X-RAY DIFFRACTION

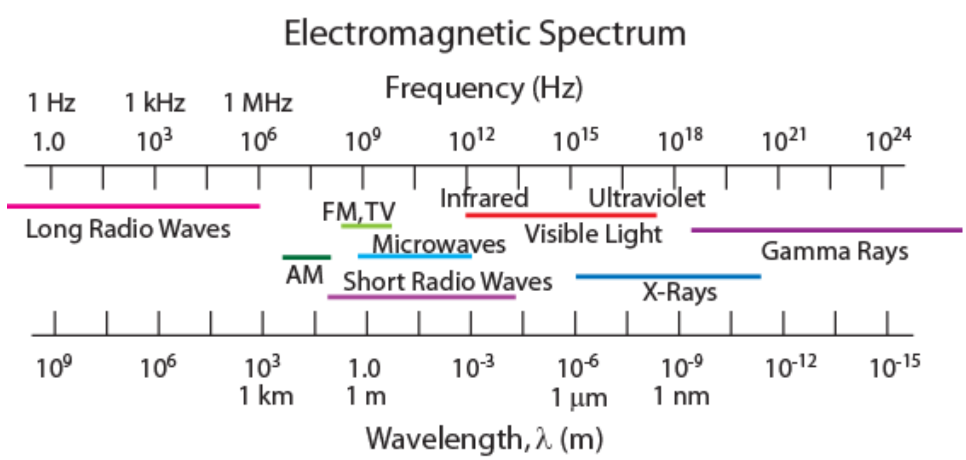
IMPORTANT POINTS FOR DISCUSSION

- Define light diffraction
- What are x-rays? who discover them, and when? Why are they called “x-rays”?
- How are x-rays produced?
- What are radiations K_α, K_β, L_α, L_β in x-rays? What is the in K_α Cu?
- What are some general applications of x-rays?
  - Why can x-rays be used in characterization of materials?
    - Describe the Von Loue’s experiment
    - What is the difference in patters between single crystals and polycrystalline materials? Explain that difference

IMPORTANT POINTS FOR DISCUSSION

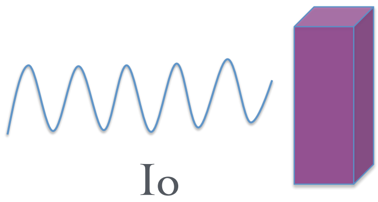
- Explain the W.L Bragg experiment
  - Why W.L Bragg and his son won the Nobel prize in 1915?
- Explain Bragg's Law
  - What is it used for?
- What are the components of an x-ray diffractometer?
- What is an x-ray pattern?
  - What kind of information can be obtained from an x-ray pattern?
- Solve examples on slides 29 - 31
- What are the applications of x-rays in characterization of materials?

INTERACTIONS OF WAVES WITH MATTER

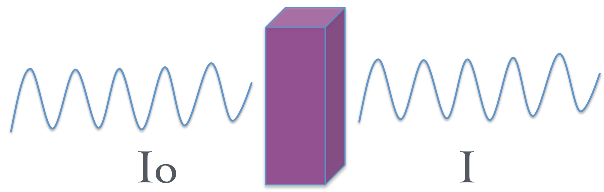


- **Absorption**
  - Fluorescence: Re-emission almost immediate after absorption
  - Phosforescence: slow re-emission
- **Diffraction**
  - **XRD**: X-Ray Diffraction
  - **DRX**: Difracción de Rayos X
- Reflection
- Refraction
- Scattering
  - SAXS: Small Angle X-ray Scattering

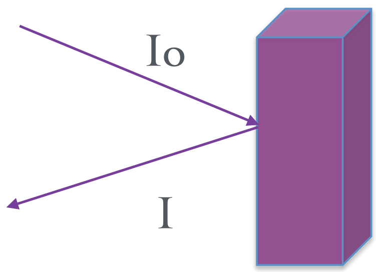
absorption



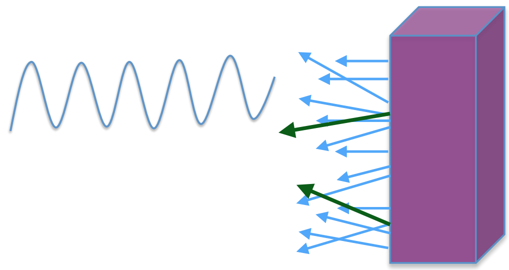
transmission



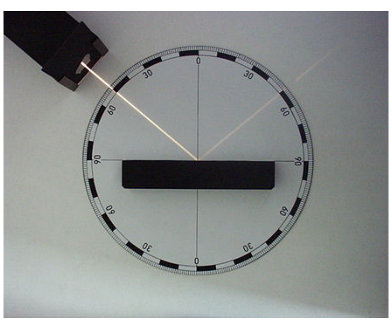
reflection



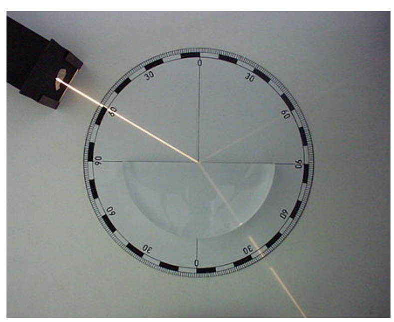
scattering



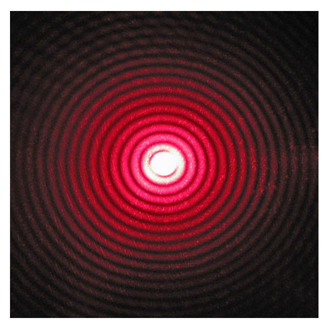
Images from wikipedia.org



reflection



refraction



diffraction

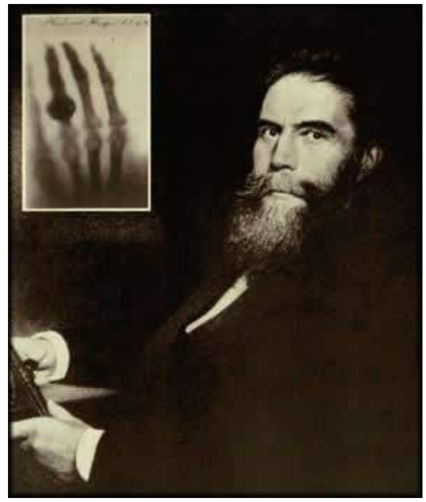
Diffraction is when a wave encounters an obstacle or a slit. It is defined as the bending of light around the corners of an obstacle or slit of size similar to the incident wavelength

X-RAY DISCOVERY

- Discovery in 1895 working with a cathode ray tube in Würzburg.

- "On a New Kind of Rays," submitted to the Proceedings of the
Würzburg Physico-Medical Society on December 1895.

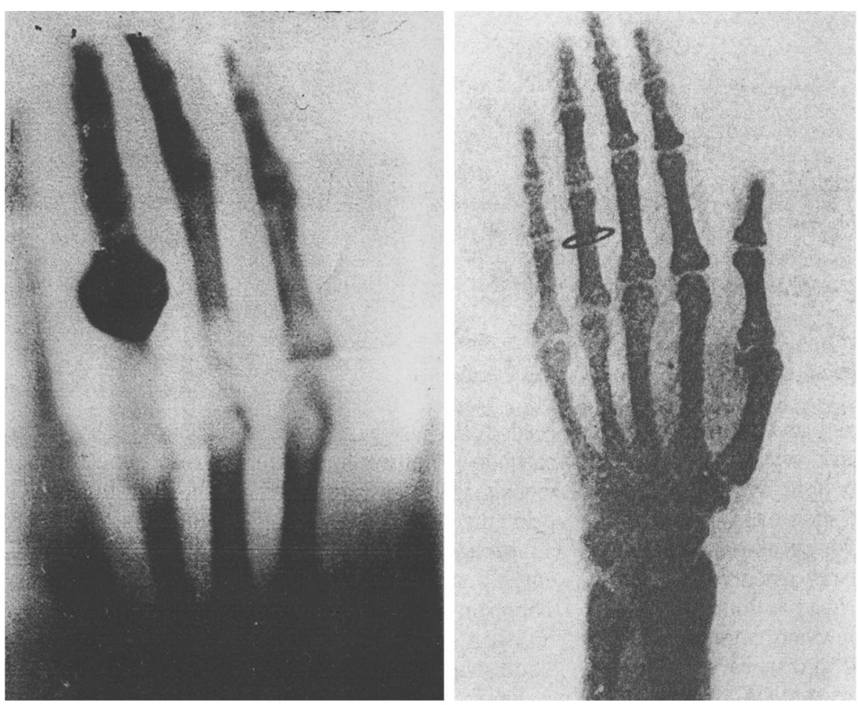
First Nobel Prize in Physics, 1901



Wilhelm Conrad Roentgen

http://www.leifiphysik.de/sites/default/files/medien/roentgen_anwendatomphy_ges.jpg

The race to produce bigger and better X-ray devices began with the publication of these X-ray images in 1895. (a) Image of `Hand Mit Ringen' taken 22 December 1895. Photograph courtesy of Otto Glasser, *"Wilhelm Conrad Rontgen und die Geschichte der Rontgenstrahlen"*, 1931, Springer-Verlag, Berlin. (b) Advertisement for images attainable using a Thomson Universal Tube produced by Edison Decorative and Miniature Lamp Department, Harrison, NJ, as published in Electrical Engineer four months after (a).



(*a*) (*b*)

JOURNAL OF SYNCHROTRON RADIATION

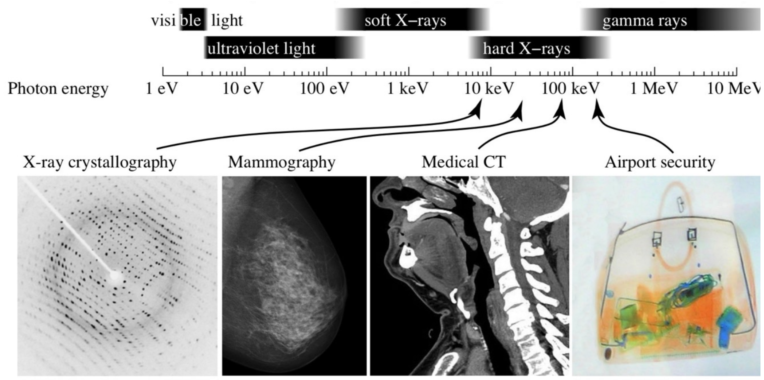
Cherezov *et al.*

Volume 9 | Part 6 | November 2002 | Pages 333–341 | 10.1107/S0909049502014528

X-RAYS

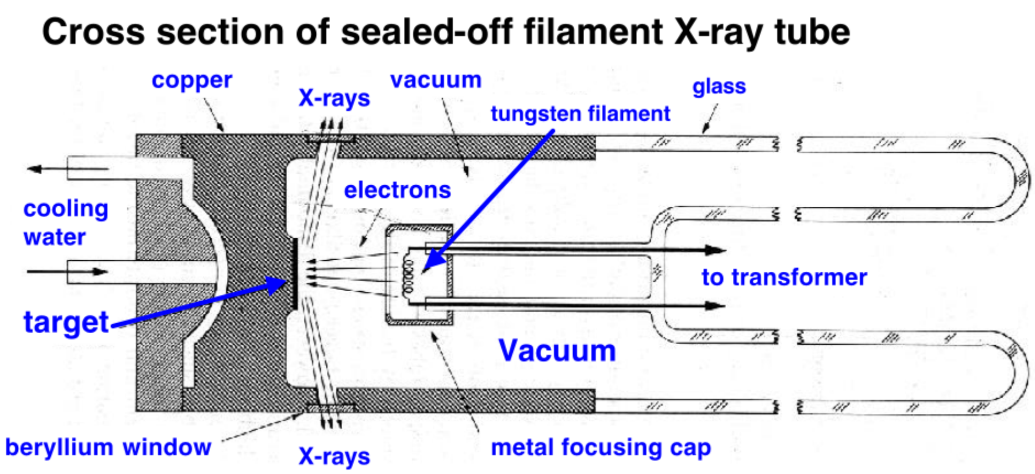
High Energy Electromagnetic Radiation

- Wavelengths 0.01 - 10 nm
- Frequencies: 30 PHz–30 Ehz (3×10^{16} to 3×10^{19} Hz)
- Energies: 100 eV–100 keV
- Ionizing radiation



"X-ray applications" by Ulflund - Licensed under CC BY-SA 3.0 via Commons – https://commons.wikimedia.org/wiki/File:X-ray_applications.svg#/media/File:X-ray_applications.svg

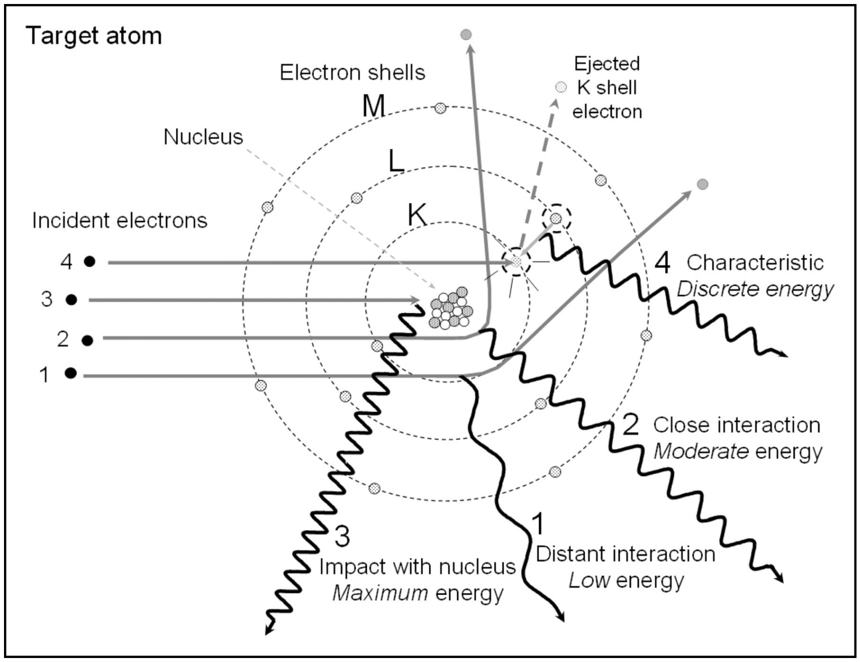
X-RAY PRODUCTION



X-rays are produced whenever high-speed electrons collide with a metal target. A source of electrons – hot W filament, a high accelerating voltage between the cathode (W) and the anode and a metal target, Cu, Al, Mo, Mg. The anode is a water-cooled block of Cu containing desired target metal.

X-RAY PRODUCTION

Element	λ k(α$_1$), Å
Fe	1.936
Ni	1.658
Cu	1.5406
Mo	0.7093
Ag	0.559
W	0.209
Au	0.180



Journal of NUCLEAR MEDICINE TECHNOLOGY

X-ray production by energy conversion. J. Anthony Seibert *J. Nucl. Med. Technol.* **2004**;32:139-147.

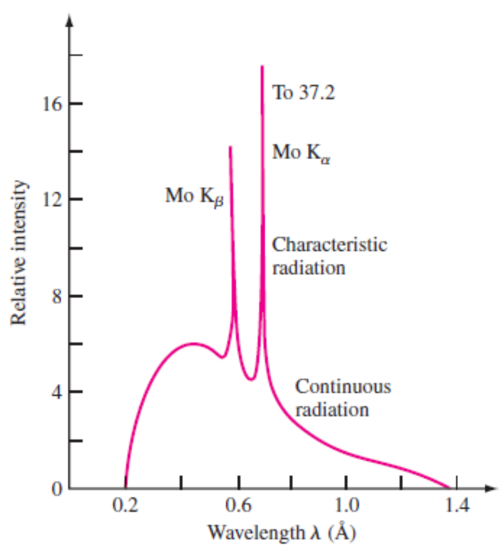


Figure 3.26
X-ray emission spectrum produced when molybdenum metal is used as the target metal in an x-ray tube operating at 35 kV.

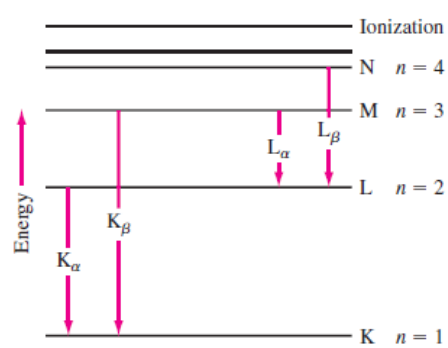


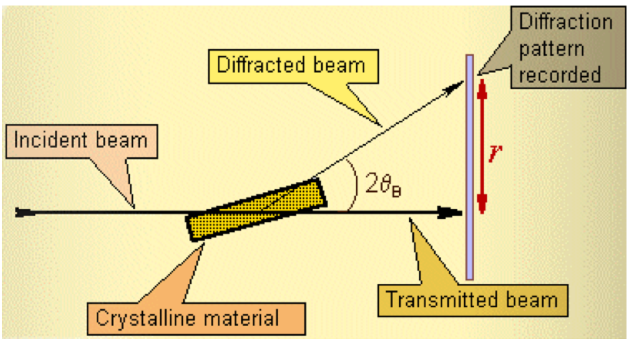
Figure 3.27
Energy levels of electrons in molybdenum showing the origin of K_α and K_β radiation.

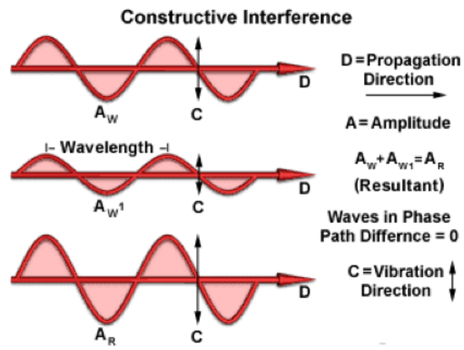
W. Smith, J. Hashemi "Foundations of Materials Science & Engineering", 4ta Edición, McGraw-Hill

DIFFRACTION

- ➤ Interference and trajectory deviation when wavelengths find an obstacle
  - ➤ Constrictive and destructive interference

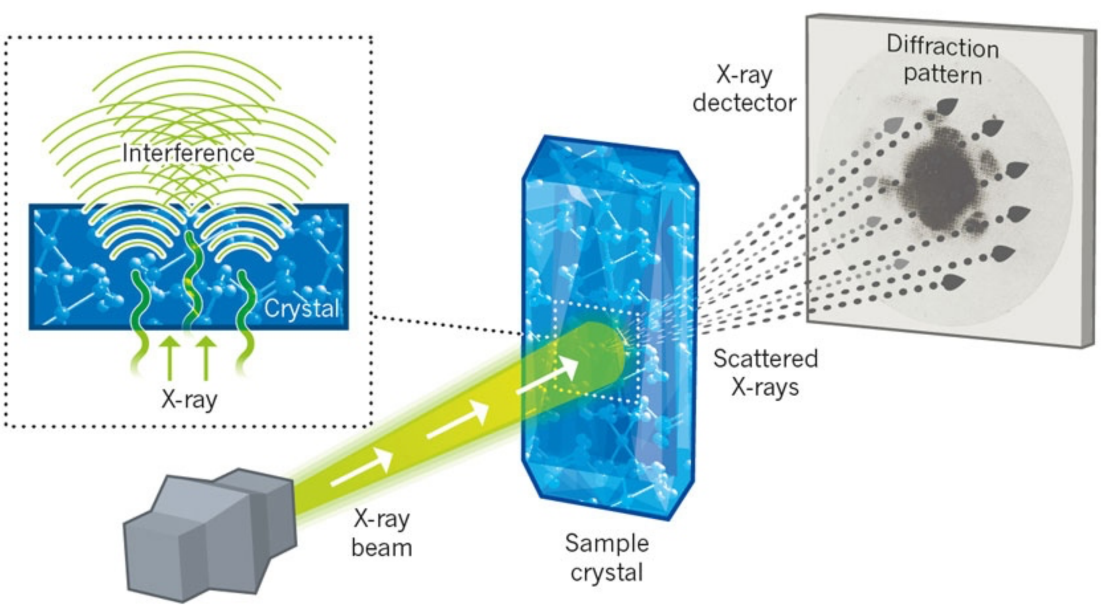
X-Ray radiation energy (0.1–102 keV) in the order of spacing between atoms in crystals and molecules (0.15–0.4 nm, 3–8 keV)



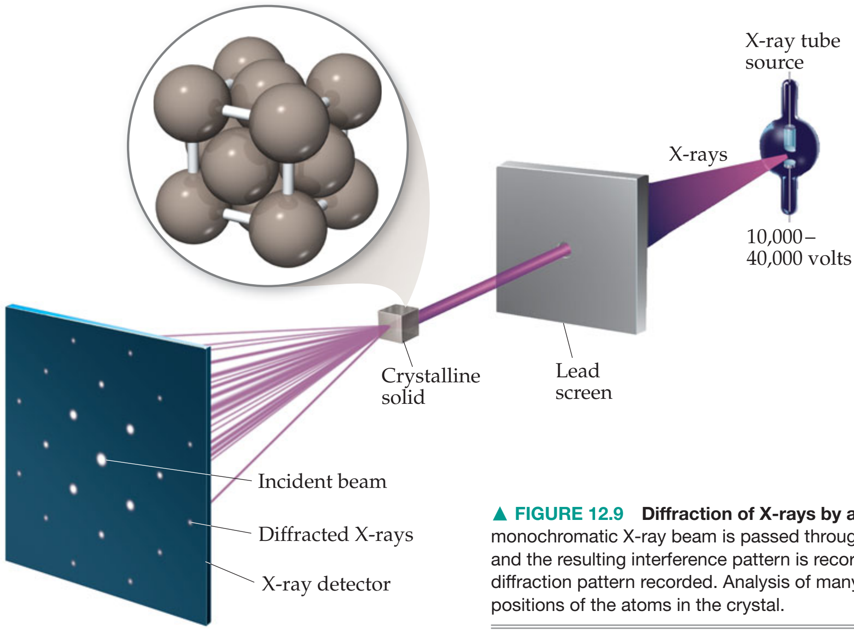


VON LAUE'S EXPERIMENT

- ➤ Max Von Laue considered that if x-rays were waves, then they should be diffracted by the atoms in a crystal



X-RAY DIFFRACTION



▲ **FIGURE 12.9 Diffraction of X-rays by a crystal.** In X-ray crystallography a monochromatic X-ray beam is passed through a crystal. The X-rays are diffracted, and the resulting interference pattern is recorded. The crystal is rotated and another diffraction pattern recorded. Analysis of many diffraction patterns gives the positions of the atoms in the crystal.

Fig. 12.9 Brown, et al Chemistry the Central Science, 12 ed

X-RAY DIFFRACTION

X-ray wavelengths are on the order of the atomic spacing in solids

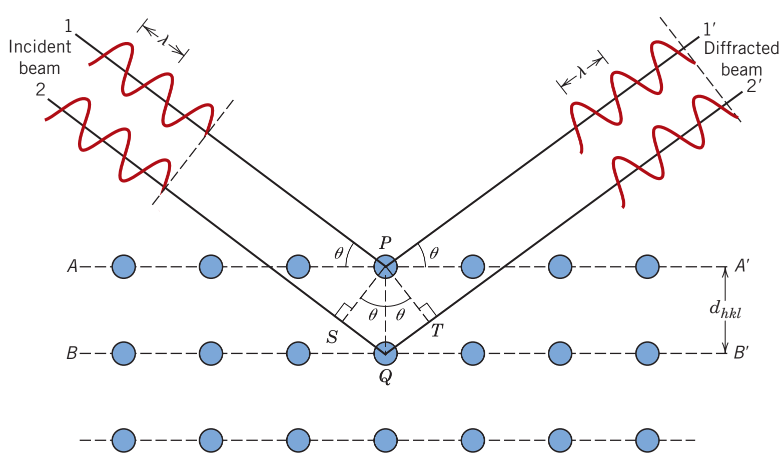
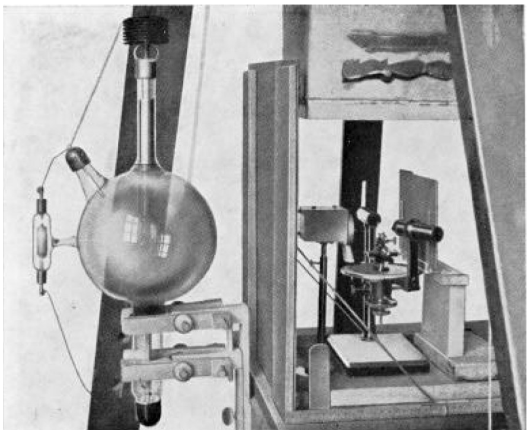
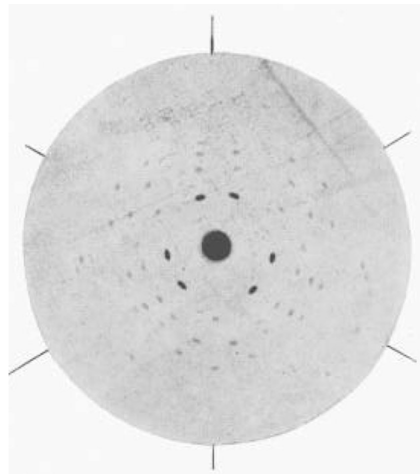


Fig. 3.20 Callister & Rethwisch, 8 ed

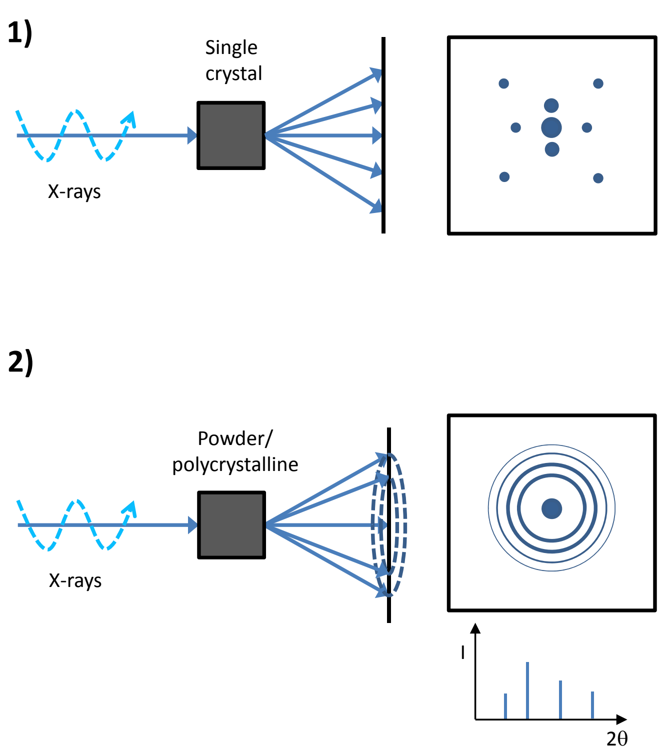
X-RAY DIFFRACTION BY CRYSTALS

➤ First patterns obtained by Walter Friedrich and Paul Knipping under von Laue orientation using copper sulphate crystals





http://www.iucr.org/publ/50yearsofxraydiffraction/full-text/laues-discovery



Single Crystals:

X-rays diffracted from a single crystal produce a series of spots in a sphere around the crystal

Each reflection peak uniquely resolved

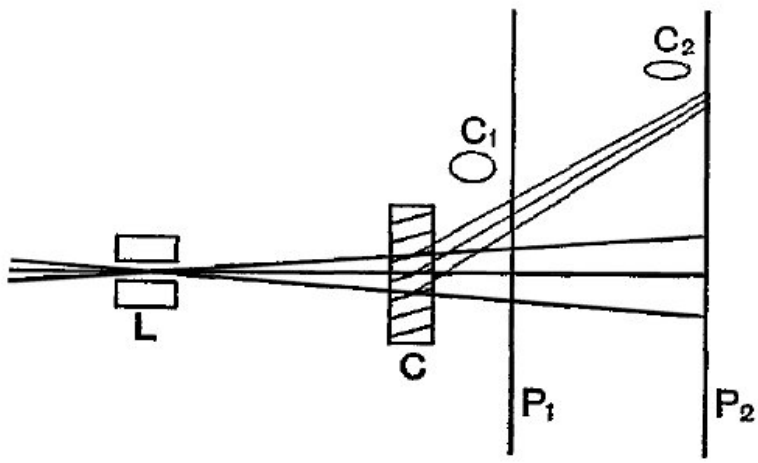
Polycrystals (Powders):

Continuos Debye rings

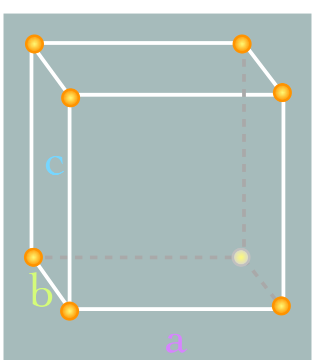
Linear diffraction patterns with discrete reflections obtained by scanning through arc that intersects each Deby cone at a single point

W.L. BRAGG: XRD REFLECTION BY CRYSTALLINE PLANES

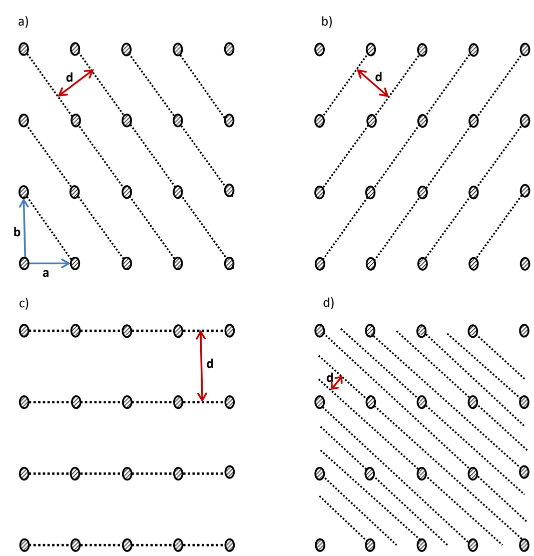
- Origen of points in a von Laue pattern due to reflection of X rays, that is why it is elliptical when photographic plaque is further from the crystal



KEY CRYSTALLOGRAPHIC CONCEPTS



d-spacing: The perpendicular separation between planes



$h = 1/a$
$k = 1/b$
$l = 1/c$

$h_x + k_y + l_z = 1$

W.L. BRAGG: X-RAY SPECTROMETER

- William Henry Bragg constructed the first X-ray spectrometer to measure intensity according with the angle
  - Different crystal phases are aligned to different angles

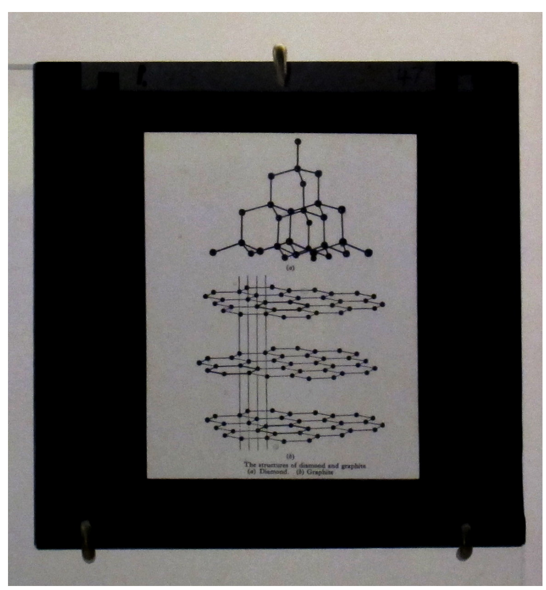
- W. Henry (father) and w. Lawrence (son) Bragg performed the first diffraction measurements and the determination of their crystalline structures

W. H. Bragg's X ray spectrometer, shown in the Royal Institution Museum in London.

X-RAY DIFFRACTION

Lawrence and Henry Bragg: Nobel Prize in Physics, 1915

W. Henry and W. Lawrence Bragg found diamond's crystalline structure by XRD in 1913, showing that carbon is tetravalent.

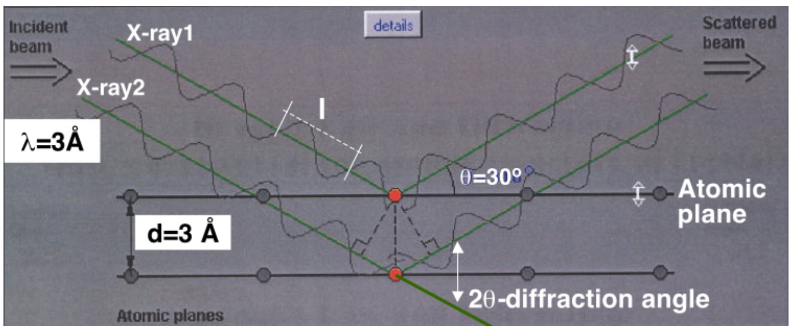


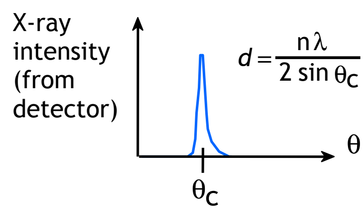
Slide showing graphite's and diamond's crystalline structures, shown in the Royal Institution Museum in London.

BRAGG'S LAW

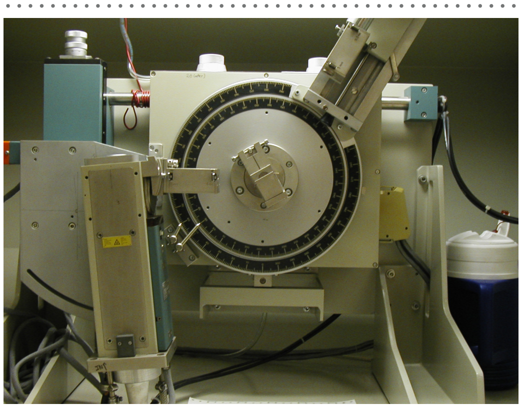
$$n\lambda = 2\, d_{hkl} \sin\theta$$

- n = reflection order, integer number
- λ = wavelength
- d = interplanar distance
- θ = incidence angle

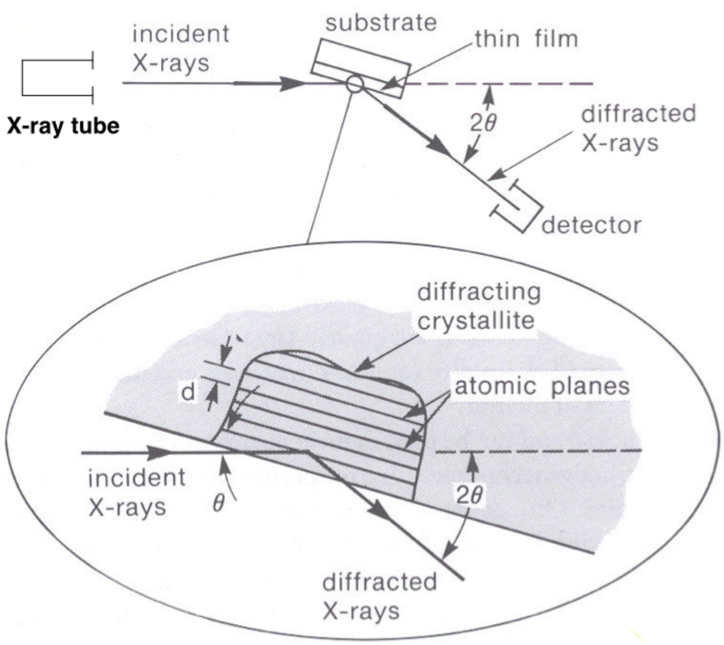




X-RAY DIFFRACTOMETER



X-RAY DIFFRACTOMETER



1) Production

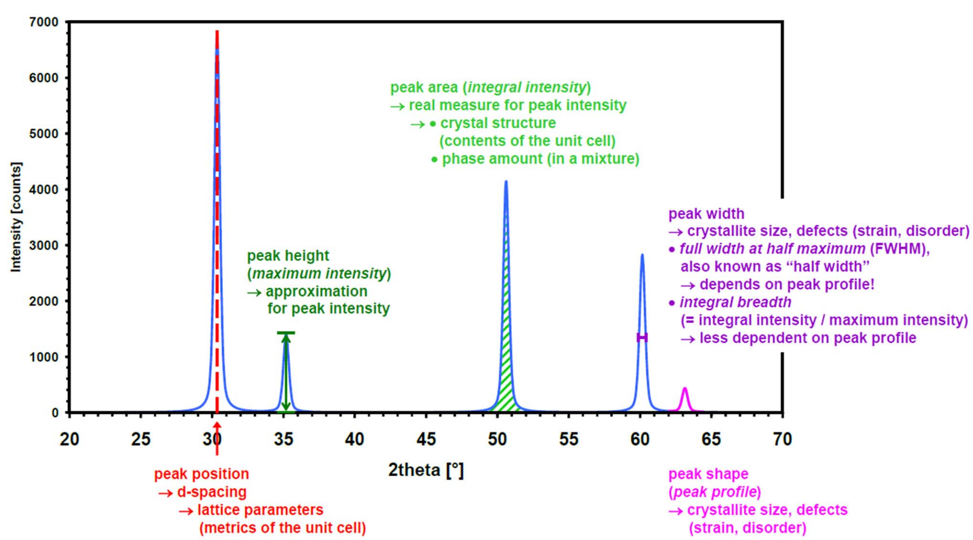
2) Diffraction

3) Detection

4) Interpretation

XRD PATTERN

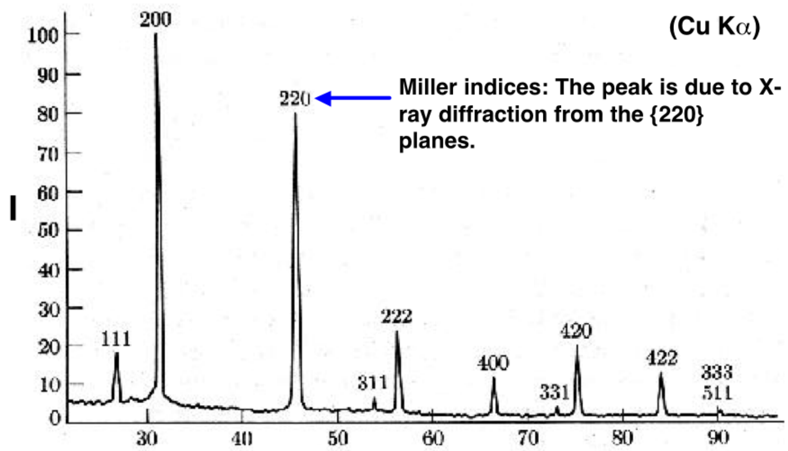
High intensity peaks result when Bragg's condition is satisfied by some set of crystallographic planes



Information content of an idealized diffraction pattern.

28

XRD Pattern of NaCl Powder



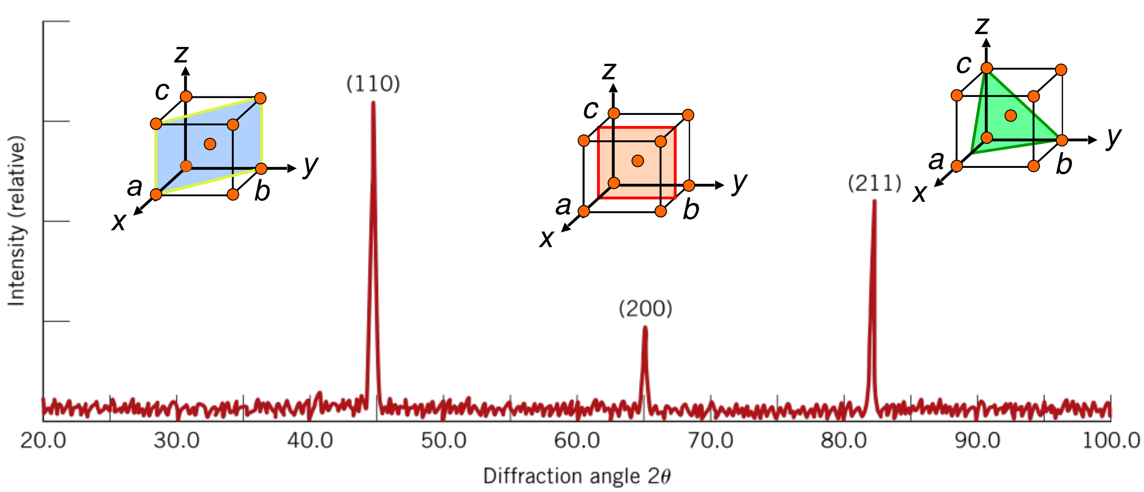
Diffraction angle 2θ (degrees)

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

- a = lattice parameters
- h, k, l = Miller indices

Not all planes are going to show in a XRD Pattern

Diffraction pattern for α-Fe



High intensity peaks result when Bragg's condition is satisfied by some set of crystallographic planes

EXAMPLE

A) Compute the inter planar spacing for iron BCC for the (220) set of planes
Lattice parameter a = 0.2866 nm

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

h = 2 k = 2 l = 0

$$d_{hkl} = \frac{0.2866 \text{ nm}}{\sqrt{(2)^2 + (2)^2 + (0)^2}} = \boxed{0.1313 \text{ nm}}$$

EXAMPLE

B) Compute the diffraction angle for iron BCC for the (220) set of planes
Radiation wavelength 0.1790 nm. Order of reflection = 1

$$n\lambda = 2\, d_{hkl} \sin\theta$$

$$\sin\theta = \frac{n\lambda}{2d_{hkl}}$$

$$\text{Sin}\,\theta = \frac{(1)\,(0.1790 \text{ nm})}{2\,(0.1313 \text{ nm})} = 0.884$$

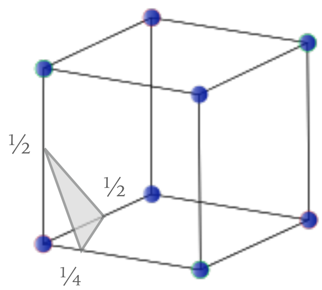
$$\theta = \sin^{-1}(0.884) = 62.13\,°$$

*** Diffraction angle is 2θ:**

$$2\theta = (2)\, 62.13\,° = \boxed{124.26°}$$

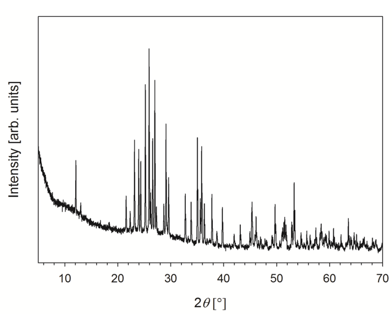
EXTRA EXAMPLE

Calculate the diffraction angle and the interlplanar spacing for the following plane in NaCl (lattice parameter, a = 5.5739 Å), if a fix wavelength (CuK$_\alpha$) of 1.54 Å was used and the order of reflection is 1.



WHAT CAN WE DETERMINE BY X-RAY DATA?

- Phase determination
  - Identification of crystalline phases



- Quantitative phase analysis
  - Relative composition of mixed phases
- Calculation of lattice parameters
  - Structural variations under different conditions
- Analysis of crystallite size and strain
  - Estimation of size of a crystallite domain and disorder
- Structure solution
  - Complete refinement of unknown phases