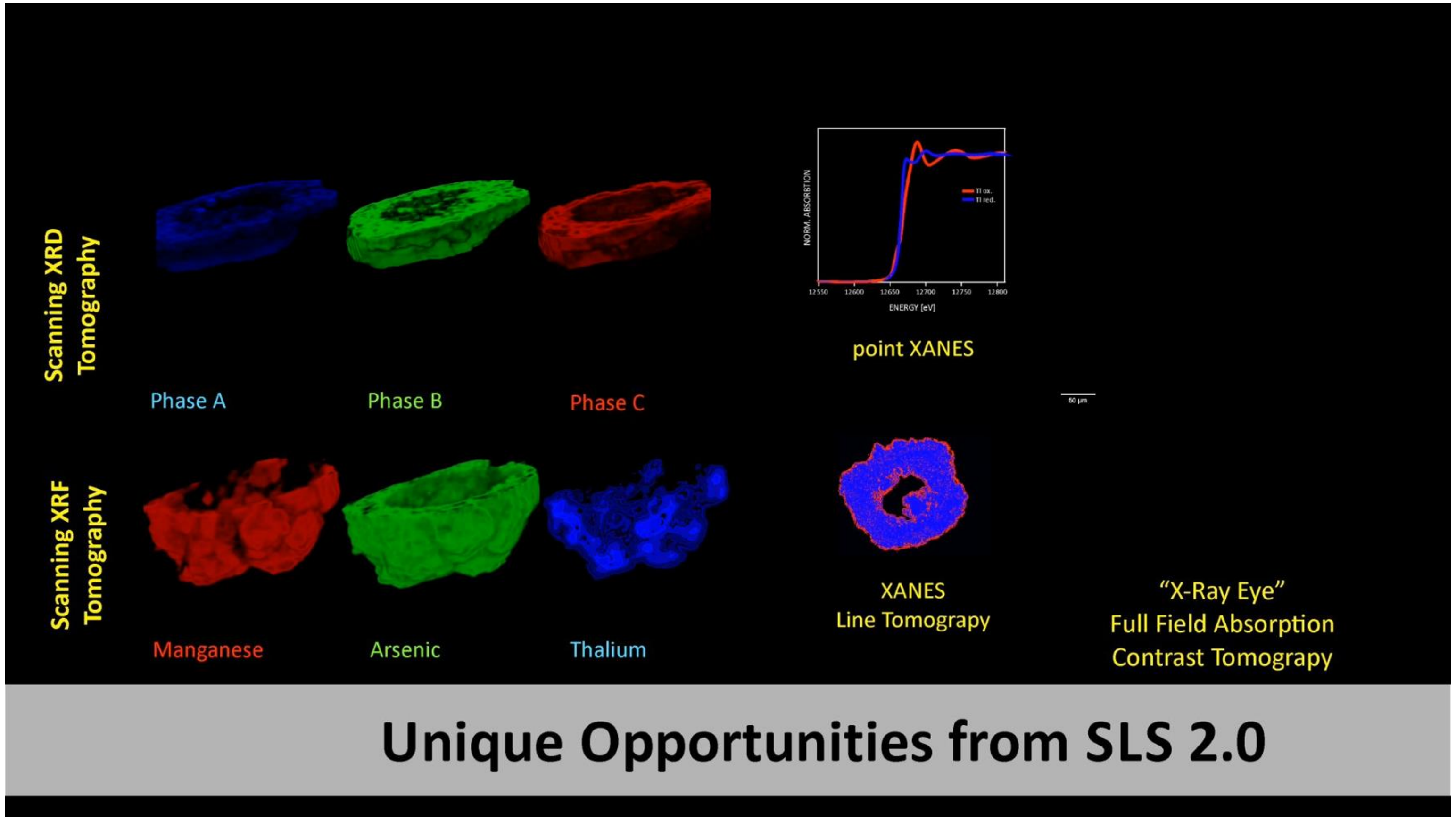


innershell transitions
→ visible to x-ray detectors



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

Example: Geological Thalium sample (Geochemistry)



Unique Opportunities from SLS 2.0

X-ray interactions with matter

X-ray interactions with matter

non-resonant

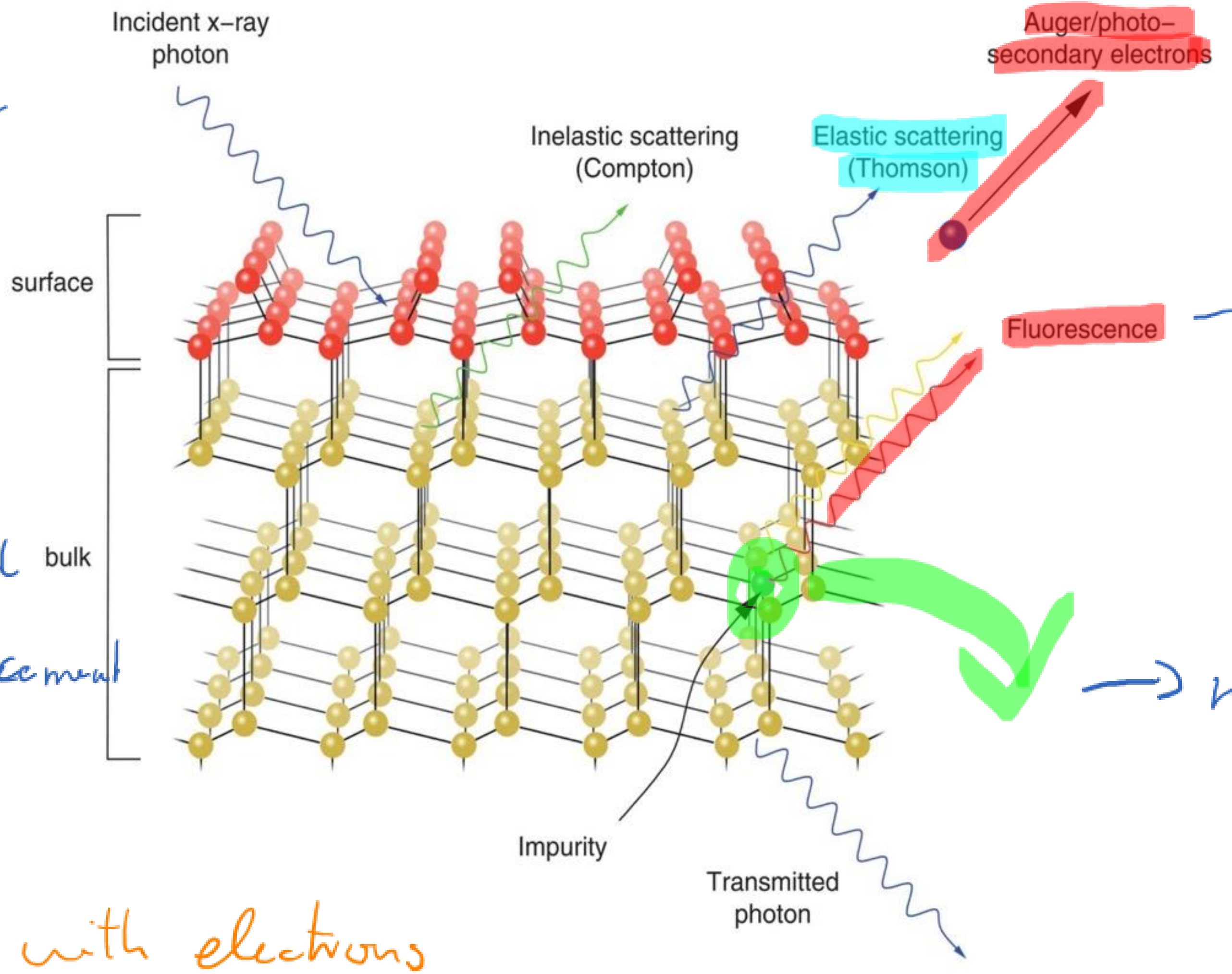
general case

cross section σ

resonant

interaction with specific core level

↳ large σ enhancement



electronic structure

↓

binding energy info

↓

local chem environment

→ resonant conditions

⇕

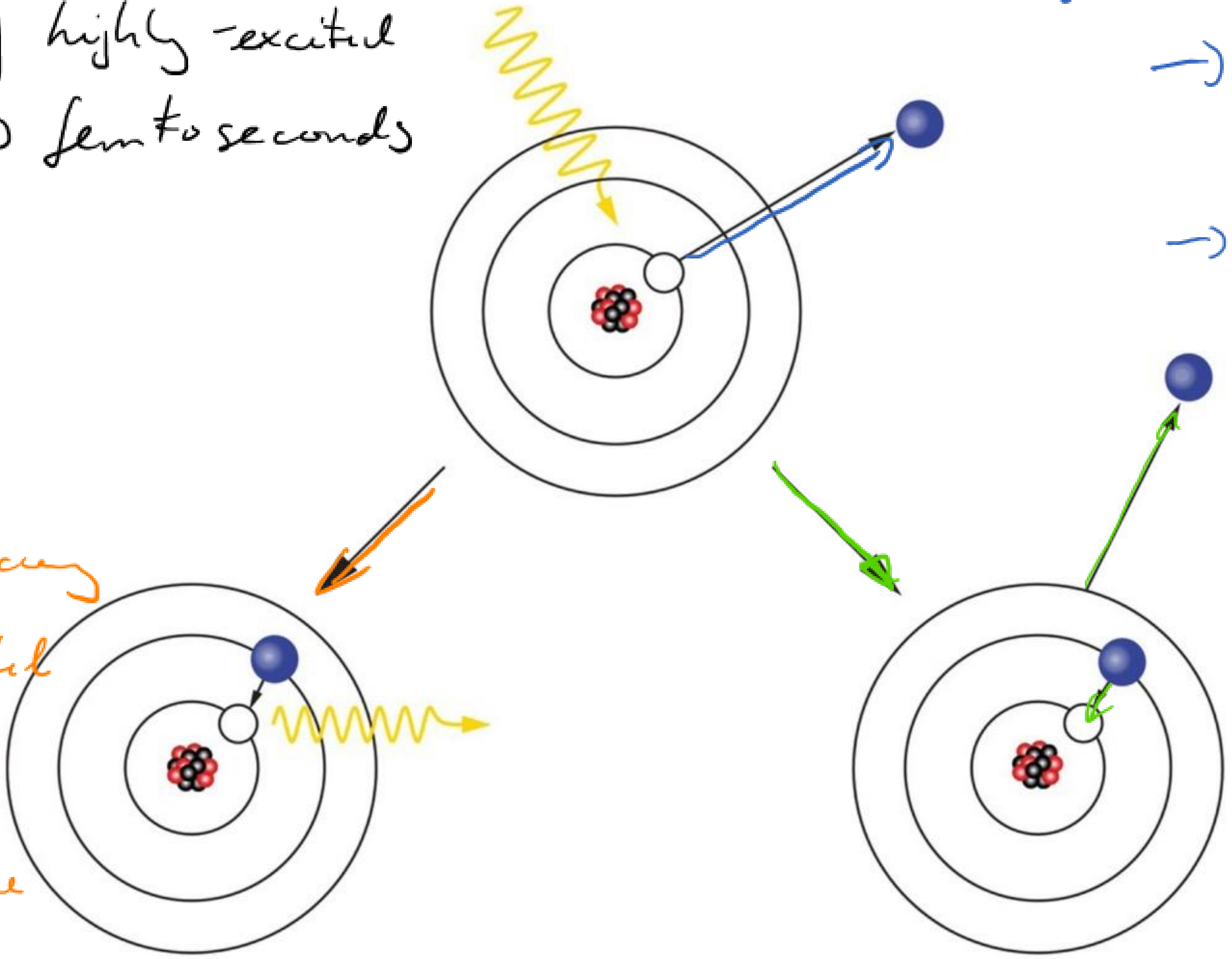
largest contrast

Remember:

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

Photoionization / absorption

Note: decay of highly-excited atoms → femtoseconds



Photoelectron

→ core-electron spectroscop

$E_{kin} = h\nu - E_B$

→ electronic structure info

fluorescence decay

→ photon emitted

dominant in hard x-ray regime

Auger decay

→ Auger electron

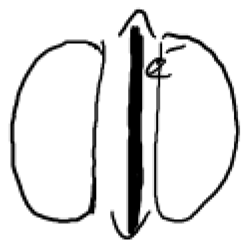
⇒ Auger spectroscopy

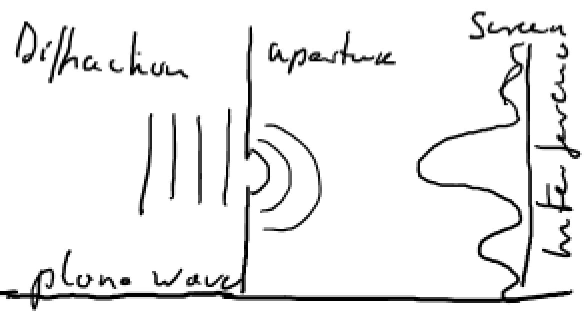
powerful tool for elemental analysis (element specific)

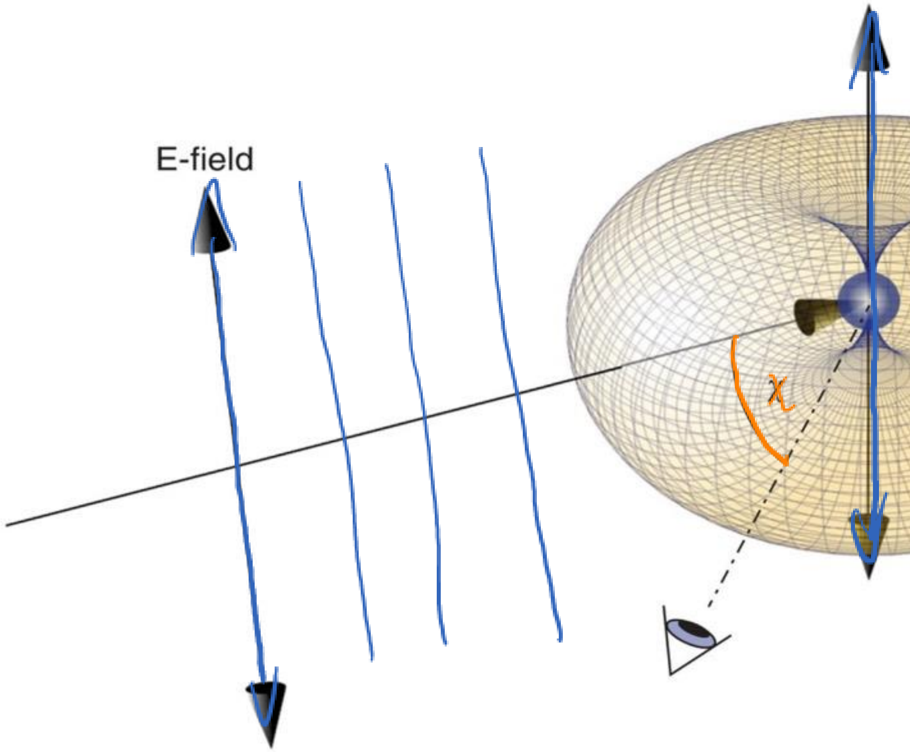
Thomson scattering

Remember from Physics

Dipole radiation







Dipole no intensity along axis

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

→ semi-classical description

→ x-rays well approximated by planar wave

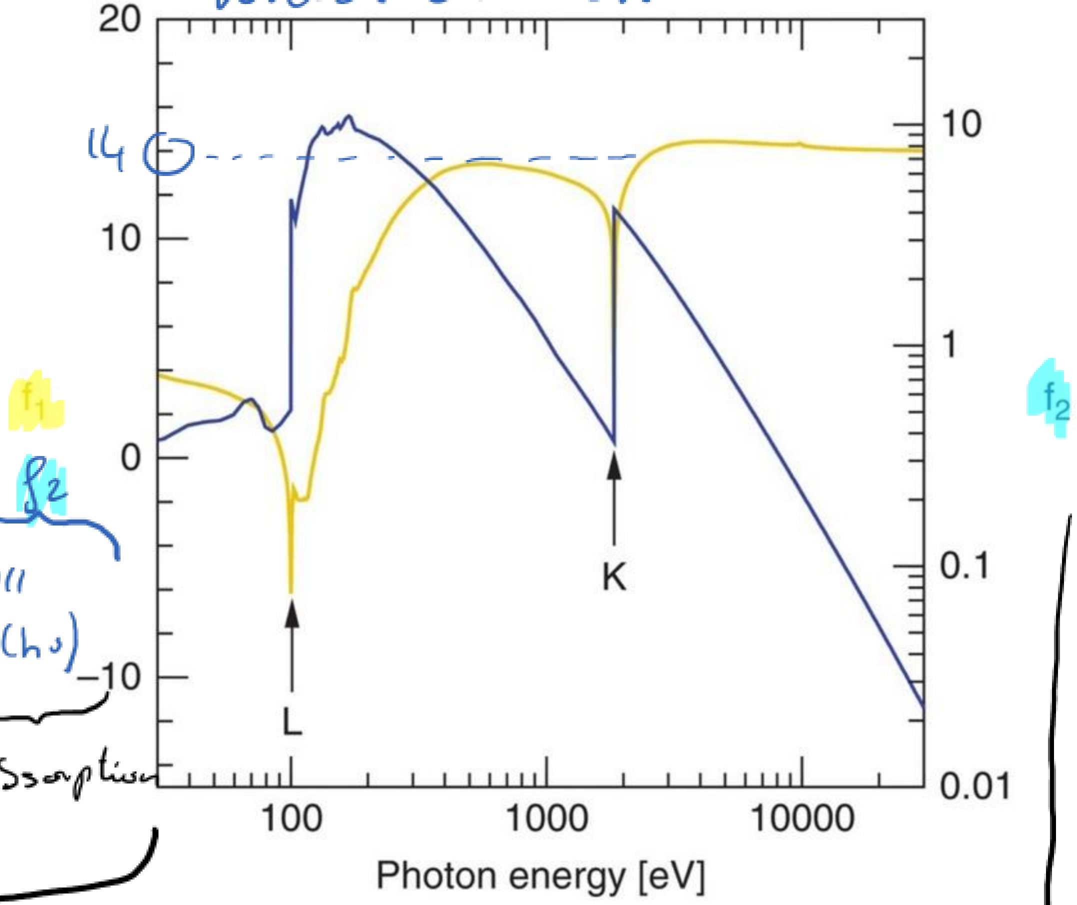
→ x-ray scattering process described by dipole radiation

Scattering process

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

Atomic scattering factors and refractive index

which element?



$$\underbrace{f(h\nu) = \underbrace{\overbrace{f_0 + f'(h\nu)}^{f_1}}_{\#\text{ electrons}} + i\underbrace{\overbrace{f''(h\nu)}^{f_2}}_{\text{absorption}}}_{\text{x-ray analogue to "refraction index"}}$$

⇒ $f_1 \sim$ # electrons

⇒ 14

⇒ $1s^2\, 2s^2 2p^6\, 3s^2\, 3p^2$

⇒ Si

⇒ double check with absorption edge / f_2

Relevance

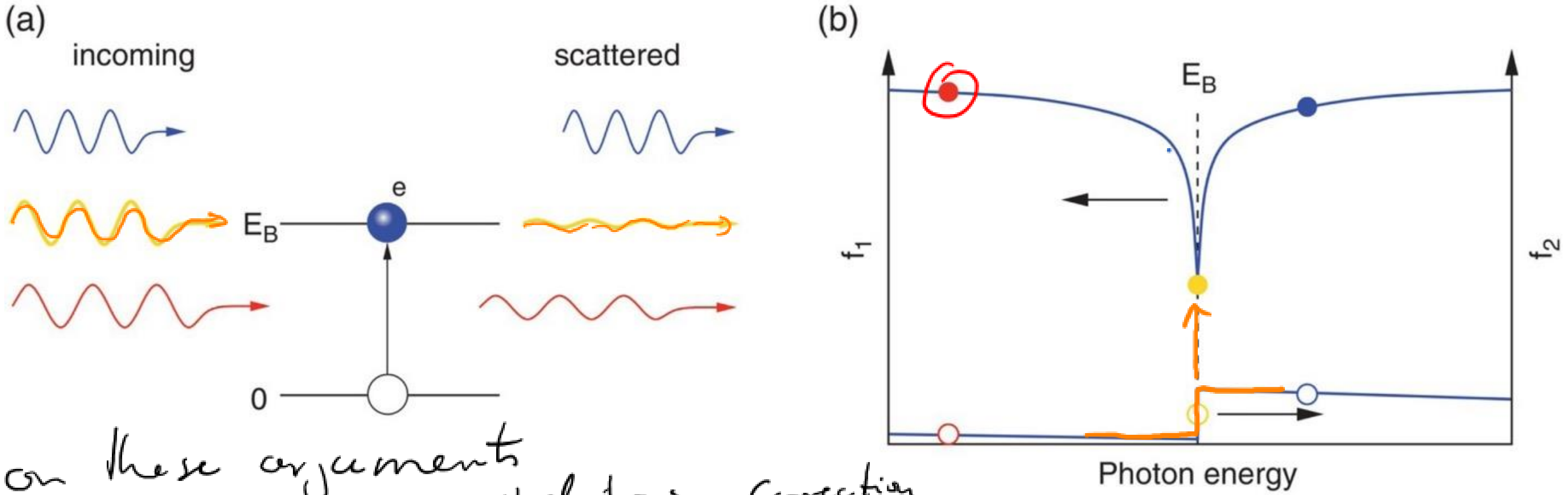
absorption → electronic levels

scattering → electronic information

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

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 3keV

$\lambda \leq$ atom

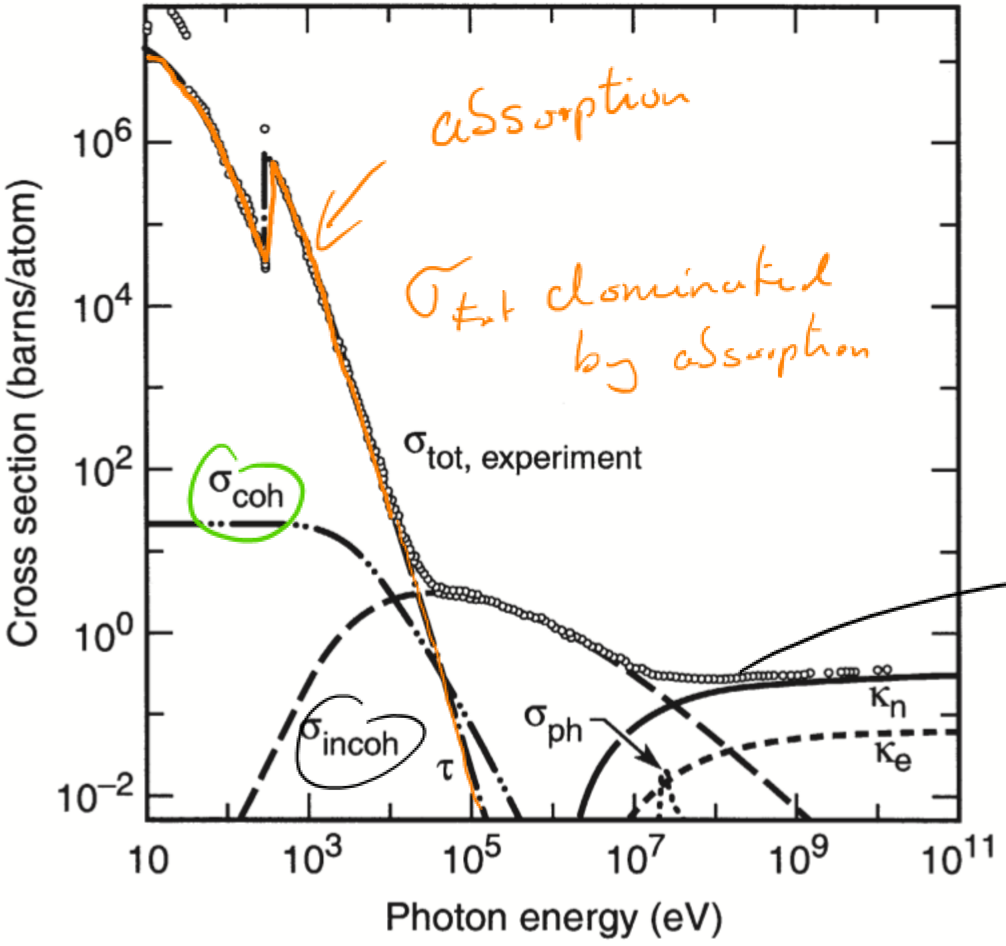


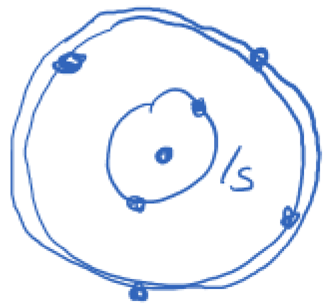
Fig. 3-1. *Total photon cross section σ_{tot} in carbon, as a*

Compton scattering

Pair production

(Physics)

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



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

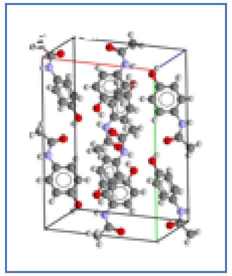
Not Polymeric
89%

Polymeric: 11%

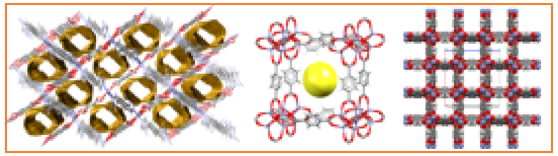
Single Component
56%

Multi Component
44%

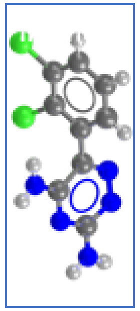
Organic
- Drugs
- Agrochemicals
- Pigments
- Explosives
- Protein ligands



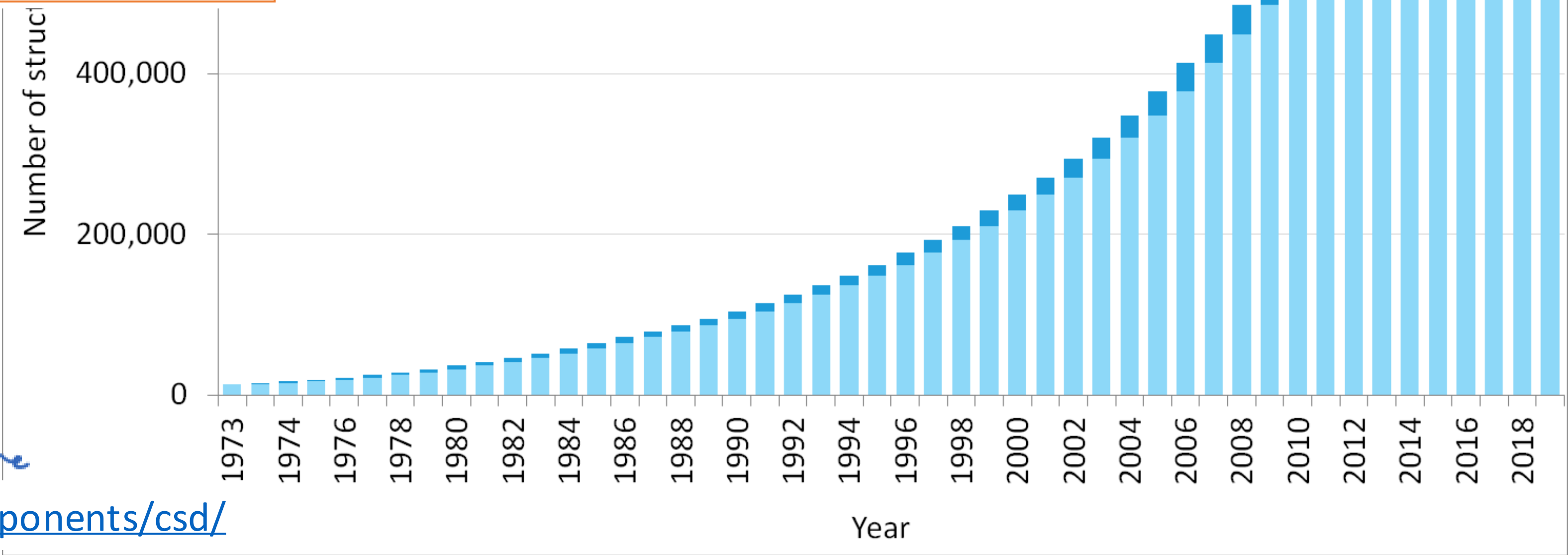
Metal-Organic
- Metal Organic Frameworks
- Models for new catalysts
- Porous frameworks for gas storage
- Fundamental chemical bonding



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



⇒ X-ray diffraction one of most important tools for structural analysis

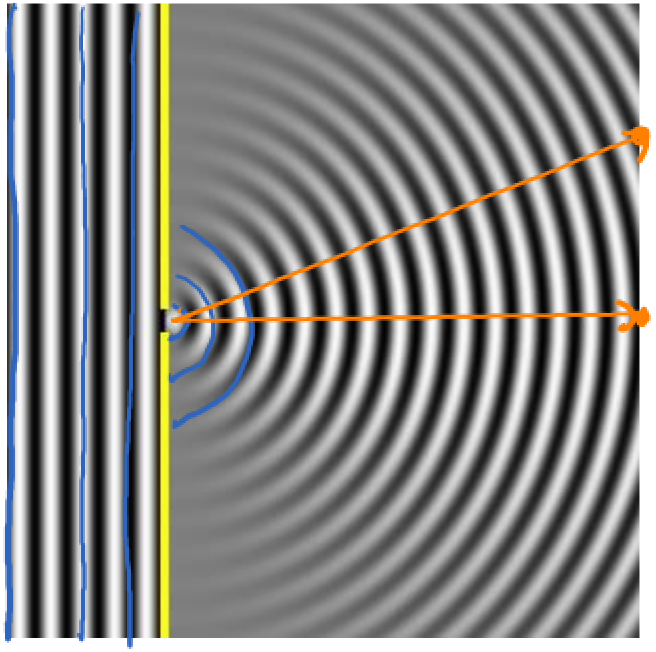
⇒ Combine with NMR, MS

⇒ X-rays provide electron densities → molecular backbone

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)

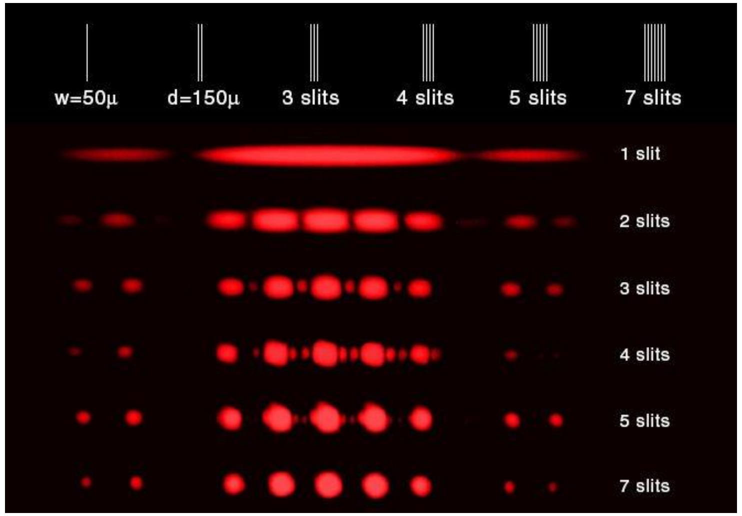


different path lengths

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

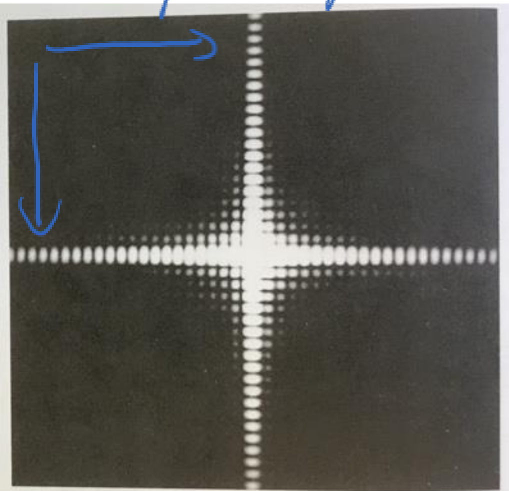
Diffraction examples

"slits"

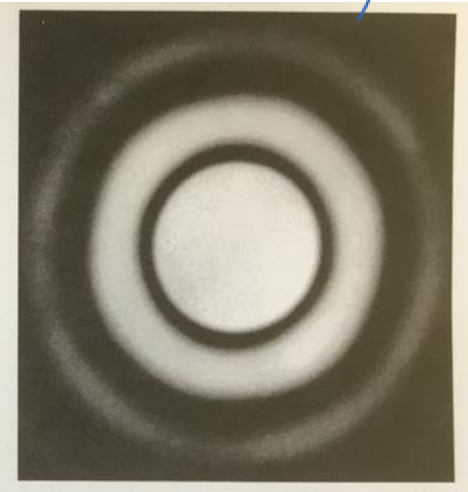


more slits
↓
finer structure

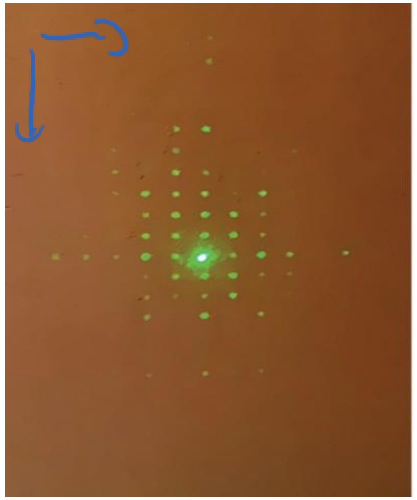
Square aperture



Circular aperture



From structure of diffraction pattern, wave-length of light
⇓
structure of sample

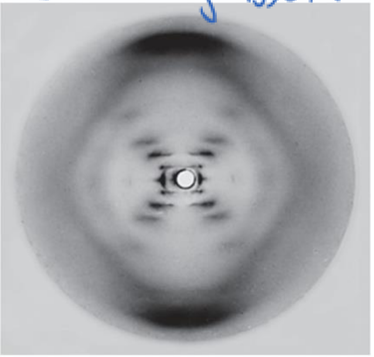


optical light diffraction
⇓
~ microns
↓
pattern of iphone pixel screen

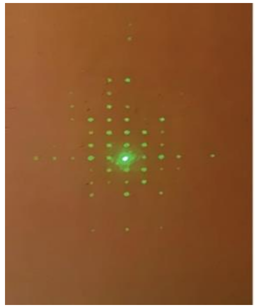
Watson, Crick
→ structure model

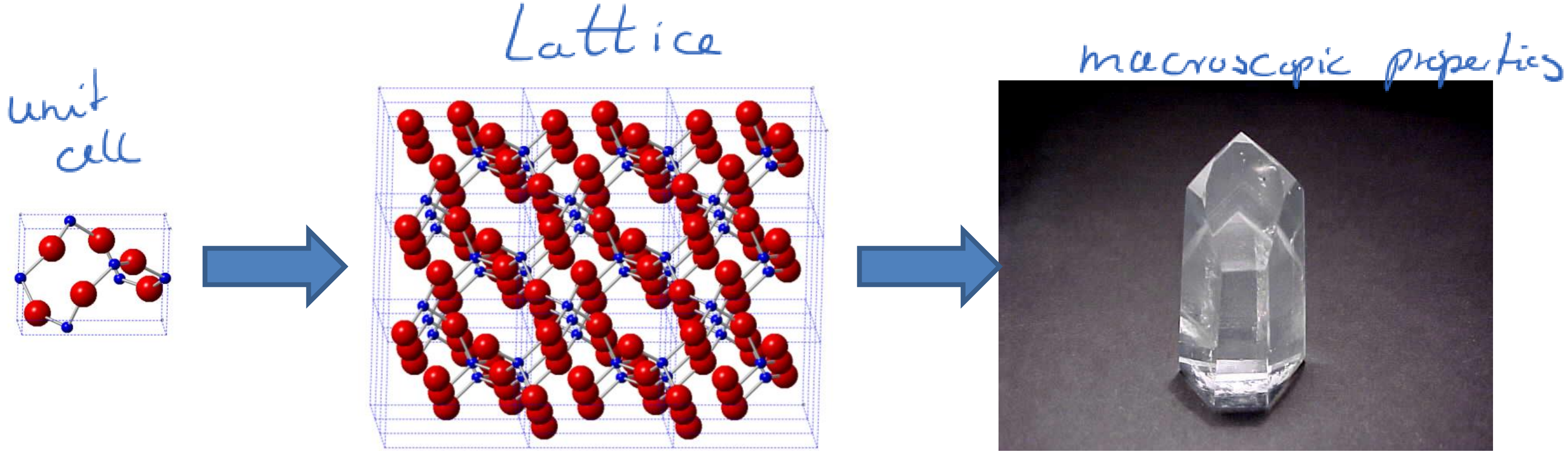
Rosalind Franklin

X-ray data of DNA



Crystaline materials are characterized by the long-range order





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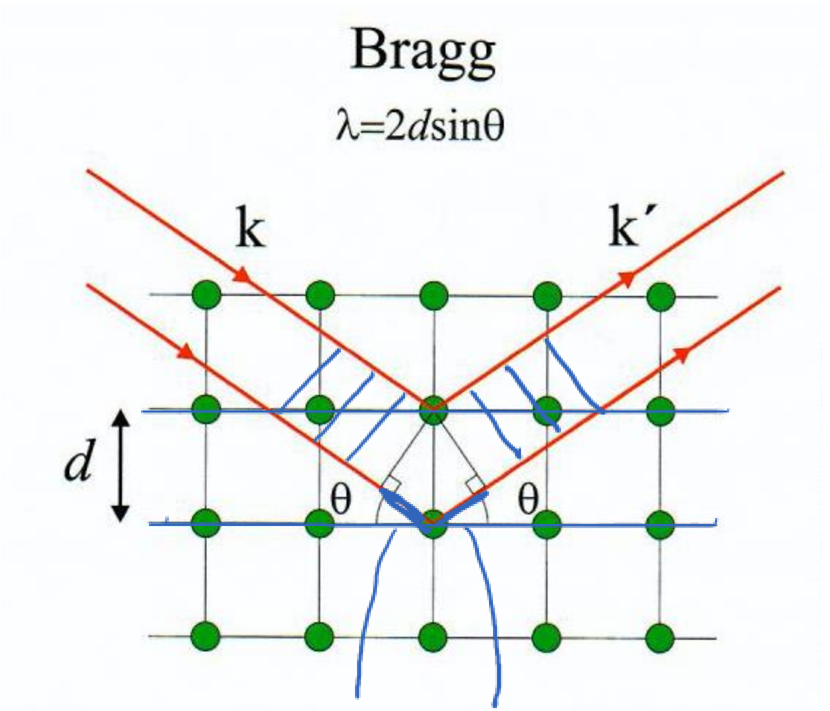
atom

Crystal

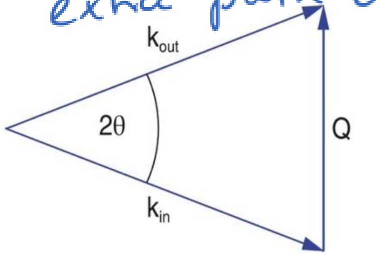
electron density

electrons localized at atoms in a periodic arrangement

Bragg scattering



$d\cdot\sin\theta + d\sin\theta$
extra path length



→ atoms in defined positions

→ defined crystal planes

→ x-rays can "reflect" from these planes

Main idea again: exploit interference phenomena

Constitute positive interference

$$\lambda = 2d\sin\Theta$$

$$\sin\Theta = \frac{n\lambda}{2d} \Rightarrow \boxed{2d\sin\Theta = n\lambda}$$

Bragg law

Note: similar formalism applies to many other sample systems

The Nobel Prize in Physics 1915

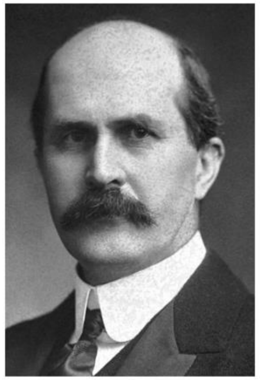


Photo from the Nobel Foundation archive.
Sir William Henry Bragg
Prize share: 1/2

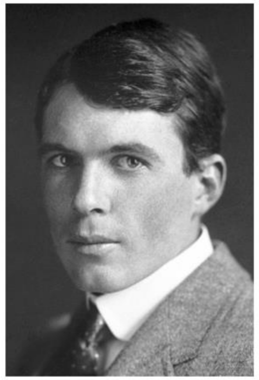
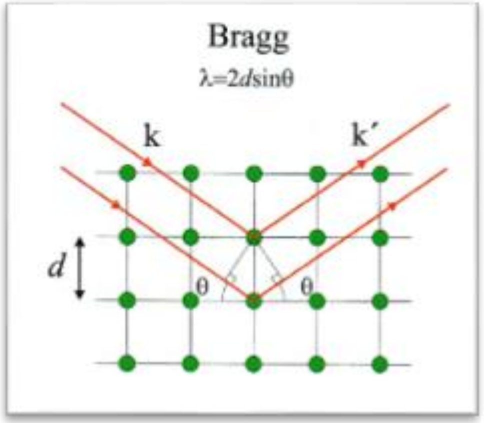


Photo from the Nobel Foundation archive.
William Lawrence Bragg
Prize share: 1/2

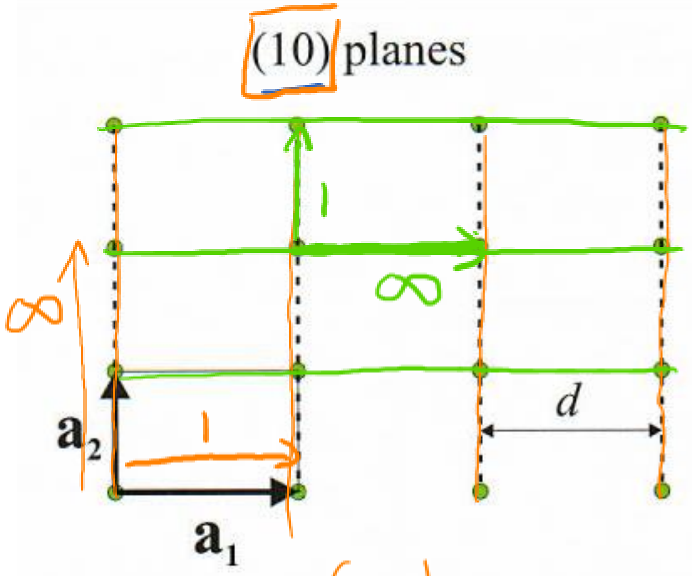
Lattice planes

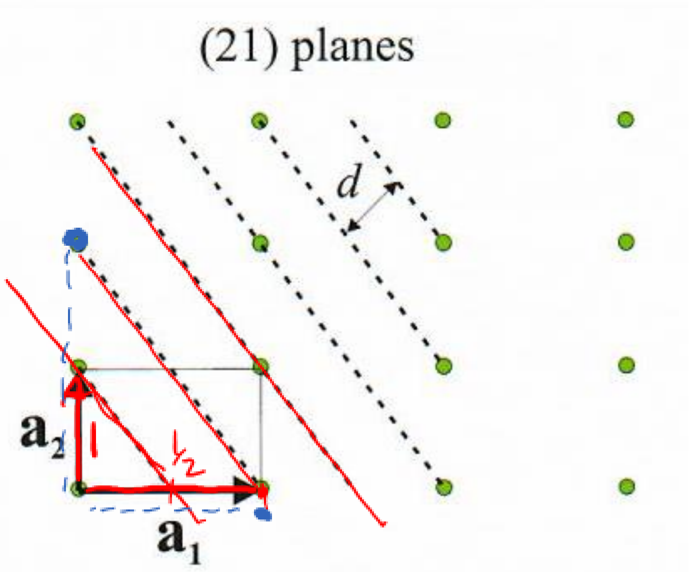
→ We need formalism to describe lattice planes



① Look where plane intersects axis

② Take inverse number & reduce to smallest integer number


(10) planes


(21) planes

$\frac{1}{1}, \frac{1}{\infty} \rightarrow (10)$ plane

$\frac{1}{\infty}, \frac{1}{1} \rightarrow (01)$ plane

$\frac{1}{\frac{1}{2}}, \frac{1}{1} \rightarrow (21)$ plane

or

$\frac{1}{1}, \frac{1}{2} \rightarrow (1, 0.5) \xrightarrow{\text{integer}} (21)$

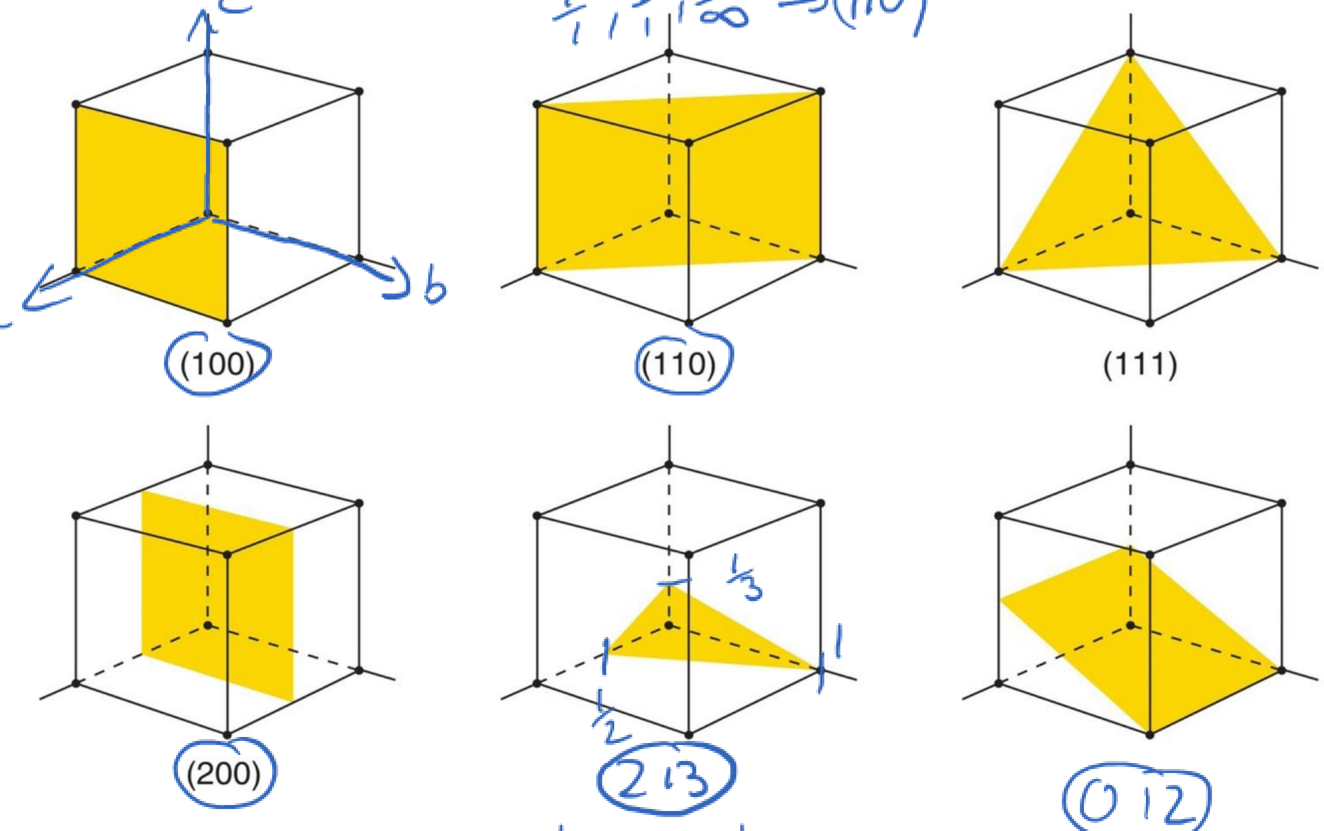
Miller indices

→ Common way to describe Lattice planes

$\frac{1}{1}, \frac{1}{1}, \frac{1}{\infty}$ → (110)

$\frac{1}{1}, \frac{1}{\infty}, \frac{1}{\infty}$

→ (100)

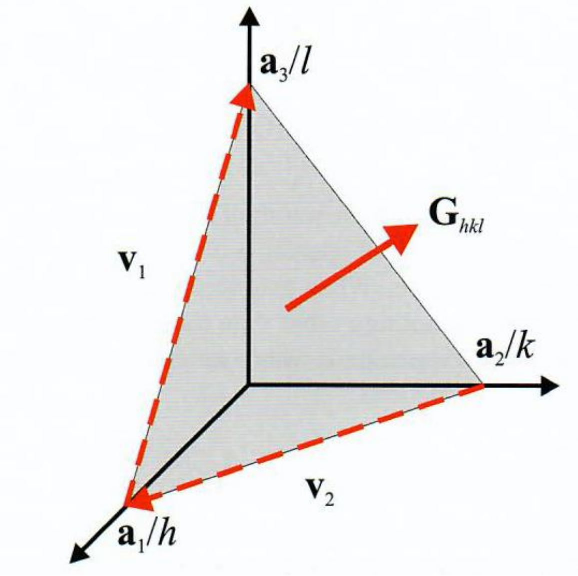


$\frac{1}{1/2}, \frac{1}{\infty}, \frac{1}{\infty}$

→ (200)

$\frac{1}{1/2}, \frac{1}{1}, \frac{1}{1/3}$

→ (2 1 3)

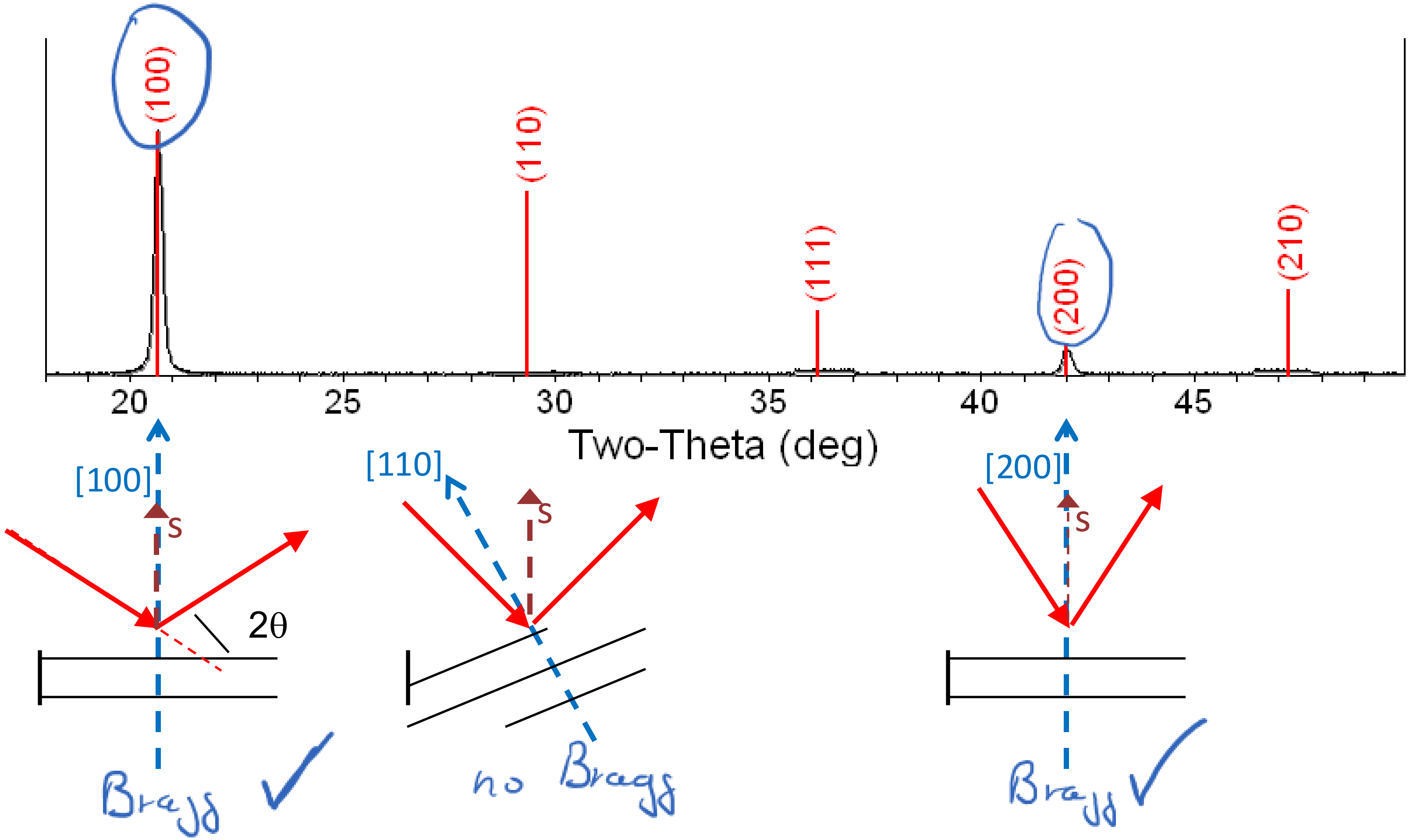


Note already now Miller indices describe vector normal to plane

Recipe:

- find the intercepts of the plane on the respective crystal axis
- take the reciprocal of these numbers, reduce to smallest integer

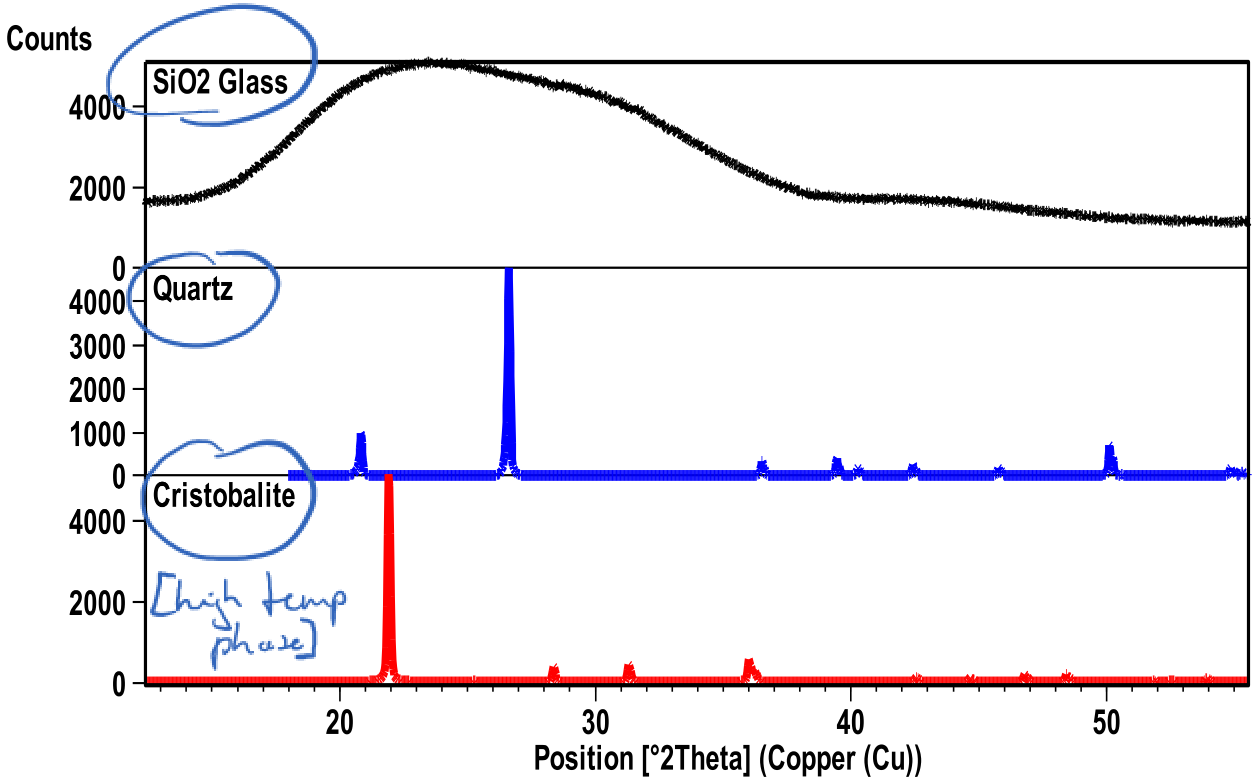
A single crystal (typically) produces one family of Bragg peaks for fixed geometry and λ



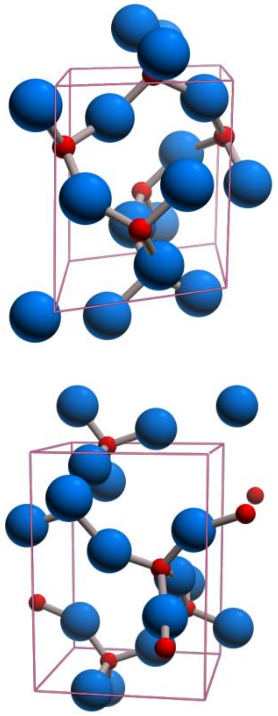
100, 200 parallel → both yield signals but at different angles

If Bragg condition is not met → no constructive interference

Characteristic signals from different – chemically identical – samples



no order (glass)



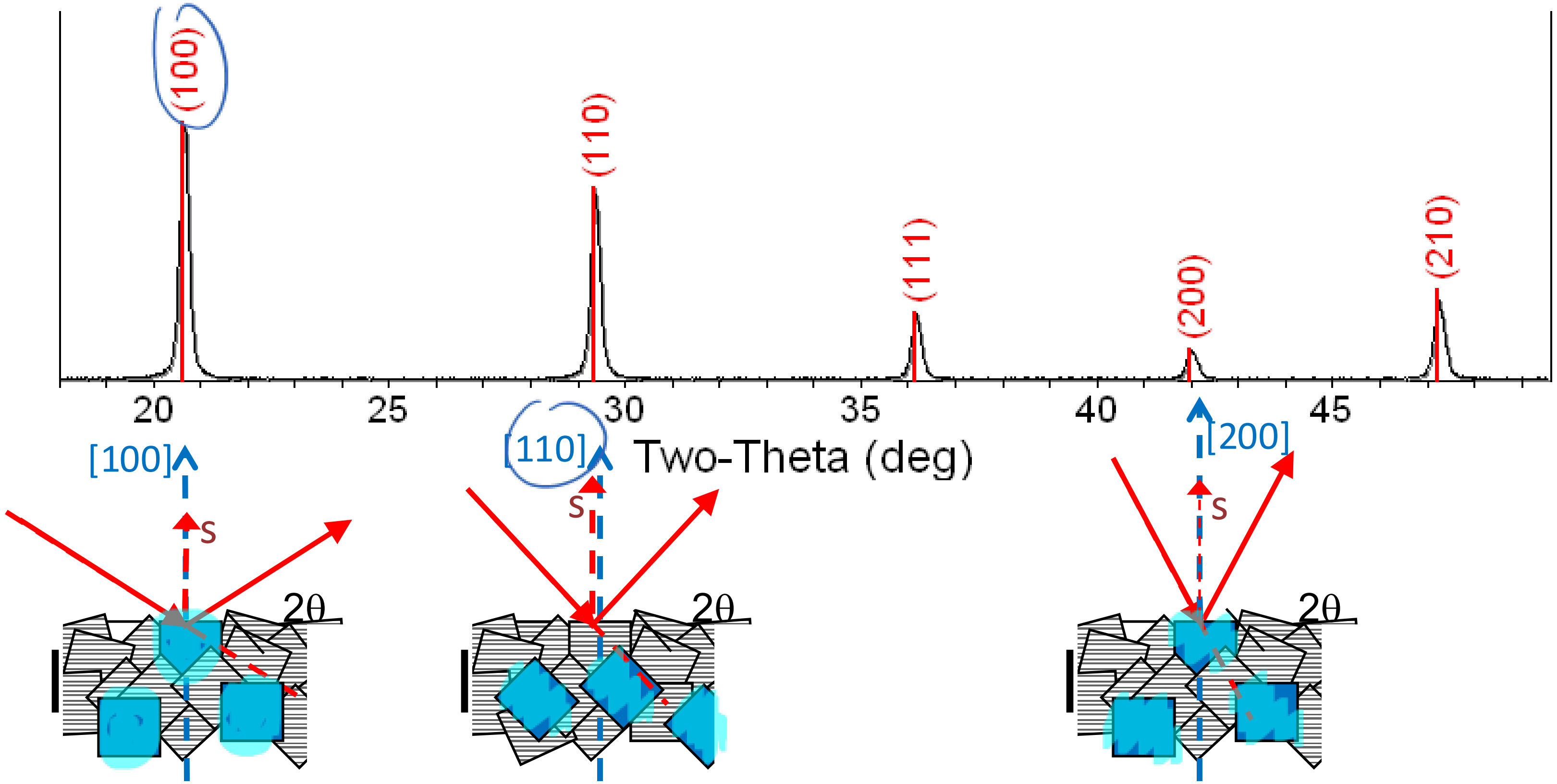
- all SiO_2 samples but different phases
- all structures are chemically identical but their structure order is different

⇓

XRD yields info about atomic arrangement

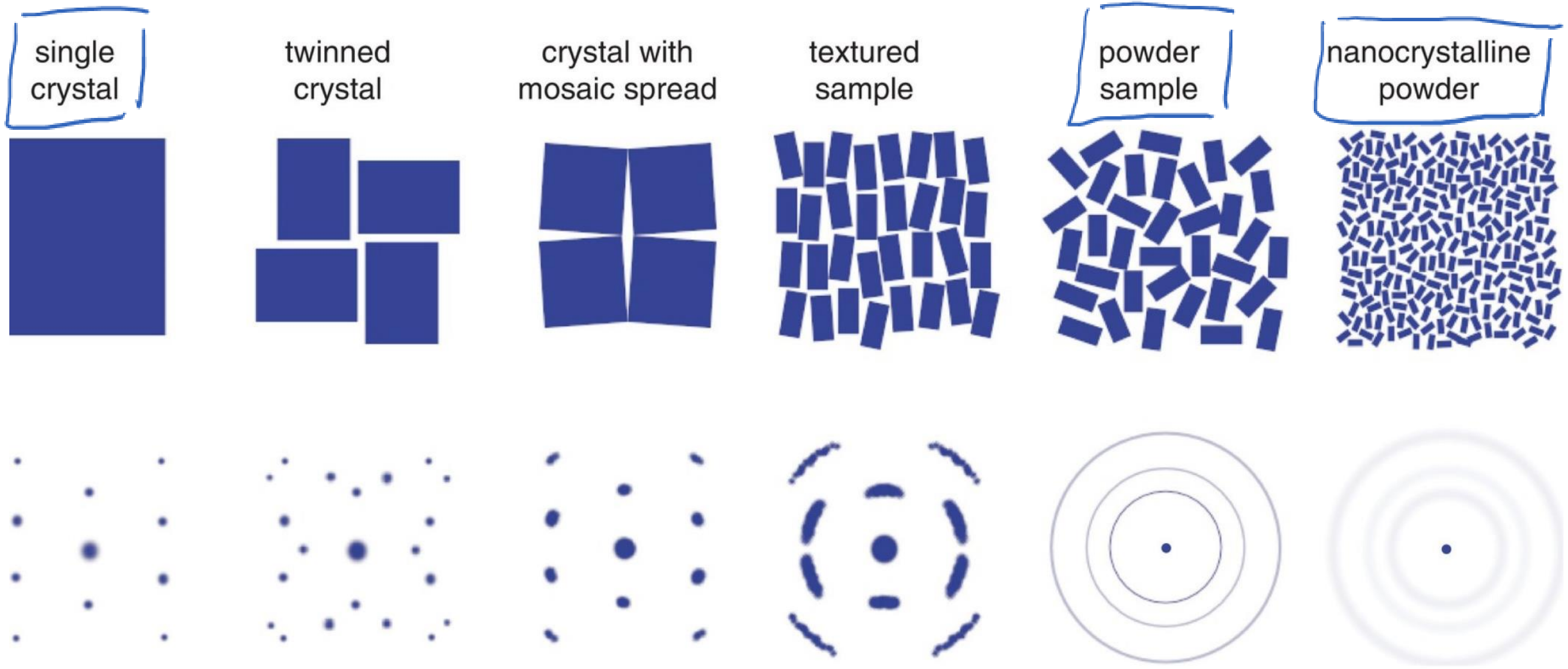
Powder diffraction

Diffraction of a polycrystalline sample



⟹ measure all possible orientations in a statistical average

Diffraction signal of different sample types



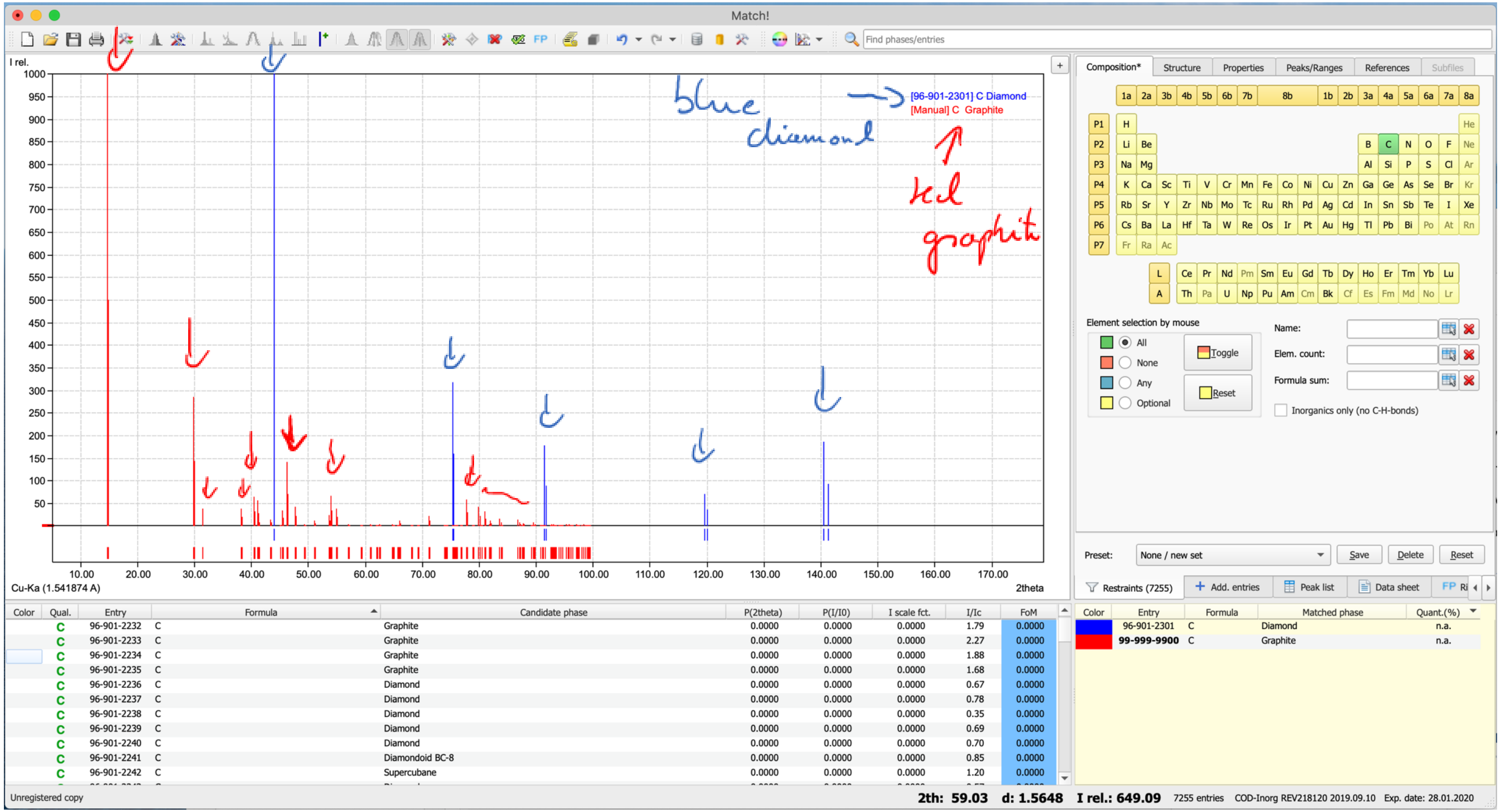
"ideal"

→ spots

→ rings

→ broadened rings

Powder diffraction data bases for elemental analysis



● All
○ None
○ Any
○ Optional

Name:
Elem. count:
Formula sum:
☐ Inorganics only (no C-H-bonds)

Color	Qual.	Entry	Formula	Candidate phase	P(2theta)	P(I/I0)	I scale fct.	I/Ic	FoM
	C	96-901-2232	C	Graphite	0.0000	0.0000	0.0000	1.79	0.0000
	C	96-901-2233	C	Graphite	0.0000	0.0000	0.0000	2.27	0.0000
	C	96-901-2234	C	Graphite	0.0000	0.0000	0.0000	1.88	0.0000
	C	96-901-2235	C	Graphite	0.0000	0.0000	0.0000	1.68	0.0000
	C	96-901-2236	C	Diamond	0.0000	0.0000	0.0000	0.67	0.0000
	C	96-901-2237	C	Diamond	0.0000	0.0000	0.0000	0.78	0.0000
	C	96-901-2238	C	Diamond	0.0000	0.0000	0.0000	0.35	0.0000
	C	96-901-2239	C	Diamond	0.0000	0.0000	0.0000	0.69	0.0000
	C	96-901-2240	C	Diamond	0.0000	0.0000	0.0000	0.70	0.0000
	C	96-901-2241	C	Diamondoid BC-8	0.0000	0.0000	0.0000	0.85	0.0000
	C	96-901-2242	C	Supercubane	0.0000	0.0000	0.0000	1.20	0.0000

Color	Entry	Formula	Matched phase	Quant.(%)
🟦	96-901-2301	C	Diamond	n.a.
🟥	**99-999-9900**	C	Graphite	n.a.

Unregistered copy **2th: 59.03 d: 1.5648 I rel.: 649.09** 7255 entries COD-Inorg REV218120 2019.09.10 Exp. date: 28.01.2020

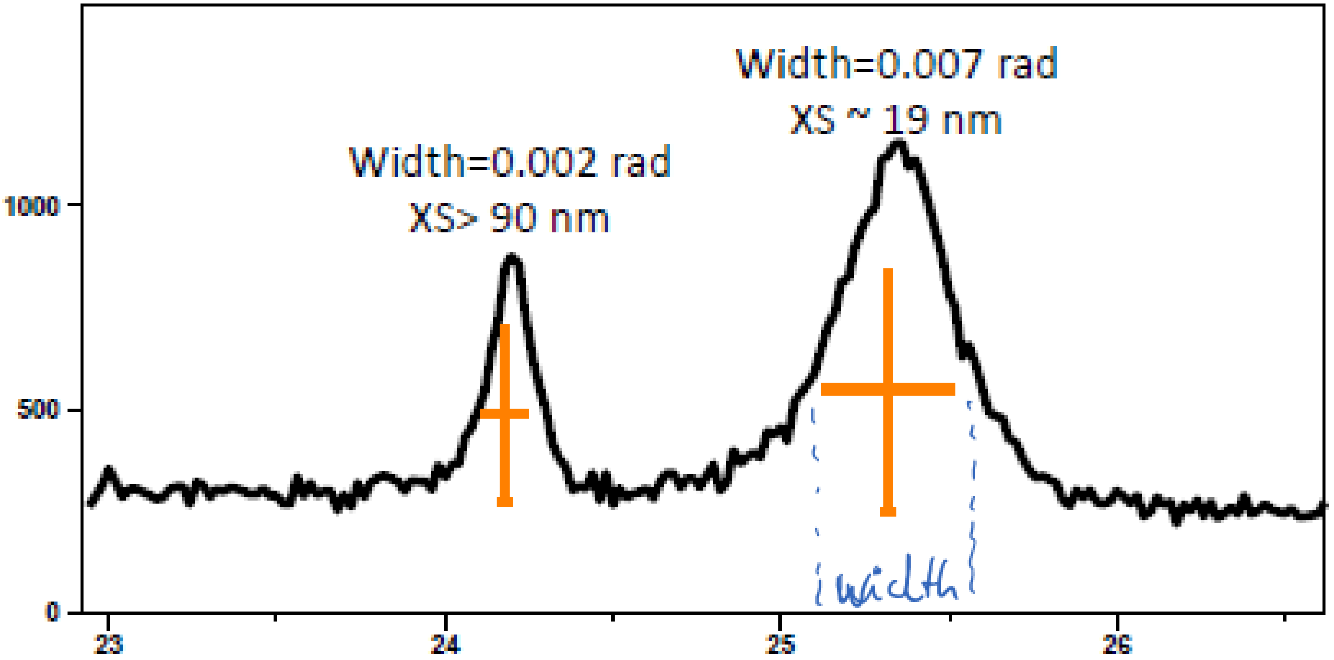
Common tool for structural and phase analysis

⇓

automated: feed in your pattern, spits out a structure (proposal)

Debye-Scherrer Formula

The diffraction peak width may contain microstructural information

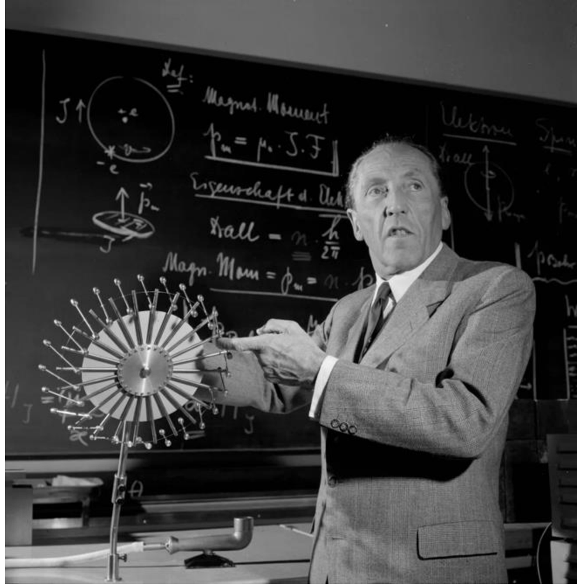


$$\underline{\text{Size}} = \frac{\overset{\overset{K\sim 0.9}{\downarrow}}{K}\lambda}{\underline{Width}*\cos\theta}$$

↑

The Debye-Scherrer formula relates the peak width with the particle siz

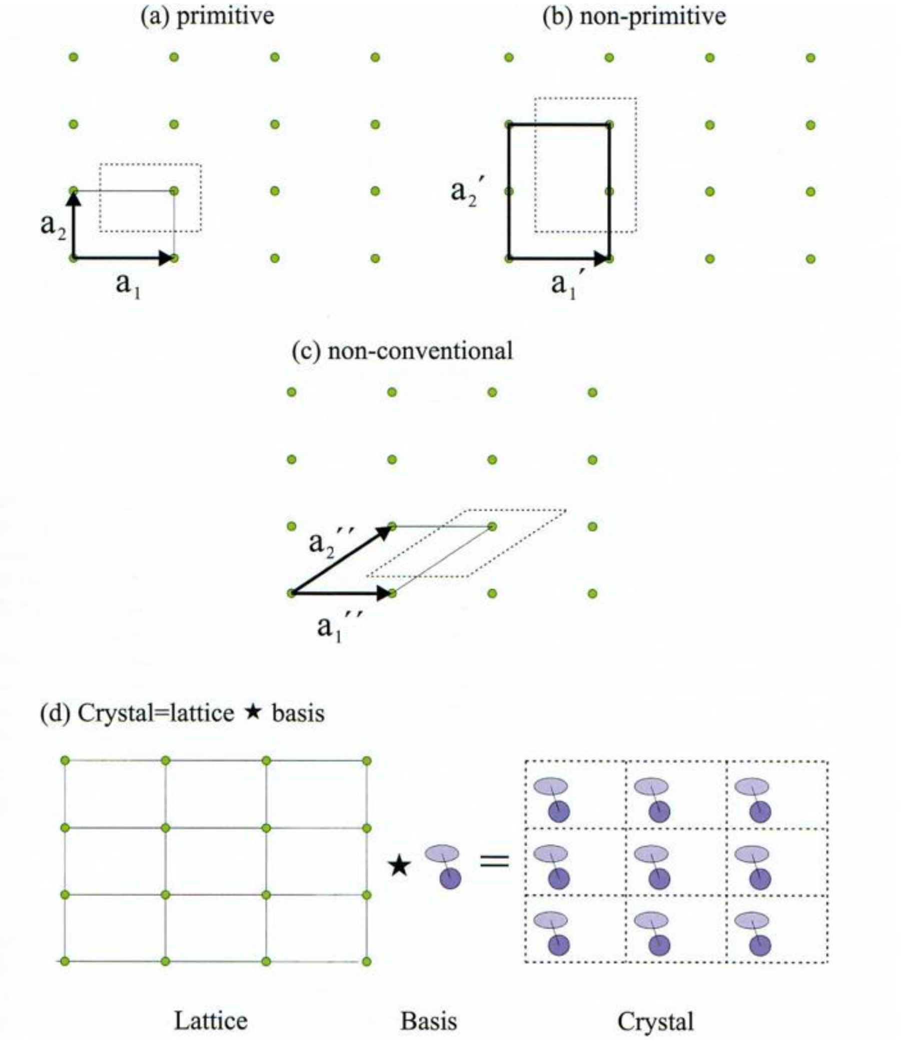
For smaller samples - without the infinite translational symmetry, the peaks are broadened.



Paul Scherrer
Swiss Physicist (1890-1969)

Note: the "natural" angle are $\underline{\text{radians}}$
↑
always use

A crystal is defined by ist lattice and basis



Convolution Lattice ⊗ Base

Remember : diffraction ⟺ Fourier transform

Diffraction: FT

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

or

$$FT_{(\text{crystal})} = FT_{(L \otimes B)} = FT_{(L)} \cdot FT_{(B)}$$

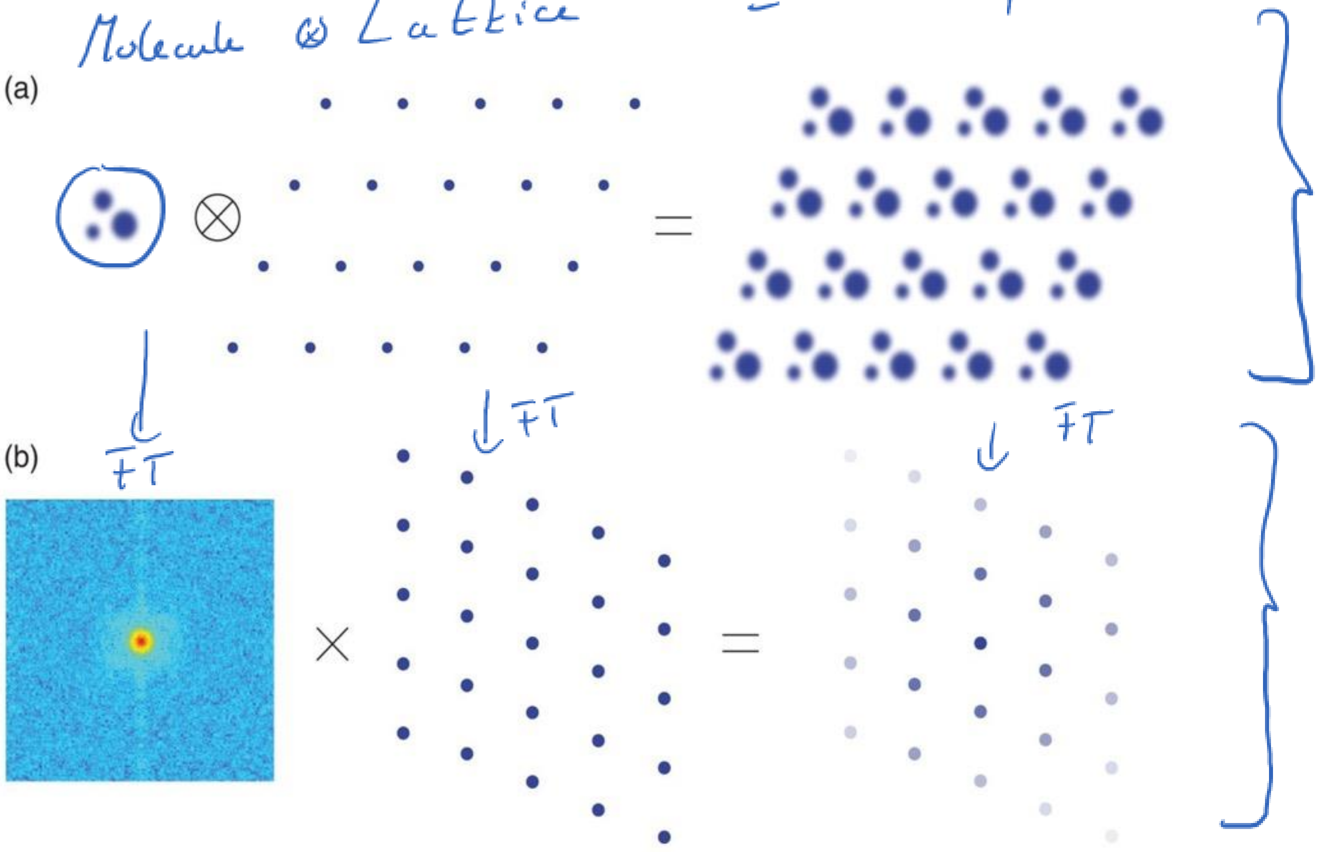
↓ physics, solved

↓ sample

Why and how does it work?

Remember last week:

Molecule ⊗ Lattice = Crystal

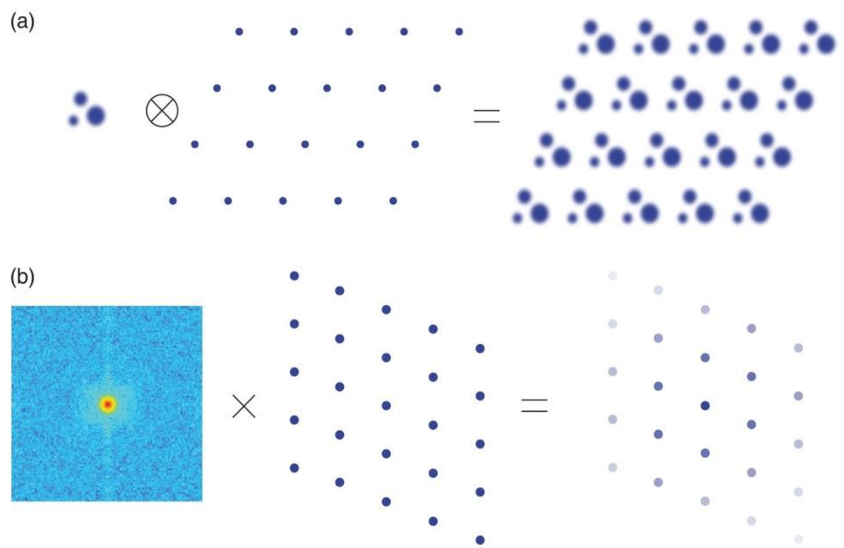


Real space

Diffraction experiment

Solving a crystal structure

Base ⊗ Lattice = Crystal



Molecular pattern   Bragg pattern = diffraction pattern

FT(Base) × FT(Lattice) = FT(Crystal)

Envelope   Peaks   Data

But ...   Phase is lost (remember?!)

Problem

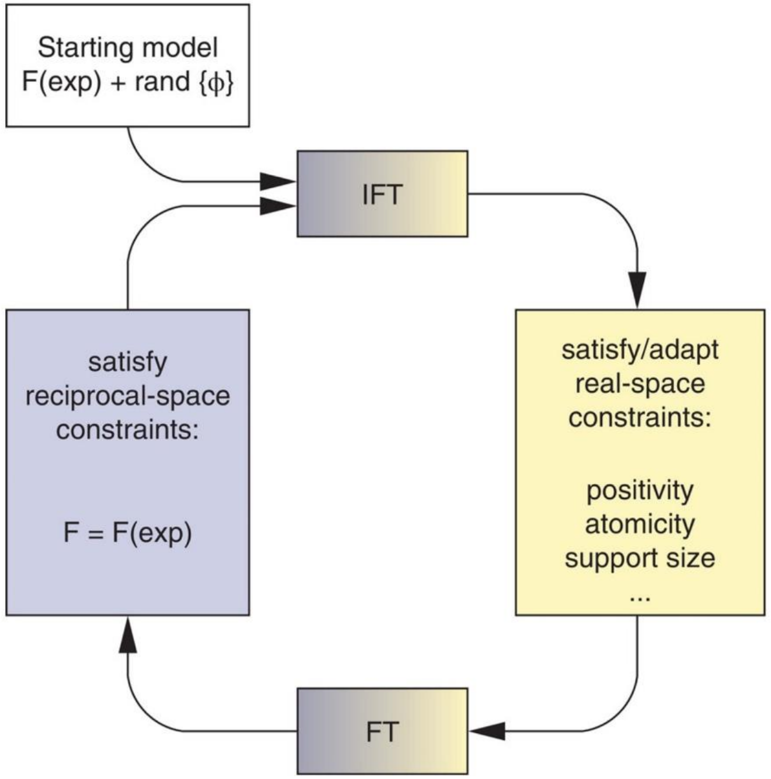
$A = A_0 \exp[\ \dots\ \phi]$

phase needed for FT

Measurement

$I = |A^2| \Rightarrow$ Phase lost !

Reconstruct:



Starting model
F(exp) + rand {ϕ}

IFT

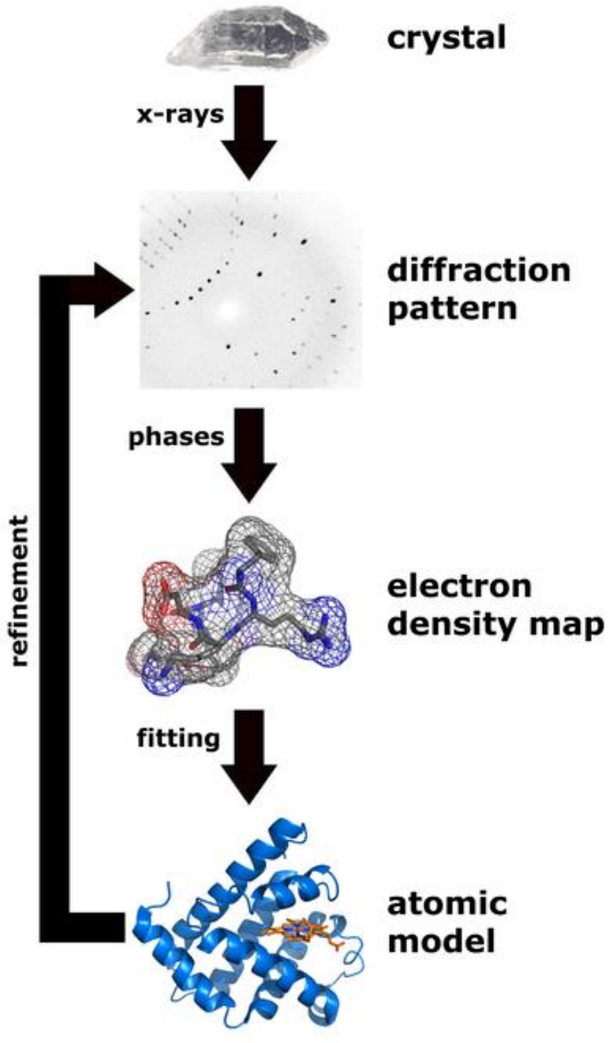
satisfy/adapt
real-space
constraints:

positivity
atomicity
support size
...

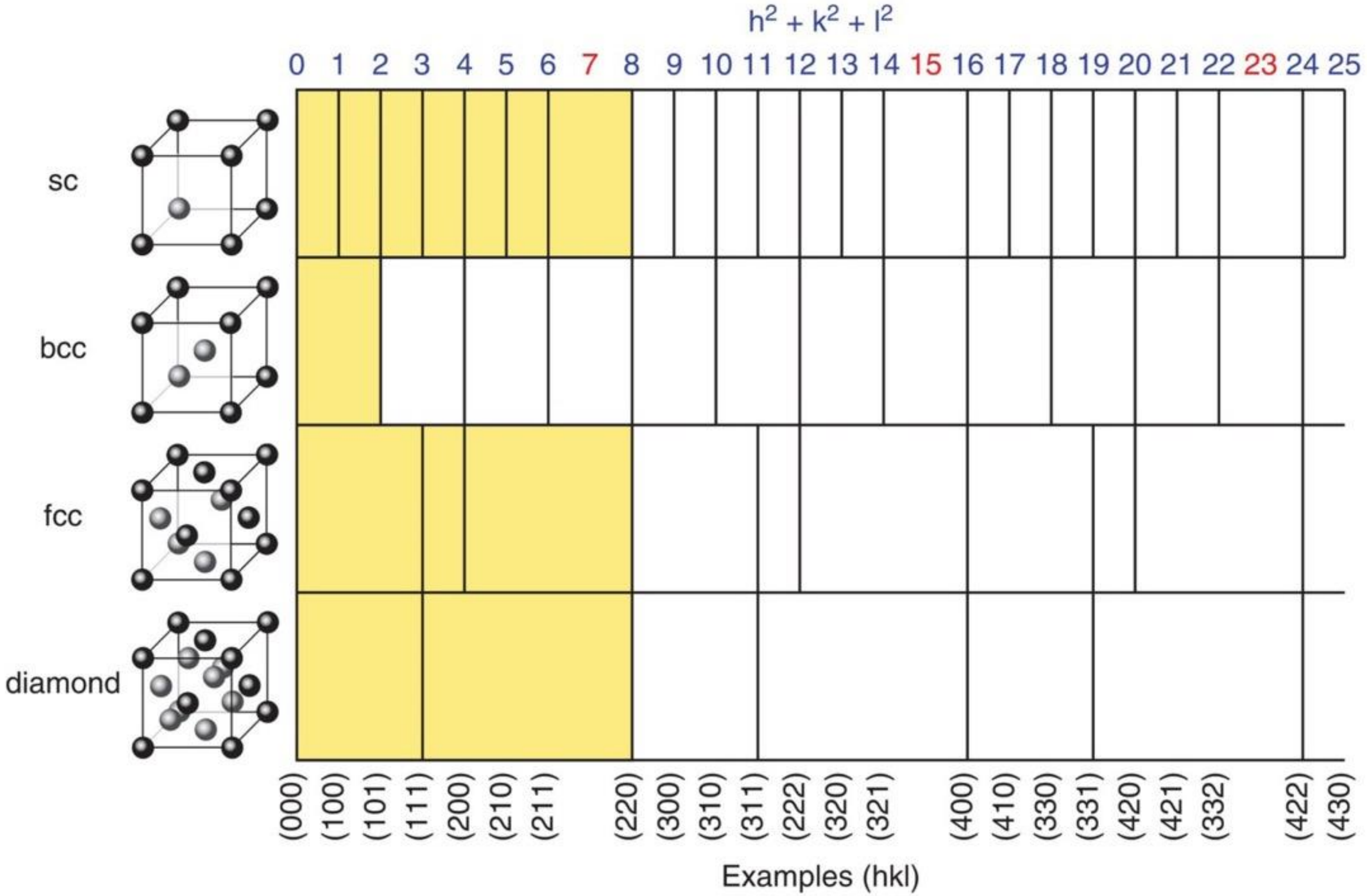
FT

satisfy
reciprocal-space
constraints:

F = F(exp)



Allowed and forbidden reflections



The end