Seminar on X-ray Diffraction

given at the
Institute of Physics
University of Silesia

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Contents

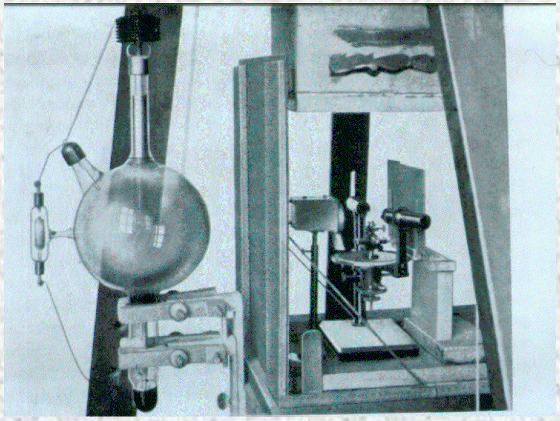
- Basic theory on diffraction of X-rays
- Analysis of X-ray diffraction
  - Fourier transform
  - Convolution theorem
- X-ray diffraction of powder samples
- X-ray diffraction of single crystals
- Applications

Basic theory of diffraction

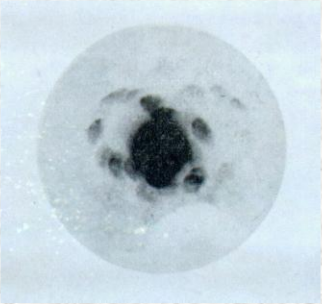
History

Two hypotheses by Max von Laue (1912):

- X-rays are **waves**
- Crystals have a 3-dimensional **periodical** structure



The original experiment

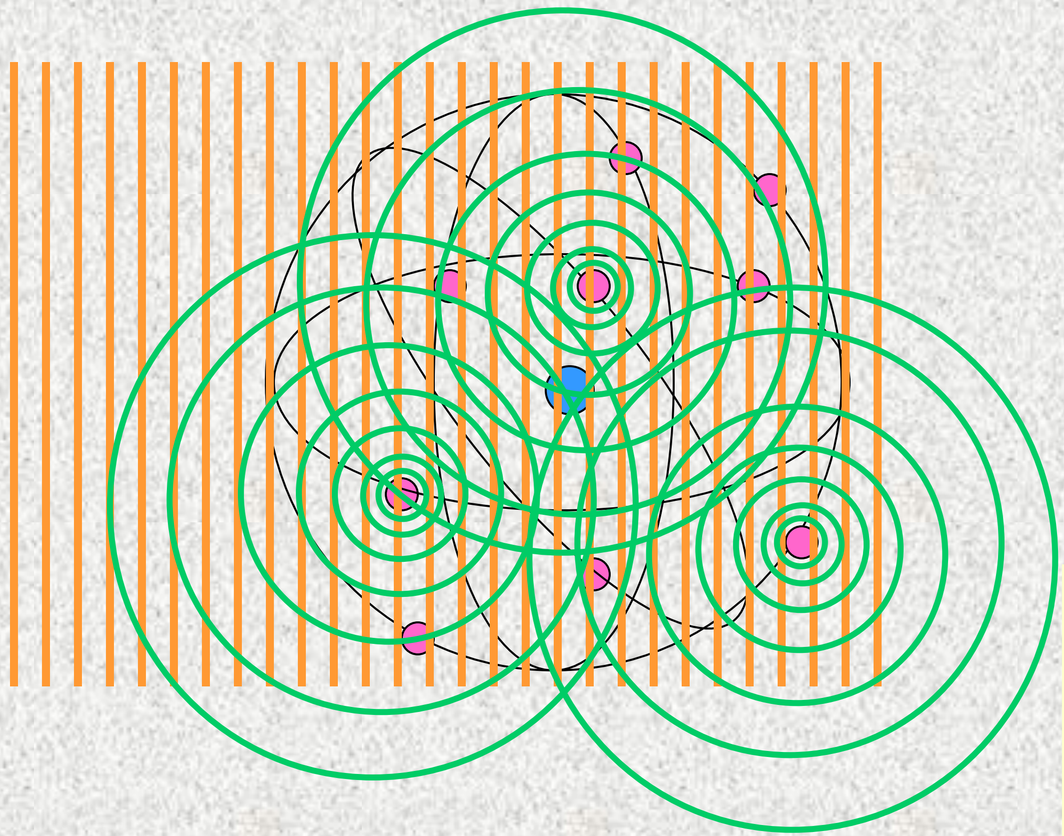


The first diffraction photograph on Coppersulfate

This was the proof of the two hypotheses

Interaction between X-rays and matter

Scattering of X-rays



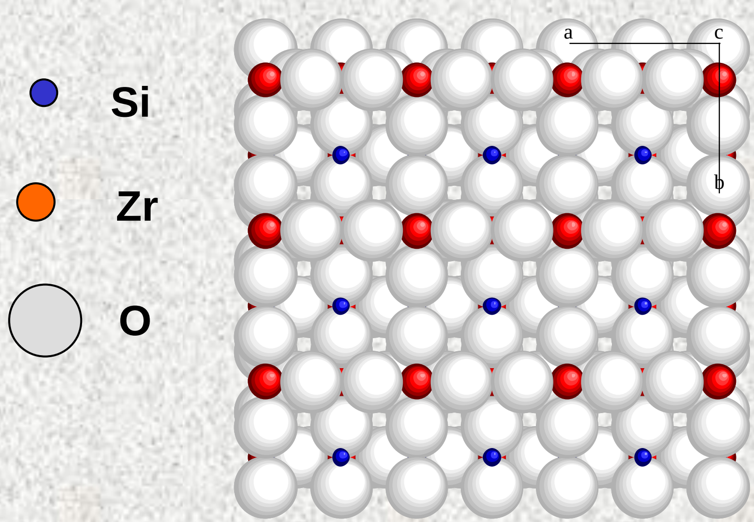
X-rays are scattered by the the individual electrons

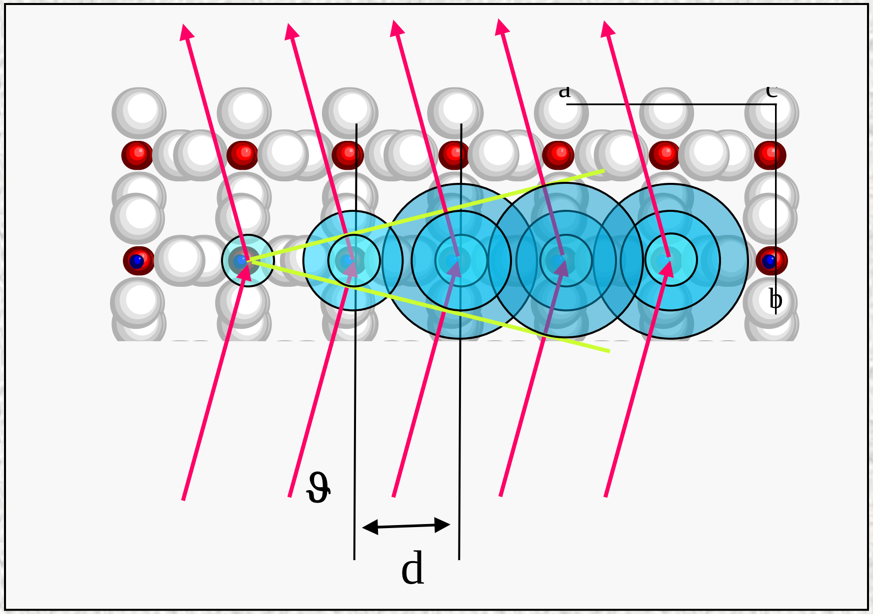
The envelope of all spherical waves is again a spherical wave

Scattering by a crystal

Example:

The crystal structure of Zircon - $ZrSiO_4$

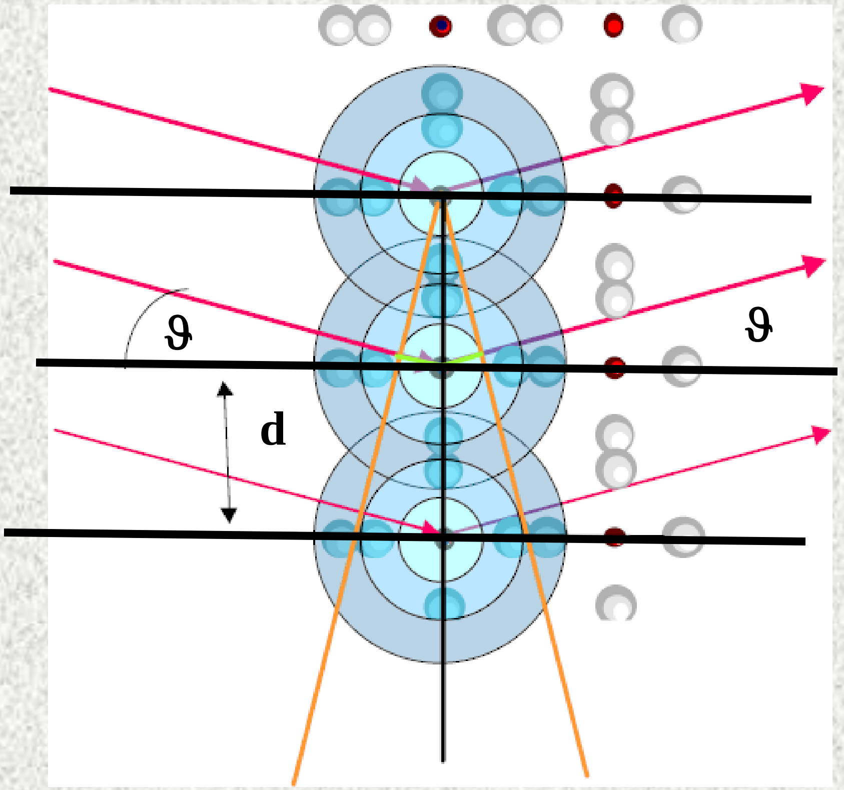




X-rays scattered by the zirconium atoms (Atomic radii are not in scale)
Analogue to Huygens Principle

Periodicity ⇒ Phase difference between scattered X-rays is constant
⇒ **Constructive interference** ⇒ **Diffraction**

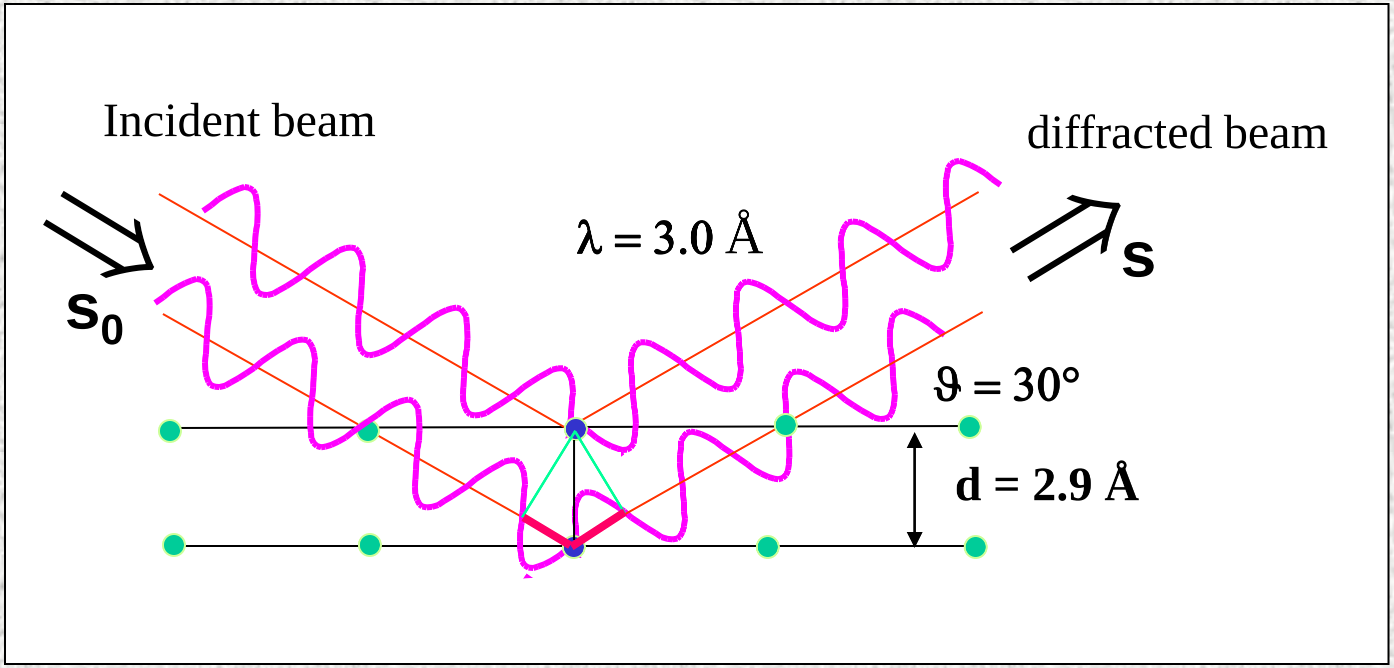
Interpretation of the diffraction by Bragg



The incident and the diffracted wave have the same angle ϑ with respect to the crystal planes with the periodic distance **d** .

$\Rightarrow$It looks like a Reflection.

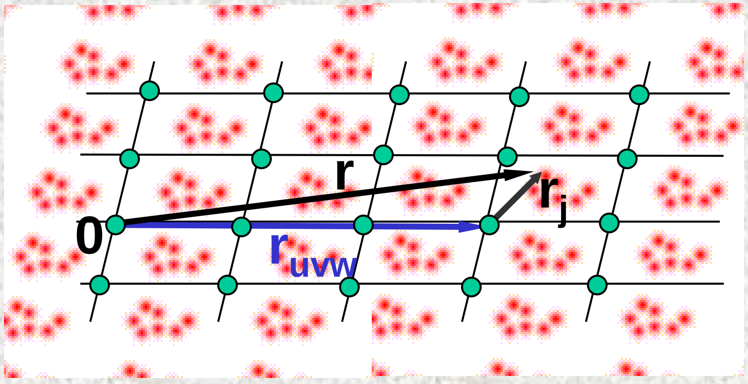
Bragg's law



<u>For constructive interference</u> the condition must hold:
The path difference between waves scattered by atoms from adjacent lattice planes (*h k l*) must be a multiple integer of λ.

$$2d_{hkl} \sin\vartheta = n\lambda$$

Diffraction by a periodic structure.



Amplitude of the scattered wave :

$$A = \Sigma f_0 \exp(2\pi i\, r\, r^*)$$

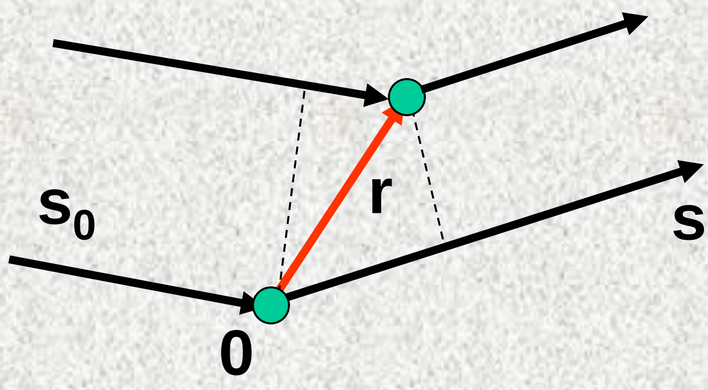
$r = r_{uvw} + r_j$ $r_{uvw} = ua + vb + wc$ $r_j = x_j a + y_j b + z_j c$

$$A = \Sigma \exp(2\pi i\, (u\vec{a} + v\vec{b} + w\vec{c})\vec{r}^*) f_{0j} \exp(2\pi i(\vec{r}_j \vec{r}^*))$$

A = G • F

G = lattice factor   **F = structure factor**

Analysis of X-ray diffraction



Path difference of a wave scattered at point r with respect to 0 :

$$r(s-s_0)$$

The phase angle is:

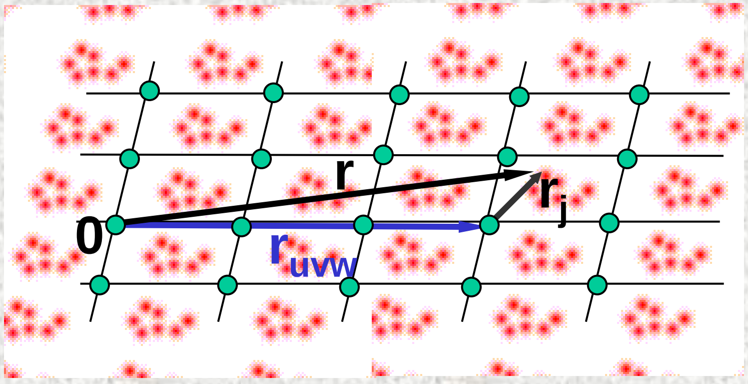
$$2\pi\, r(s-s_0)\,/\lambda$$

$$(s-s_0)\,/\lambda = r^*$$

Amplitude of the scattered wave :

$$A = \exp(\,2\pi i\; r\; r^*)$$

Diffraction by a periodic structure.



Amplitude of the scattered wave :

$$A = \Sigma f_0 \exp(\,2\pi i\ r\ r^*)$$

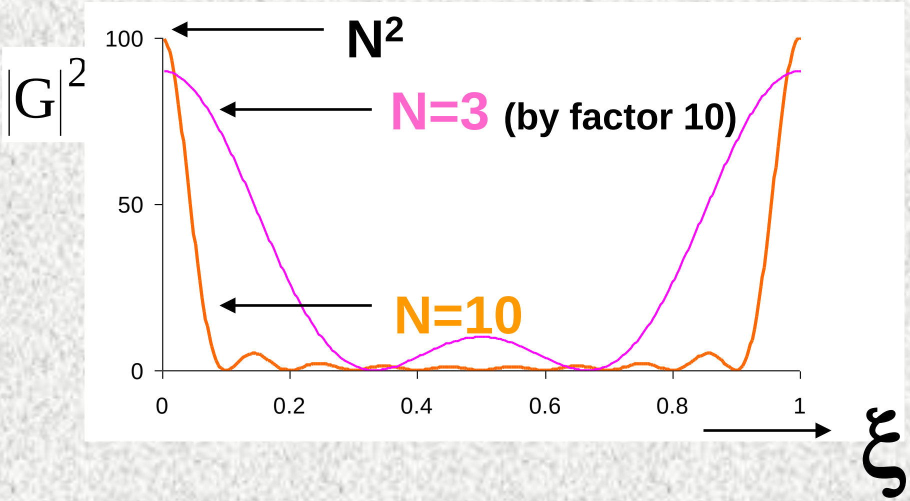
r = $\mathbf{r_{uvw}}$+$\mathbf{r_j}$ $\quad$ **$\mathbf{r_{uvw}} = ua + vb + wc$** $\quad$ **$\mathbf{r_j = x_j a + y_j b + z_j c}$**

$$A = \Sigma \exp(\,2\pi i\ (u\vec{a} + v\vec{b} + w\vec{c})\vec{r}^*) f_{0j}\ \exp(2\pi i(\vec{r}_j \vec{r}^*))$$

A = G • F

G = lattice factor $\qquad$ **F = structure factor**

The lattice factor.

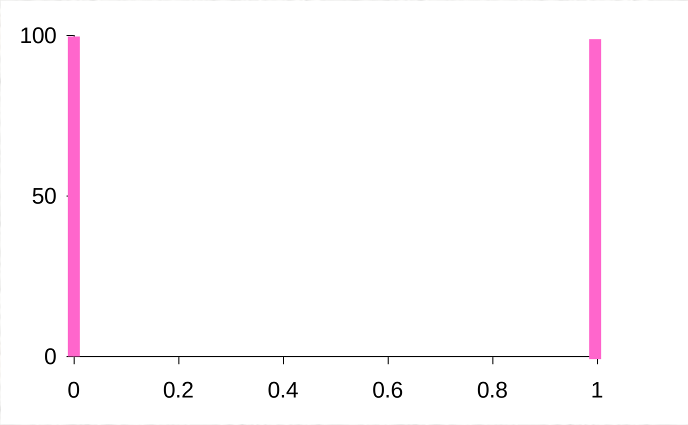


$$G = \sum^{N} \exp(\xi u + \eta v + \zeta w)$$

r*=(ξ,η,ζ)

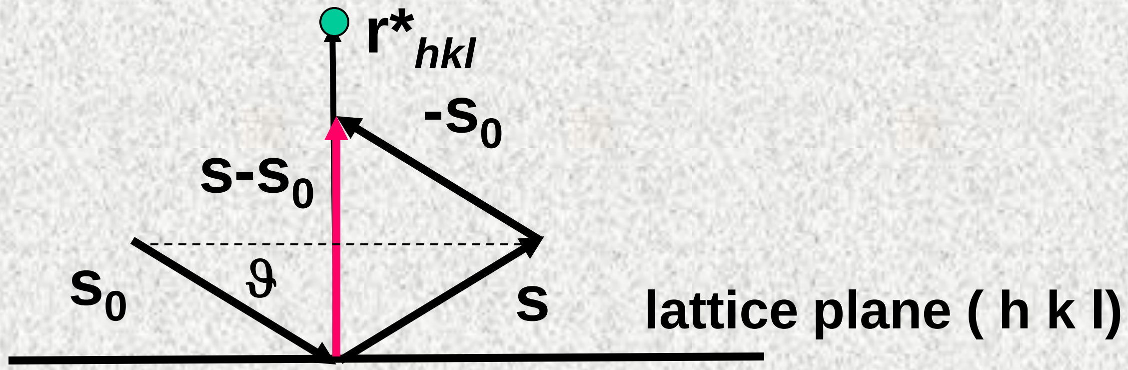
Laue's approximation for N → ∞

$$|G| = \delta(\xi - h)$$



⇒r* = (point) lattice
h, k, l = integer

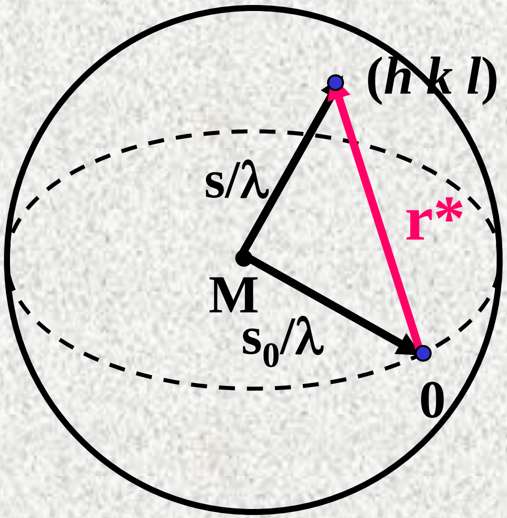
Laue's equations in vector notation



$$(s-s_0)/\lambda = r^*_{hkl} = ha^* +kb^* +lc^*$$

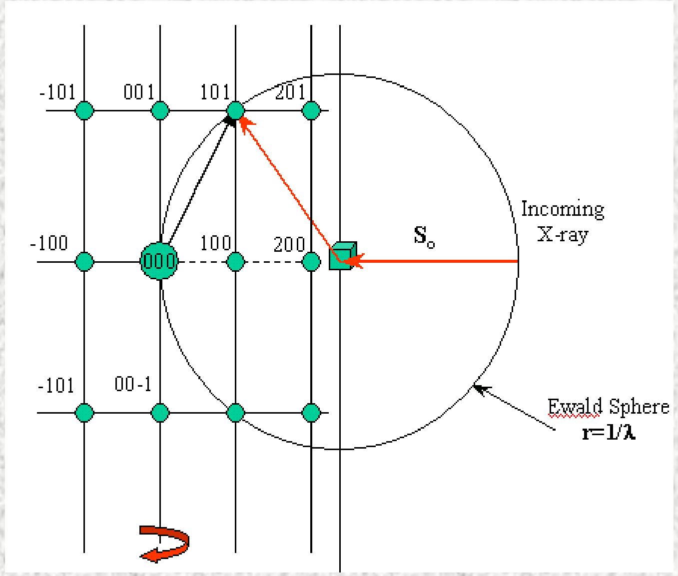
Ewald's interpretation

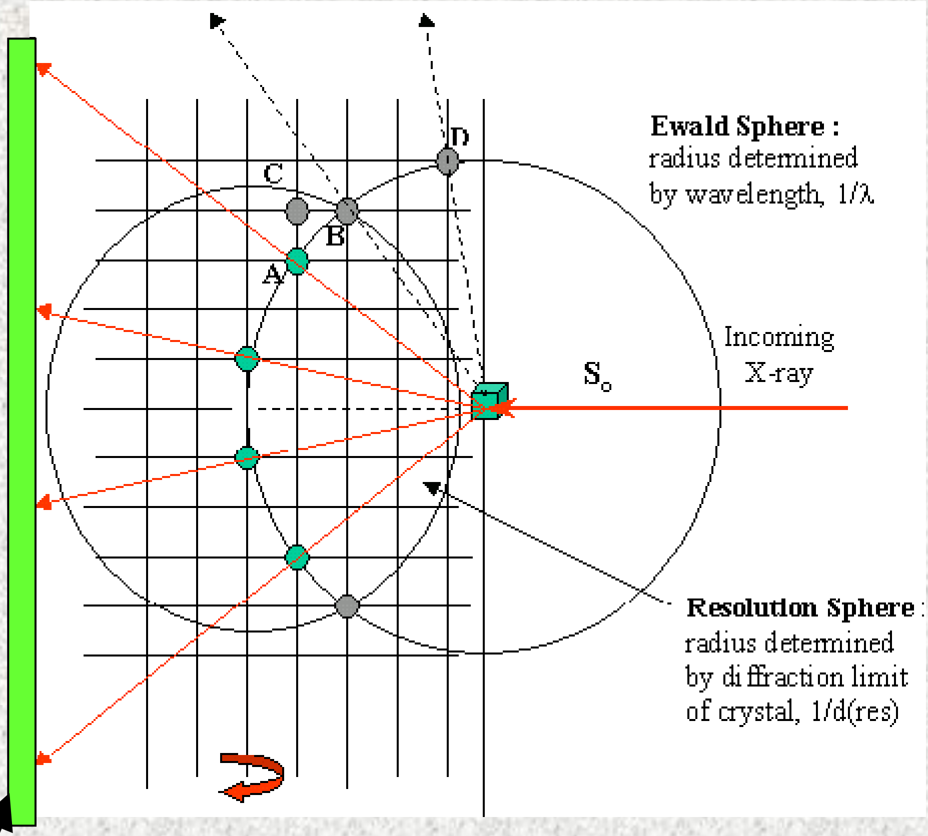
Crystal at the centre M of a sphere with the radius $1/\lambda$.
The origin of the reciprocal lattice is on the sphere with M-0 equal to s_0/λ.



Diffraction occurs in the direction of s if a point of the reciprocal lattice intersects the Ewald-sphere

Measurement of X-ray reflections

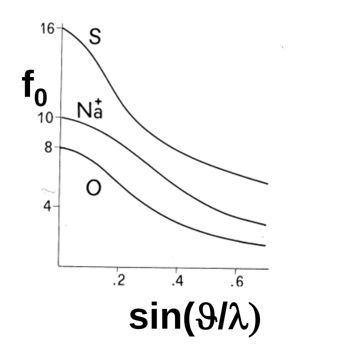




Film, Detector

The structure factor.

$$F(h,k,l) = \sum_j f_{0j} \exp(2\pi i(hx_j + ky_j + lz_j))$$



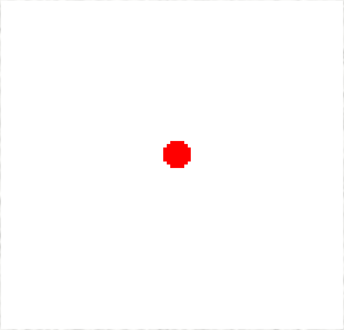
f_{0j}= scattering factor of atom j

The structure factor for a density $\rho(x,y,z)$

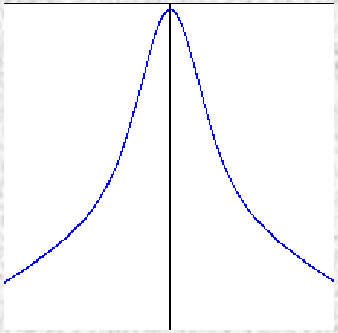
$$F(h,k,l) = \int \rho(x,y,z) \exp(2\pi i(hx_j + ky_j + lz_j))dV$$

The operator which transforms the density of the <u>crystal space</u> to the amplitude of the <u>reciprocal space</u> is the Fourier Transform

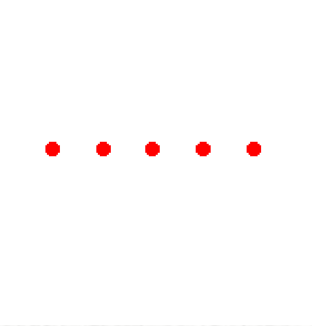
Examples of Fourier Transforms.



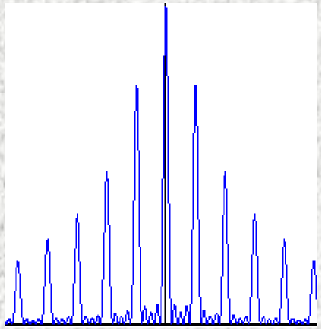
A silicon atom



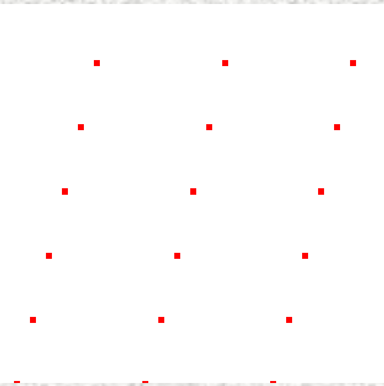
Its transform



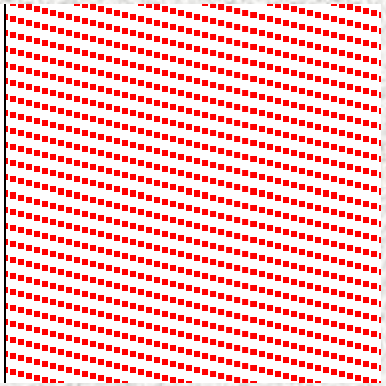
Fife atoms



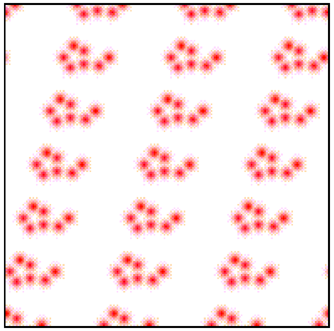
Their transform



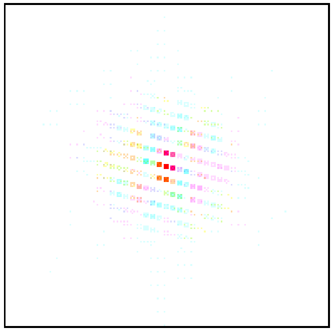
A lattice



Its transform



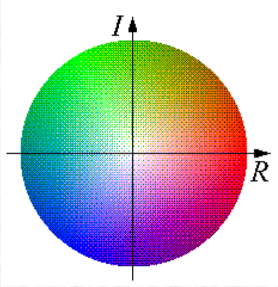
A structure



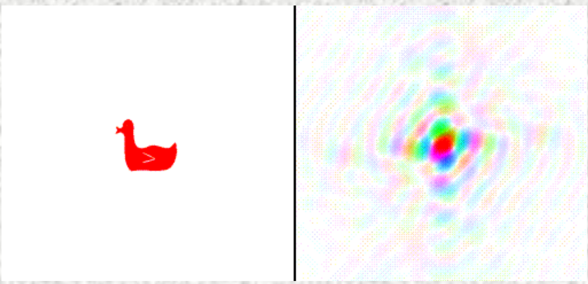
Its transform

Information from the structure factor.

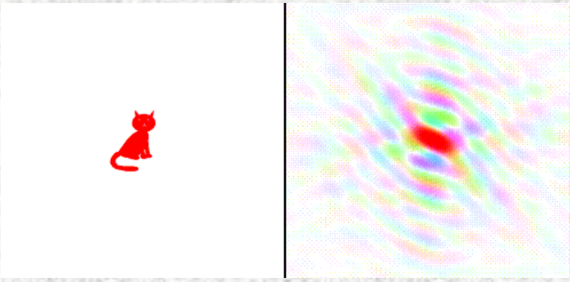
The structure factor is a complex quantity: It consists of real and imaginary part (or magnitude and phase)



graphic representation in the Gaussian plane:
colour = phase
brightness= magnitude

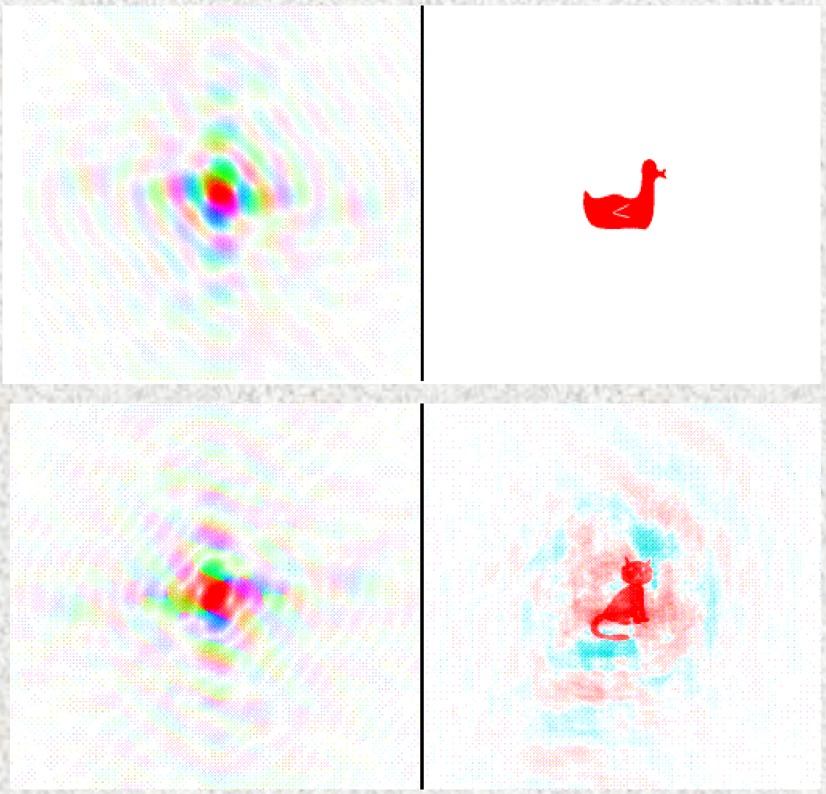


A motif and its
Fourier Transform
(example found in the internet)



A motif and its
Fourier Transform
(example found in the internet)

A motif can be reconstructed from phase and magnitude



Reconstruction of the duck

Reconstruction with the magnitude of the duck and the phase of the cat

Phase problem:

In diffraction experiments only intensities are measured, i.e. the square of the magnitude.
For reconstruction of the structure from diffraction data the more important part is not known : the phases

Convolution

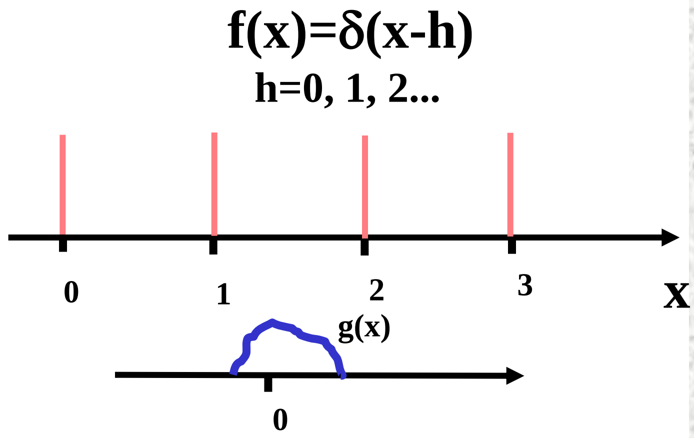
The operator that produces the function $f(x) * g(x)$ from two functions f(x) and g(x) is called a **convolution**

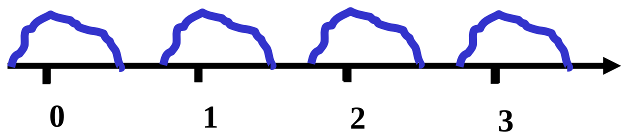
$$f(x) * g(x) = \int g(x-u) f(u) du$$

Consider for f(x) a special case

f(x)=δ(x-h)

This describes a point lattice
Let g(x) be the electron density of a unit cell





$f(x) * g(x)$

density of the unit cell $*$ lattice $\Rightarrow$ periodic structure

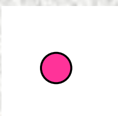
Convolution theorem.

$$\mathcal{F}(f(x) * g(x)) = \mathcal{F}(f(x)) \bullet \mathcal{F}(g(x))$$

The Fourier transform $\mathcal{F}$ of a convolution of two functions is equal to the product of their Fourier transforms.

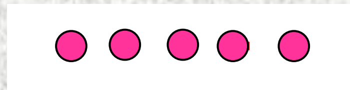
The periodic structure is a convolution of a contents of a unit cell and a point lattice
Their Fourier transform is the product of the lattice factor and the structure factor

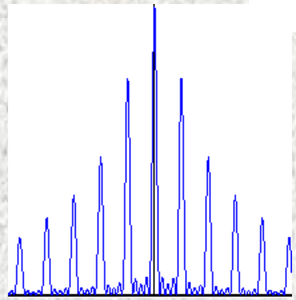
Example: A train of 5 atoms is a convolution of one atom with 5 lattice points



$*$

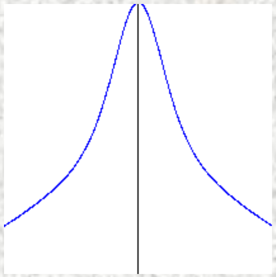
$\Rightarrow$





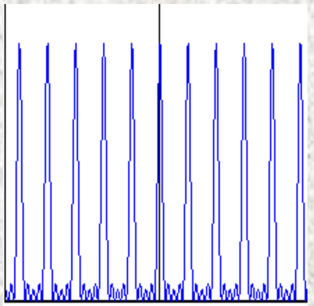
Fourier transform of a train of 5 atoms

$=$



Fourier transform of one atom

$\bullet$



Fourier transform of a train of 5 lattice points