

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

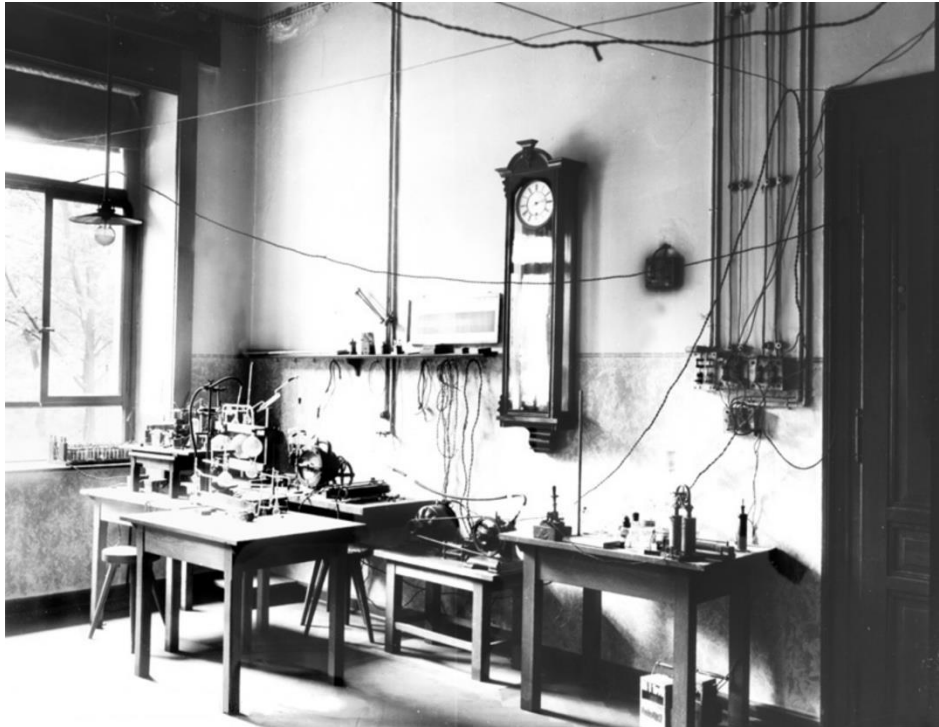
Today:

Lets get going with x-rays

Some new ideas and many applications of previous material

Introduction and historical perspective

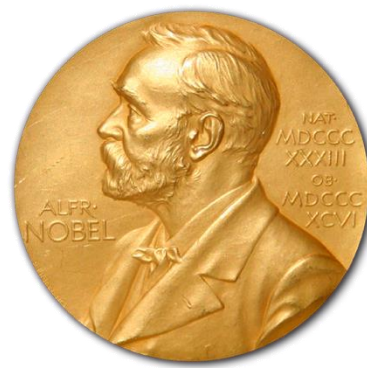
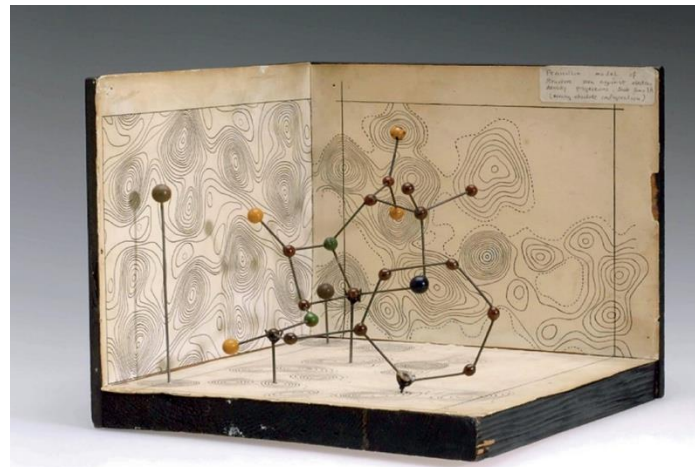
The discovery of x-rays in 1895



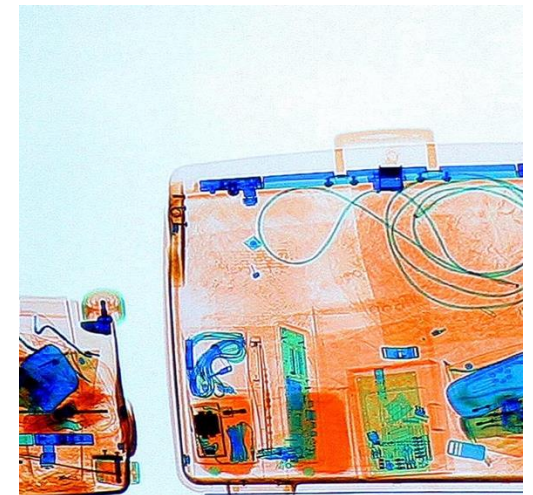
- Röntgens lab in Würzburg
- Experiments with vacuum tube
- Noticed fluorescence on a screen despite light-tight packaging of tube
- Postulated mysterious x-rays

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

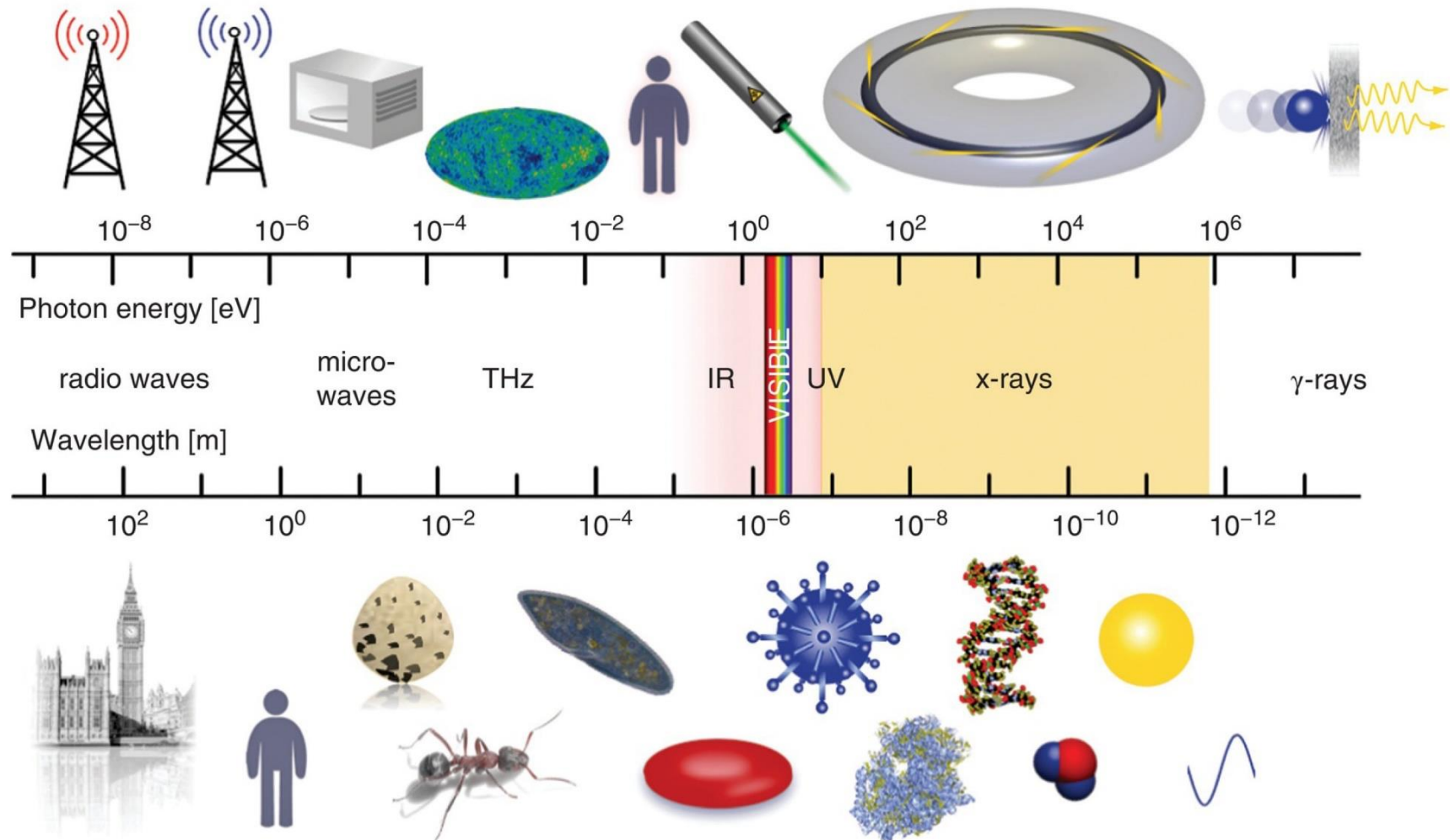
Discovery of X-rays triggered many technological and scientific developments



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.

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

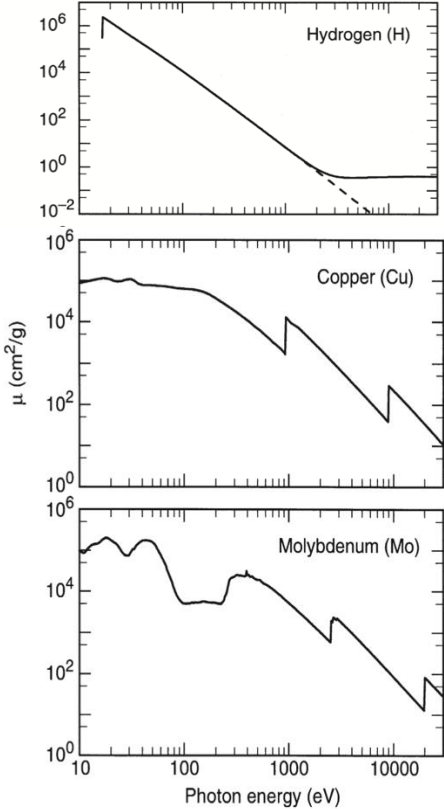
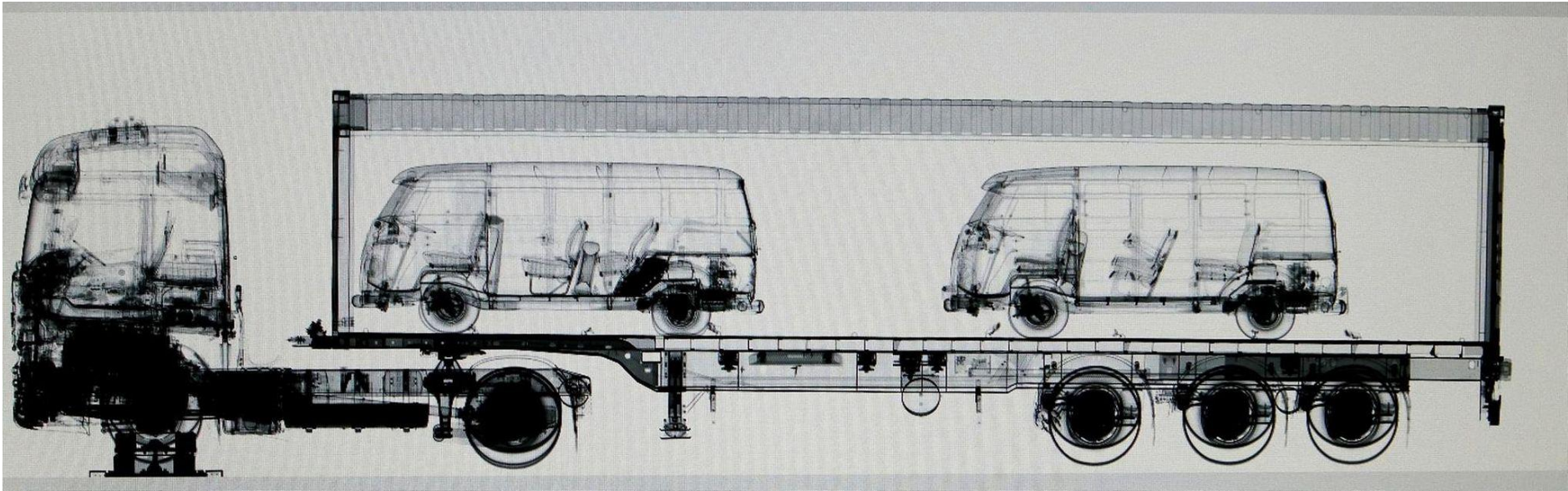
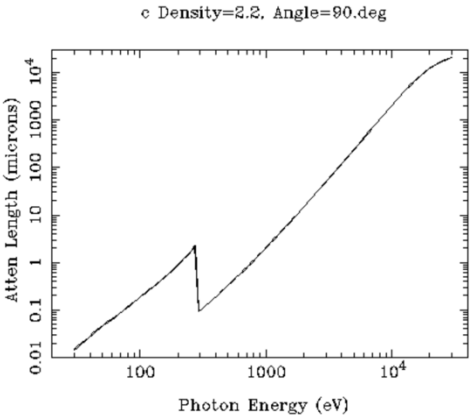
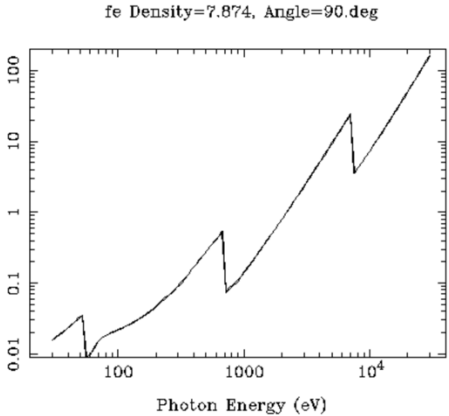


Fig. I-5. Mass absorption coefficients (continued).

X-Ray Attenuation Length



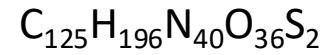
X-Ray Attenuation Length



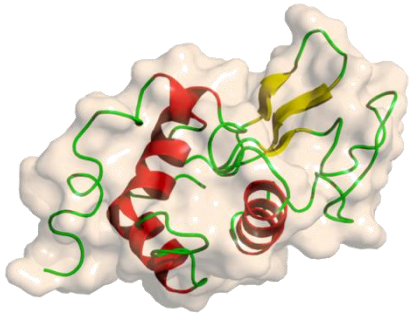
Scattering with atomic resolution

Lysozym (Protein, Immunsystem)

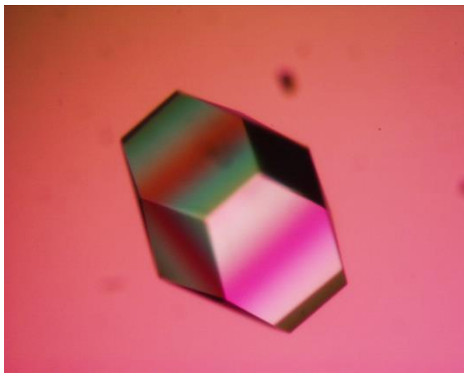
Stoichiometric formula



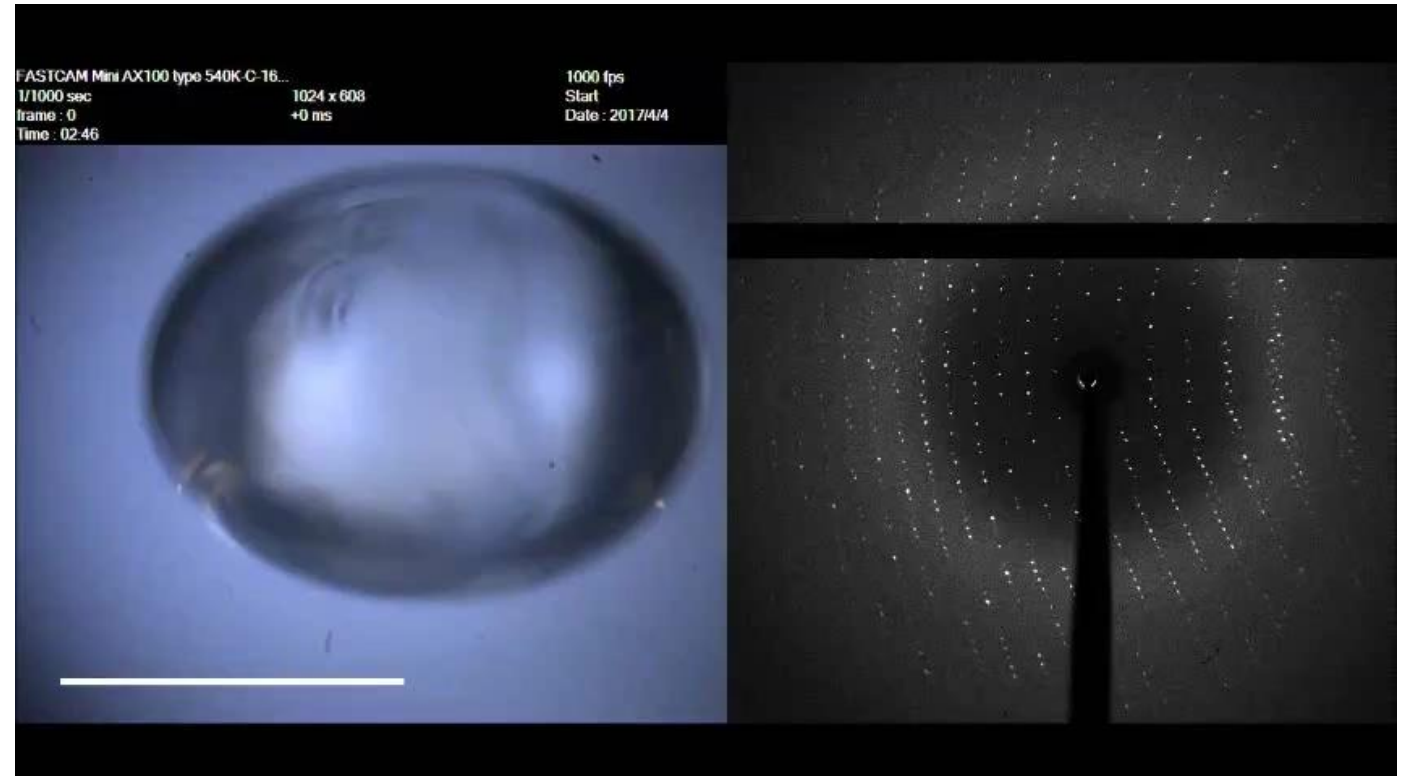
Structure



Crystal



Experiment at the Swiss Light Source

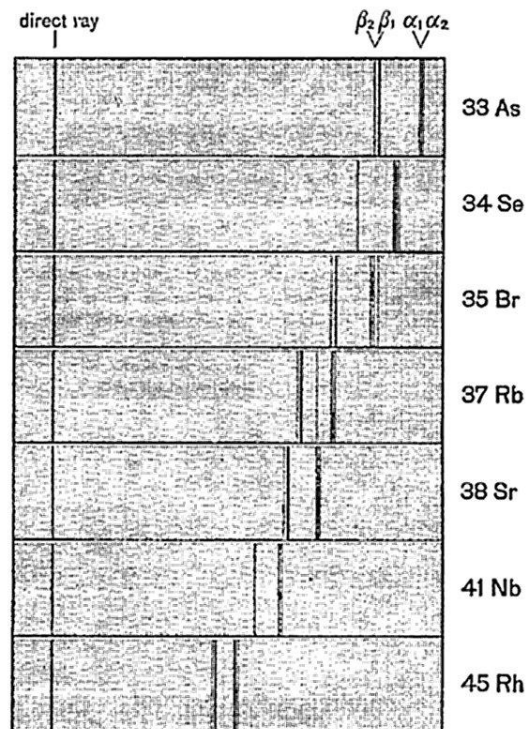


Elements possess specific colors – also in X-ray spectral regime

Rose of Lausanne:
Characteristic visible colors



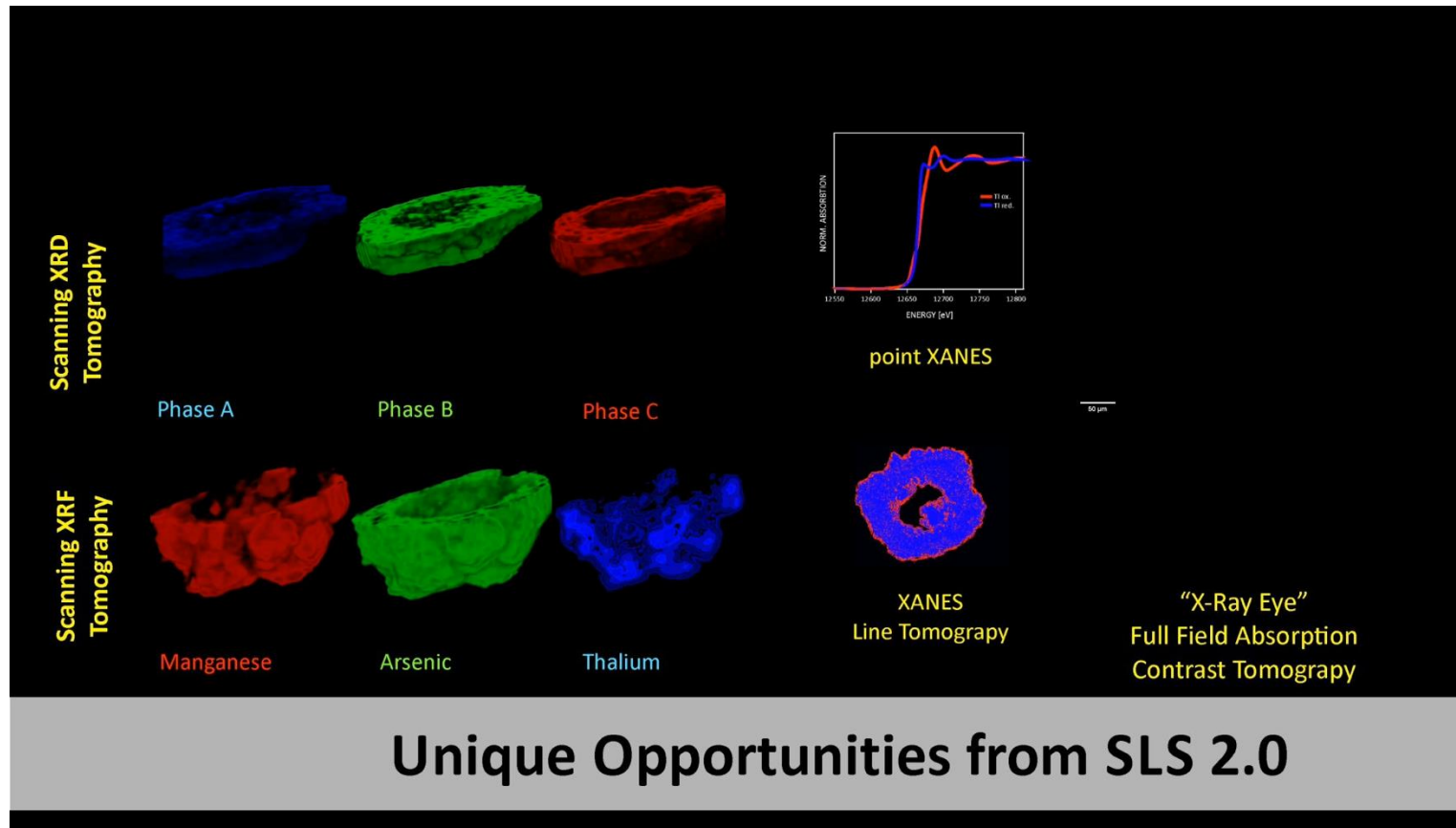
Barkla:
Characteristic emission lines of
elements in x-ray regime



Barkla, Nobel Prize in 1917

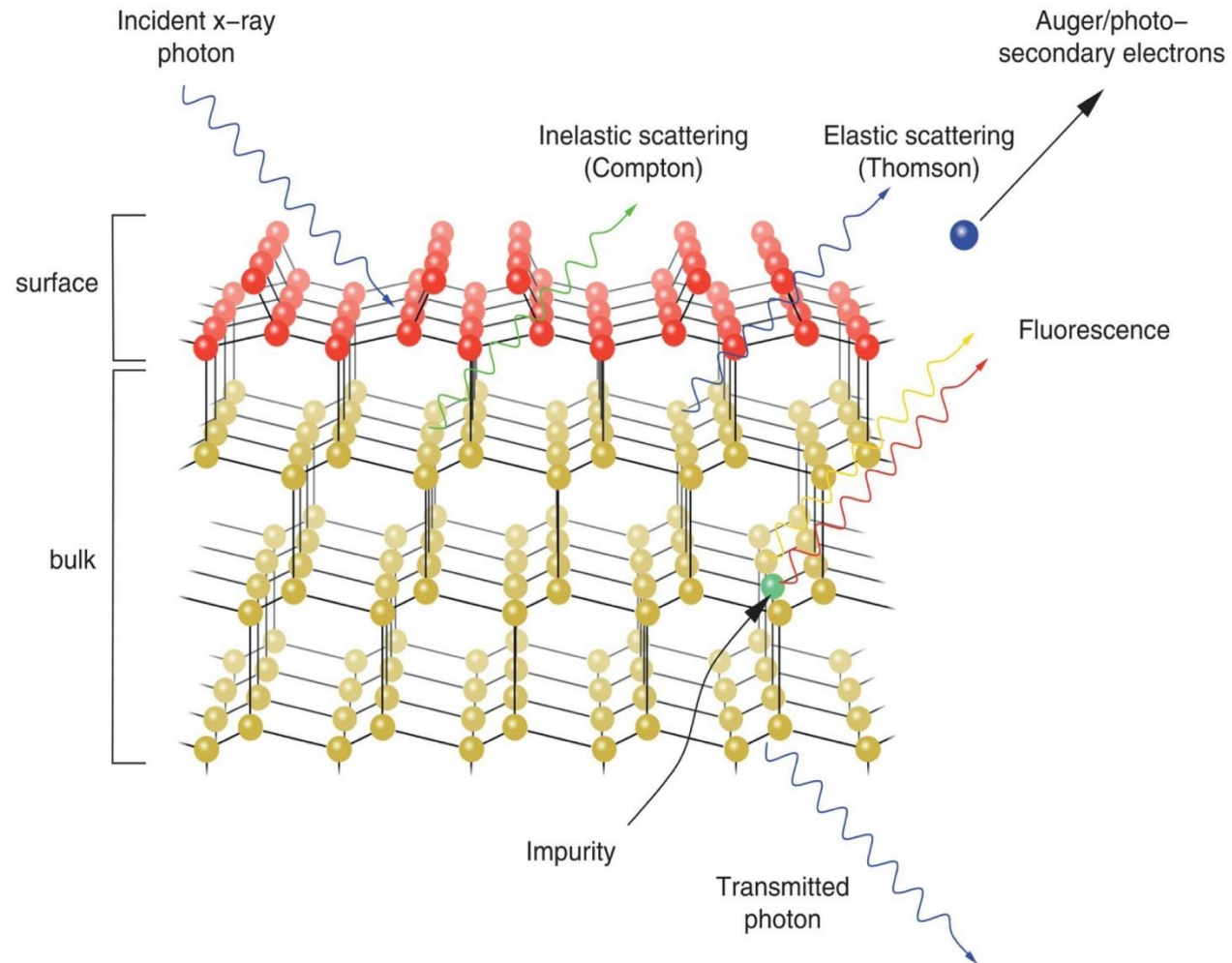
Combination of large penetration depth, elemental information, and high resolution

Example: Geological Thallium sample (Geochemistry)

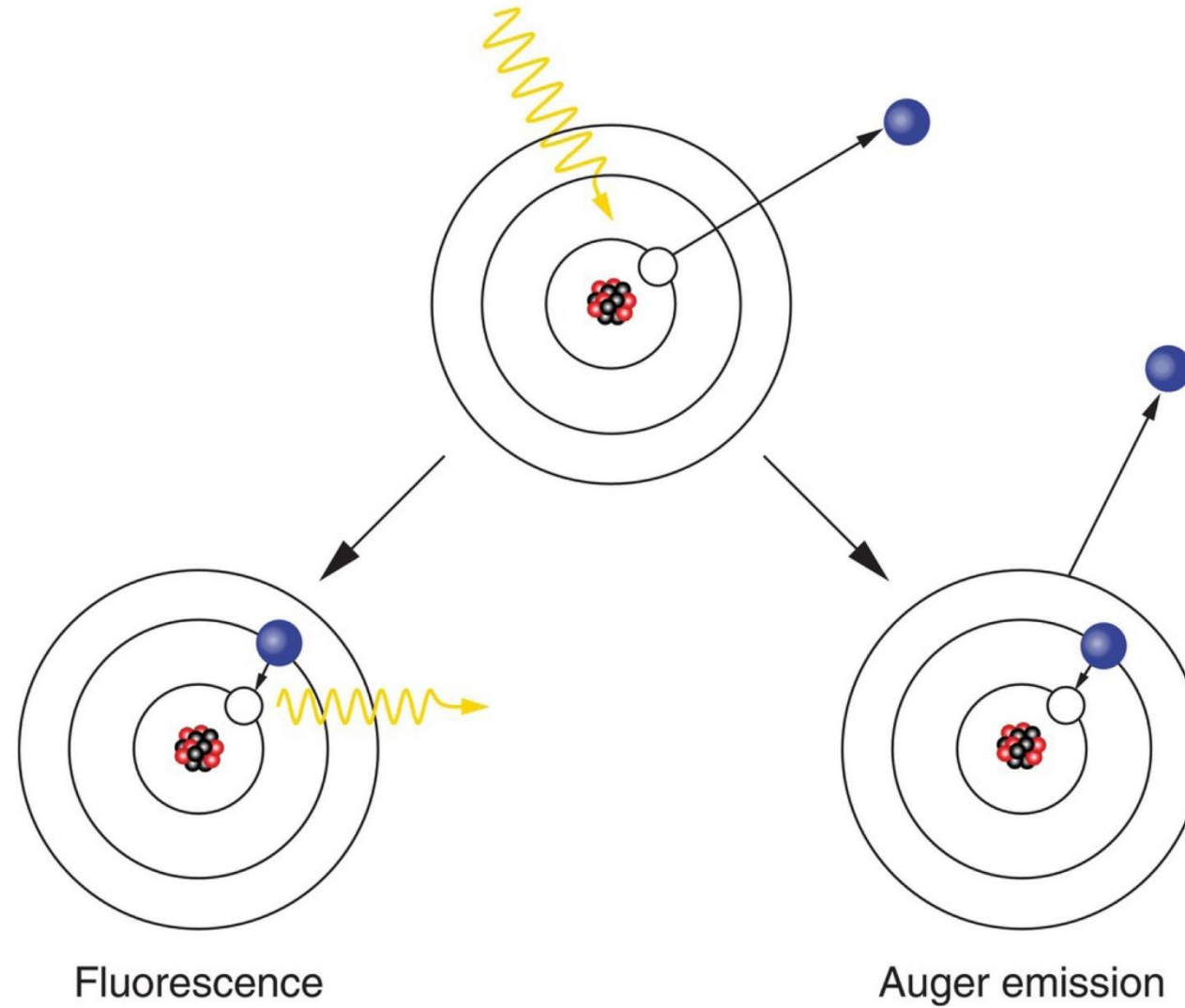


X-ray interactions with matter

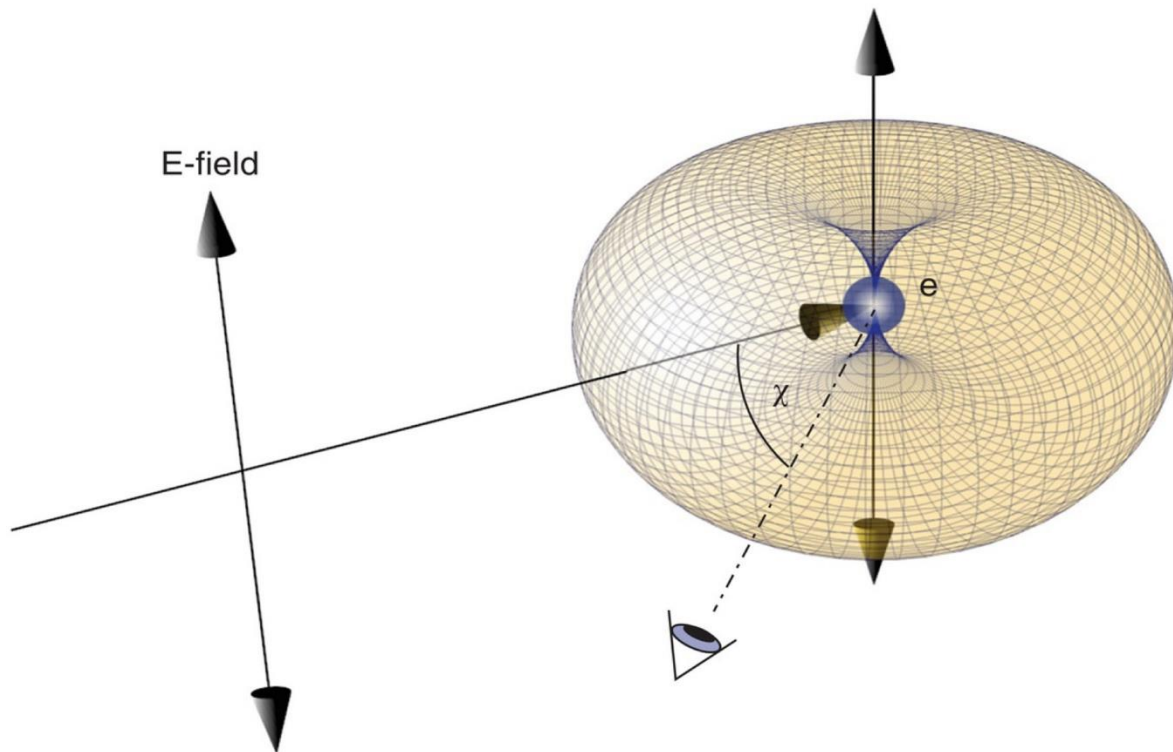
X-ray interactions with matter



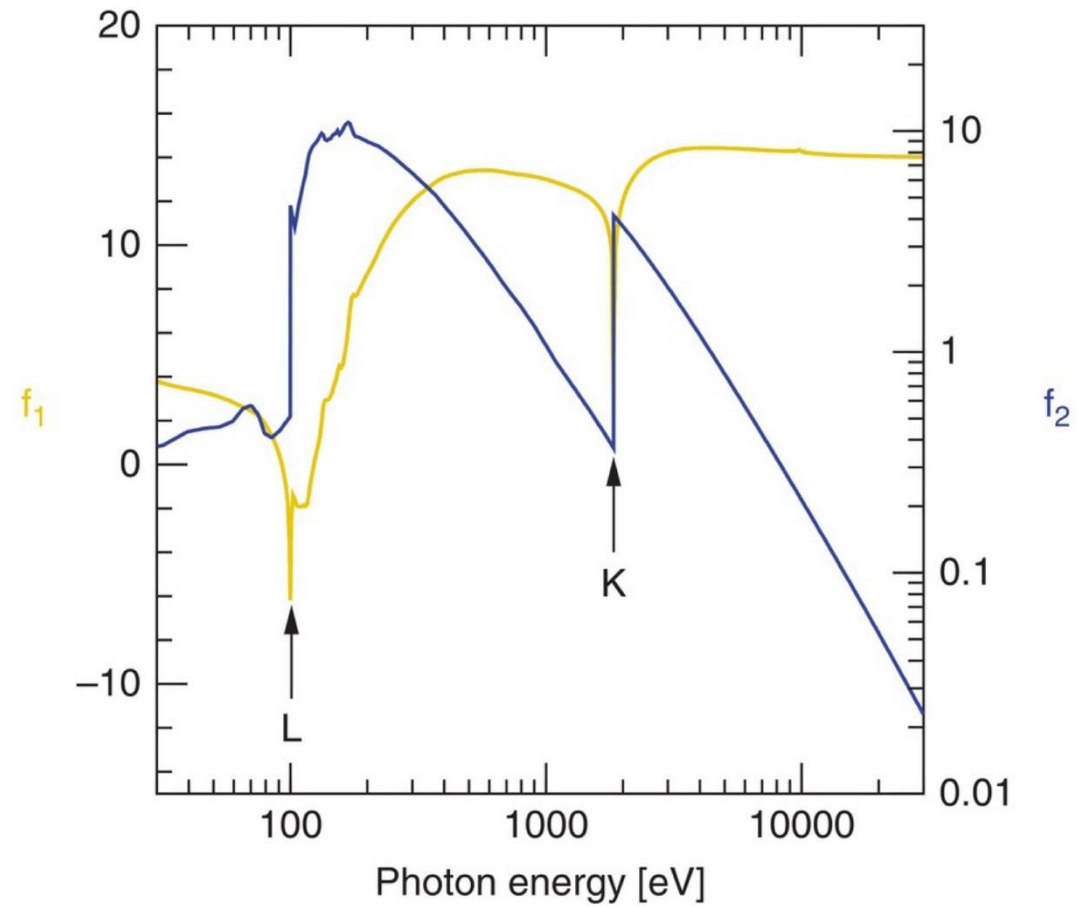
Photoionization / absorption



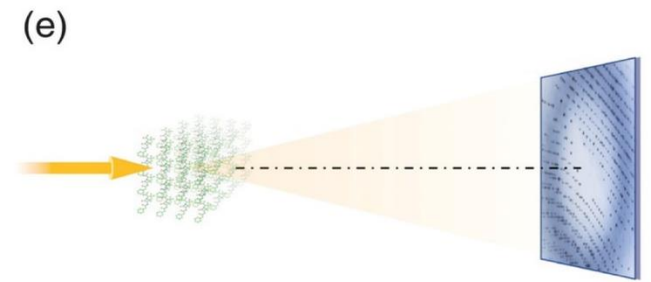
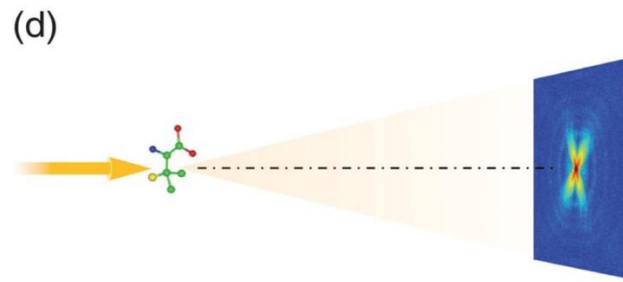
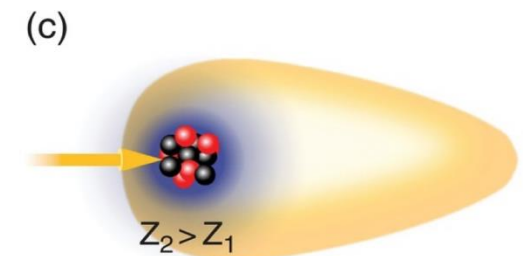
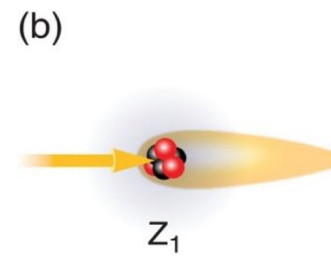
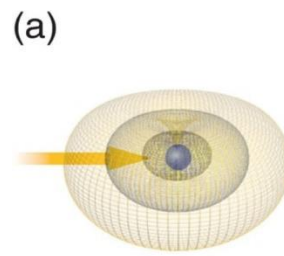
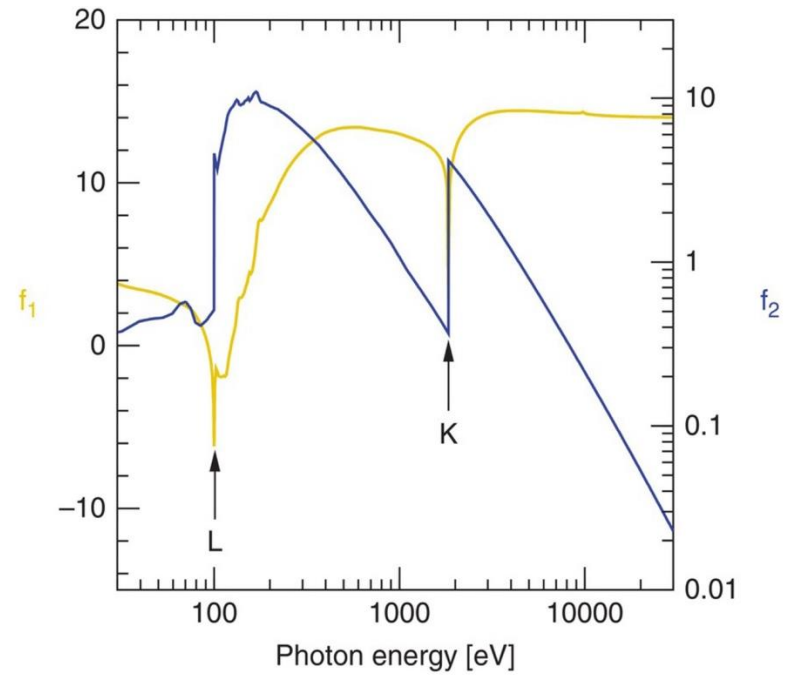
Thomson scattering



Atomic scattering factors and refractive index



Atomic scattering factors again



X-ray cross sections

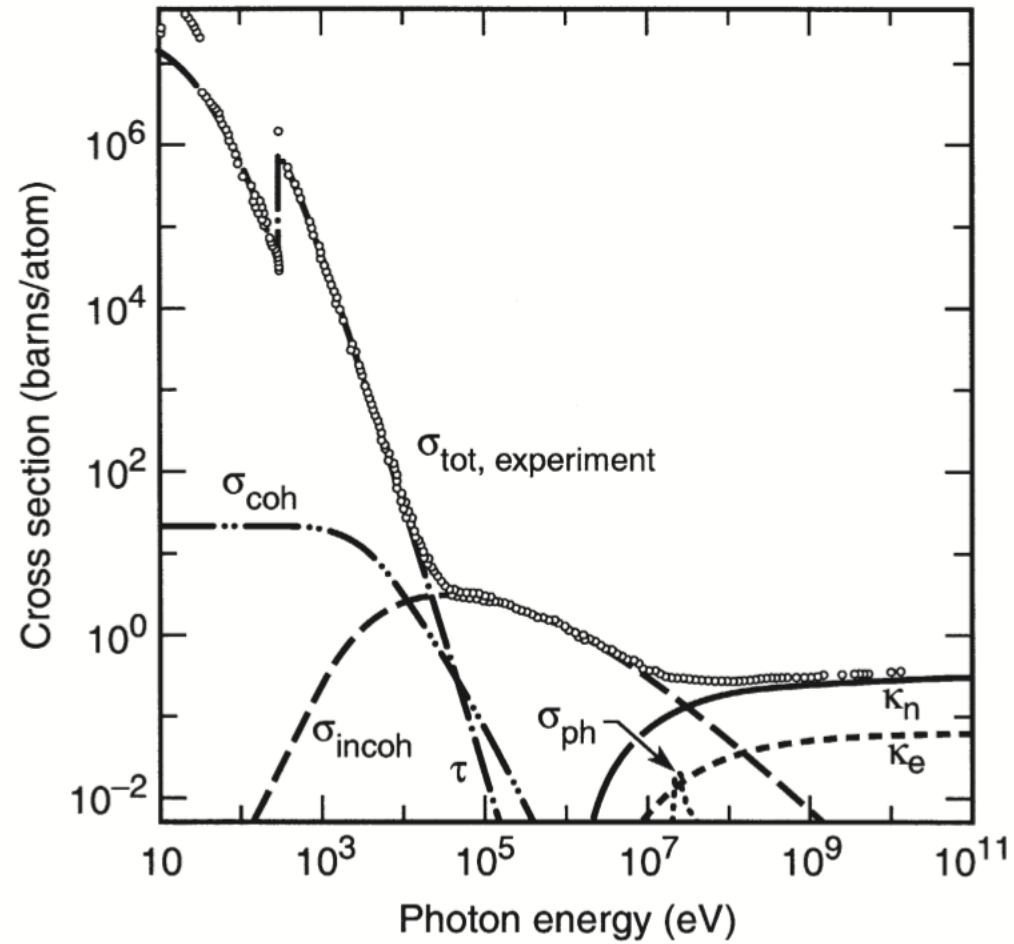
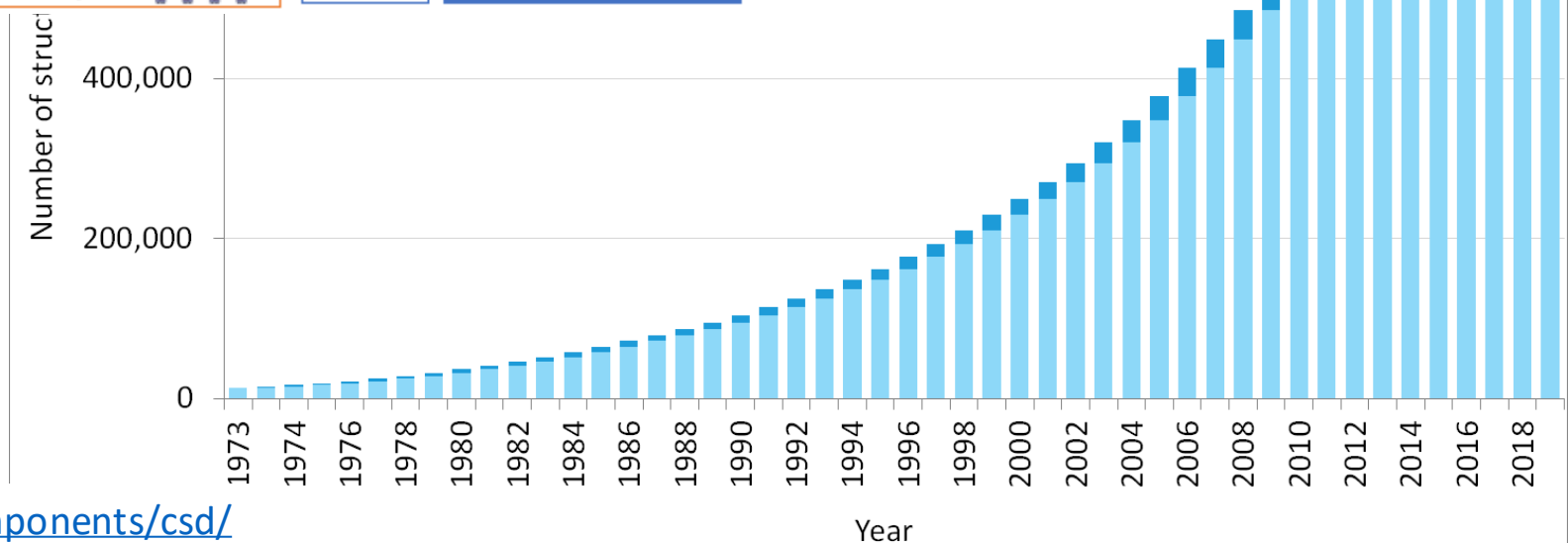
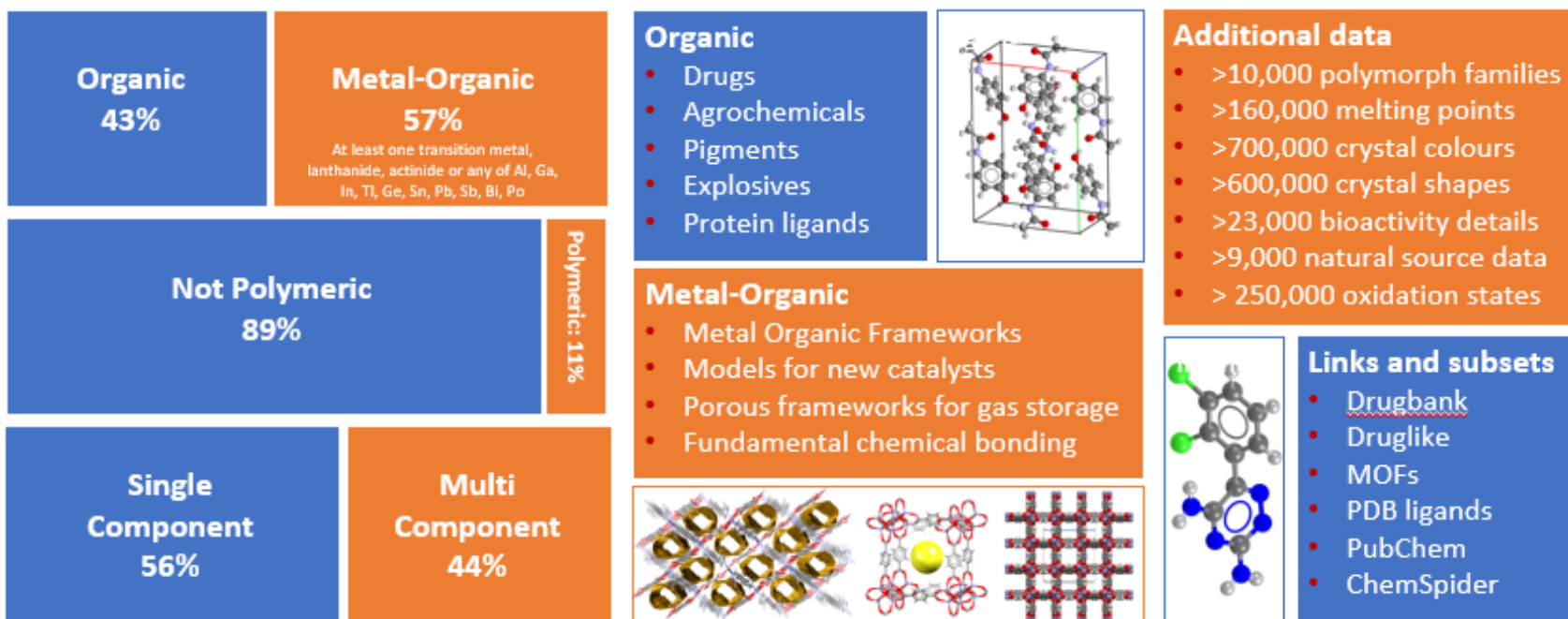


Fig. 3-1. Total photon cross section σ_{tot} in carbon, as a

Diffraction by crystals

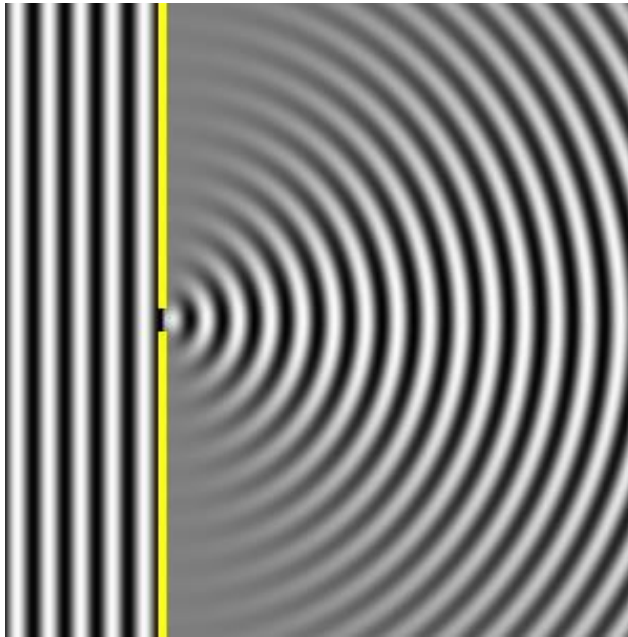
Why should we care about x-rays, crystals, lattices, etc?

Source:
The Cambridge Structural Database (CSD)

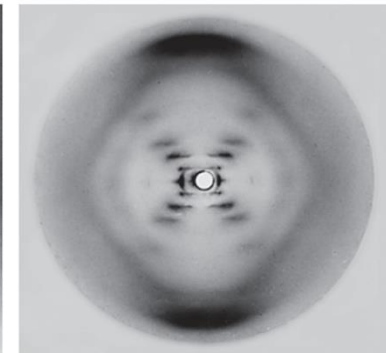
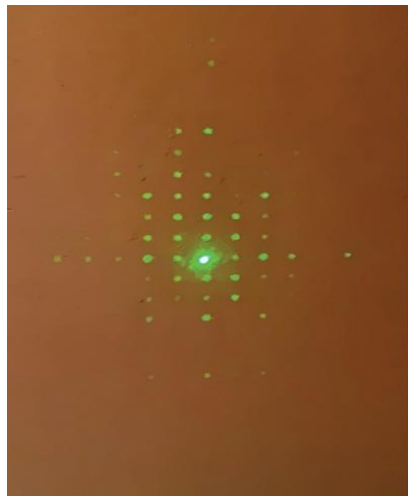
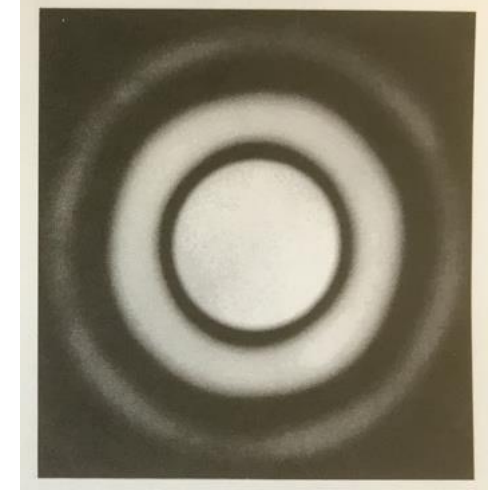
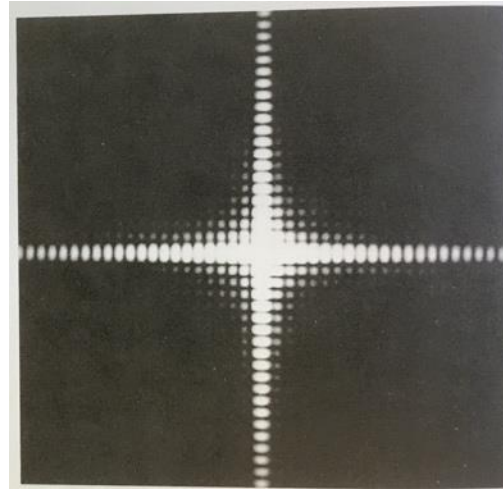
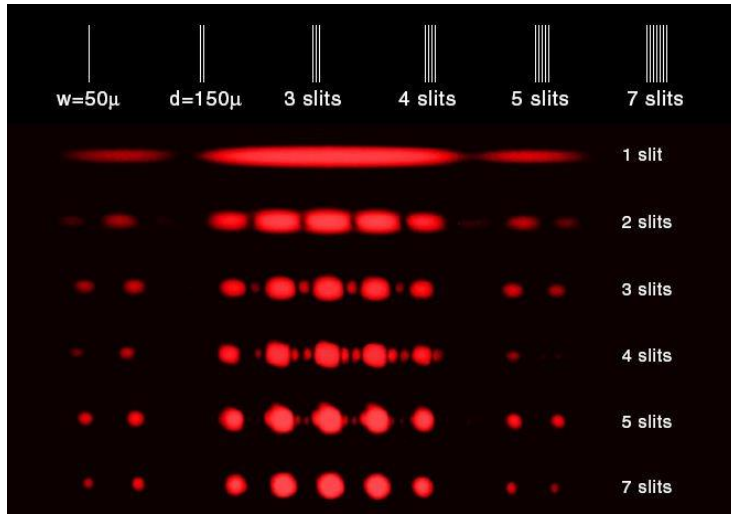


The Huygens-Fresnel Principle

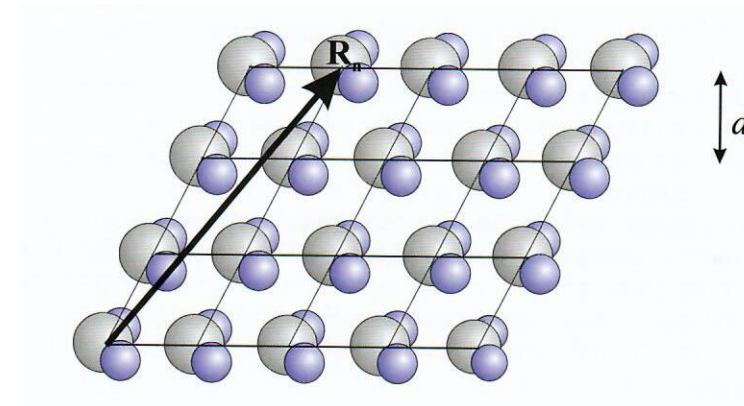
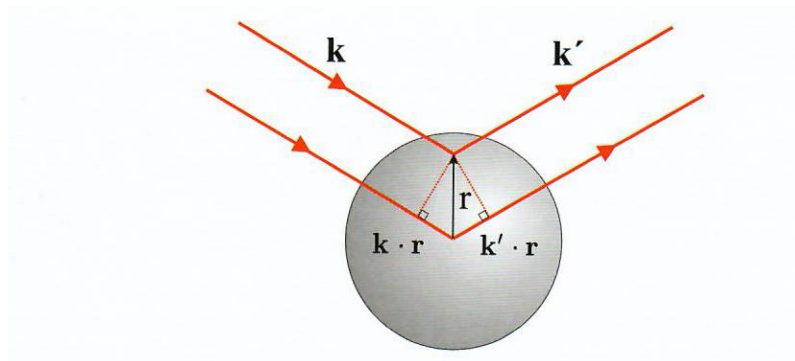
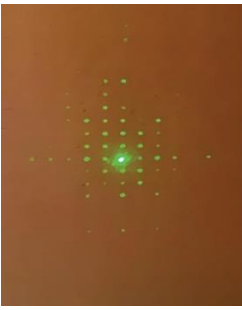
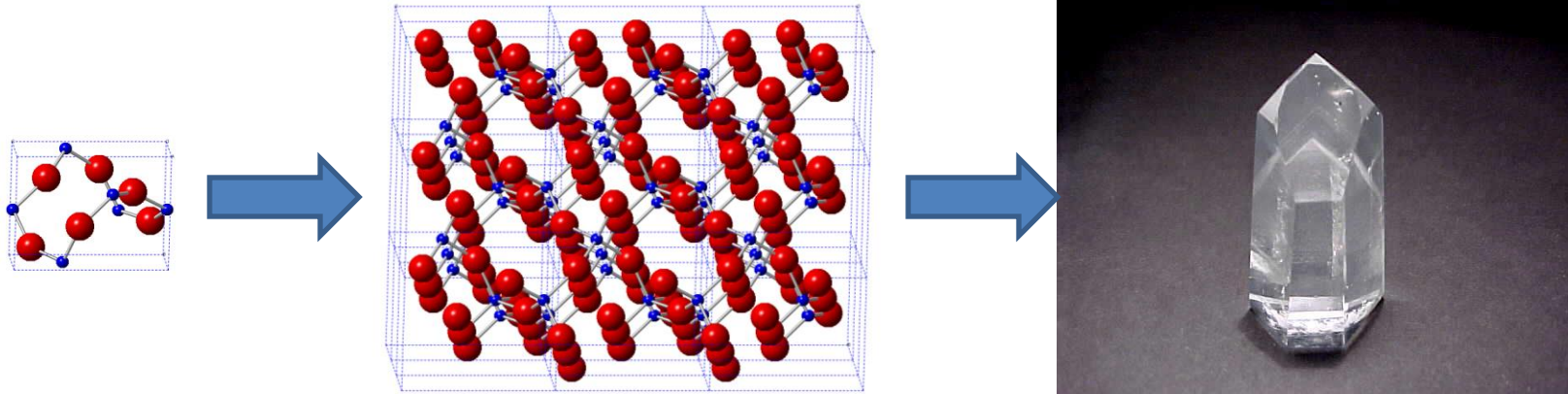
- Hugen: every point a wave (a luminous disturbance) reaches becomes a source of a spherical wave; the sum of these secondary waves determines the form of the wave at any subsequent time.
- Huygens-Fresnel: every unobstructed point of a wavefront serves as a source of spherical secondary wavelets. The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



Diffraction examples



Crystalline materials are characterized by the long-range order



Bragg scattering

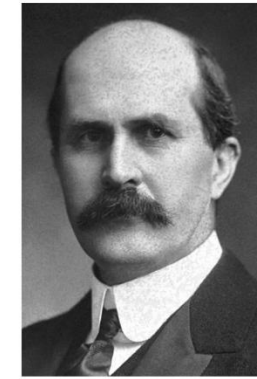
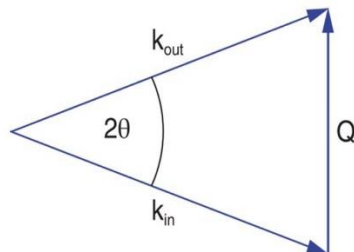
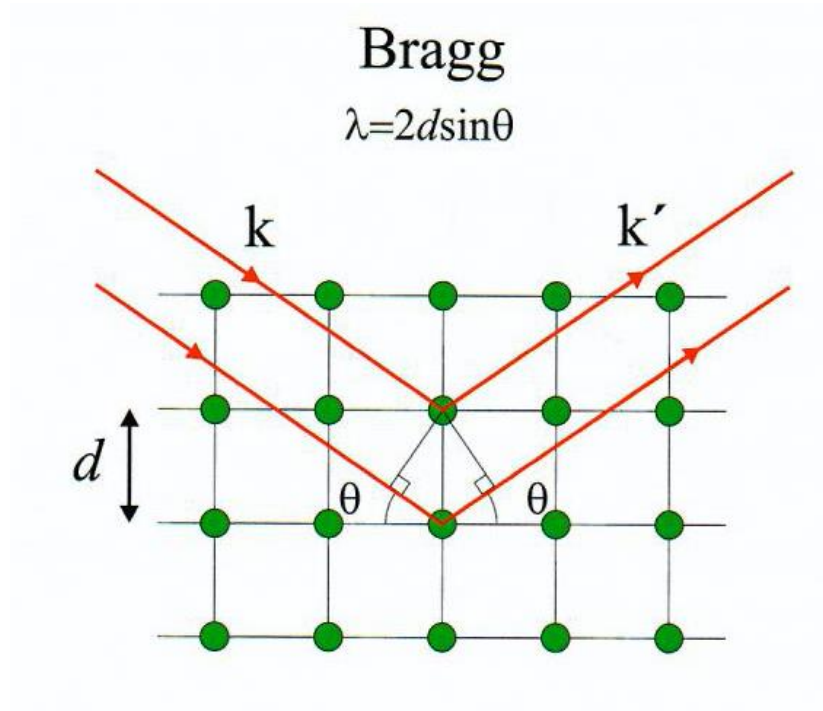


Photo from the Nobel Foundation archive.

Sir William Henry Bragg

Prize share: 1/2

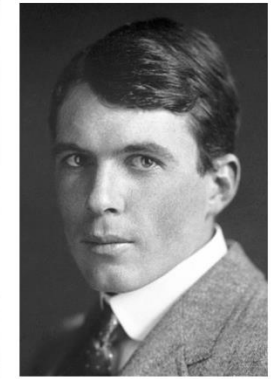
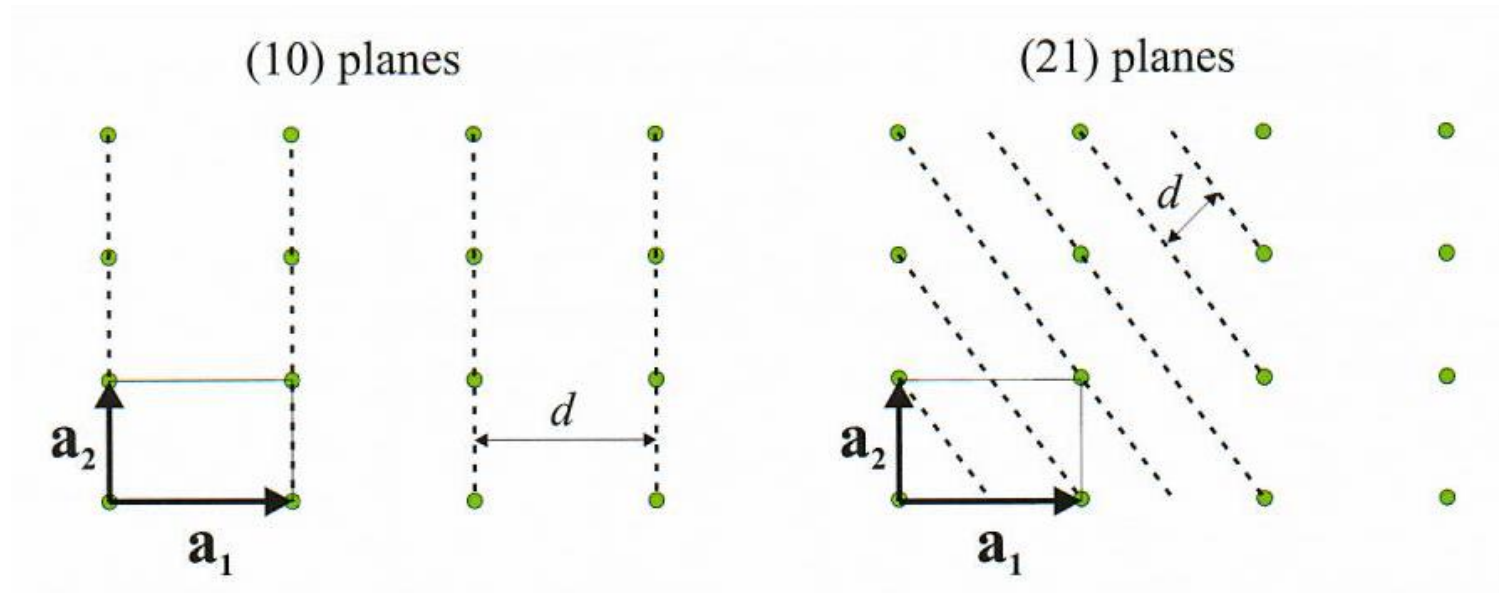
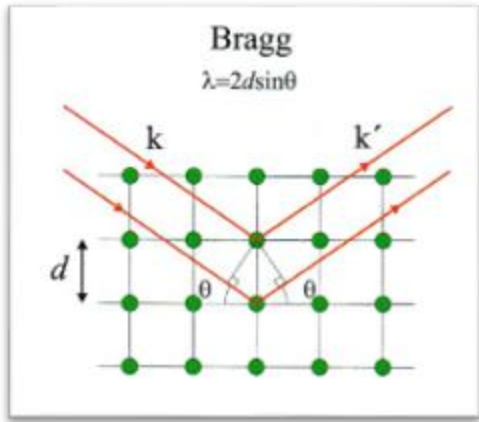


Photo from the Nobel Foundation archive.

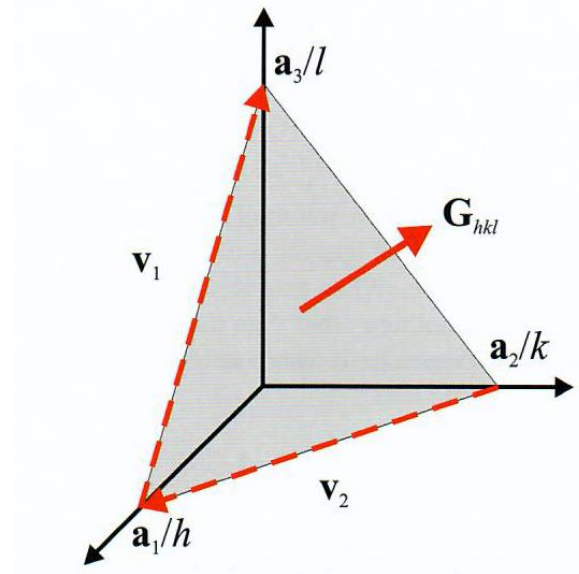
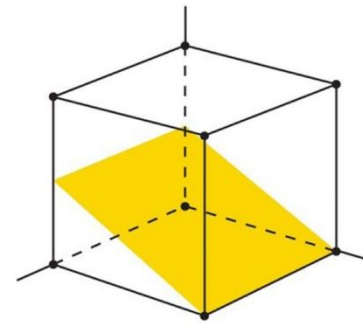
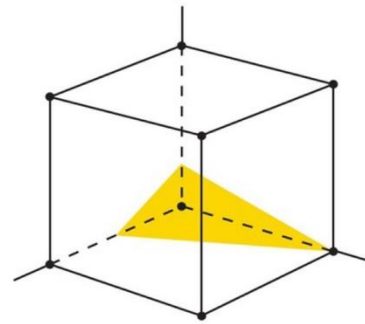
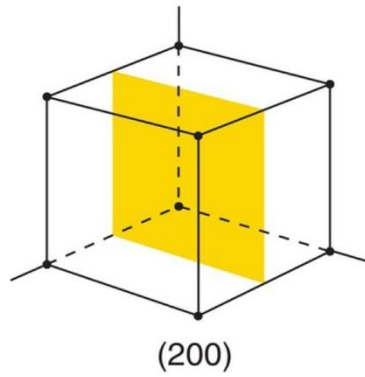
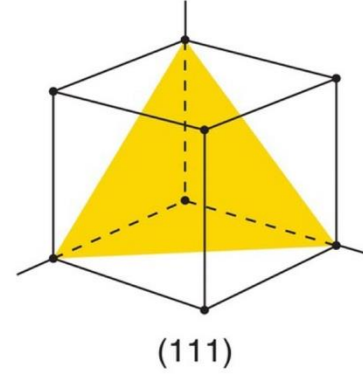
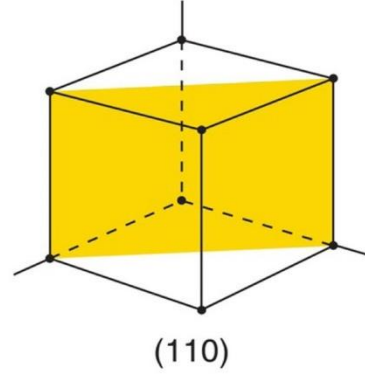
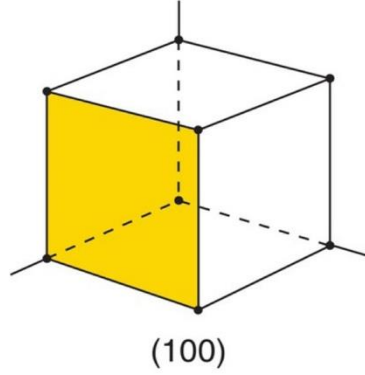
William Lawrence Bragg

Prize share: 1/2

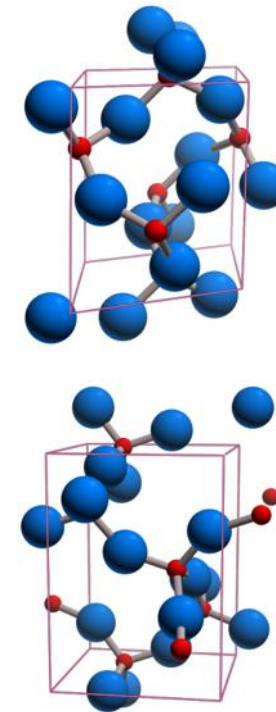
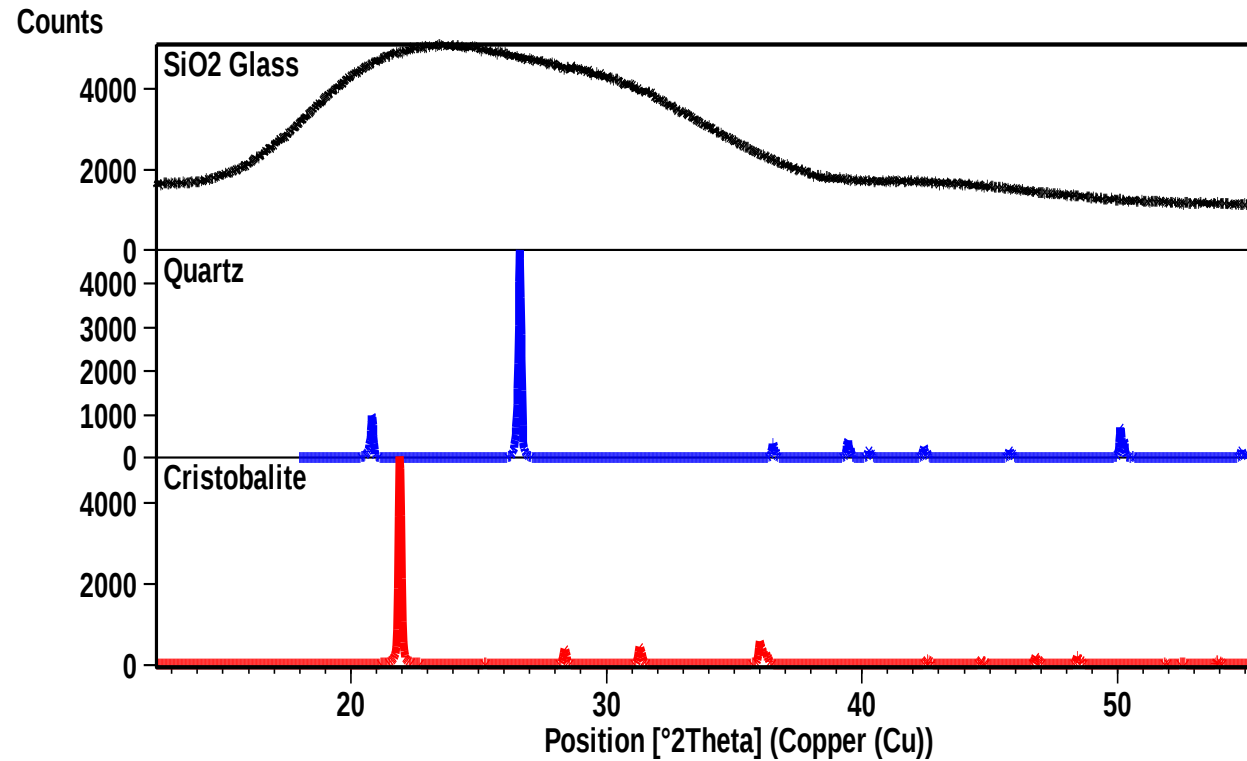
Lattice planes



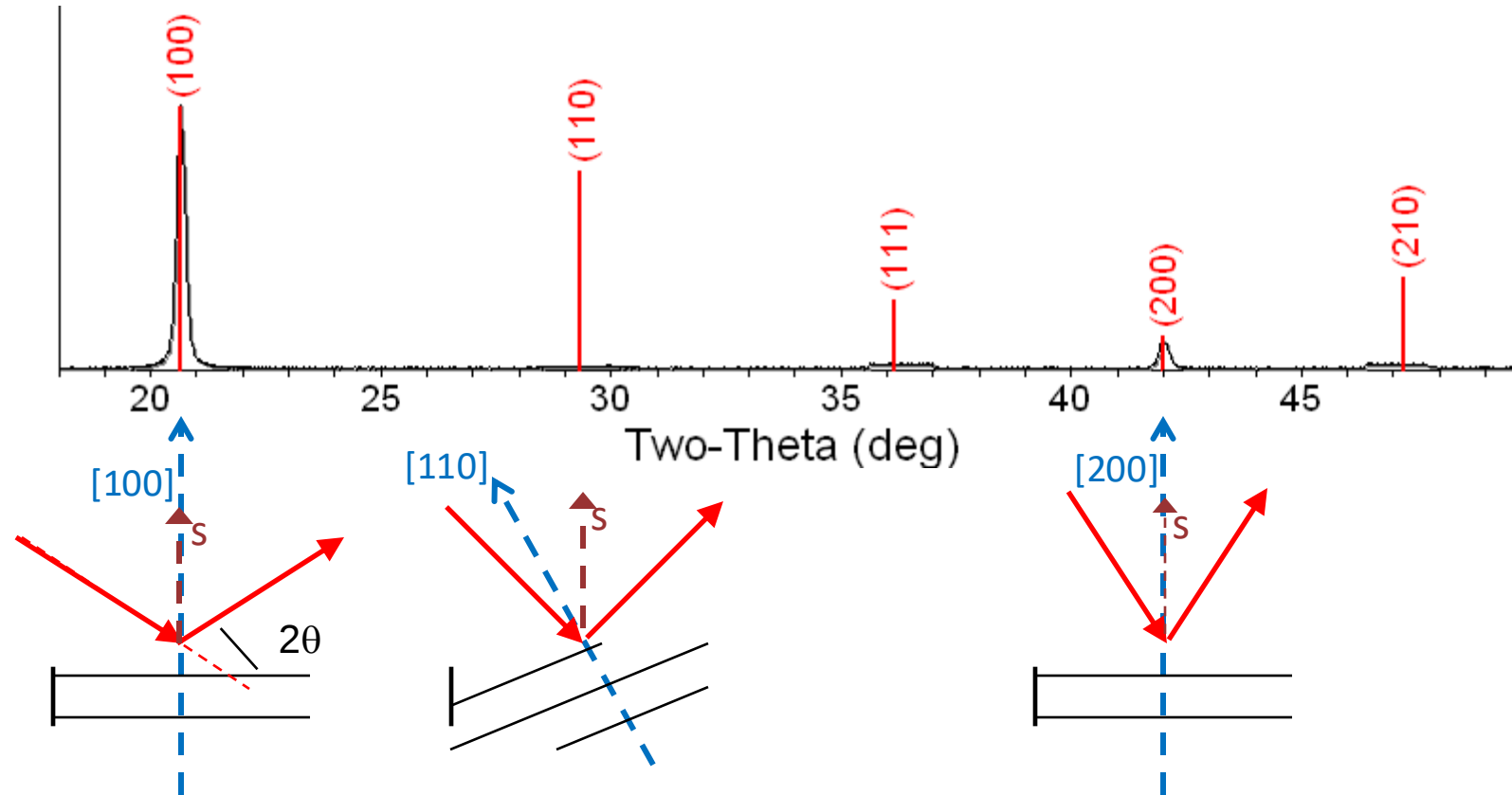
Miller indices



Characteristic signals from different – chemically identical – samples

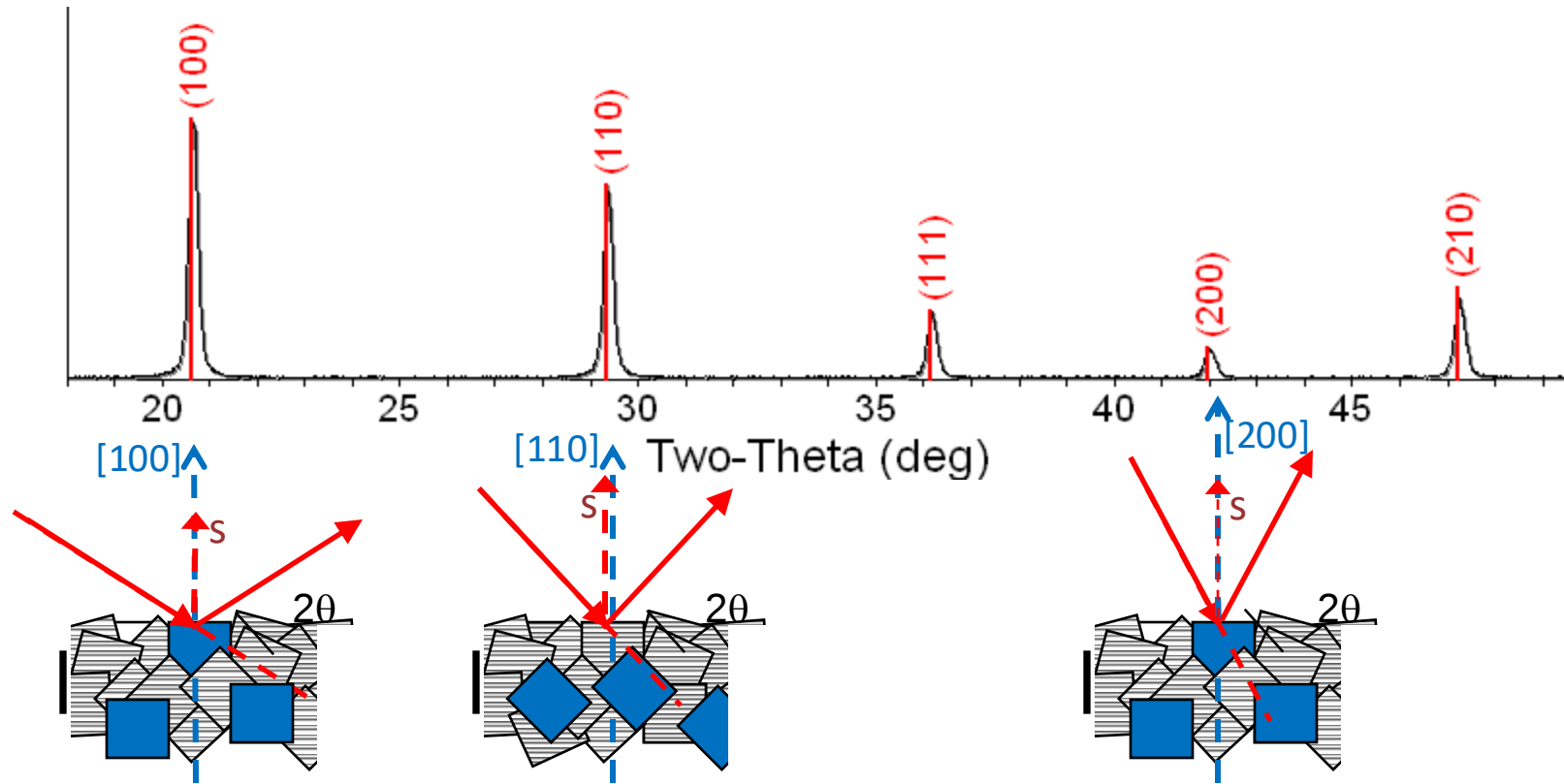


A single crystal (typically) produces one family of Bragg peaks for fixed geometry and λ

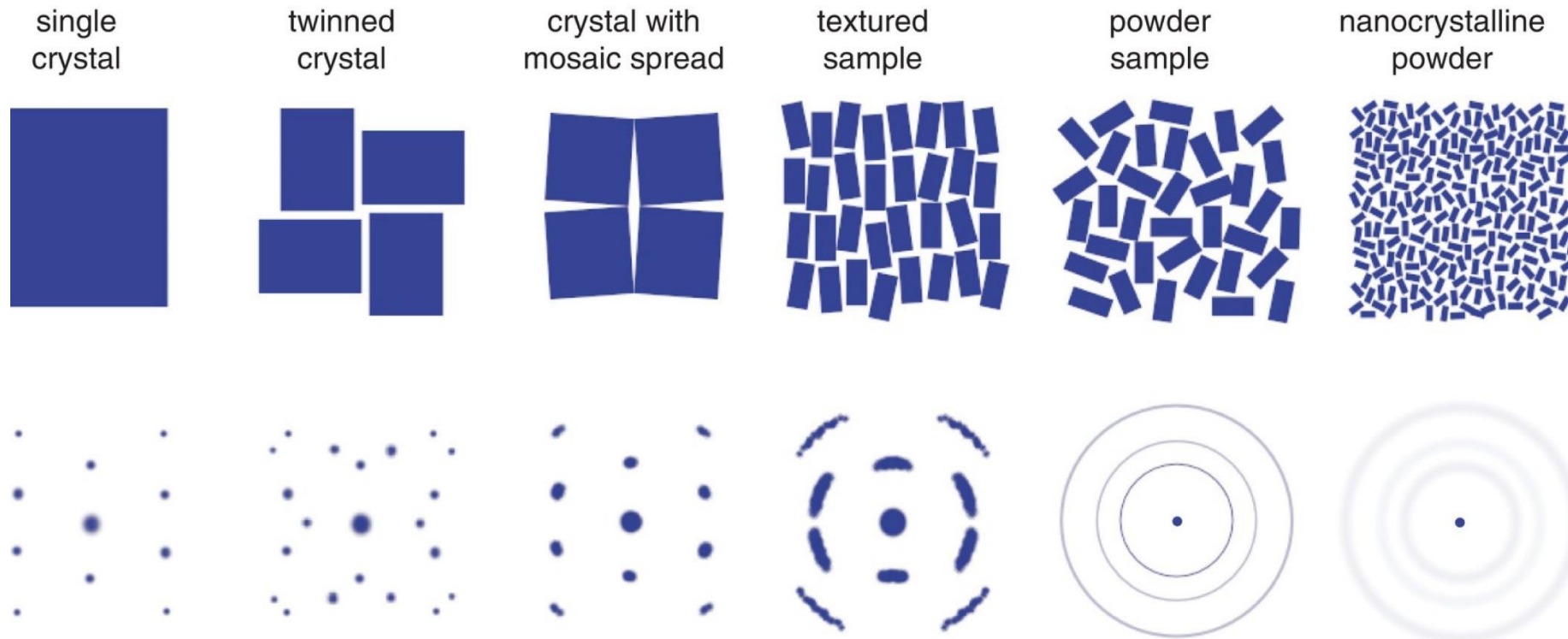


Powder diffraction

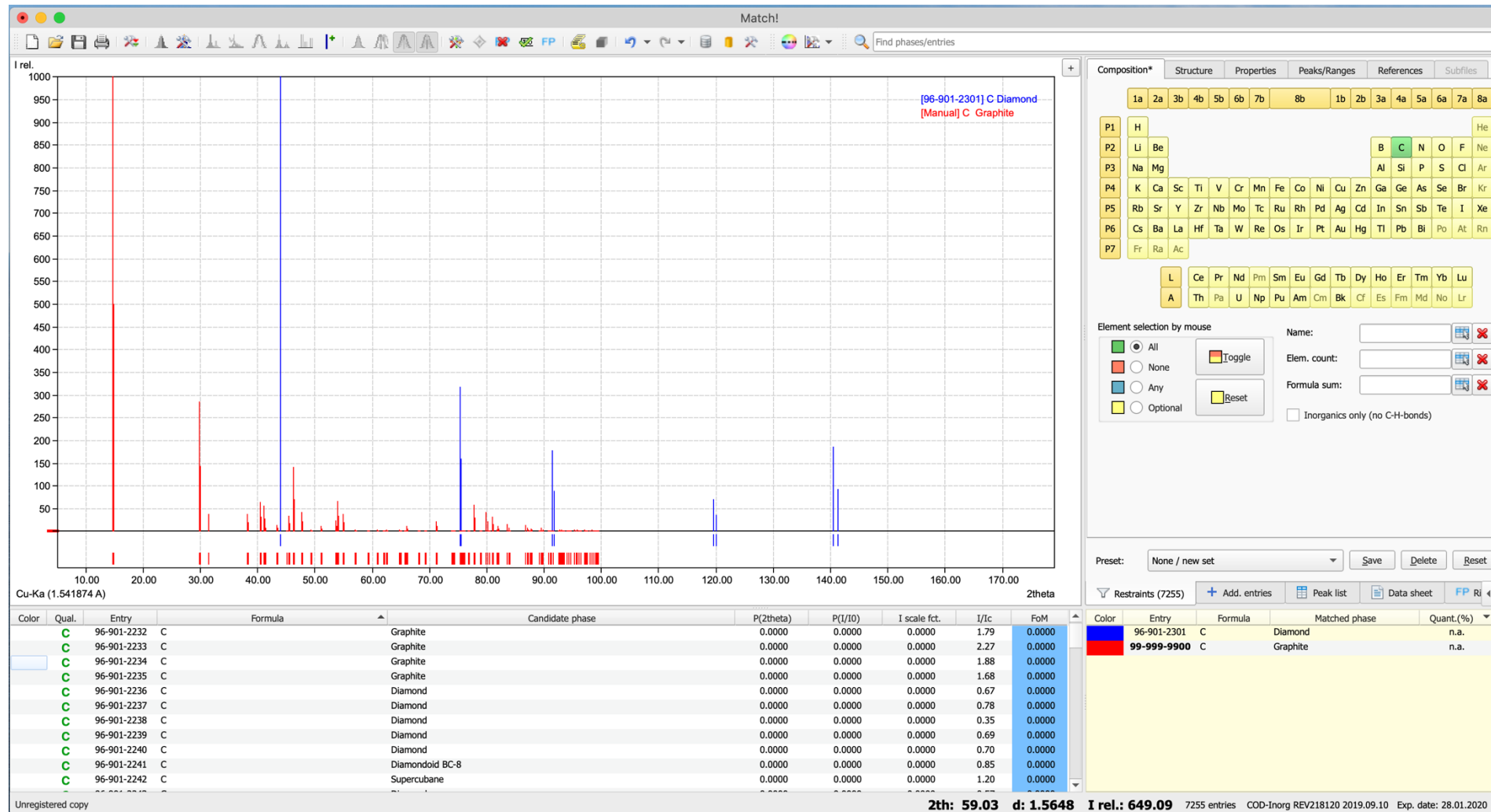
Diffraction of a polycrystalline sample



Diffraction signal of different sample types

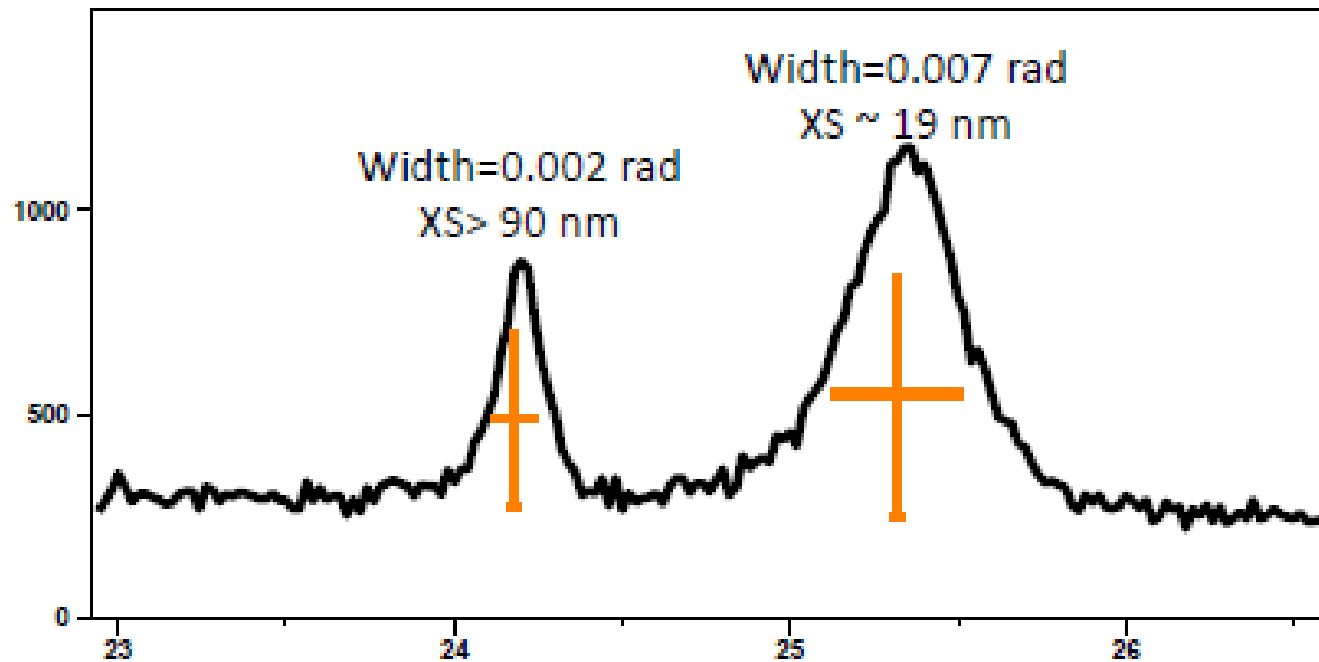


Powder diffraction data bases for elemental analysis

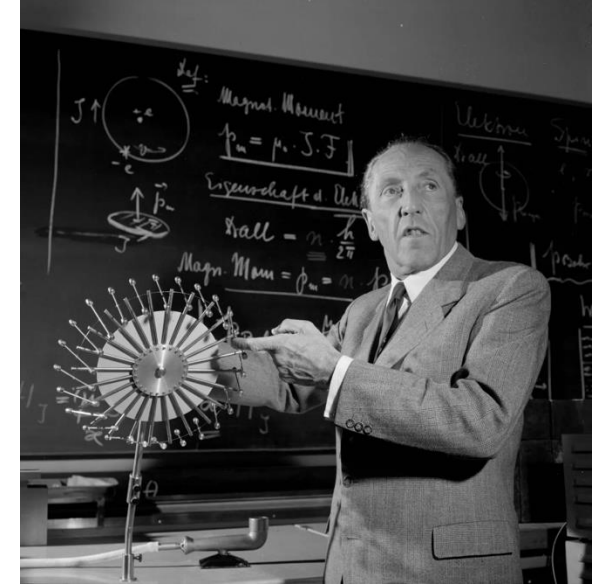


Debye-Scherrer Formula

The diffraction peak width may contain microstructural information

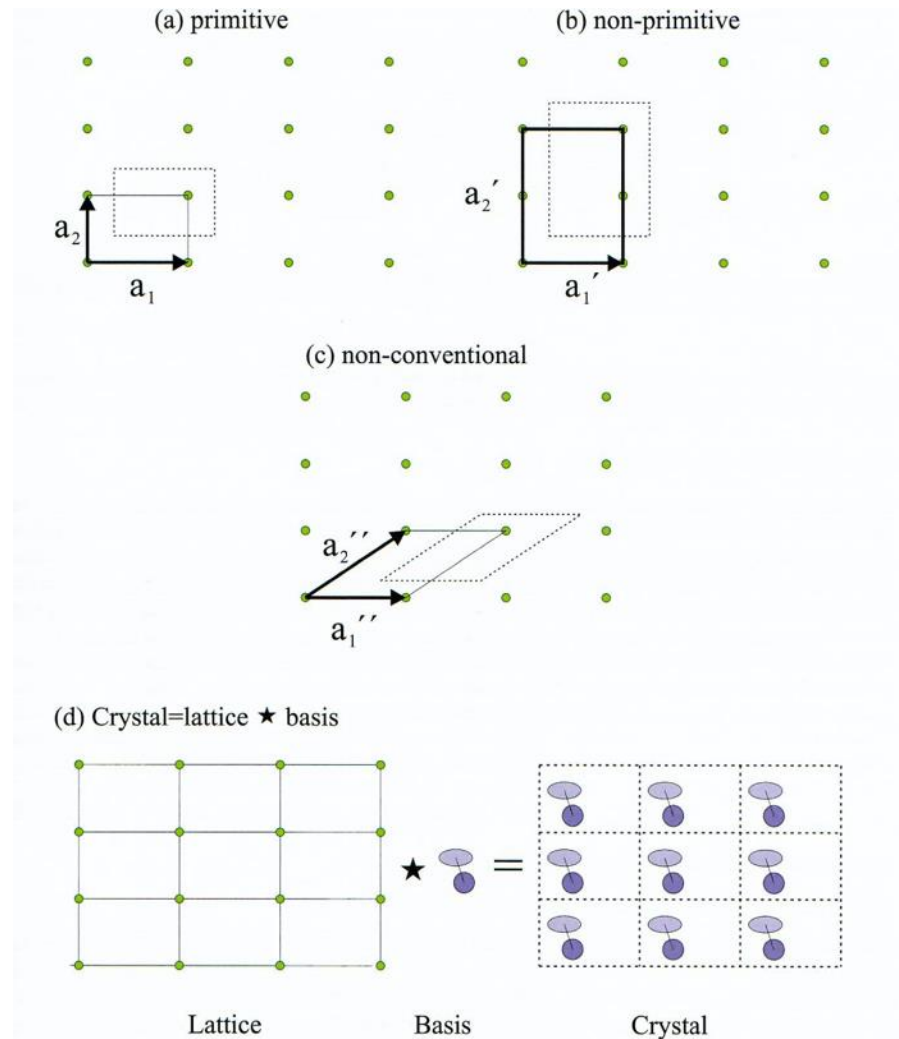


$$\text{Size} = \frac{K\lambda}{\text{Width} \cdot \cos \theta}$$



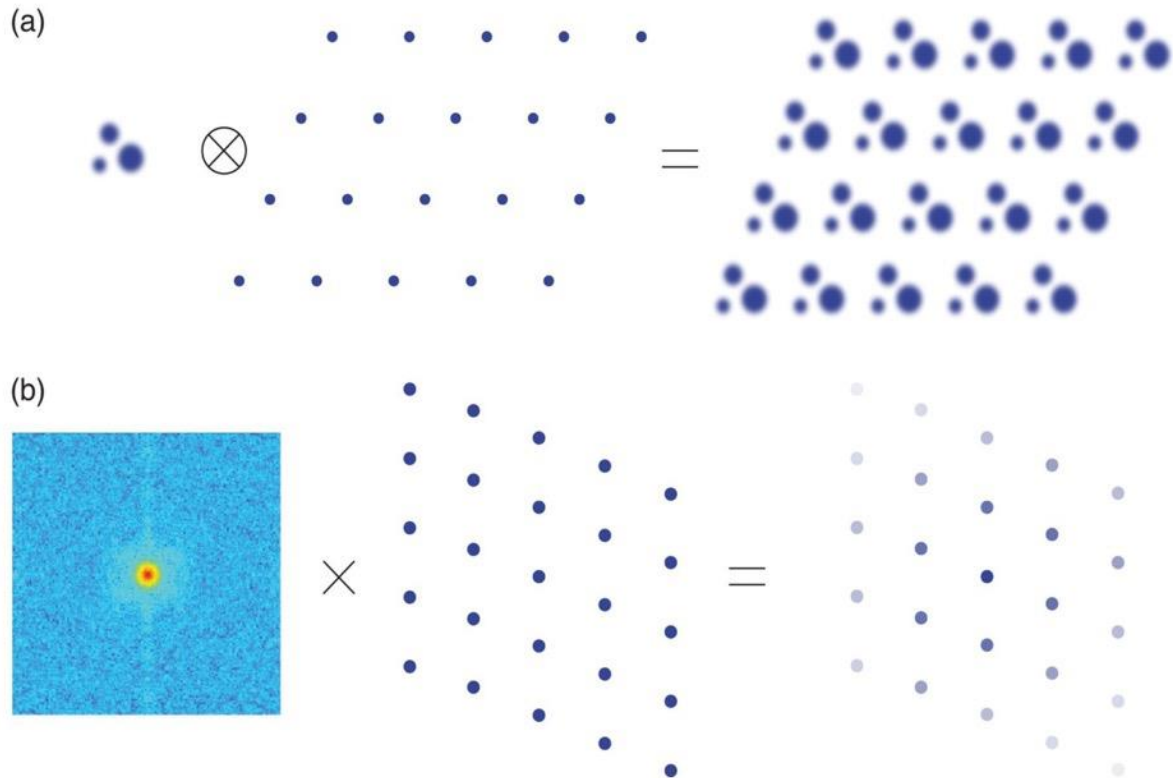
Paul Scherrer
Swiss Physicist (1890-1969)

A crystal is defined by its lattice and basis

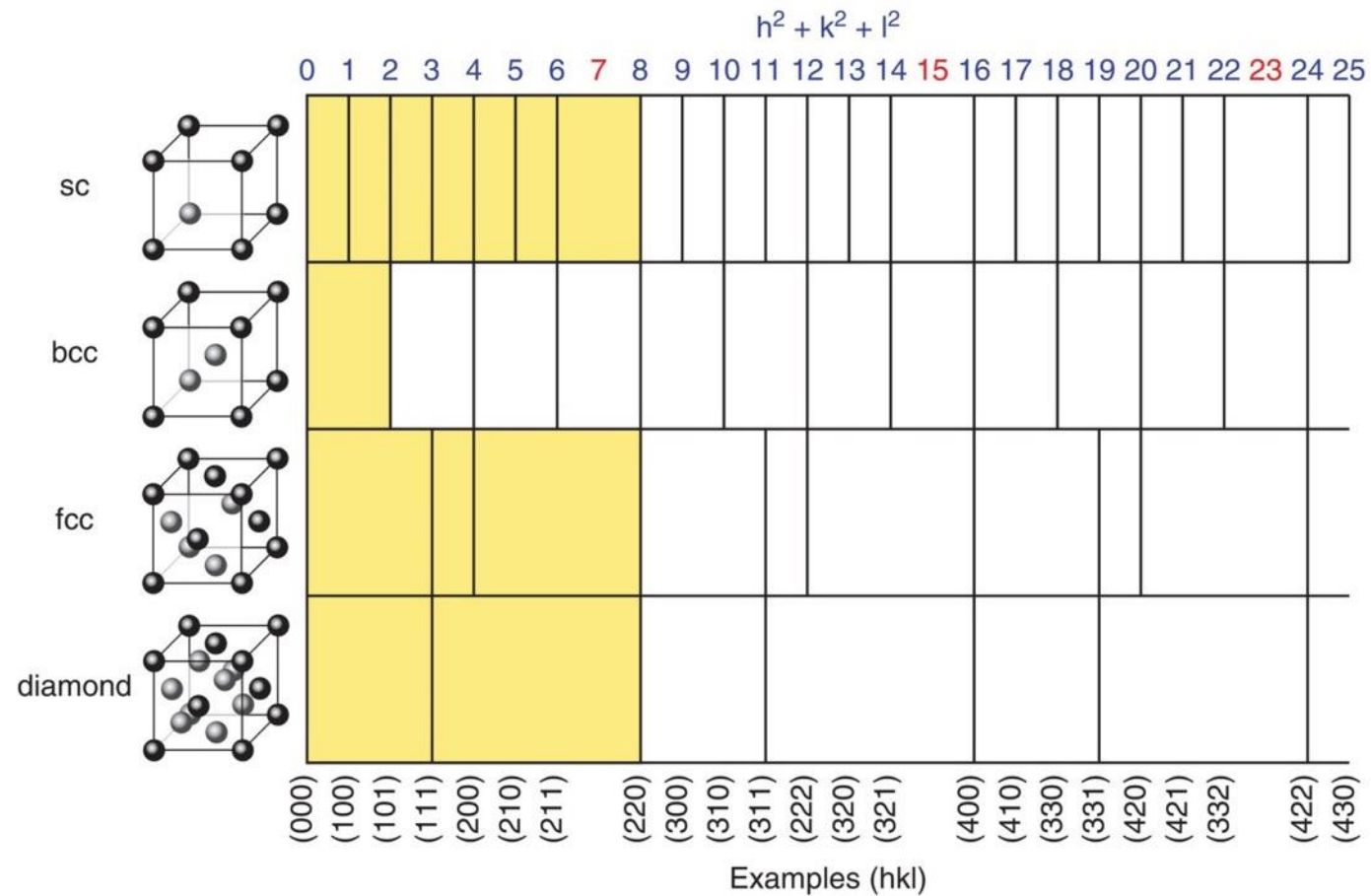


Why and how does it work?

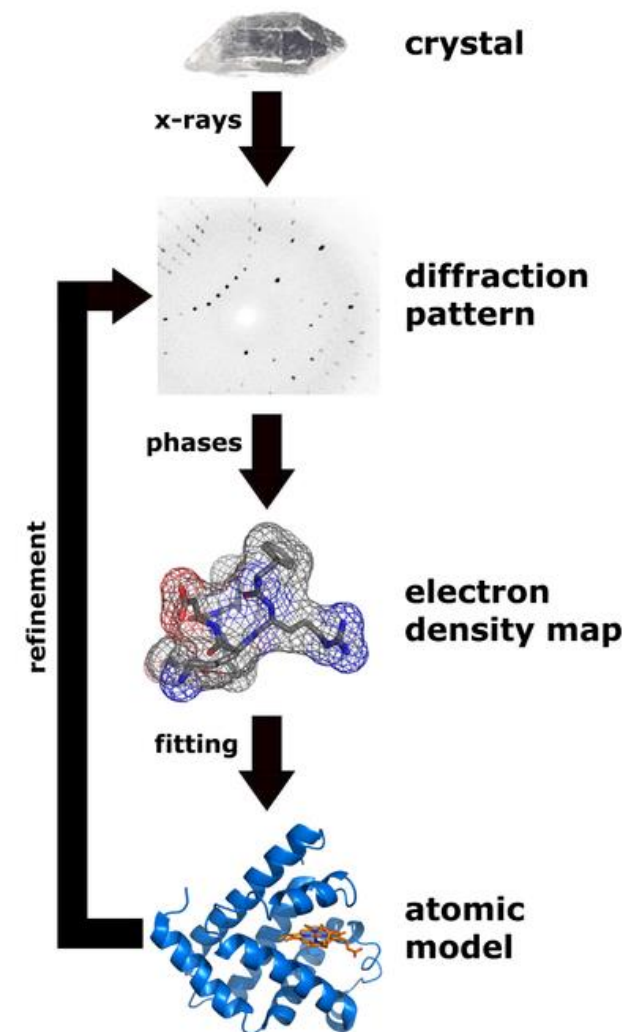
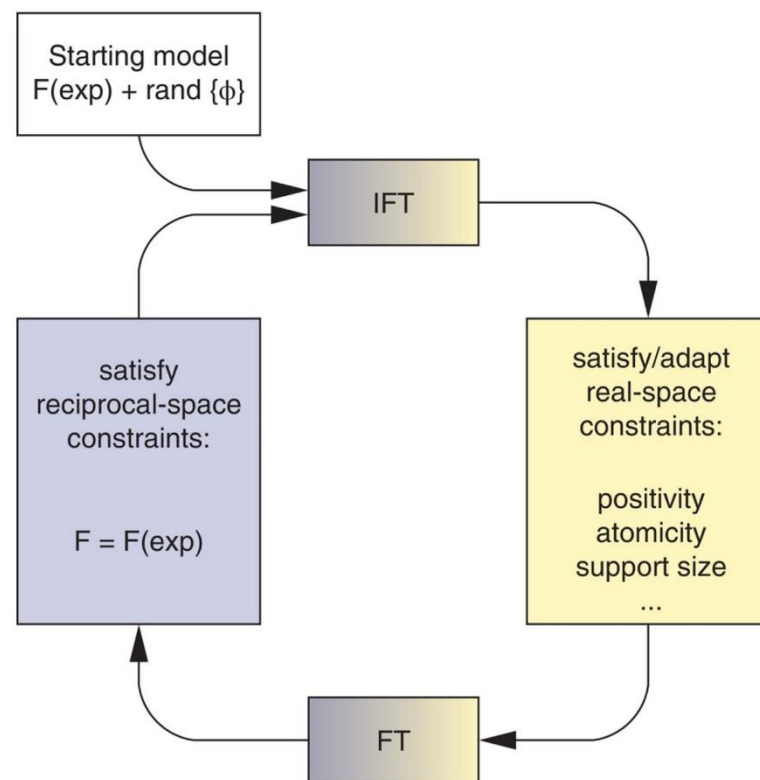
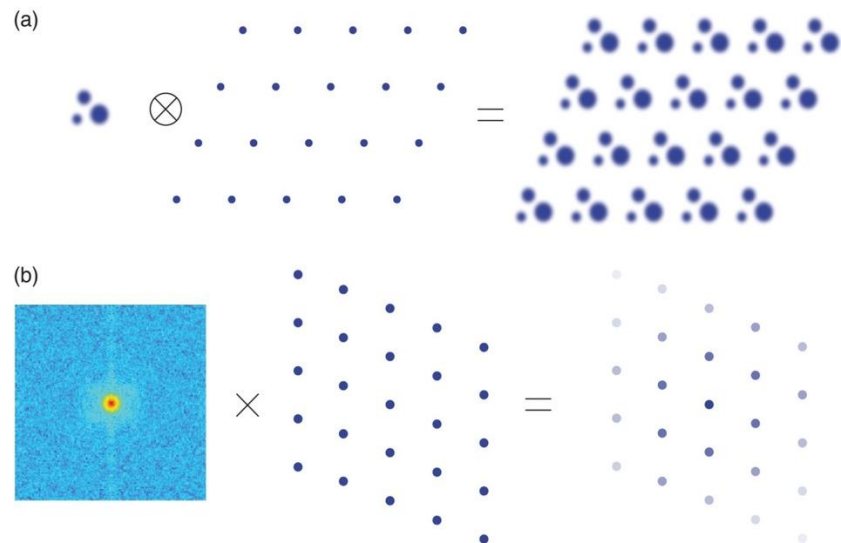
Remember last week:



Allowed and forbidden reflections



Solving a crystal structure



The end