X-rays & quantitative analysis of functional materials

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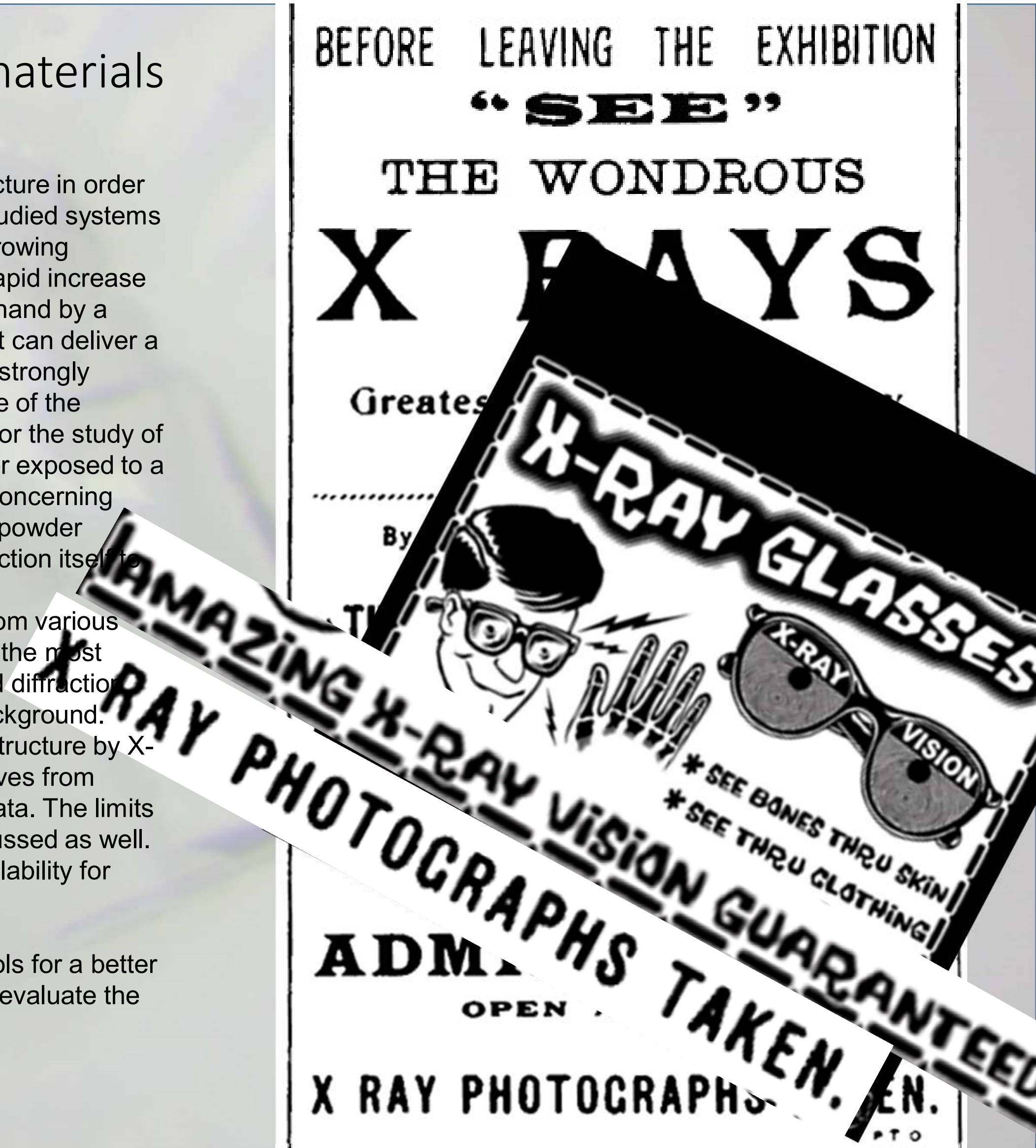
X-rays are used since over a century to analyze and understand Materials and their structure in order to explain their macroscopic properties. With the acceleration of the complexity of the studied systems in what in a wider sense is called “Nanotechnology” the importance of analysis tools is growing constantly. In the field of X-rays this growing importance is met on the one hand by the rapid increase of availability and performance of tools based on synchrotron radiation and on the other hand by a more widespread use of laboratory X-ray equipment for materials analysis. As a tool that can deliver a lot of different quantitative information the output of X-ray diffraction analysis of any kind strongly depends on the planning of the measurement. This requires in general a good knowledge of the material system and of the parameters accessible by X-ray diffraction. This is also valid for the study of powders using lab XRD equipment. In only a restricted amount of cases is the researcher exposed to a new structure that needs to be resolved. The more common case addresses questions concerning details to be resolved that are unlikely to fall into the resolution capacity of refinement of powder patterns. More often it requires an application of a more profound understanding of diffraction itself to interpret diffraction data.
It is the intention of this lecture series to encourage materials scientists and engineers from various backgrounds to understand basic X-ray-matter interactions. It will supply an overview on the most prominent use cases of X-rays. A phenomenological approach to structure resolution and diffraction makes it easy to follow the basics and motivates for a deeper study of the theoretical background. After an introduction to basic questions of material science and the discovery of crystal structure by X-rays a step by step derivation of a few fundamental equations about the scattering of waves from periodic objects delivers a practical tool box for the quantitative treatment of diffraction data. The limits of the most conveniently used techniques based on kinematic scattering theory are discussed as well. An introduction to synchrotron radiation and its still rapidly progressing potential and availability for material science will be part of the second half of the lecture series.

The first lecture will be and introduction, historical review and motivation for analytical tools for a better understanding of materials’ structure. It will include questions to the audience in order to evaluate the needs and expectations and adapt the lectures accordingly.



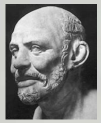
X-rays & quantitative analysis of matter, basic topics addressed in this course:

- -Short review on Materials, Structure and Properties: Science, tools, and the people behind
- -X-rays and their interaction with materials
- -phenomenological approach to diffraction & structure resolution
- -introduction of the reciprocal lattice
- -scattering concepts/ reciprocal space / kinematical interpretation/ limits
- -real experiments with real samples: 1D, 2D and 3D data sets
- -X-ray sources: from sealed tubes to synchrotron radiation (some electrodynamics of light generation)
- -what else beyond average structure ?

Some equations are unavoidable, but I know none of these myself by heart. $\Delta x \Delta p \geq \hbar$ all the rest can be looked up or derived. Understanding a relation does not mean to remember by heart a mathematical equation

History of the structure of materials = history of human civilization

By convention sweet, by convention bitter, by convention hot, by convention cold, by convention color:
<u>but in reality **atoms** and void</u>.
Democritus ~ 400 BC

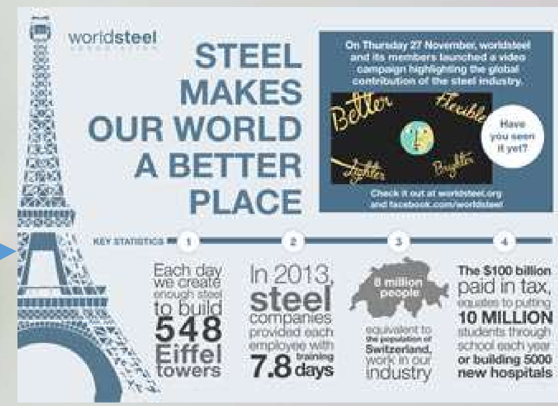


The discovery and analysis of the atomic structure of materials has much accelerated technological progress beyond trial-and-error approaches.

It goes along with the most important examples of quantitative 3D material analysis based on scattering/ diffraction methods.

Beginning of iron age (1000-2000 BC)

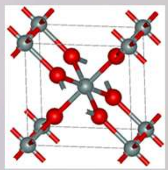
Few 1000 years or trial and error

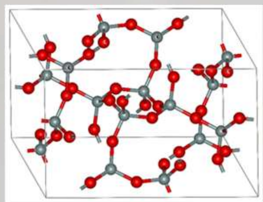


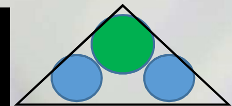
Exploration of crystal structure (1915)& "understanding" of quantum physics of the solid state:
100 years of high level analysis

Macroscopic material properties can be explained by…

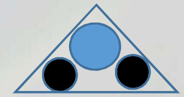
Chemistry (and crystal structure)







SiO_2



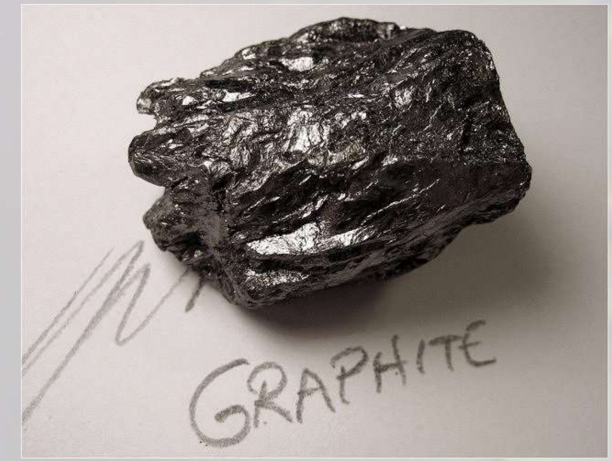
H_2O

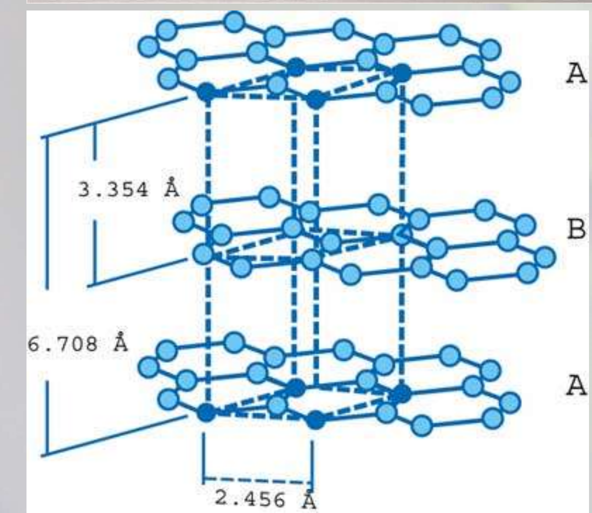
Crystal structure

Micro-structure

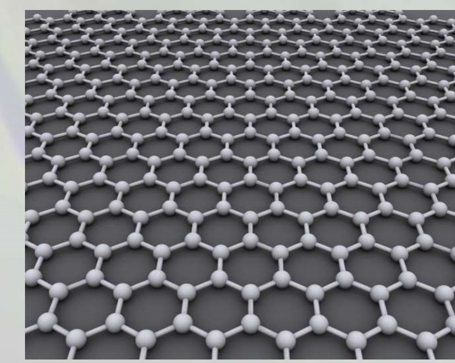
All these properties can be studied with X-rays, (essentially by using X-ray diffraction)

Structure function relationship





Novoselov & Geim Nobel Price 2010:
Using scotch tape to lift of one atomic layer of *Graphene,*
With outstanding mechanical and electrical properties



2010: single layers of MoS_2 turn out to have outstanding electronic properties.

Crystalline structure of matter - History

Niels Stensen (1638-1686)
Danish Anatomist, Geologist and Bishop, observes and describes the constancy of angles between facets of different quartz crystals

Arnould Carangeot & Jean-Baptiste Romé de L'Isle
Mineralogists, build and use a goniometer to measure precisely angles between facets of crystals (around 1780)
Carangeot is convinced that crystals can be classed by the sole description of the geometrical arrangement of their facets.
He proposes and starts a « database » of crystals.

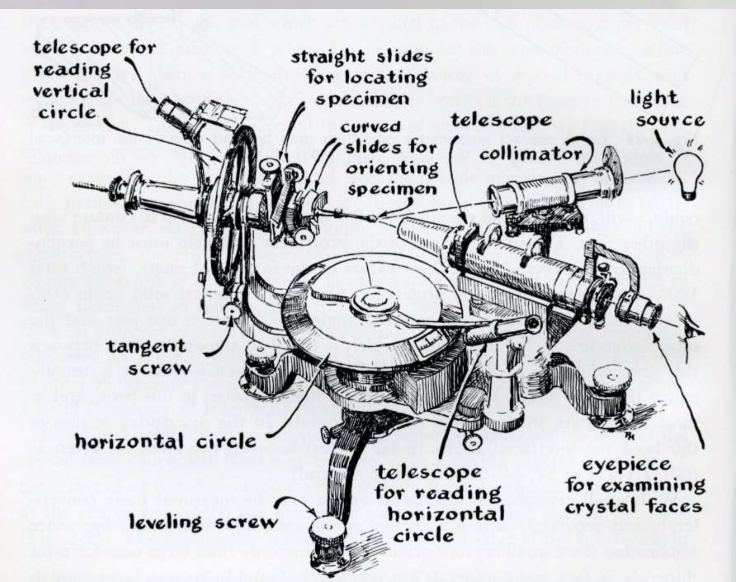
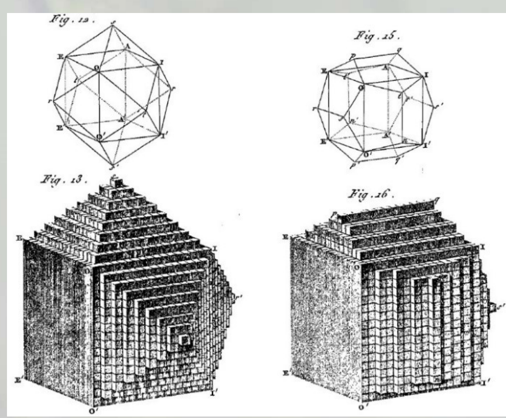


Fig. 2-26 A two-circle reflecting goniometer.

His student **René Just Haüy** continues to fill this crystallographic database and formulates the law of rational indices (1781):

*For the given crystal species it is always possible to choose three vectors, **a**, **b** and **c** so that all the natural faces of this crystal cut the lengths proportional to the three integer numbers*



Haüy brings up the idea of "parallelepiped molecules".

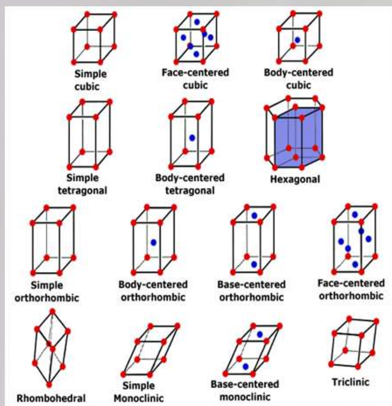
-> explained the symmetric shape by the periodic nature of the internal structure.

He even started to study the electrical properties of crystals in 1817.

Crystalline structure of Matter

Bravais discovers (1848) that 14 regular point lattices suffice to describe the basis of any periodic structure that fills space when reproduced by 3 basic translations.

14 lattices



Operations of
Rotation
Reflection
Inversion

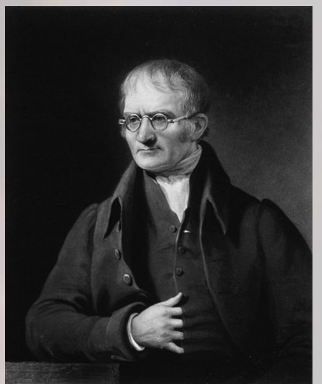
32 point groups

Glide planes
Screw axis

230 space groups

Incomplete enumeration by Fedorov and Schoenflies in 1891. Completed in 1892. Although Schoenflies invented a notation the most generally used one is the one published by C. Hermann (1928) and completed by C.-V. Maugin (1931)

Atomic structure of Matter – History



John Dalton (1766-1844): Proposes the modern Atom theory in 1803 with a first table of six identified elements (H, N, C, O, P, S) and their combinations.

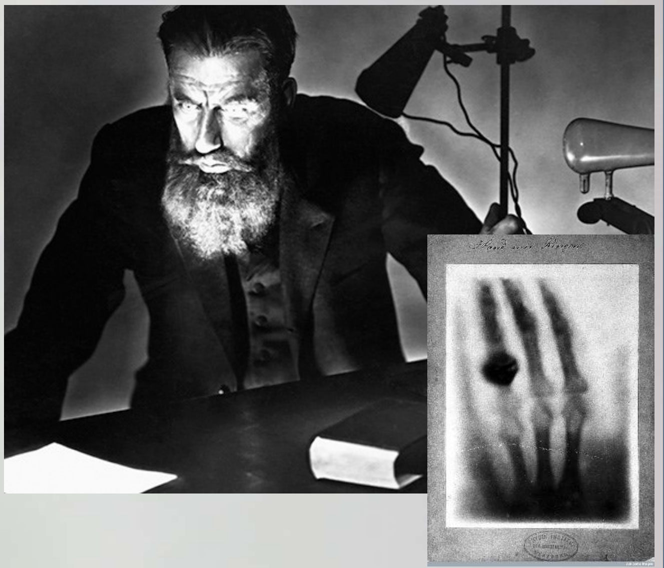
Daltons' proportionality law and Haüys' Cristal "Molecules" lead to speculations in the early 19th century about the existence of Atoms. For 100 years this is often harshly criticised

J.-B. Dumas in 1836: « If I would have the power, I would delete the word « Atom » from science, convinced that it goes further than our experiences reach. »
Marcellin Berthelot (around 1880): « I do not want chemistry to degenerate into a religion where one believes in the real existence of these Atoms »

19th century: anisotropies of crystal shapes is associated to the anisotropies of their physical properties. 1880: discovery of piezoelectricity in quartz by Pierre Curie.

The properties "order" and "symmetry" become linked to the physical properties.

A short history of X-rays



Nov 8th 1895: Wilhelm C. Roentgen (50 yrs old) discovers a new kind of radiation while experimenting with a “cathode-ray tube”. Realizing that the radiation he discovered had entirely new properties, he ate and slept in his laboratory for two weeks, continuing experiments and taking notes .

The analysis and publications from this time set the state of the art of knowledge about X-rays for about 10-15 years.
In January and February 1896 several articles in the New York Times report about “Roentgen Ray” photographs “ that have nothing in common with ordinary photographs.”

N-YT Feb. 1896: Already numerous successful applications of it to surgical difficulties are reported from various countries.

1901: Roentgen is awarded the 1st Noble prize in physics

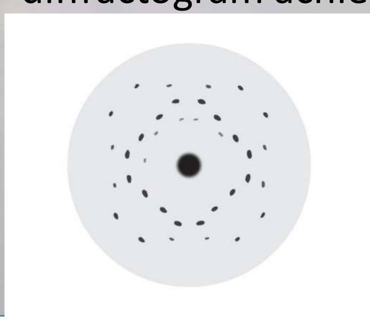
A short history of X-rays

Until 1912, imaging remains the “only” application, although scientists around the world try to explain what X-rays really are (waves, or new particles ?)

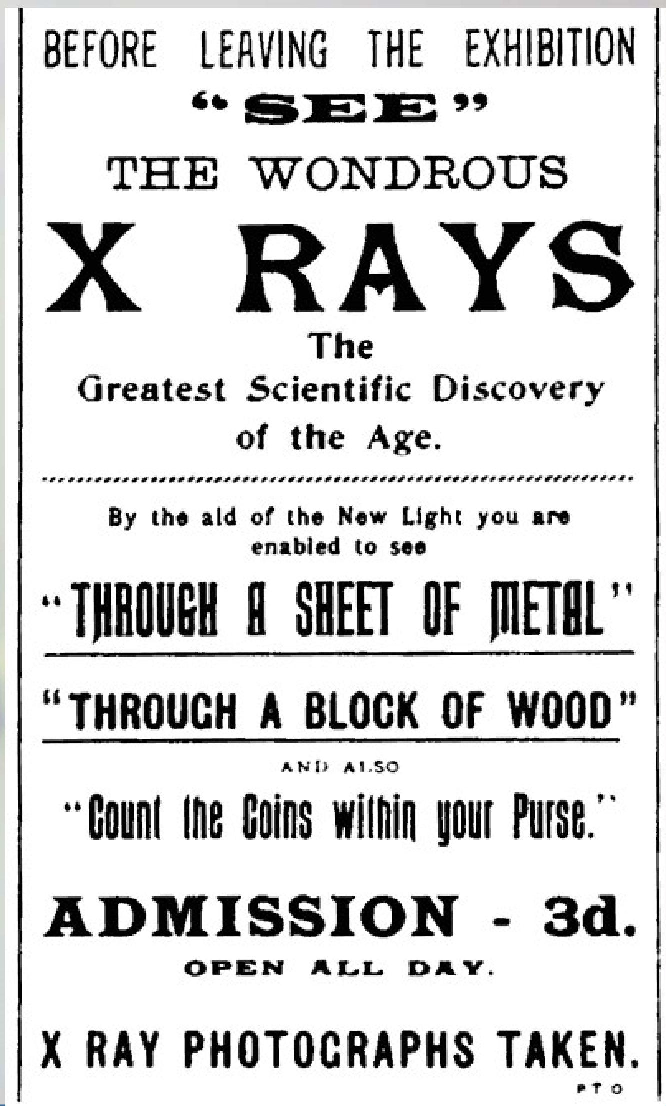
In 1910 the wave nature of X-rays and the idea of Crystals as “atomic gratings” where still discussed

Max v. Laue (1874-1960), former student of Max-Planck and assistant to A. Sommerfeld proposes in 1911 that the characteristic radiation rather than the chaotic Bremsstrahlung be used to make a diffraction experiment that could solve both issues at once.

1911/1912 his ideas matured in discussions with P.P. Ewald (1888-1985) and in April 1912, Laue directed his students P. Knipping and W. Friedrich to shine X-rays through ZnS and CuS cristals leading to the first “Laue diffractogram achieved by white X-ray light (Nobel Prize of 1914)



Public lecture flyer from London, 1896



Crystalline, atomic structure of matter - History

Around 1900

Even “without atoms” the physical properties of crystals are described by scientists as linked to their symmetries. This is often referred to as Franz Neumann’s (1795- 1898) principle published in his lecture notes in 1885:

“If a crystal is invariant with respect to certain symmetry operations, any of its physical properties must also be invariant with respect to the same symmetry operations, or otherwise stated, the symmetry operations of any physical property of a crystal must include the symmetry operations of the point group of the crystal”

As late as 1910 (W. Voigts textbook on Crystal physics) many experts in the field preferred a continuum description of crystals and physical properties.

After 1913: the “diffraction revolution” catapults the point lattices and space-groups from a mathematical curiosity of group theory to the model describing the structure of almost all solid materials.
New Journals emerge, like “Strukturbericht” that aim at publishing the determined space-groups of all known Materials.

1944: to unify international efforts and to end “chaotic” publishing Ewald and Bragg initiate the foundation of the International Union for Crystallography IUCr, the Hermann-Maugin notation of space groups becomes the standard.

X-rays & their diffraction from lattices

The basic principles of diffraction where known from visible light experiments.

Structure resolution requires the calculation not only of diffraction peak *positions* but also of *intensities*.

It became quickly clear that for “big” crystals the intensity of a diffraction pattern becomes a difficult parameter to calculate as. It requires the taking into account several possible pathways, as e.g. a very intense diffraction peak might itself excite other diffraction peaks etc..

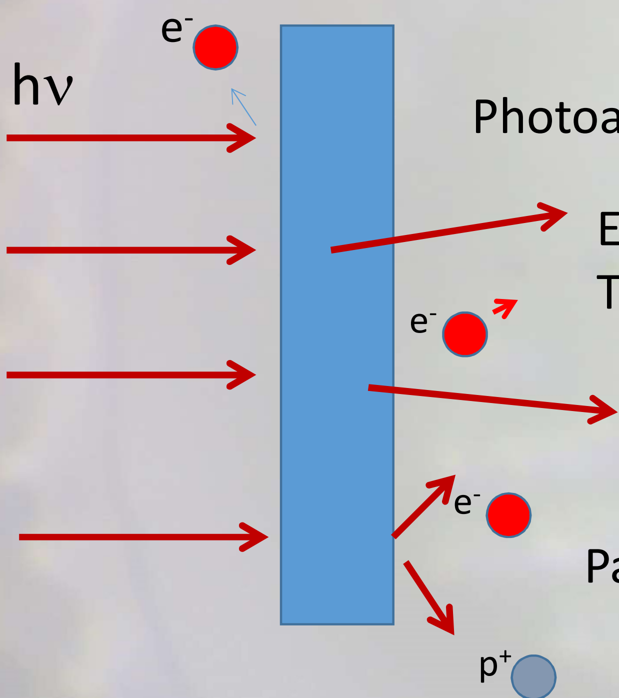
This complete treatment of light-lattice interaction is generally referred to as “dynamic scattering theory”.
The first developments were done by C. G. Darwin (*The theory of X-ray reflection*, Phil. Mag. **27**, 315 (1914), and P. P. Ewald who spent much of WW I completing his first geometrical approaches.

In many cases, a simpler approach is possible, called the kinematic scattering theory. This approach is the basis and the reason of success of structure resolution by X-ray diffraction

Impact of crystallography

29 Noble prices linked to Crystallography (10 in physics, 18 Chemistry, 1 Medicine)

Principal interactions in the X-ray regime



Photoabsorbtion

Elastic scattering (Coherent scattering or Thompson scattering)

Compton scattering (incoherent scattering)

hν'

Pair formation (for hν> 1 MeV)

Process	Probability to happen for 8 keV photons in 10 µm Carbon
Photo absorption	0.01
Elastic scattering	0.00005
Compton scattering	0.00002
Pair formation	0

Scattering Cross-sections

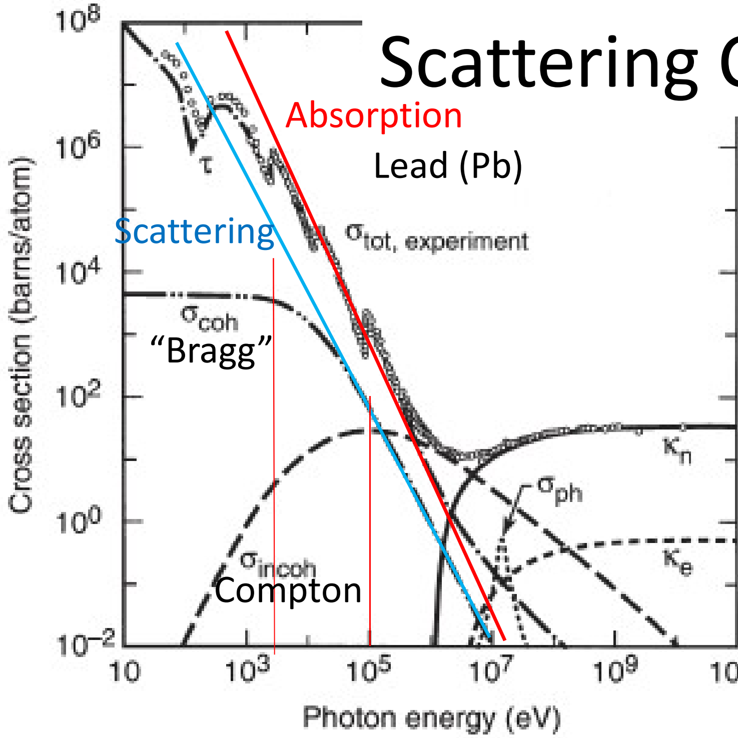


Fig. 3-2. *Total photon cross section σ_{tot} in lead, as a function of energy. See Fig. 3-1. (From Ref. 3; figure courtesy of J. H. Hubbell.)*

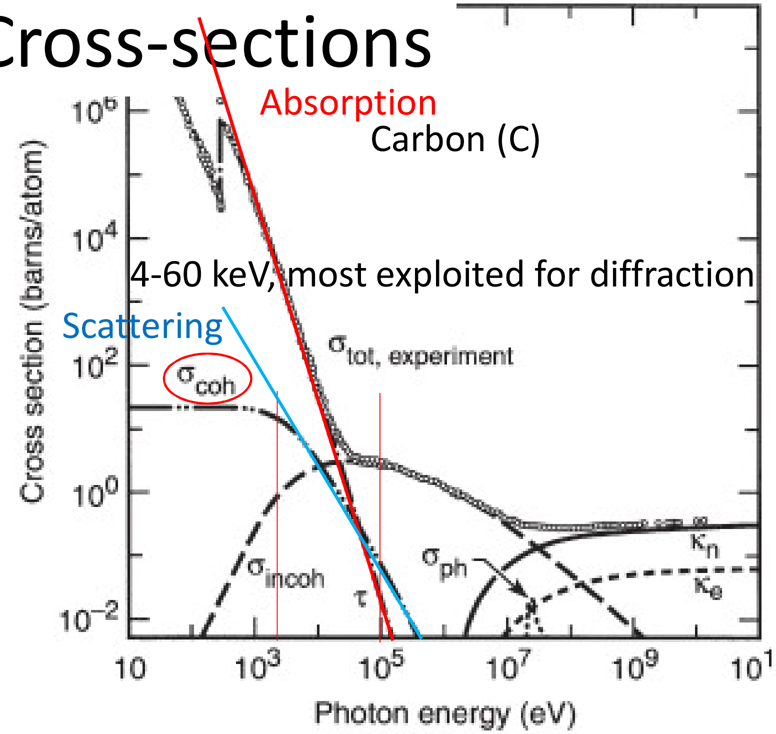


Fig. 3-1. *Total photon cross section σ_{tot} in carbon, as a function of energy, showing the contributions of different processes: τ, atomic photo-effect (electron ejection, photon absorption); σ_{coh}, coherent scattering (Rayleigh scattering—atom neither ionized nor excited); σ_{incoh}, incoherent scattering (Compton scattering off an electron); κ_n, pair production, nuclear field; κ_e, pair production, electron field; σ_{ph}, photonuclear absorption (nuclear absorption, usually followed by emission of a neutron or other particle). (From Ref. 3; figure*

Rule of thumb

Photo effect ~E^{-3}

Elastic Scattering ("Bragg") ~E^{-2}

Photo effect ~Z^4

Elastic scattering ("Bragg") ~Z^2

Figures: the X-ray data booklet
http://xdb.lbl.gov

Why can we treat all these contributions separately ?

Elastic scattering (~ “Bragg Peak”): information on the ensemble of all interacting particles, as no “individual” trace (no kicked out electron, no energy transfer), that is why diffraction leads to “sharp” peaks in angular space as

$$\Delta x \Delta p \geq \hbar$$

i.e. the angular deviation can be well defined (small Δp), as the zone of spatial interaction is large (Δx many 10s of nanometres).