Basic X-ray experimental techniques - WAXS

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Suggested readings

[1] Attwood, D., & Sakdinawat, A. (2017). X-Rays and Extreme Ultraviolet Radiation: Principles and Applications (2nd ed.). Cambridge: Cambridge University Press.

[2] Willmott P. (2011), An introduction to synchrotron radiation: techniques and applications. John Wiley & Sons, Ltd.,

[3] Jens Als-Nielsen, Des McMorrow (2011) Elements of Modern X-ray Physics. John Wiley & Sons, Ltd.

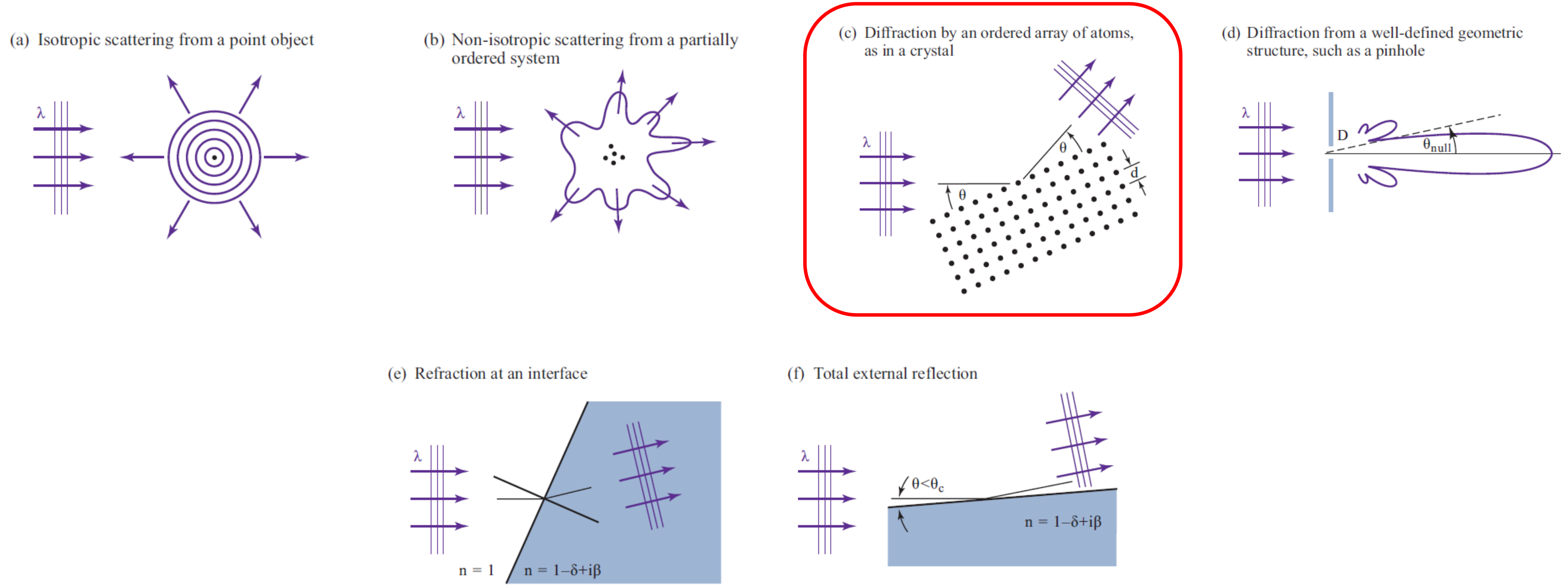
[4] D.B. Cullity, S.R. Stock (2001), Elements of X-Ray Diffraction (3rd ed.), Prentice Hal.

Terminology

Wide-**A**ngle **X**-ray **S**cattering (WAXS) is an X-ray **diffraction** technique based on analysis of the scattering of X-rays by sub-nanometer size structures.

WAXS is complementary to SAXS (**S**mall-**A**ngle **X**-ray **S**cattering), which is caused by the scattering of X-rays by structures with a characteristic size beyond a nanometer.

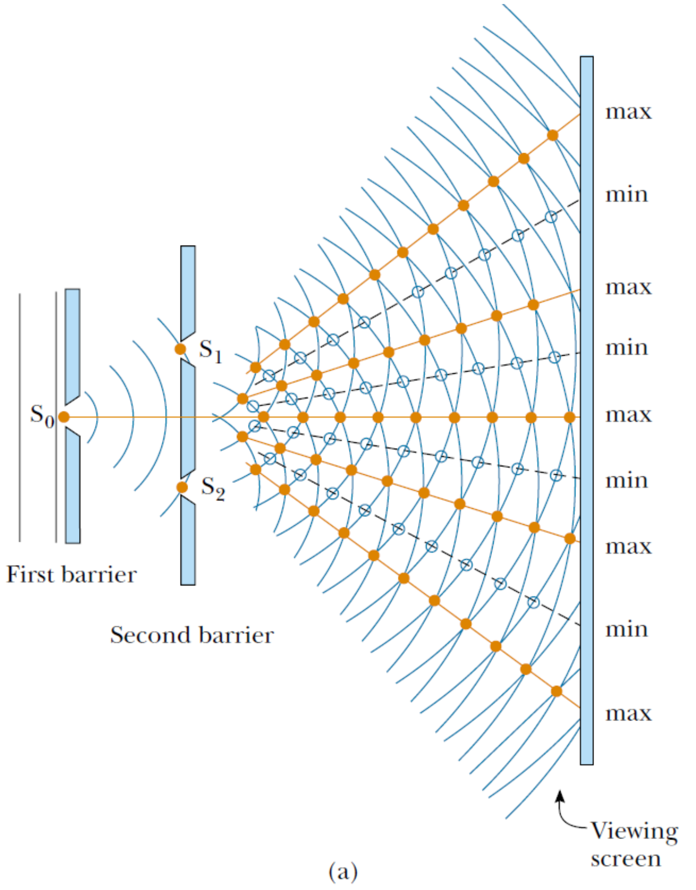
Scattering, diffraction and reflection of X-rays

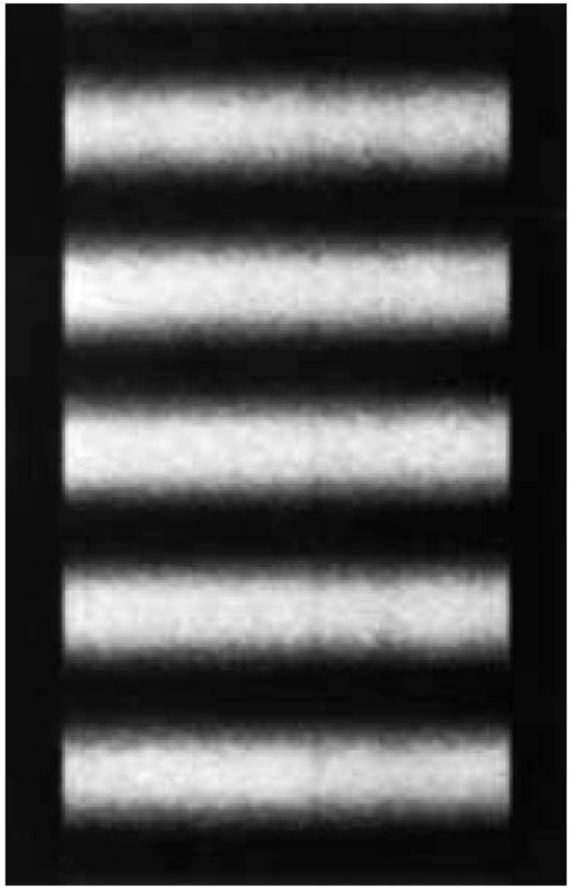


source: [2]

Double slit diffraction of visible light

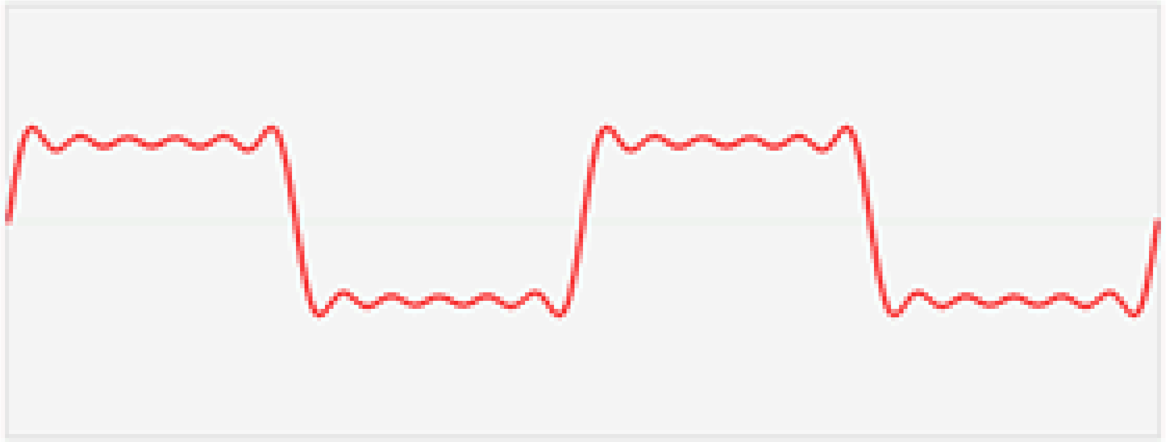
source: Halliday, Resnick & Walker – Fundamentals of Physics





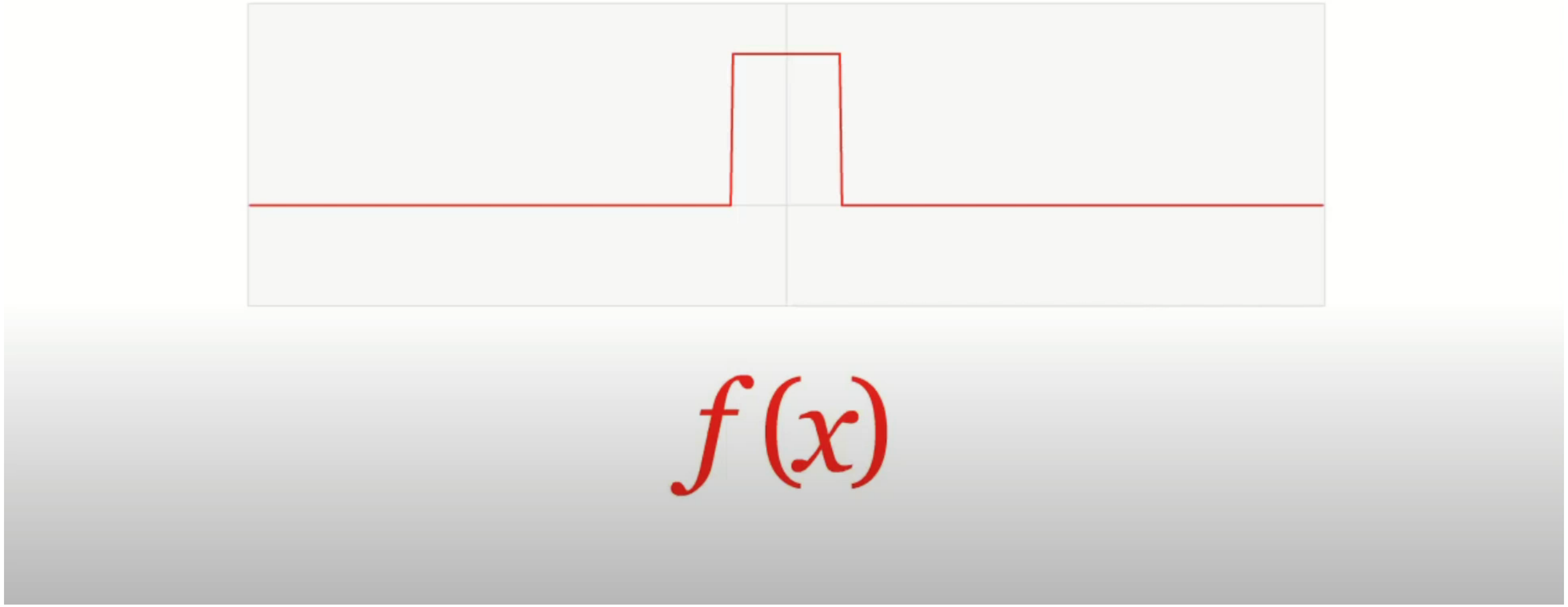
The diffraction pattern forms by adding waves and their constructive or destructive interference.

Fourier series



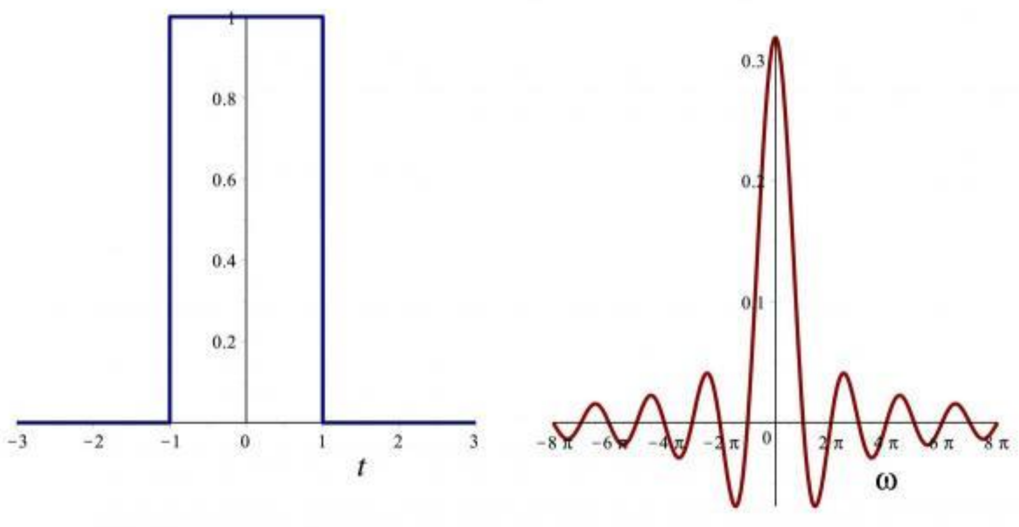
source: Wikipedia

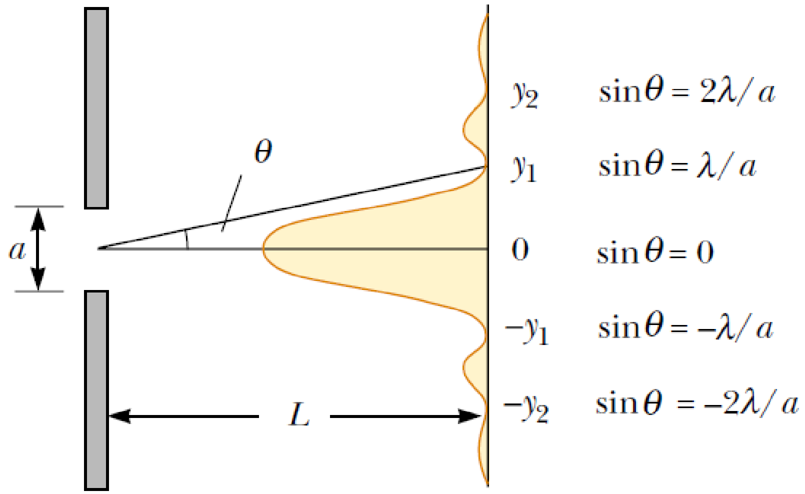
Fourier transform



source: YouTube

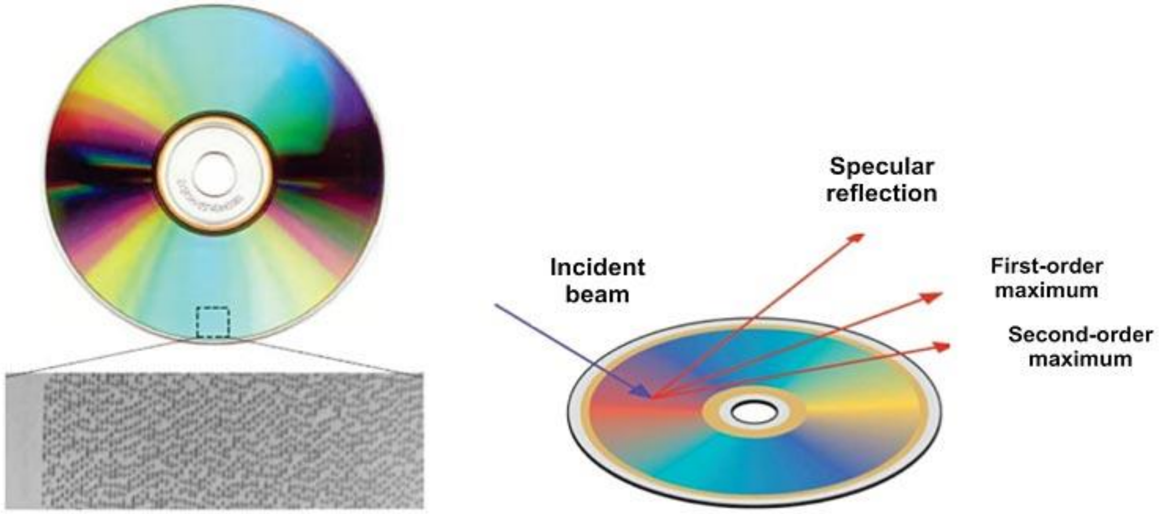
Fourier transform



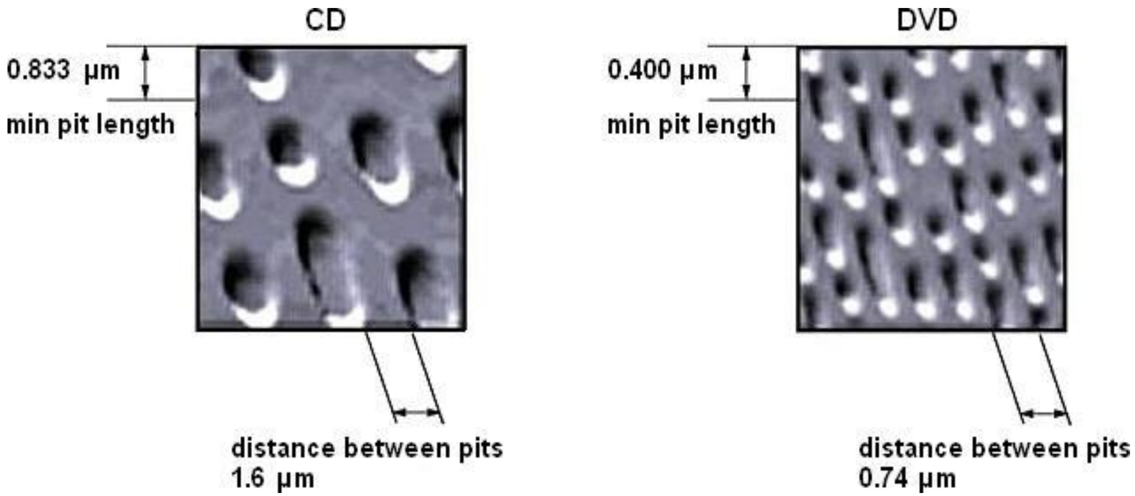


When light diffracts on an object, it performs a Fourier transform of the object.

Diffraction of visible light



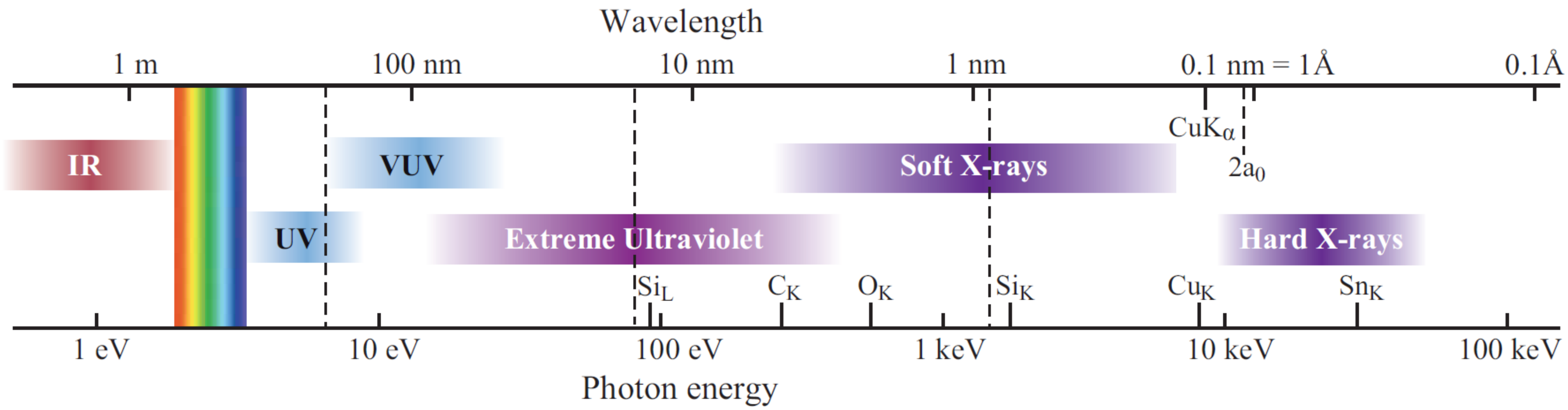
source: https://holmarc.com/differ_reflection_grating.php



source: https://onlinehelp.avs4you.com/AVS-Disc-Creator/Introduction/DiscStructure.aspx

A compact disc (modulation length about a micrometer) acts as a diffraction grating for a visible light (wavelength equal to fraction of a micrometer).

Electromagnetic spectrum



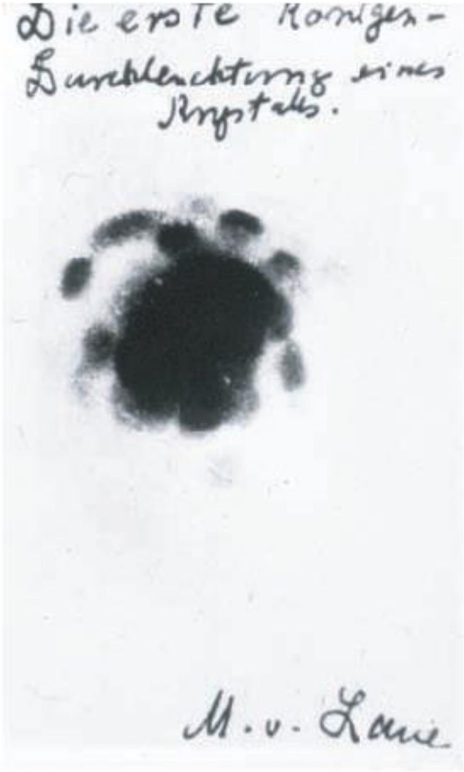
source: [1]

$\mathcal{E}$ – photon energy
h – Planck's constant
ω – wave frequency
c – speed of light
λ – wavelength

$$\mathcal{E} = \frac{h\omega}{2\pi} = \frac{hc}{\lambda}$$

$$\lambda[\text{Å}] = \frac{hc}{\mathcal{E}} = \frac{12.4}{\mathcal{E}[\text{keV}]}$$

Max von Laue

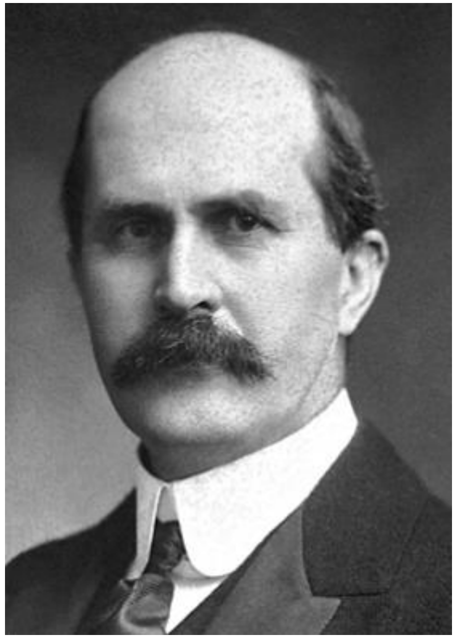


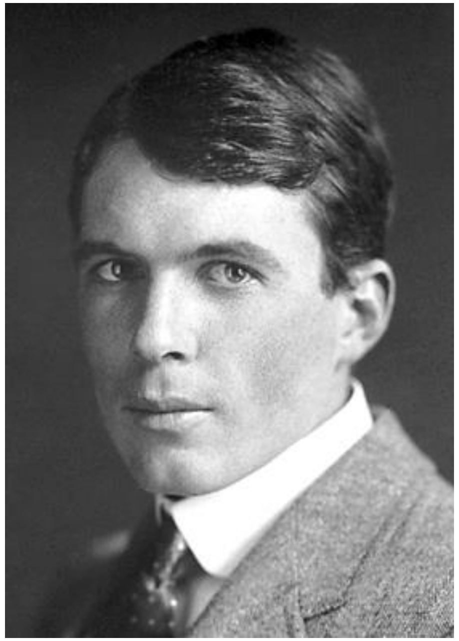
source: Wikipedia

source: [2]

The Nobel Prize in Physics 1914 was awarded to Max von Laue *"for his discovery of the diffraction of X-rays by crystals"*.

W.H. i W.L. Bragg



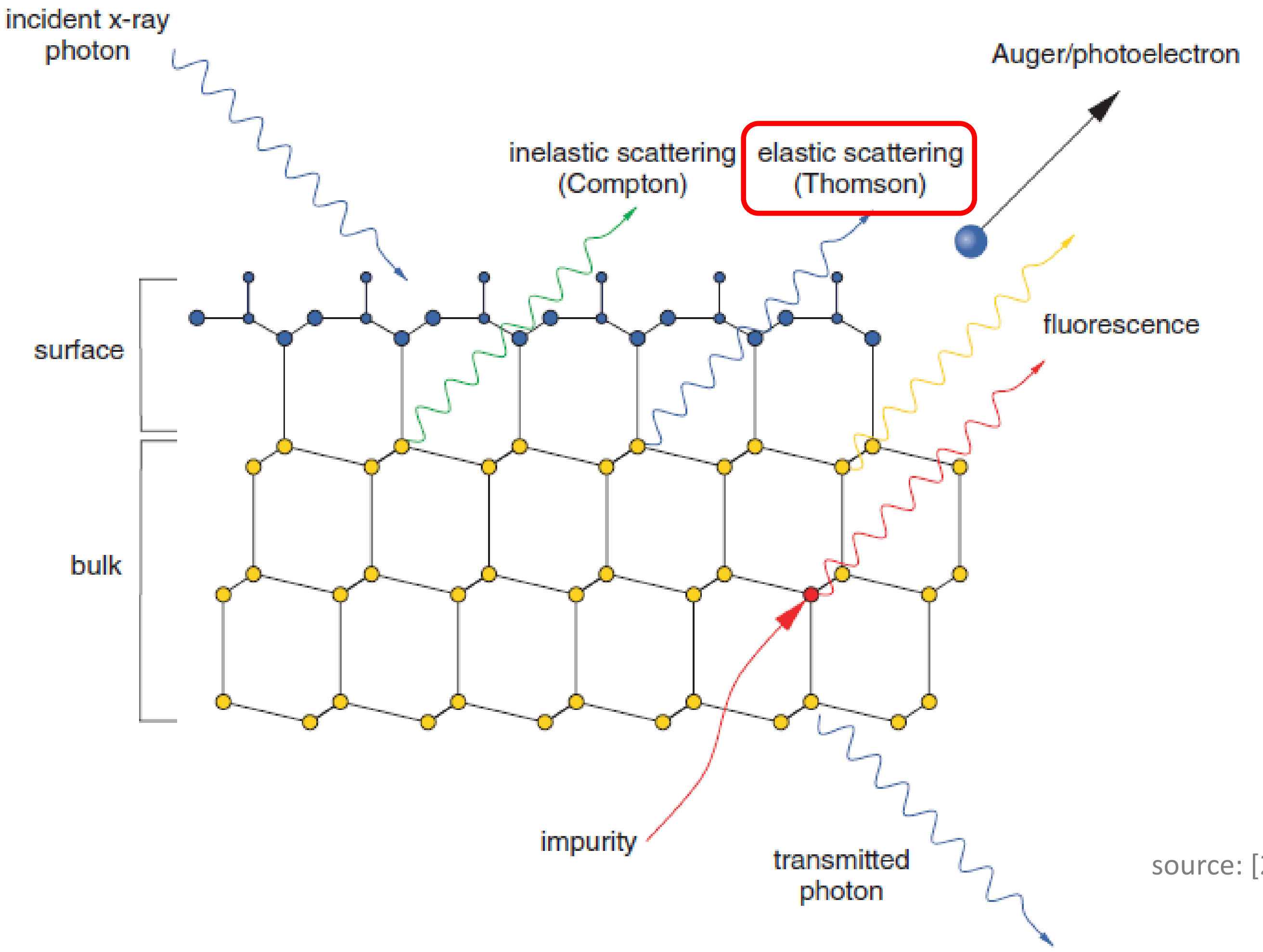


source: [2]

The Nobel Prize in Physics 1915 was awarded jointly to Sir William Henry Bragg and William Lawrence Bragg *"for their services in the analysis of crystal structure by means of X-rays"*

source: Wikipedia

X-ray interactions mechanisms

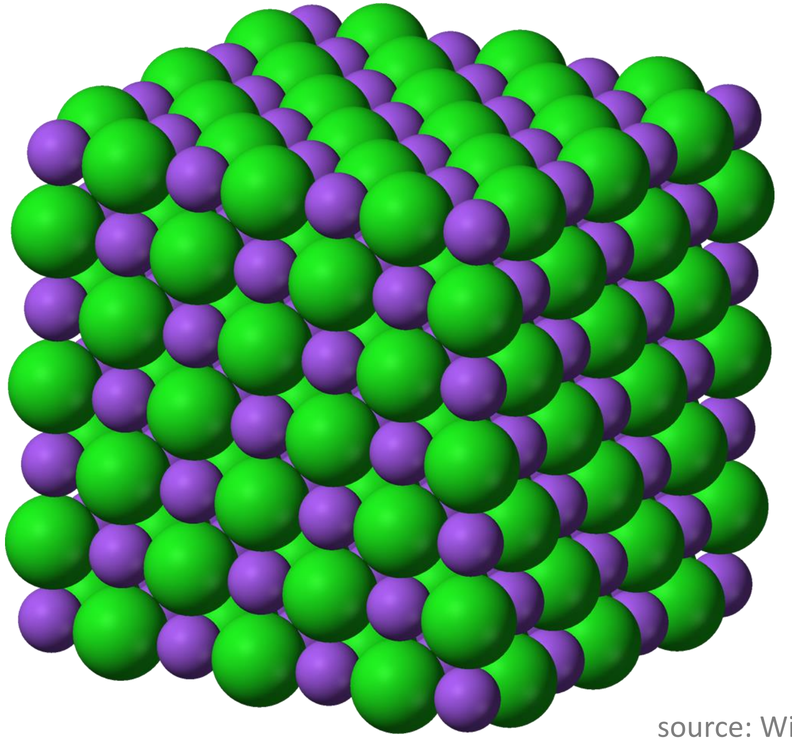


source: [2]

Crystalline structure

Rock salt crystal

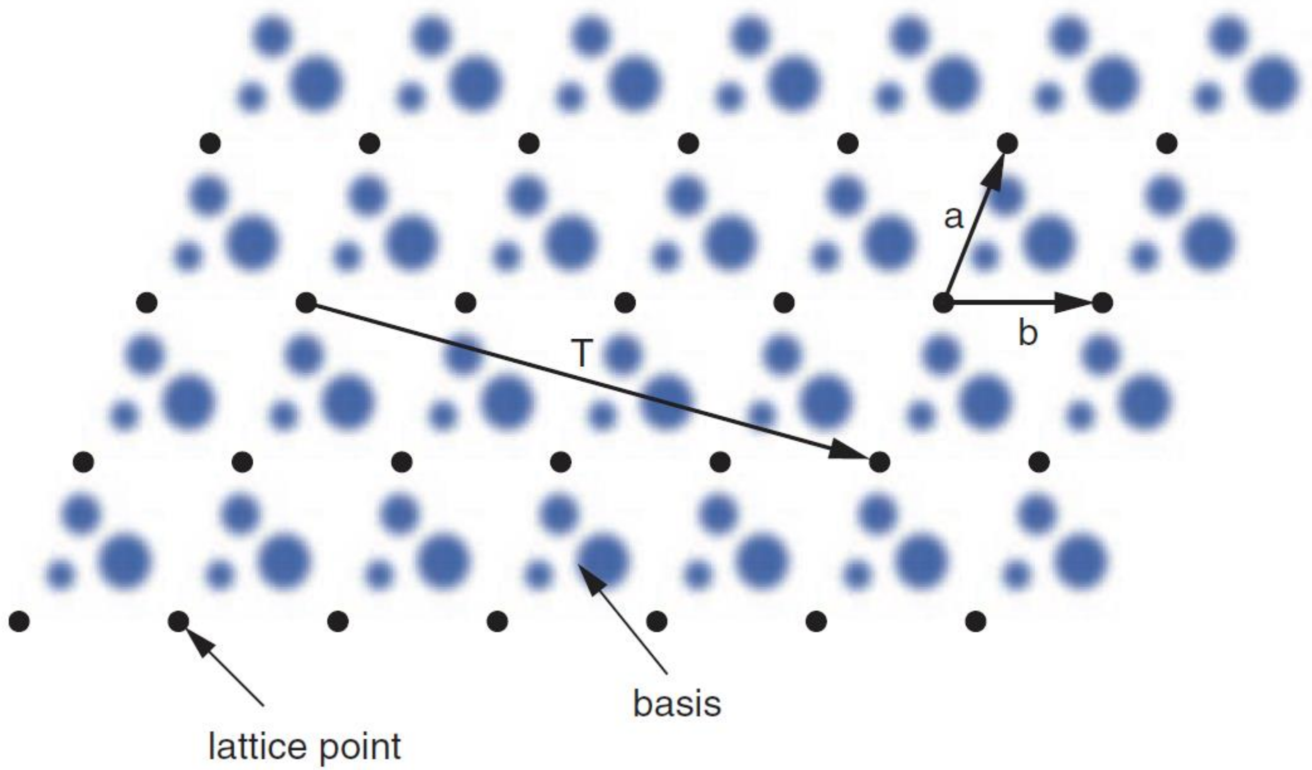
source: Wikipedia



source: Wikipedia

Translational symmetry of crystals

$$\mathbf{T} = u_1\mathbf{a} + u_2\mathbf{b} + u_3\mathbf{c}$$



source: [2]

Bravais lattices

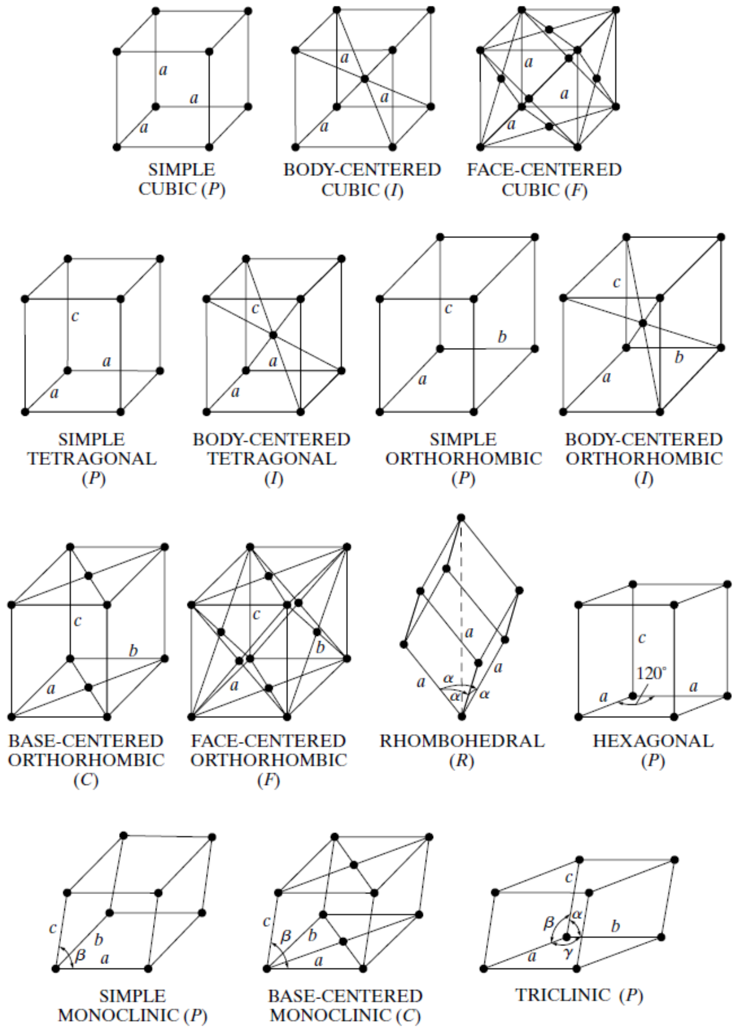
TABLE 2 CRYSTAL SYSTEMS AND BRAVAIS LATTICES

(The symbol ≠ means that equity is not required by symmetry. Accidental equality may occur, as shown by an example in Sec. 4.)

System	Axial lengths and angles	Bravais lattice	Lattice symbol
Cubic	Three equal axes at right angles $a = b = c,\quad \alpha = \beta = \gamma = 90°$	Simple Body-centered Face-centered	P I F
Tetragonal	Three axes at right angles, two equal $a = b \neq c,\quad \alpha = \beta = \gamma = 90°$	Simple Body-centered	P I
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c,\quad \alpha = \beta = \gamma = 90°$	Simple Body-centered Base-centered Face-centered	P I C F
Rhombohedral*	Three equal axes, equally inclined $a = b = c,\quad \alpha = \beta = \gamma \neq 90°$	Simple	R
Hexagonal	Two equal coplanar axes at 120º, third axis at right angles $a = b \neq c,\quad \alpha = \beta = 90° \quad (\gamma = 120°)$	Simple	P
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c,\quad \alpha = \gamma = 90° \neq \beta$	Simple Base-centered	P C
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c,\quad (\alpha \neq \beta \neq \gamma \neq 90°)$	Simple	P

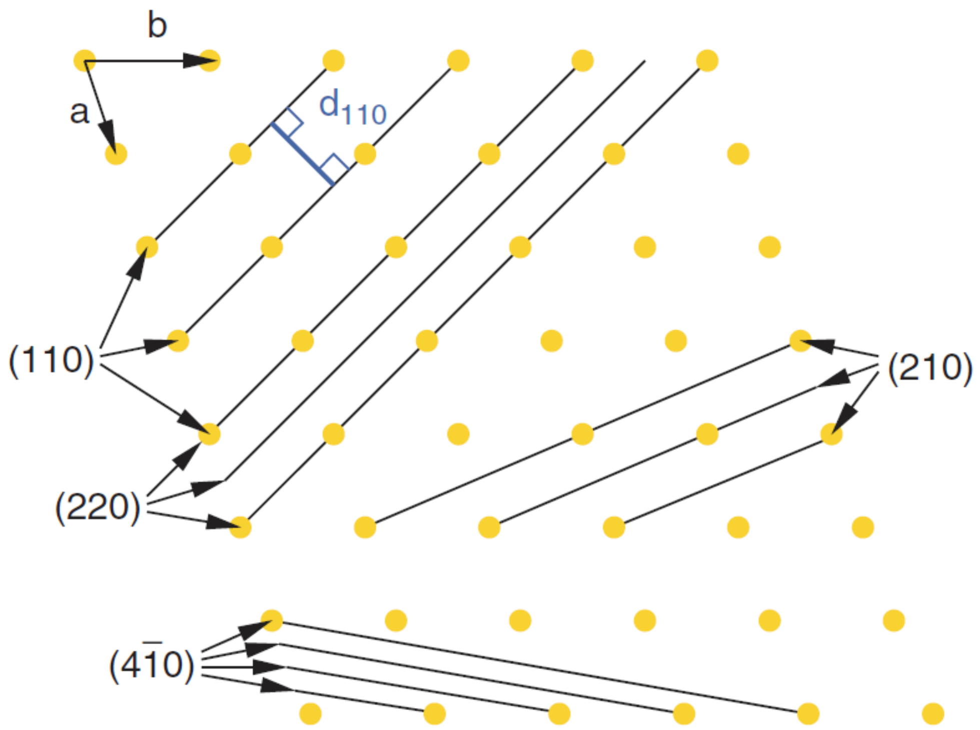
* Also called trigonal.

source: [4]



source: [4]

Atomic planes in crystals



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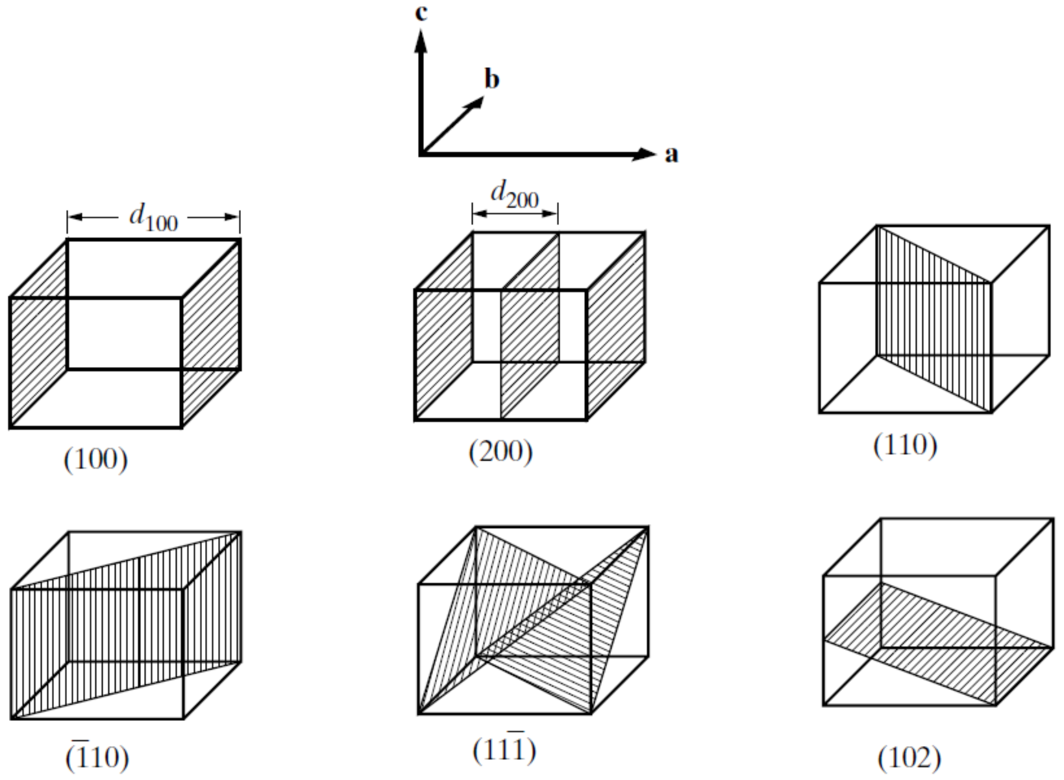
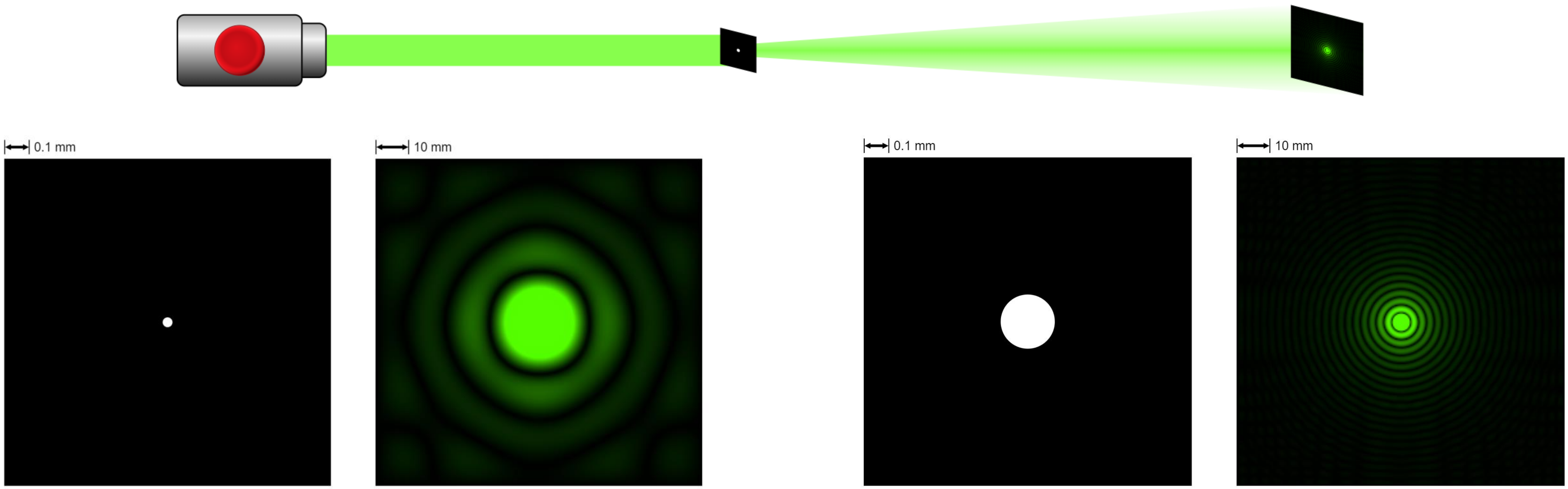
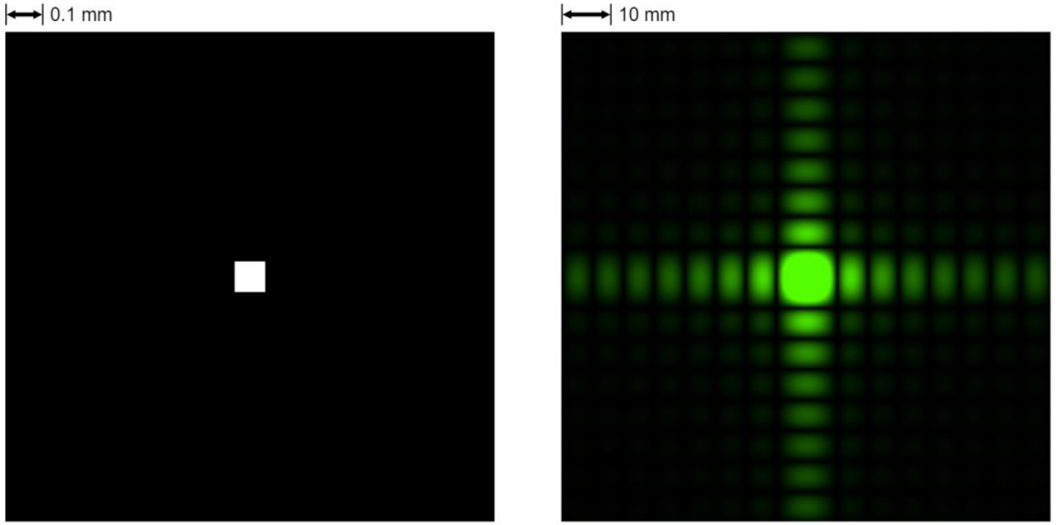


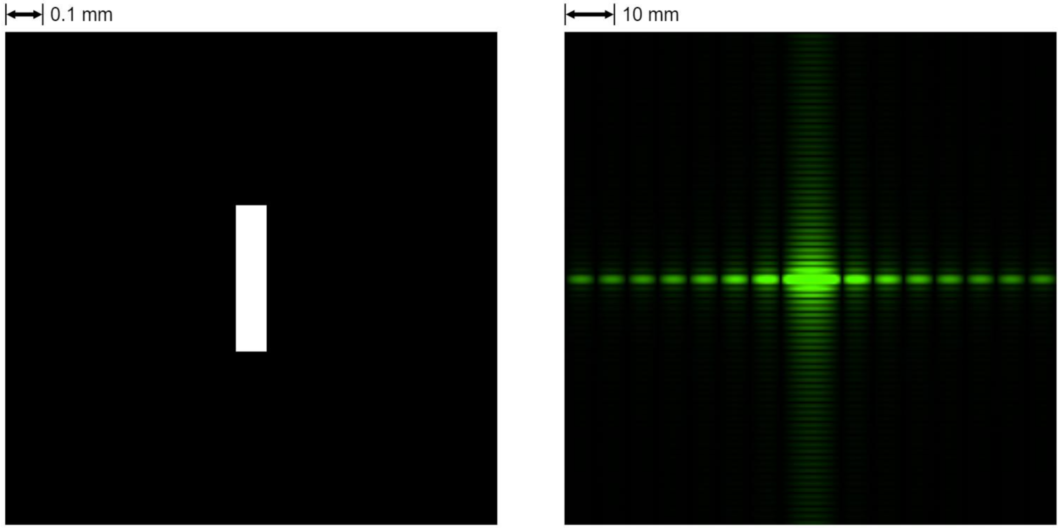
source: [4]

Diffraction of visible light

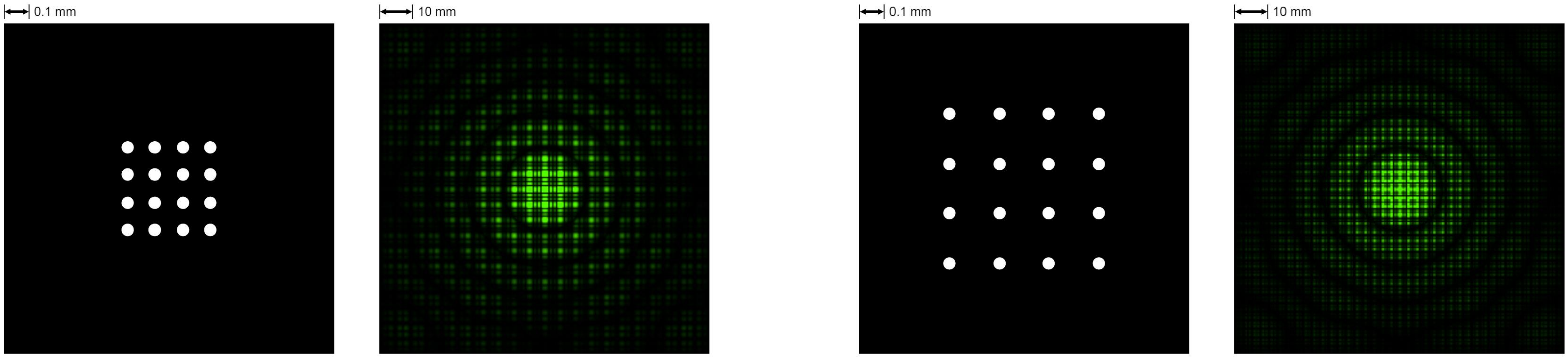


Diffraction of visible light



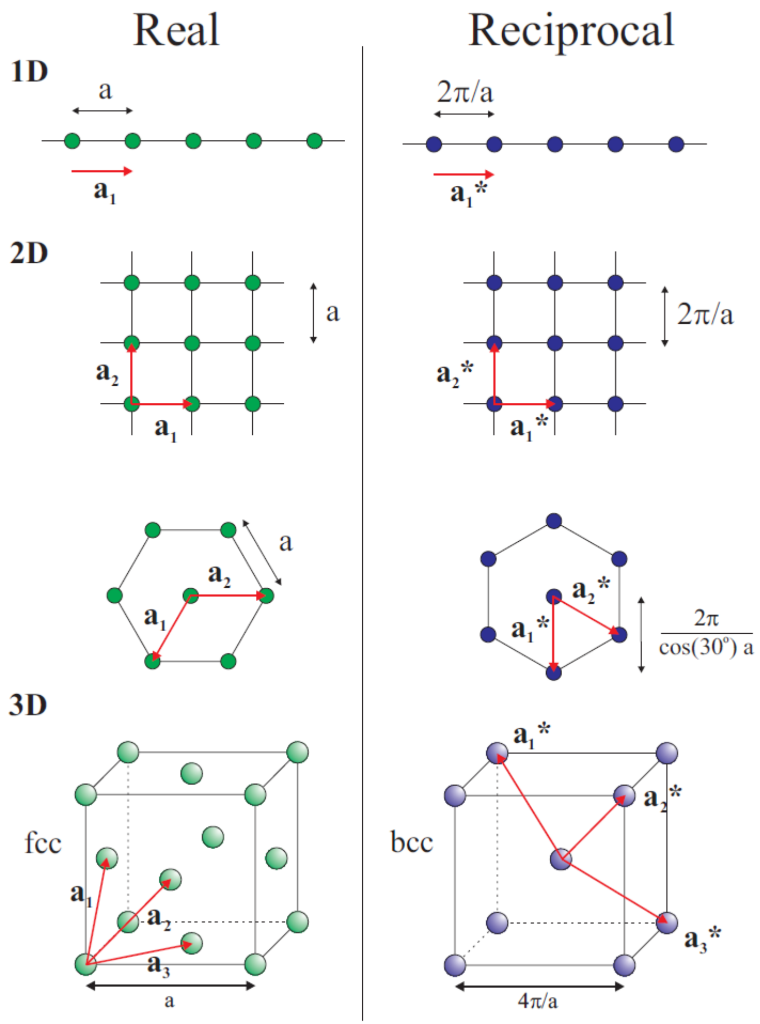


Diffraction of visible light



- The symmetry of the diffraction pattern is related to the symmetry of the scattering object.
- The characteristic distance in the diffraction pattern is **inversely proportional** to the distance in the real space.
- The diffraction can be viewed as a projection of the **reciprocal space.**

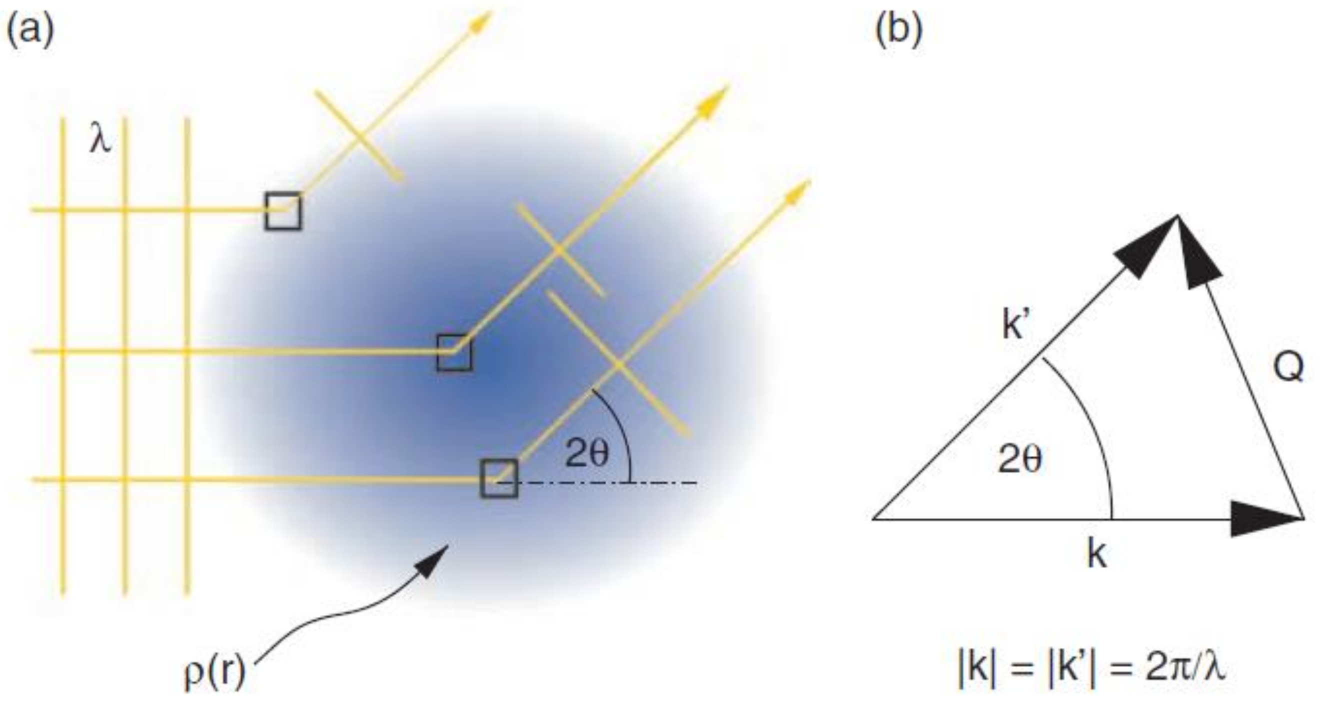
Reciprocal lattice



source: [3]

- **The reciprocal lattice is the Fourier transform of the Bravais lattice**.
- A **set of planes** in the real lattice corresponds to a **point** in the reciprocal lattice.
- A magnitude of a vector in the reciprocal lattice is **inversely proportional** to a magnitude of a corresponding vector in the real lattice ($2\pi/a$).

X-ray scattering by a cloud of free electrons



source: [2]

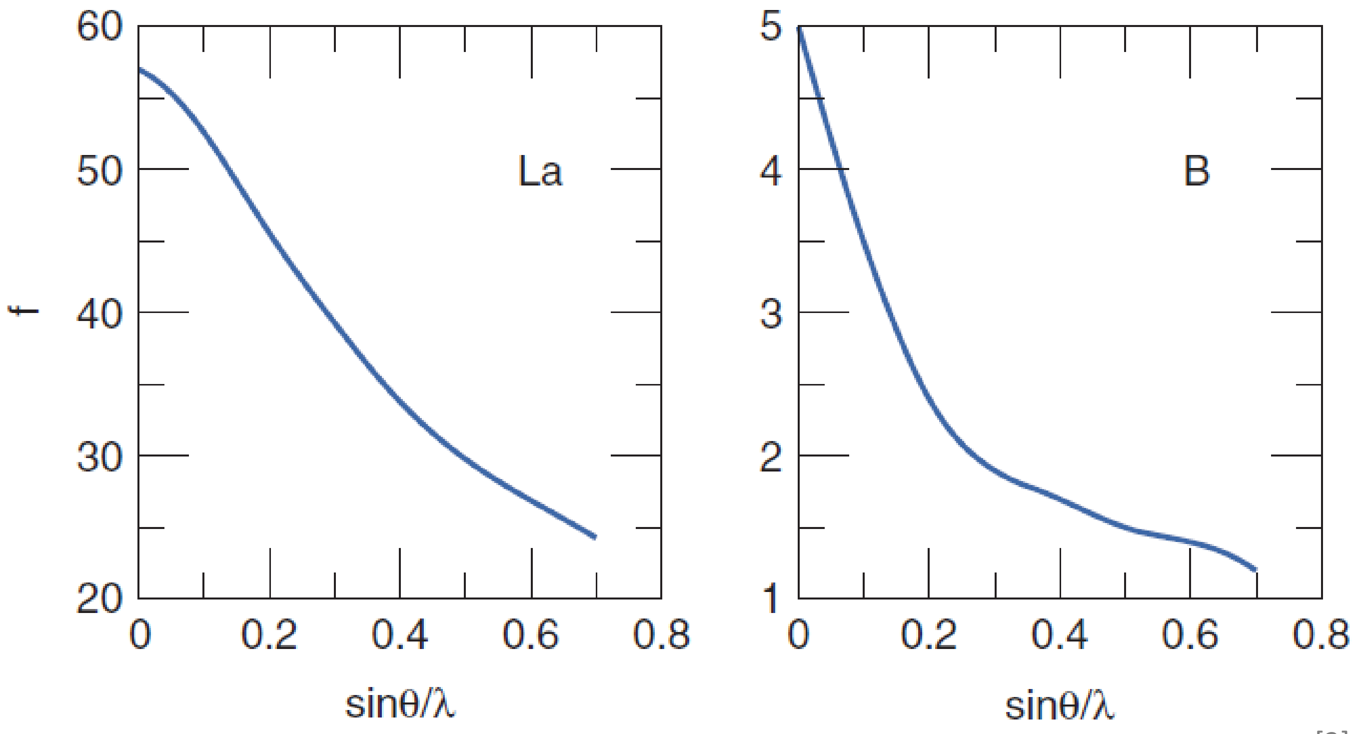
$$\mathbf{Q} = \mathbf{k} - \mathbf{k}'$$

$$\boxed{Q = \frac{4\pi}{\lambda}\sin\theta}$$

$\mathbf{k}$ – incident wave wave vector
$\mathbf{k}'$ – scattered wave wave vector
$\mathbf{Q}$ – scattering vector

Atomic scattering factor

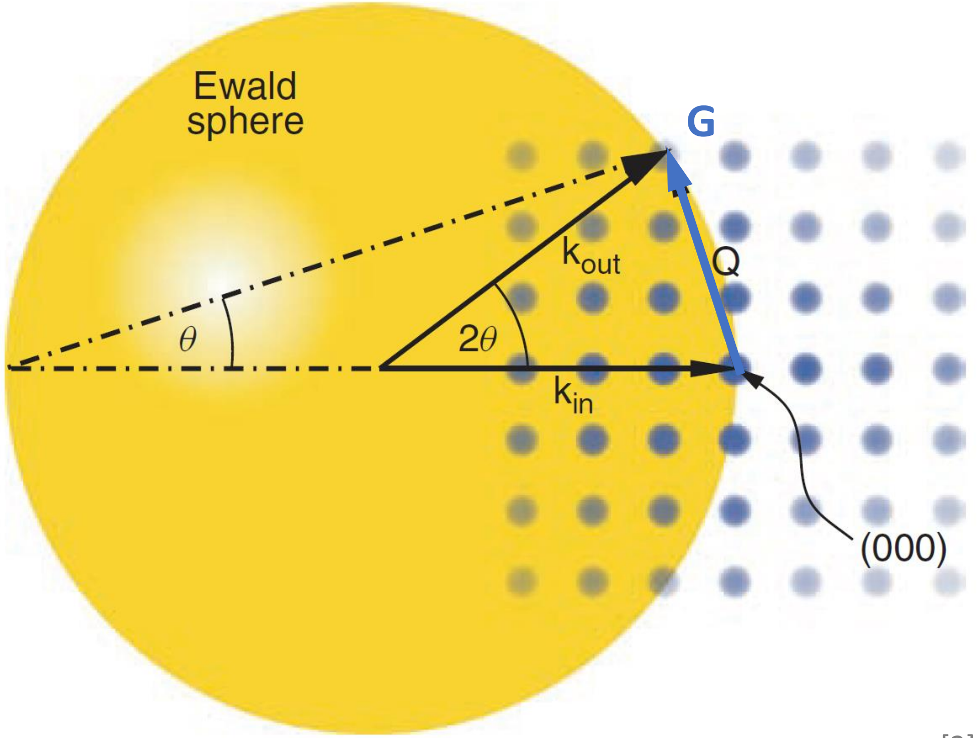
$$f\,(\mathbf{Q}) = \int \rho(\mathbf{r})\, e^{i\,\mathbf{Q}\cdot\mathbf{r}} d\mathbf{r} = \begin{cases} Z & \text{for } \mathbf{Q} \to 0 \\ 0 & \text{for } \mathbf{Q} \to \infty \end{cases}$$



source: [2]

Atomic scattering (form) factor involves a Fourier transform of a spatial charge distribution from real space to Q-space.

The Ewald construction



source: [2]

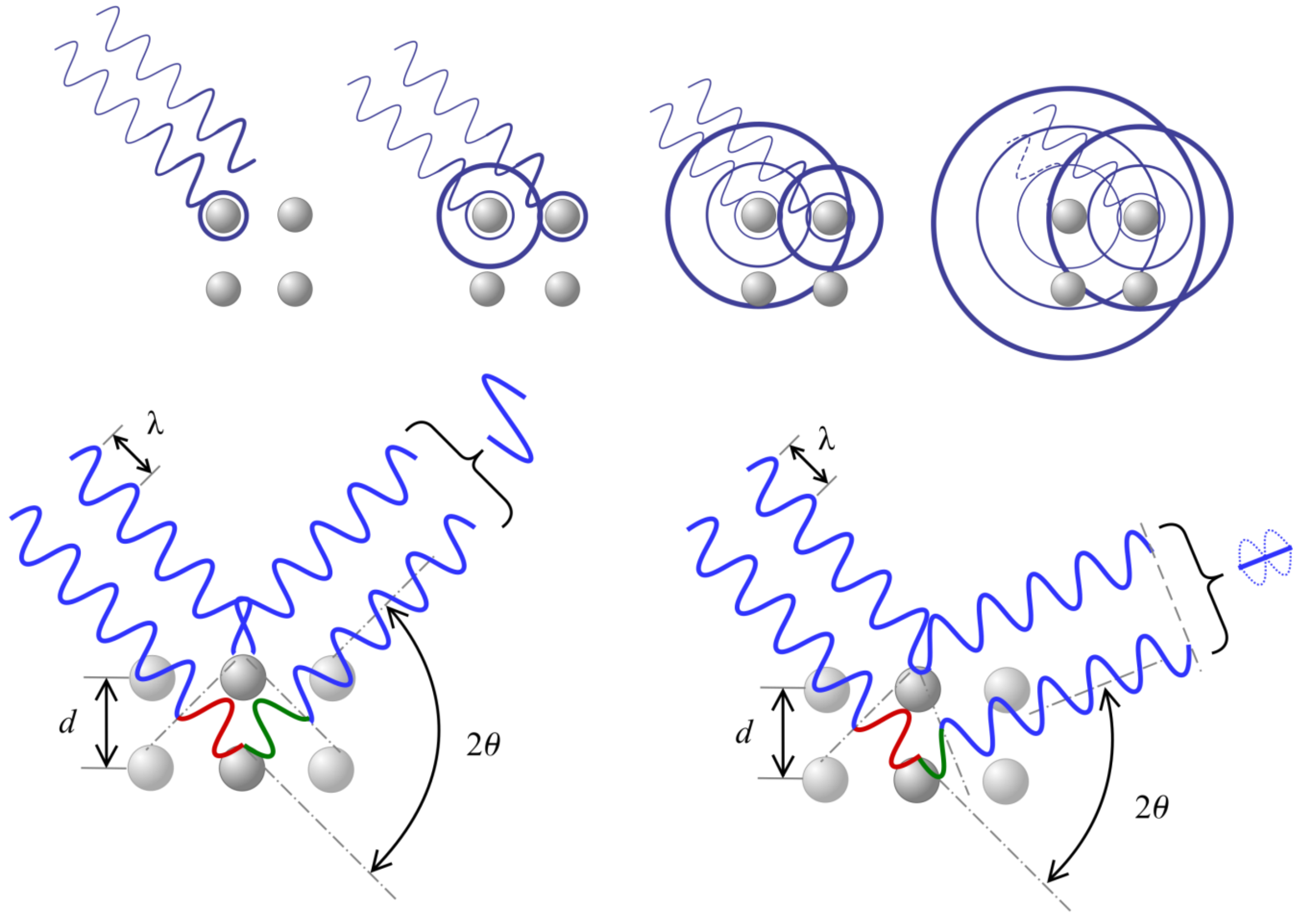
$$|k_{in}| = |k_{out}| = |k| = \frac{2\pi}{\lambda}$$

$$|Q| = 2|k| \sin\theta = \frac{4\pi}{\lambda} \sin\theta$$

$$|G| = \frac{2\pi}{d_{hkl}}$$

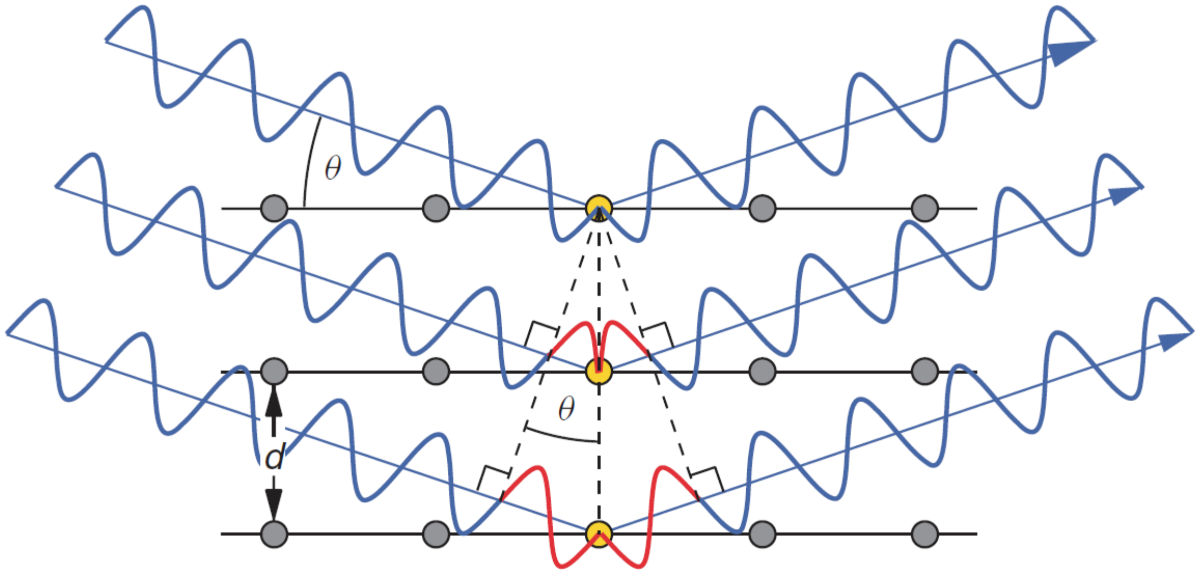
Diffraction occurs when the scattering vector **Q** is equal to the reciprocal lattice vector **G**.

Bragg’s law



source: Wikipedia

Bragg's law



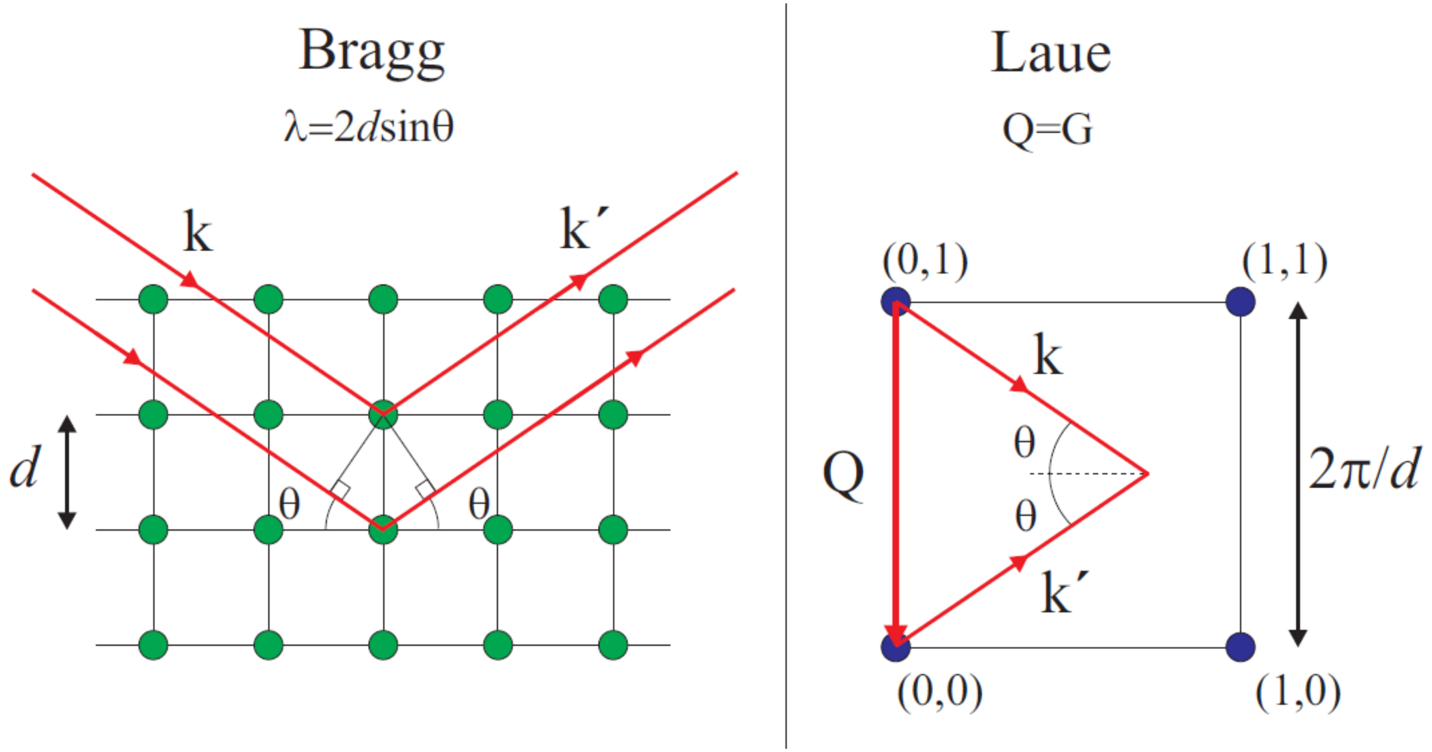
source: [2]

$$\boxed{m\lambda = 2d_{hkl}\sin\theta}$$

$$m = 1, 2, 3, \ldots$$

Bragg condition for a given set of atomic planes with spacing d_{hkl} is met when angle θ corresponds to the maximum of the constructive interference of the scattered waves.

Equivalence of real space and reciprocal space view on diffraction

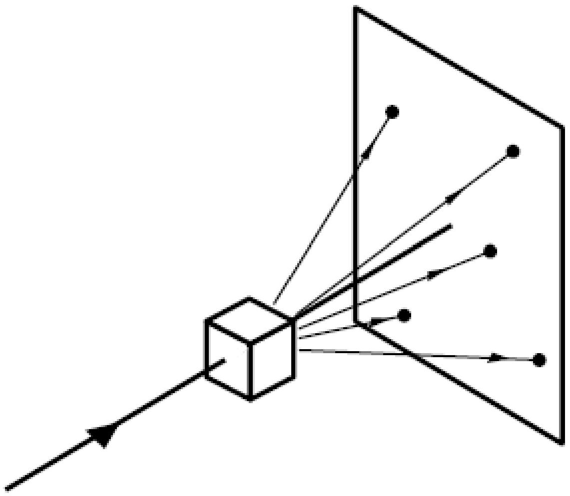


Real space (Bragg) view:
diffraction occurs when Bragg condition is satisfied.

Reciprocal space (Laue) view:
diffraction occurs when the scattering vector is equal to the reciprocal lattice vector.

source: [3]

Diffraction from monocrystals – Laue method



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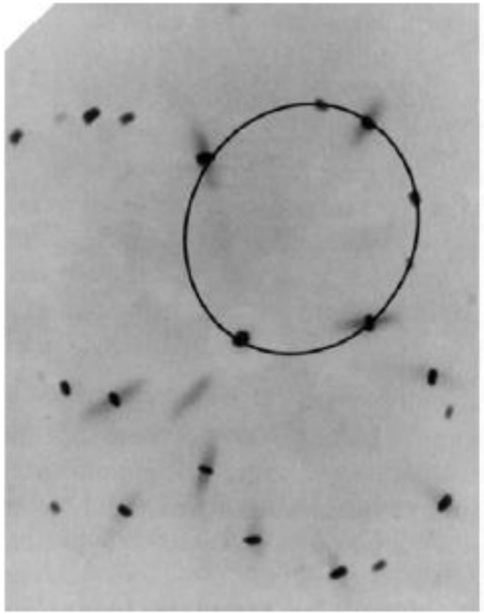
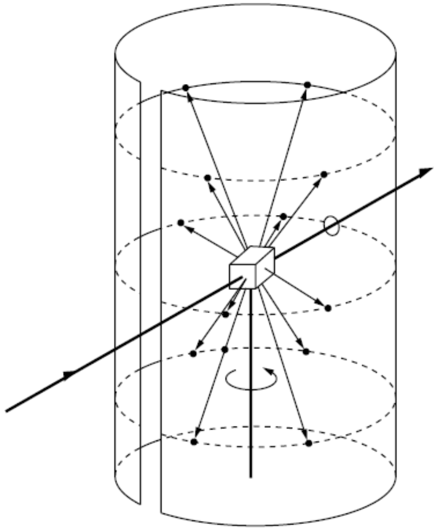


source: [4]

In the **Laue method**, a polychromatic ('pink') beam is focused on a sample. Because there is a continuum of wavelengths in the incident beam, specific wavelengths will satisfy the Bragg condition for some crystal planes and thus form a diffracted beam.

Diffraction from monocrystals – rotating crystal method



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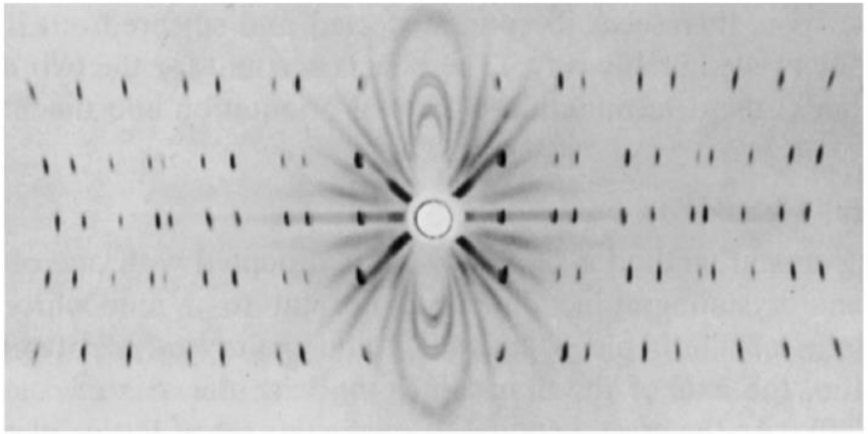
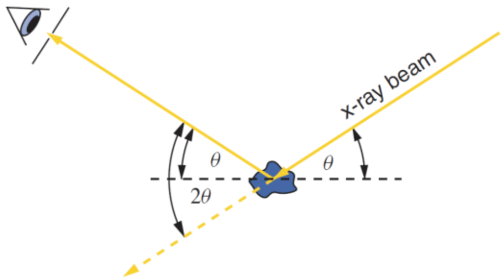
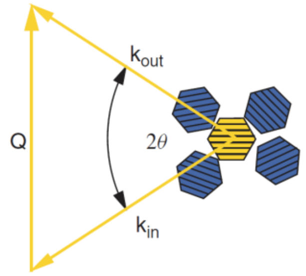


source: [4]

In the **rotating crystal method**, a <u>monochromatic</u> beam is focused on a sample. As the crystal rotates, a particular set of lattice planes will, for an instant, make the correct Bragg angle for diffraction and at that instant a diffracted beam will be formed.

Diffraction from polycrystals - powder method





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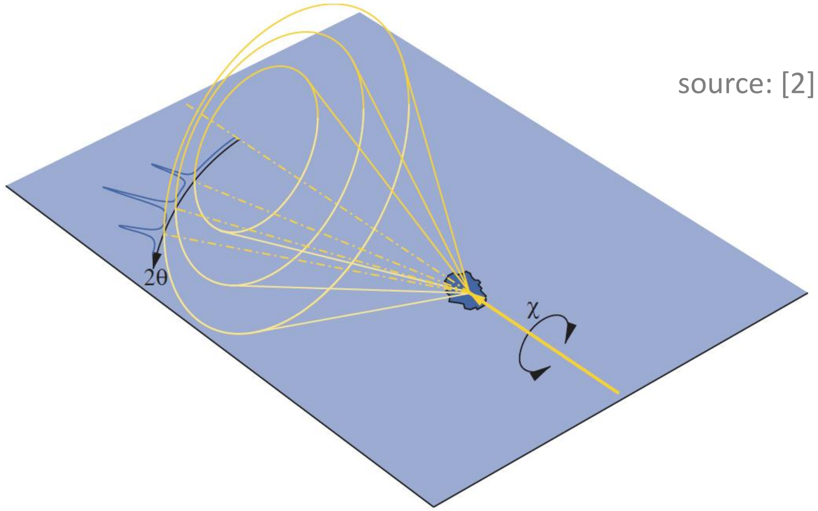
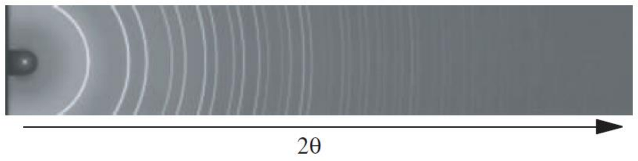
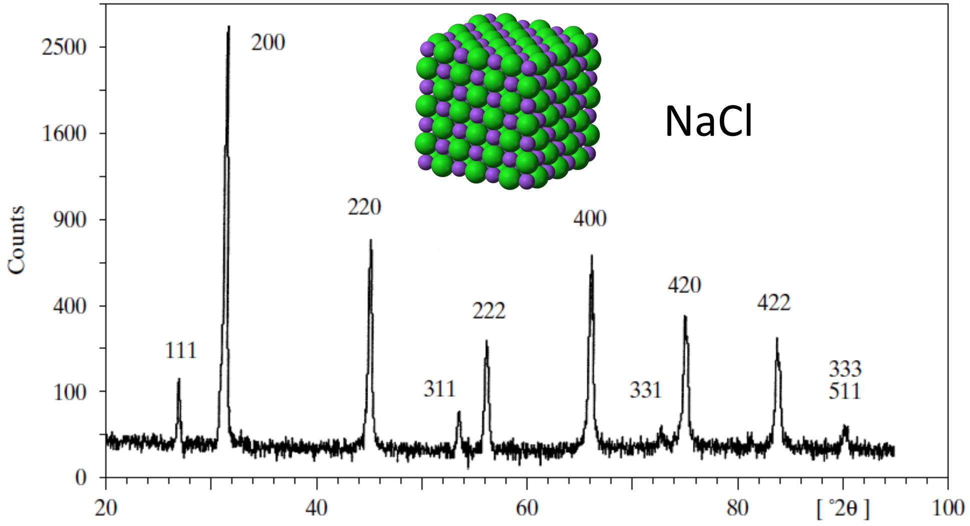




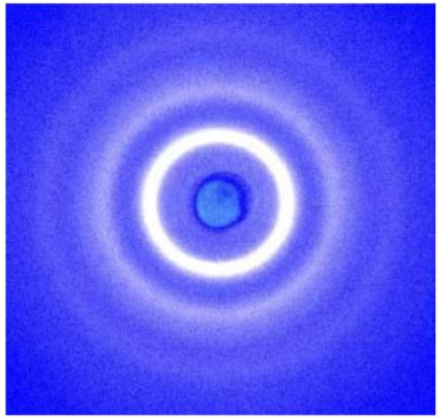
source: [2]

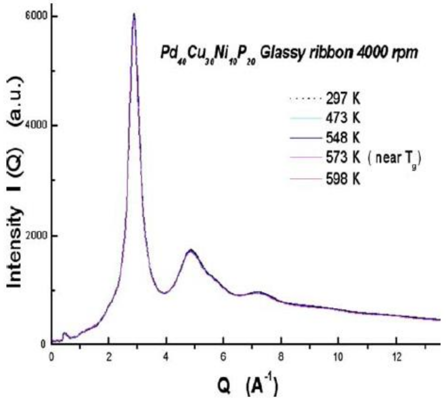
In the **powder method**, a monochromatic beam is focused on a polycrystalline sample. Each crystalline grain in the sample is randomly oriented with respect to the incident beam. By chance, some of the crystals will be oriented for diffraction from a set of planes (other crystals will be correctly oriented for other reflections). The result is that every set of lattice planes will be capable of diffraction.

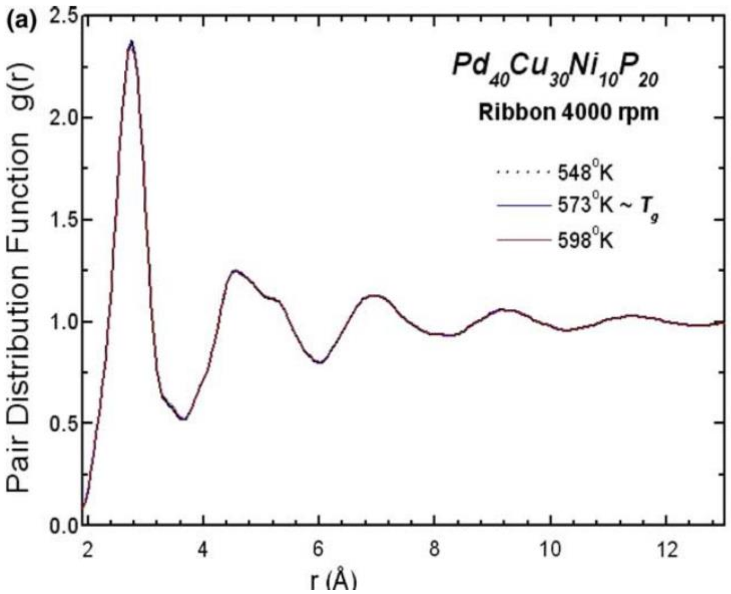


source: [4]

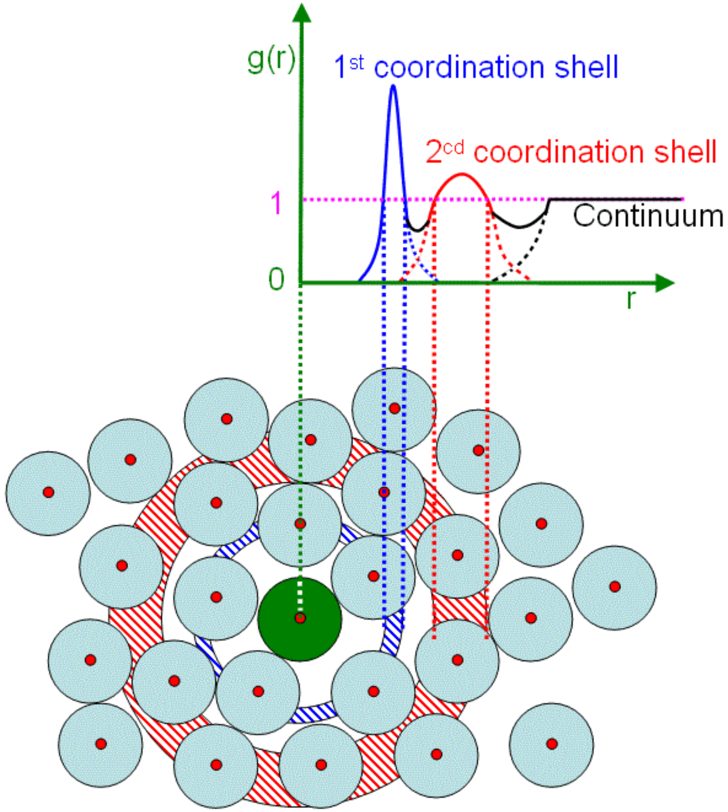
Diffraction patterns of amorphous samples





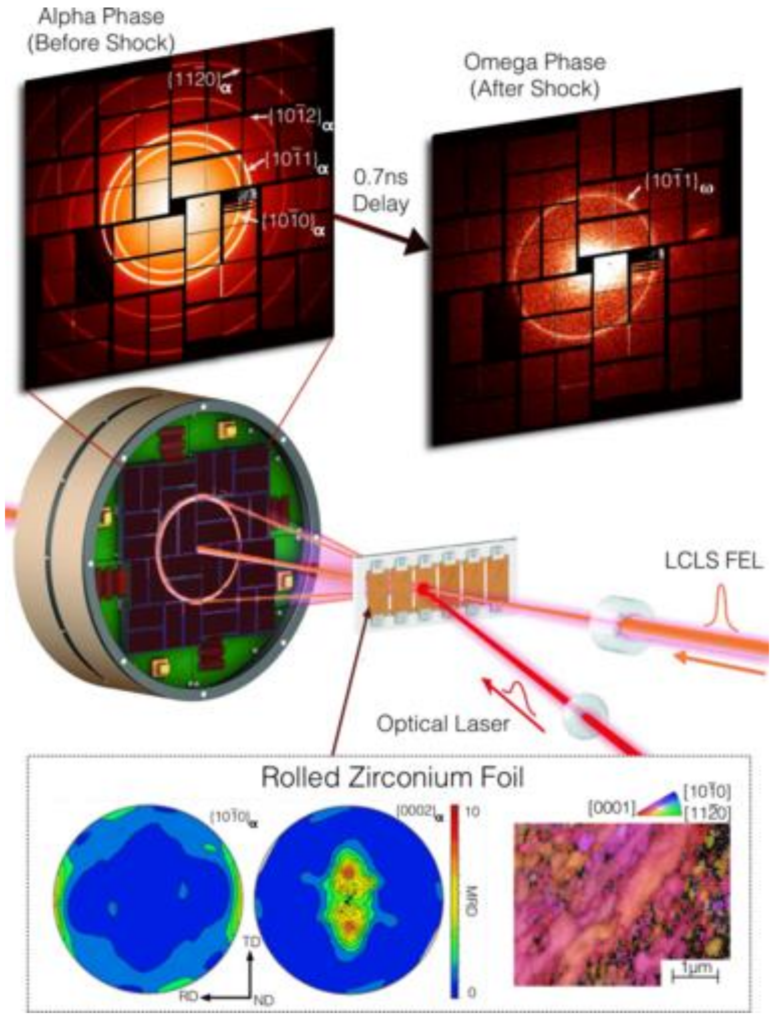


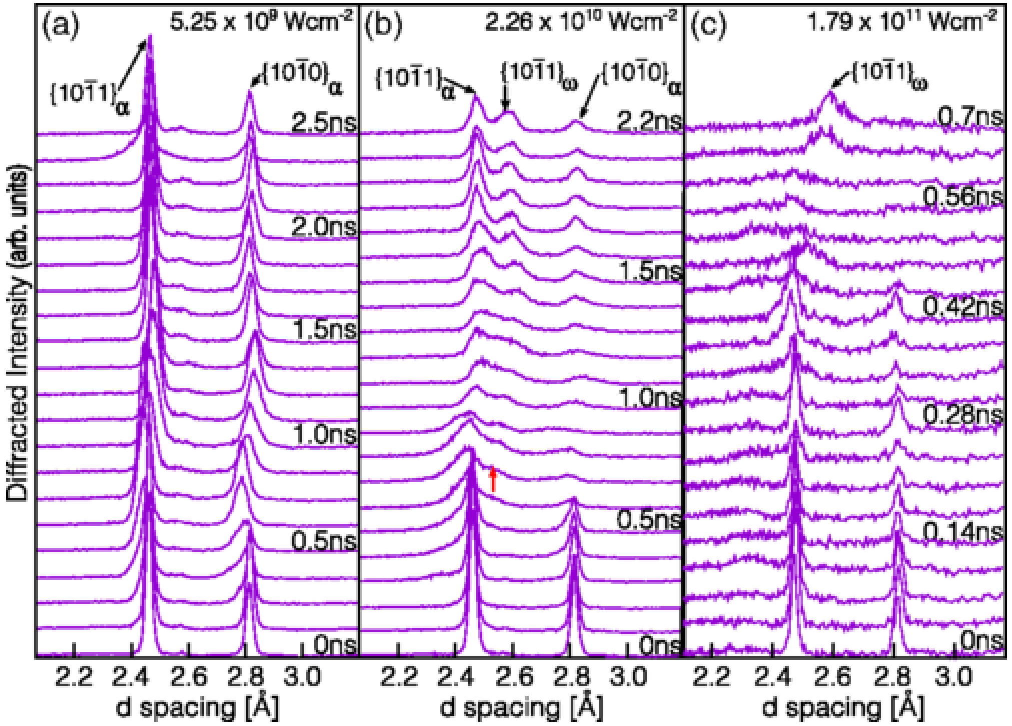
source: A. R. Yavari *et al.*, vol. 53, no. 6, pp. 1611–1619, 2005



source: https://www.globalsino.com/EM/page3097.html

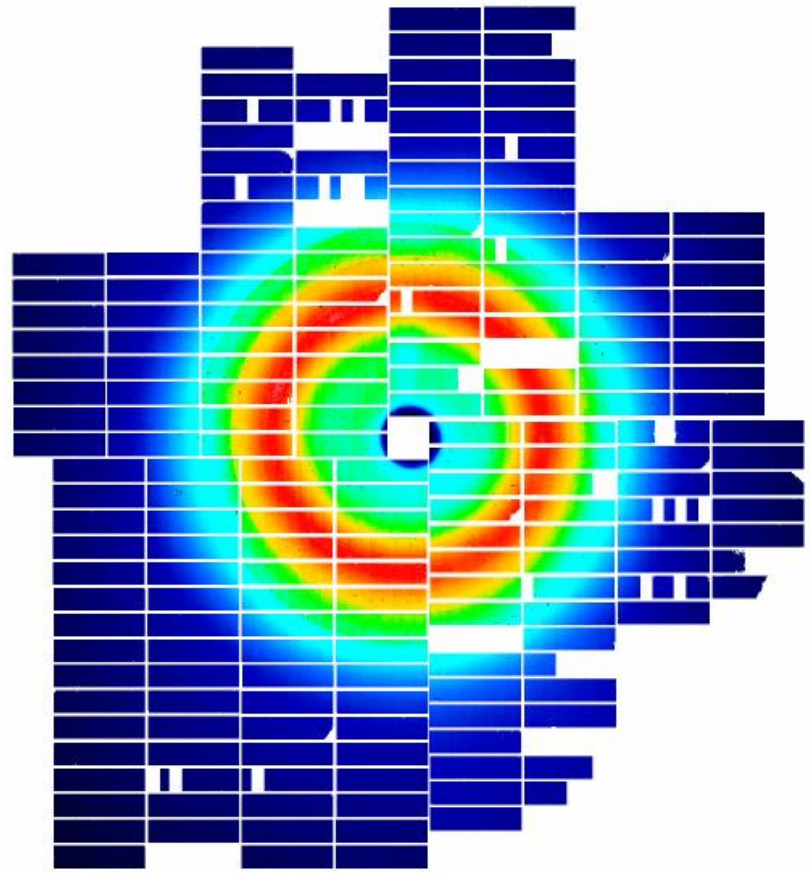
Example: picosecond dynamics of a shock-driven phase transformation in zirconium metal

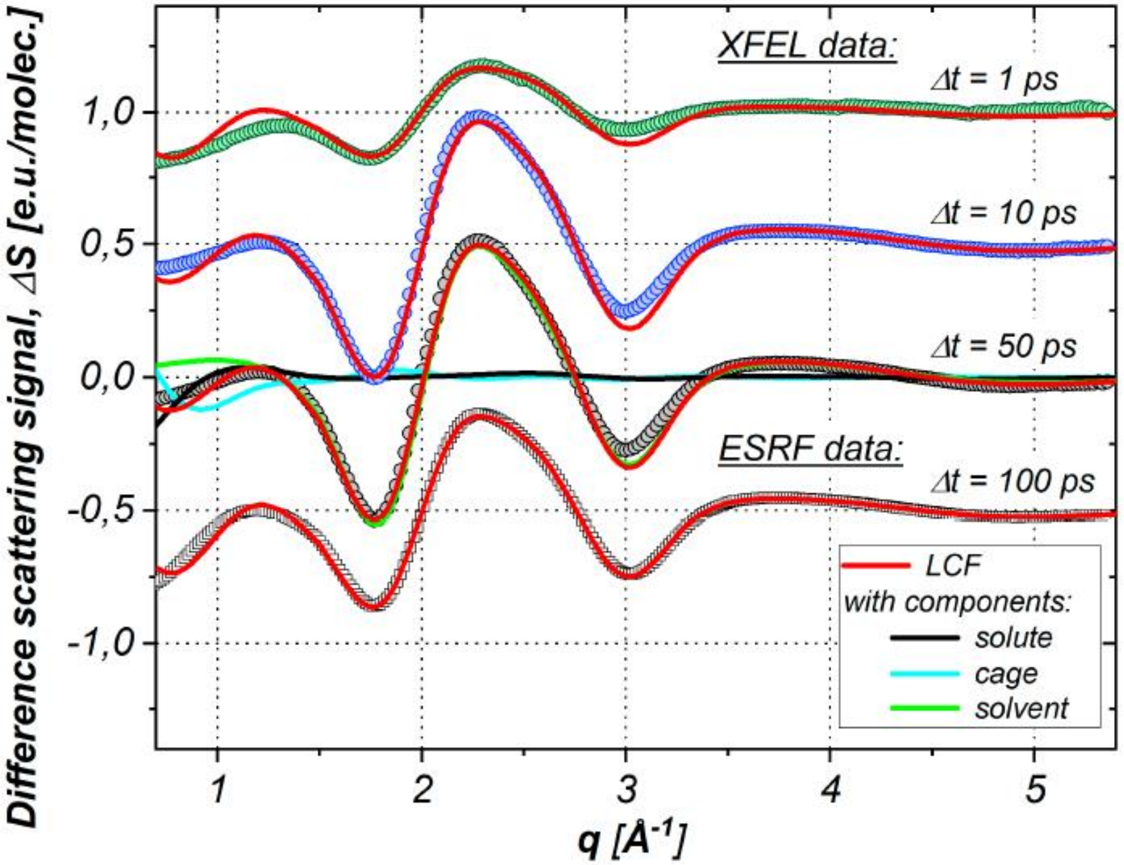




T. D. Swinburne *et al.*, Phys. Rev. B 93, 2016, 144119

Example: WAXS from an aqueous solution of $[Fe(bpy)_3]^{2+}$





source: D. Khakhulin *et al.*, Appl. Sci. 2020, 10, 995

Summary

What kind of questions can be answered using X-ray diffraction (WAXS):

- Is the sample crystalline or amorphous?
- What is the atomic structure of the crystalline sample (type of crystal structure, strain, texture, crystal size, etc.)?
- What is the pair distribution function of the liquid/amorphous sample (distances between the pairs of atoms/particles)?