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Introduction to X-ray diffraction

1) Diffraction: the basic concepts

What it is
When it occours
How it is interpreted fenomenologically and matematically

2) The Fourier Transform

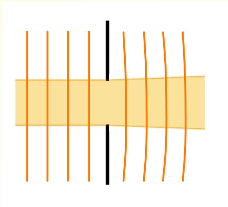
How it works
The convolution function
Examples of optical transforms

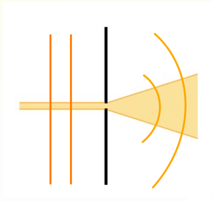
3) Elements of X-ray diffractions

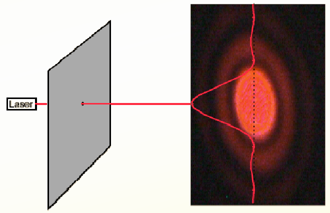
Diffracton by electrons, atoms, molecules, crystals
Laue equations, Bragg equation, Ewald description
Rotating crystal method, Powder method
The temperature effect

What's Diffraction?

Diffraction is the spreading of waves around obstacles.







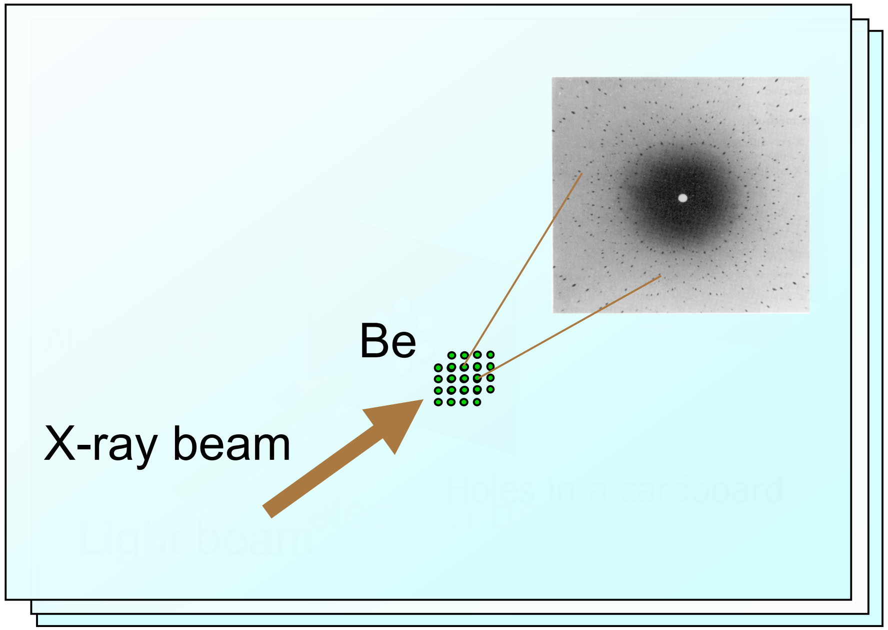
consequences of **diffraction** are that sharp shadows are not produced and interference patterns appear.

Diffraction takes place

1. Mechanical waves
water waves, sound;

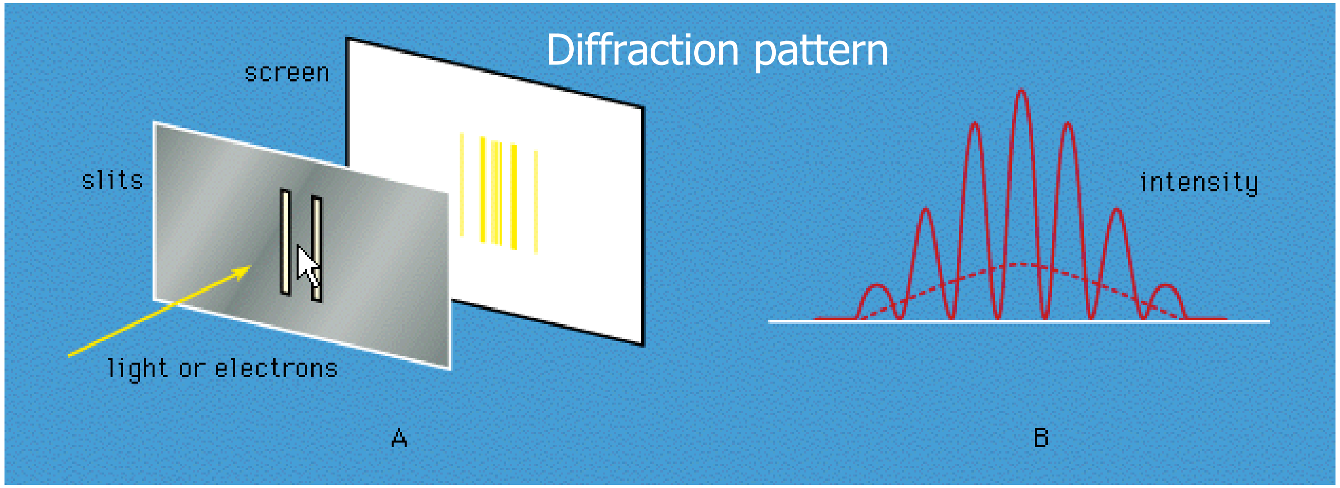
2. very small moving particles which show wavelike properties
electrons, neutrons, atoms,

3. with electromagnetic radiation:
light, X-rays, gamma rays;



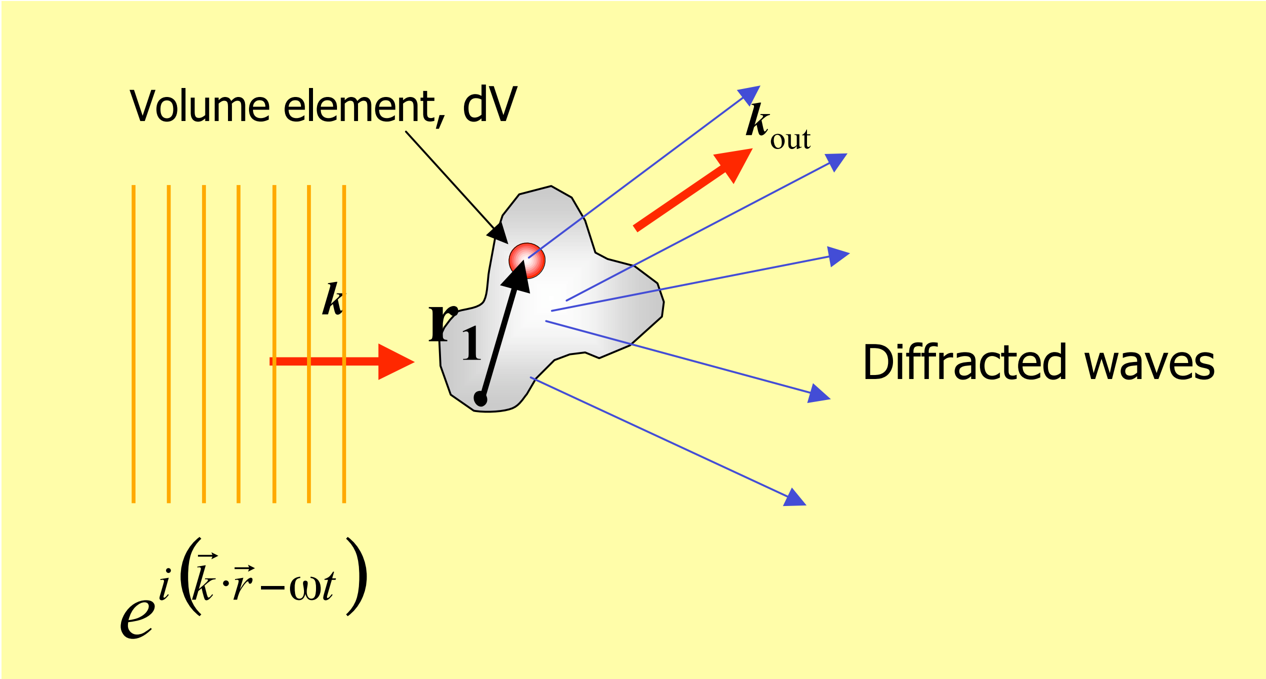
How is it interpreted ?

The phenomenon is the result of interference
i.e., when waves are superimposed, they may reinforce or cancel each other out



and is most pronounced when the wavelength of the radiation is comparable to the linear dimensions of the obstacle.

How is diffraction described?



$e^{i\left(\vec{k}\cdot\vec{r}_1-\omega t\right)}$ incoming wave interacting with the elementar volume dV

The perturbation of dV on the incoming wave is proportional to $f\left(\vec{r}_1\right)dV$

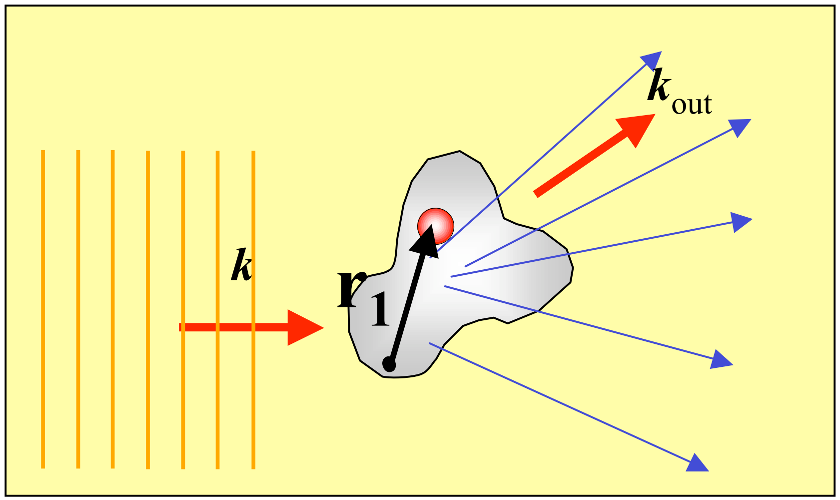
DIFFRACTED WAVE by dV $= f\left(\vec{r}_1\right)dV \; e^{i\left(\vec{k}\cdot\vec{r}_1-\omega t\right)}$

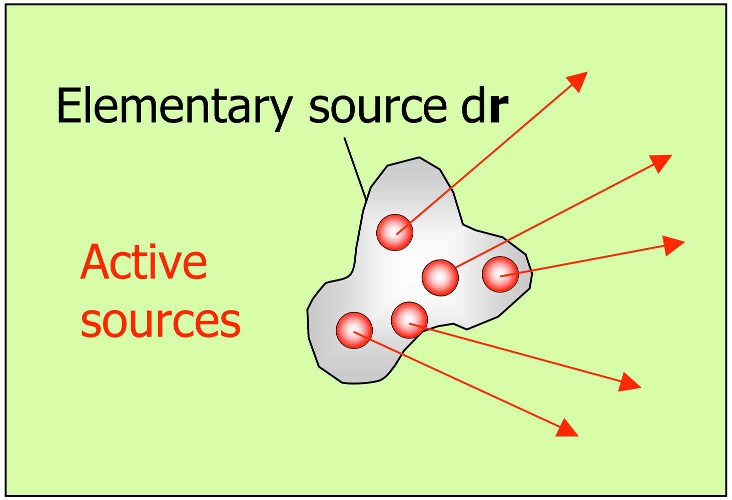
How is diffraction described ?

… Superimposition theorem ⇒

Diffraction pattern= $f(\mathbf{r}_1)\, e^{i\,(\mathbf{k}\cdot\mathbf{r}_1-\omega t)}\, d\mathbf{r}_1 + f(\mathbf{r}_2)\, e^{i\,(\mathbf{k}\cdot\mathbf{r}_2-\omega t)}\, d\mathbf{r}_2 + \ldots$

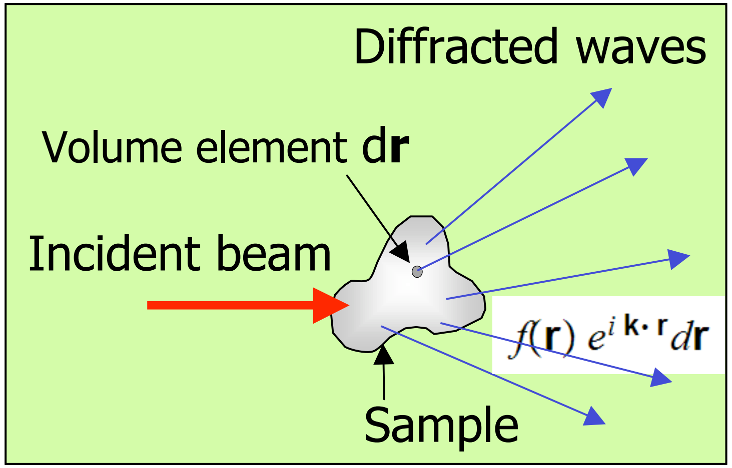
$$F\left(\vec{k}\right) = \int_V f\left(\vec{r}\right) e^{i\left(\vec{k}\,\vec{r}-\omega t\right)}\, d\vec{r}$$

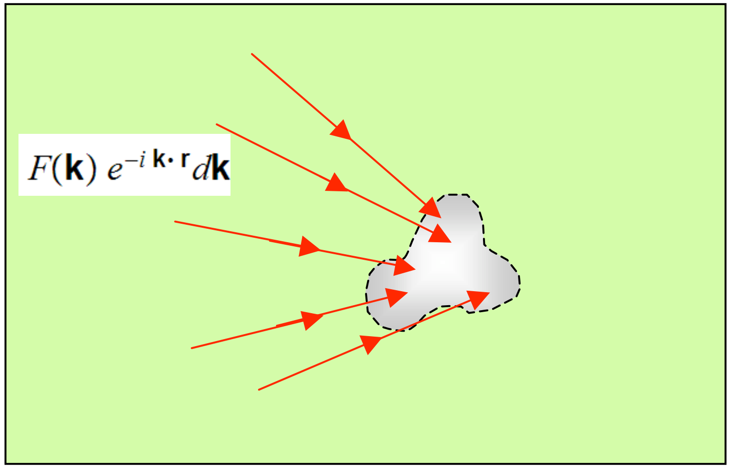




The significance of the inverse transform

The principle of the reversibility light paths

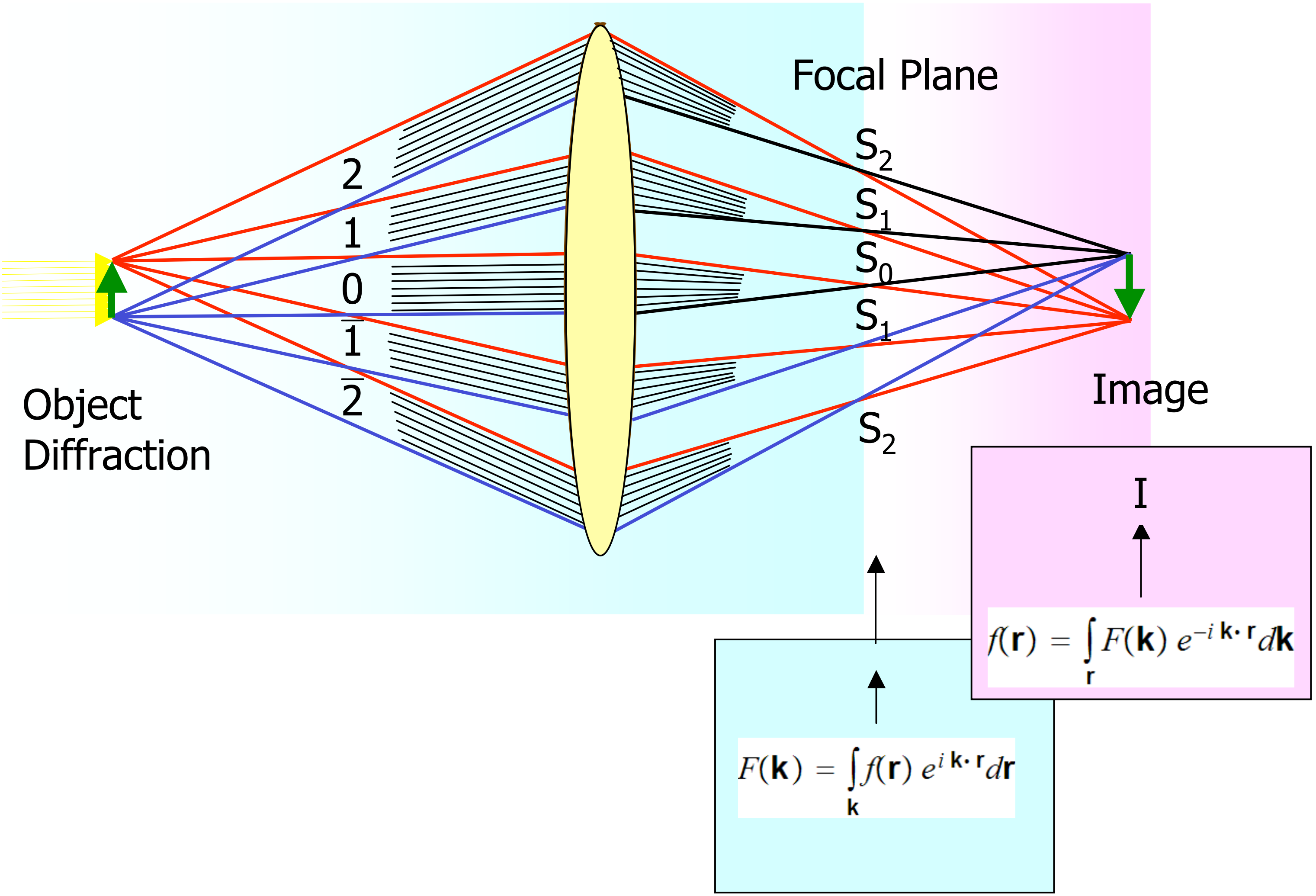




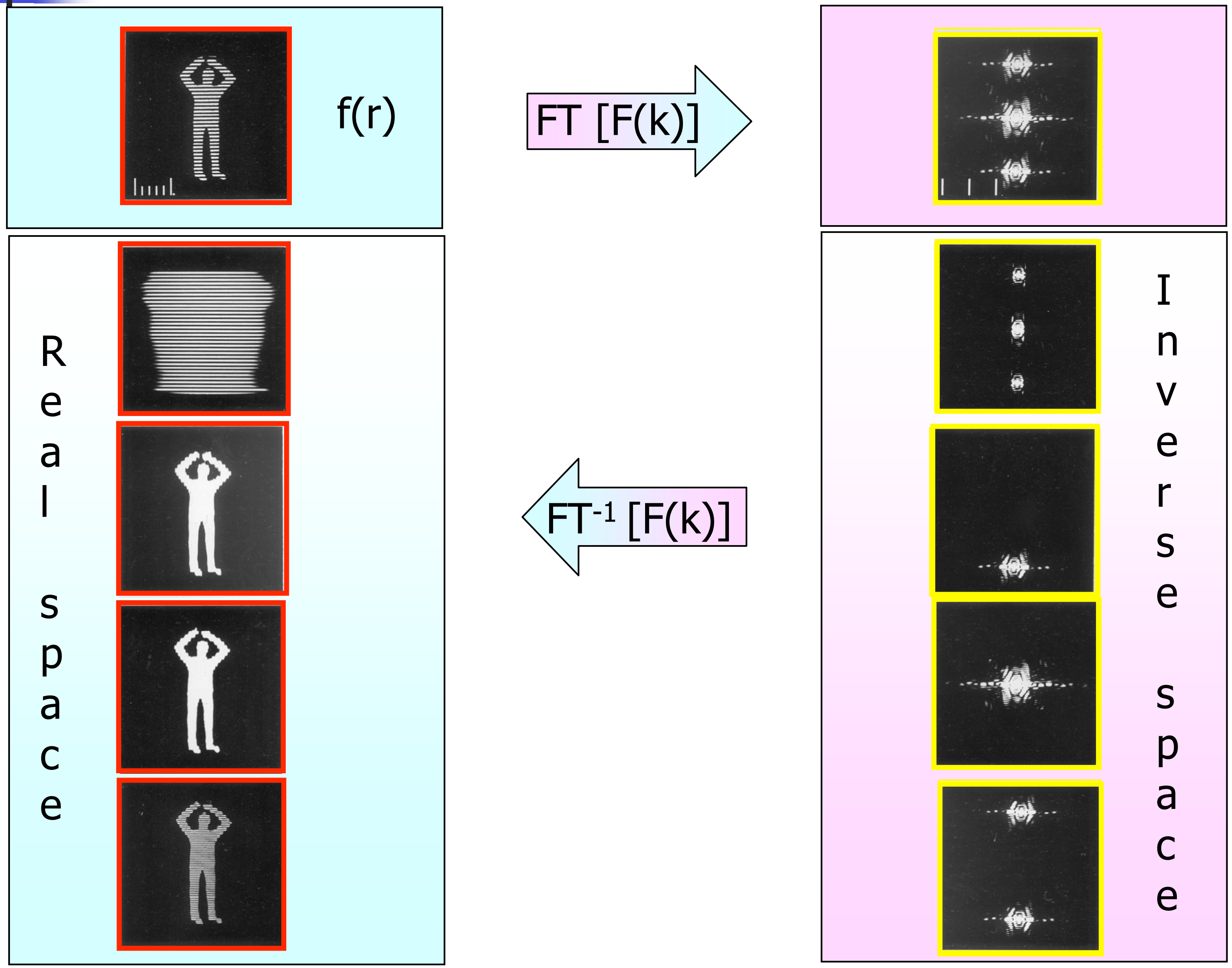
$$F(\mathbf{k}) = \int_{\mathbf{k}} f(\mathbf{r})\, e^{i\,\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}$$

$$f(\mathbf{r}) = \int_{\mathbf{r}} F(\mathbf{k})\, e^{-i\,\mathbf{k}\cdot\mathbf{r}} d\mathbf{k}$$

Diffraction in the back plane of a lens



Spatial filtering



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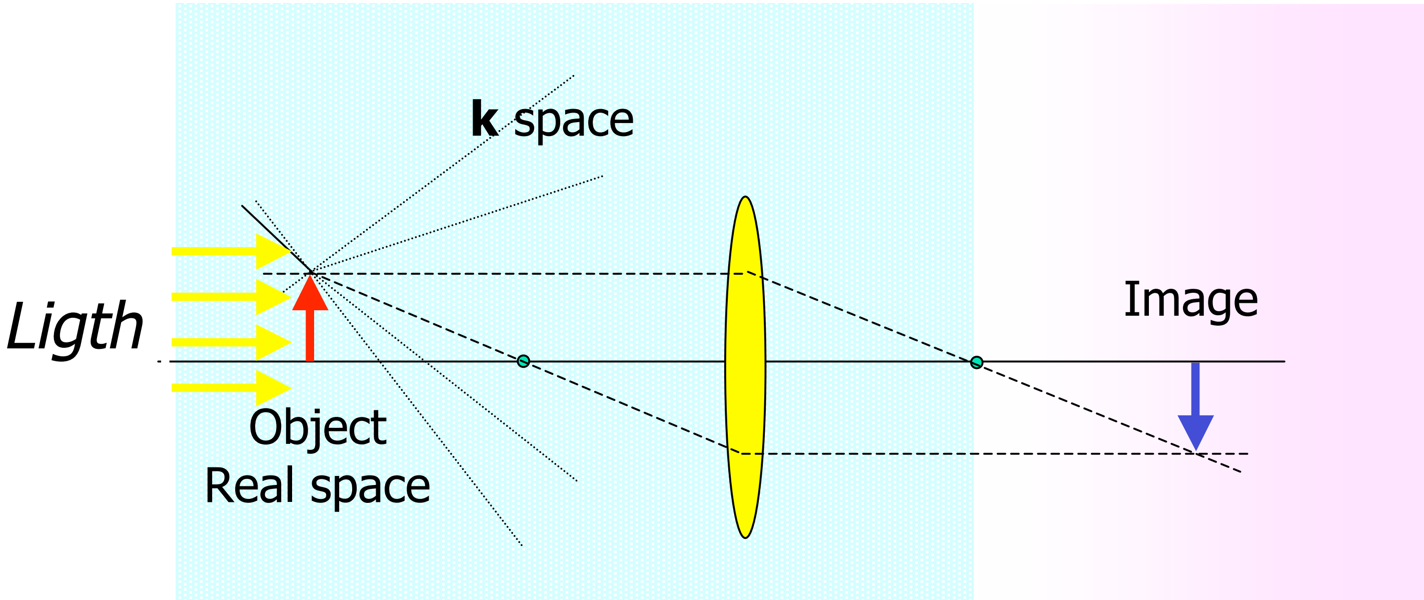
Operation of a lens

Lens as back Fourier transform analog device

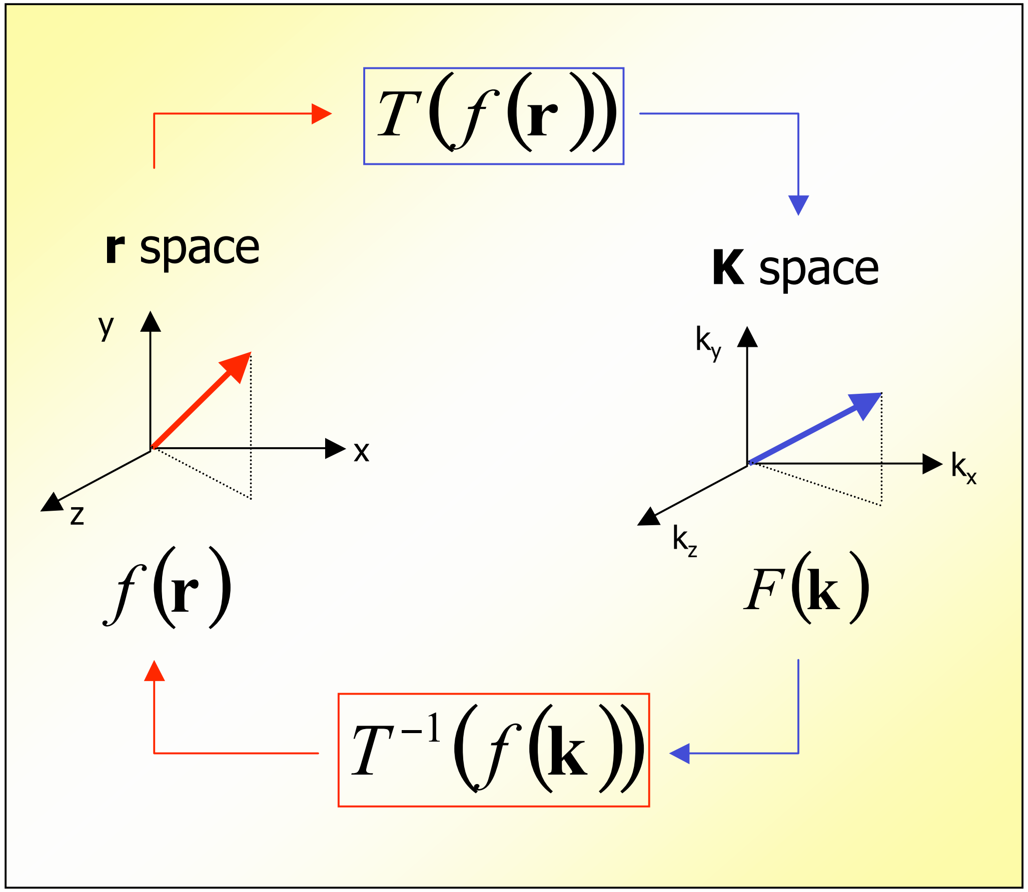


$$F(\mathbf{k}) = \int_{\mathbf{k}} f(\mathbf{r})\, e^{i\,\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}$$

$$f(\mathbf{r}) = \int F(\mathbf{k})\, e^{-i\mathbf{kr}}\, d\mathbf{k}$$

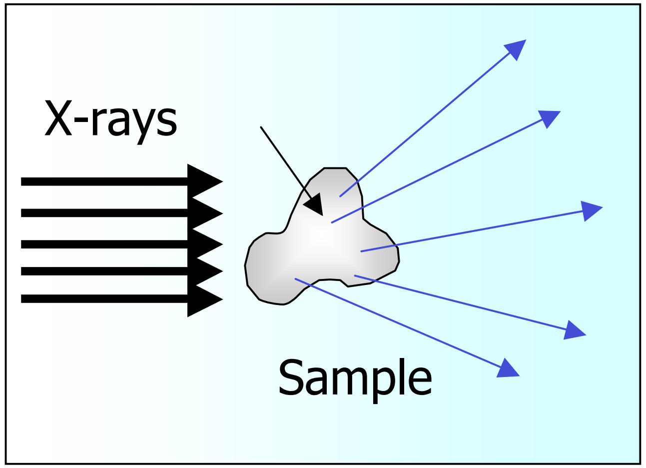
From real to reciprocal space and vice-versa

f(**r**) and F(**k**) carry the same information expressed in terms of different variables



Mathematical Fourier-backtransform

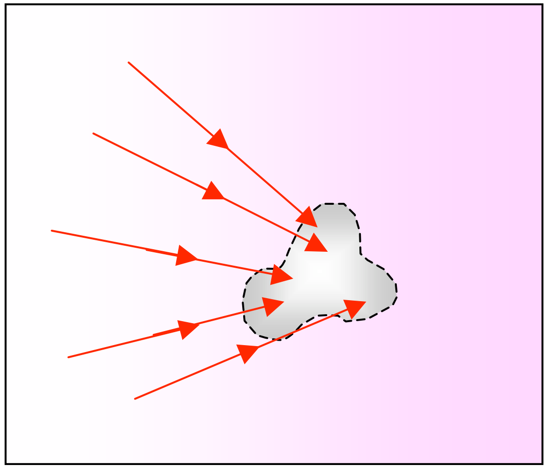
…still no lenses for atomic X-rays "microscopy"



Data collection

+

Back-Fourier transformation



Data collection

$$F(\mathbf{k}) = \int_{\mathbf{k}} f(\mathbf{r})\, e^{i\,\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}$$

⇩

X-ray diffractometer

Back-Fourier transformation

$$f(\mathbf{r}) = \int_{\mathbf{r}} F(\mathbf{k})\, e^{-i\,\mathbf{k}\cdot\mathbf{r}} d\mathbf{k}$$

⇩

Computer

Fourier transforms

1) Diffraction: the basic concepts

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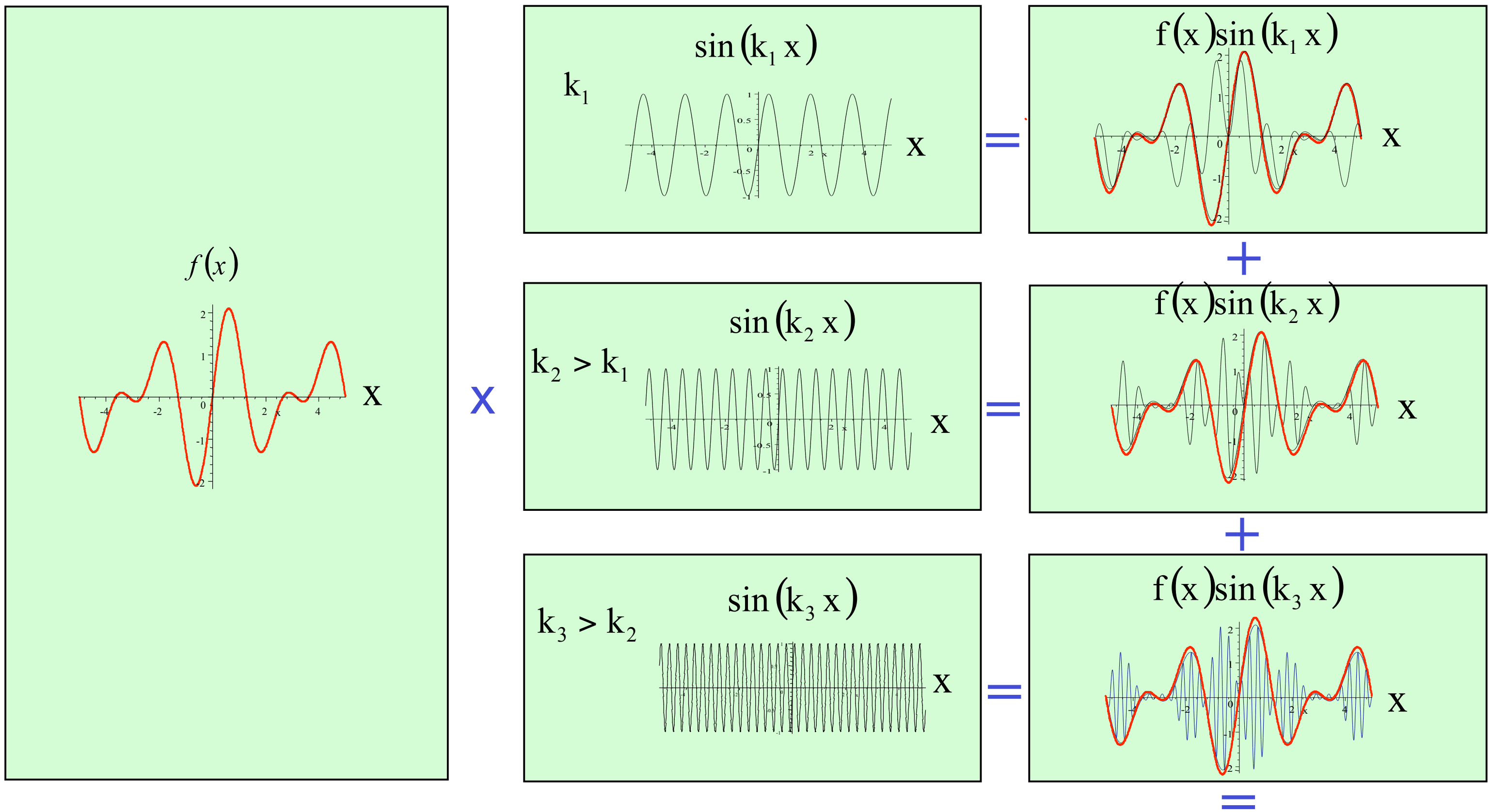
Fourier Transforms

$$F(k) = \int_{-\infty}^{+\infty} f(x) e^{ikx} dx$$ Fourier transform of $f(x)$



$$F(k) = \int_{-\infty}^{+\infty} f(x) \sin kx \, dx$$

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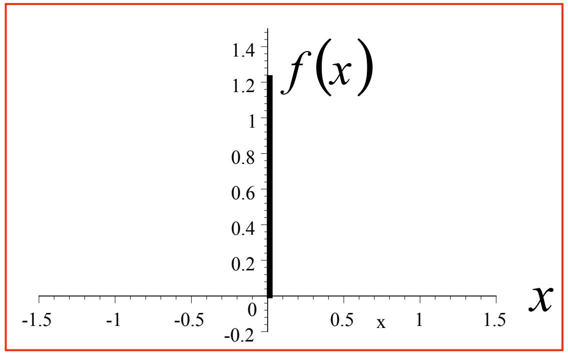
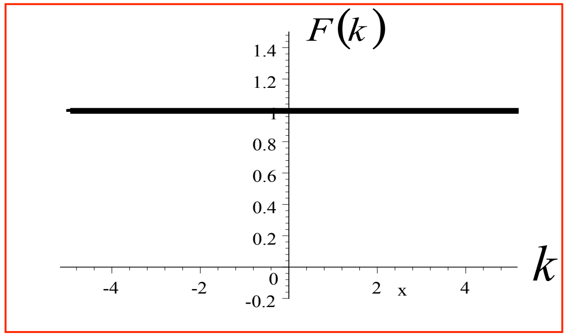
FT of one δ functions

f(x)=δ(x)



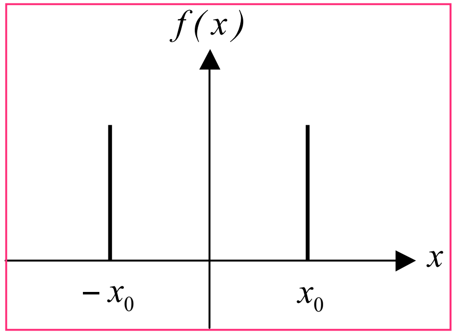
$$F(k) = \int_{-\infty}^{+\infty} f(x)e^{ikx}dx = \int_{-\infty}^{+\infty} \delta(x)e^{ikx}\,dx = [e^{ikx}]_{x=0} = 1$$

F(k)=T(f(x))=T(δ(x))

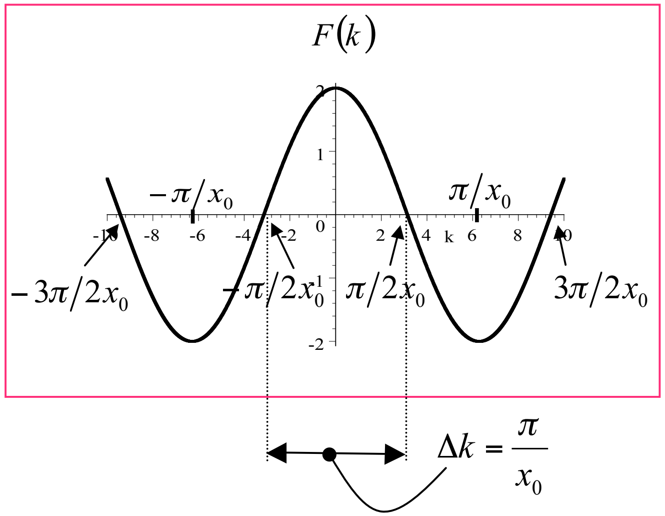


FT of two δ functions

$f(x)=\delta(x+x_0)+\delta(x-x_0)$



$F(k)=2\cos kx_0(x)$



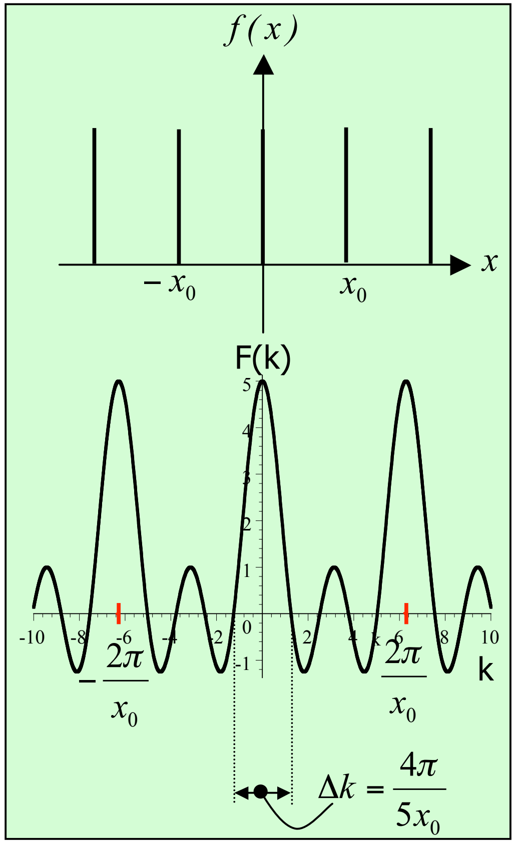
$$F(k) = \int_{-\infty}^{+\infty} f(x)e^{ikx}dx = \int_{-\infty}^{+\infty} (\delta(x+x_0)+\delta(x-x_0))e^{ikx}\,dx =$$

$$= \int_{-\infty}^{+\infty} (\delta(x+x_0))e^{ikx}\,dx + \int_{-\infty}^{+\infty} (\delta(x-x_0))e^{ikx}\,dx$$

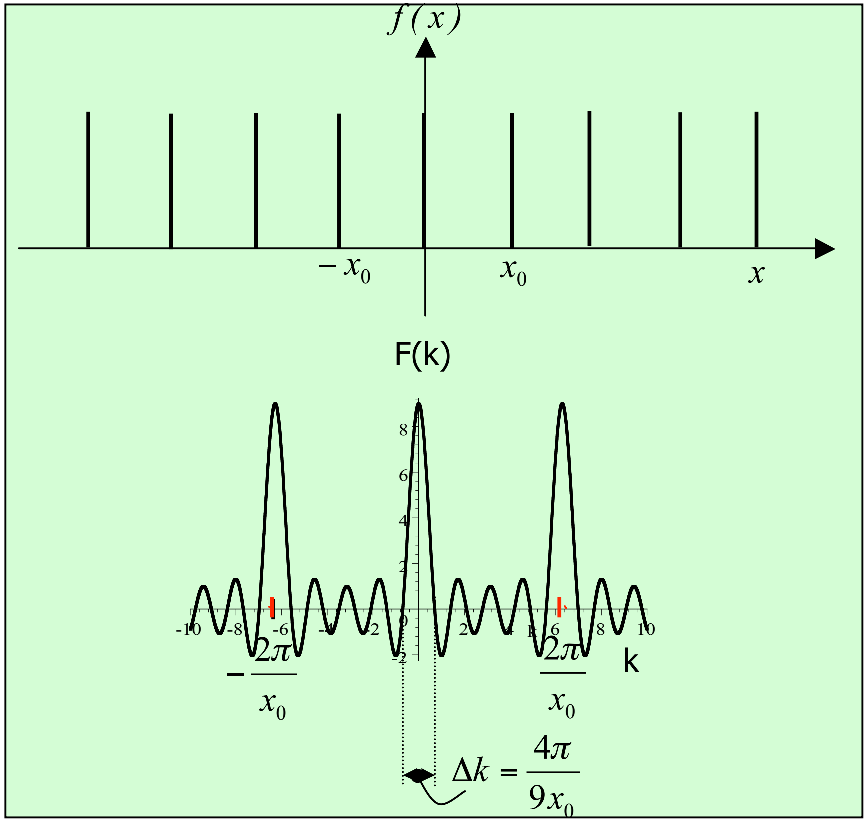
$$= \left[e^{-ikx_0} + e^{+ikx_0}\right] = 2\cos kx_0$$

FT of N δ functions

N=5

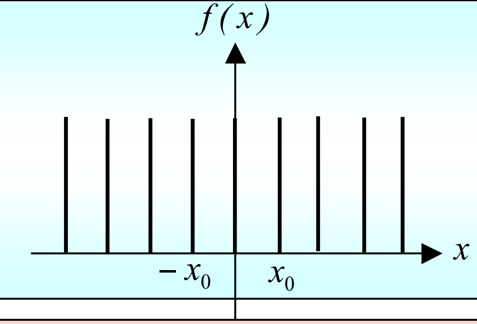


N=9

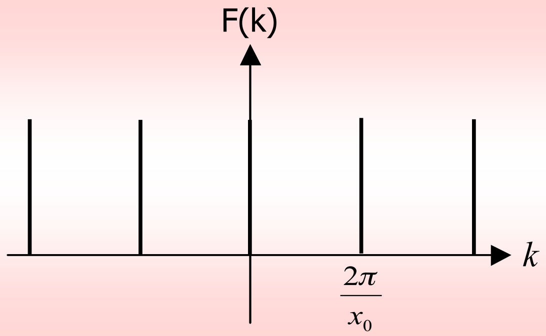


$$F(k) = \frac{\sin \frac{Nkx_0}{2}}{\sin \frac{kx_0}{2}}$$

FT of an infinite series of δ function



$$f(x) = \sum_{n=-\infty}^{n=\infty} \delta(x - nx_0)$$

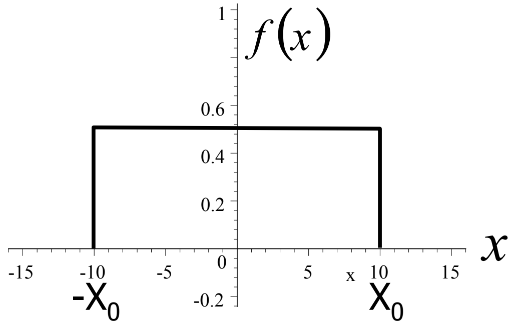


$$F(k) = \sum_{n=-\infty}^{n=\infty} \delta\left(k - 2n\frac{\pi}{x_0}\right)$$

Summary

- The positions of the main peaks in a FT are determined by the spacing x_0 of the δ functions in the original array
- The higher is the number of the δ functions the narrower is the width of the main peak in the FT
- The number of the subsidiary peaks is determined by the total number of the δ functions in the original array

Rectangular window FT

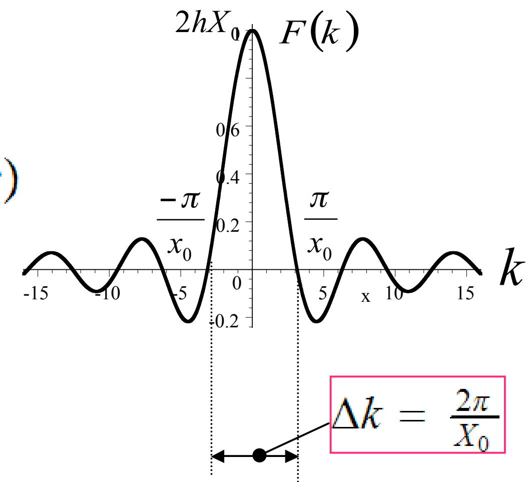


$$F(k) = h\int_{-X_0}^{X_0} e^{ikx}dx = h\left[\frac{e^{ikx}}{ik}\right]_{-X_0}^{X_0} = h\,\frac{e^{ikX_0}-e^{-ikX_0}}{ik}$$

⇨ $\sin\alpha = \frac{e^{i\alpha}-e^{-i\alpha}}{2i} \qquad \alpha = kX_0$

⇨ $$F(k) = 2hX_0\,\frac{\sin kX_0}{kX_0}$$

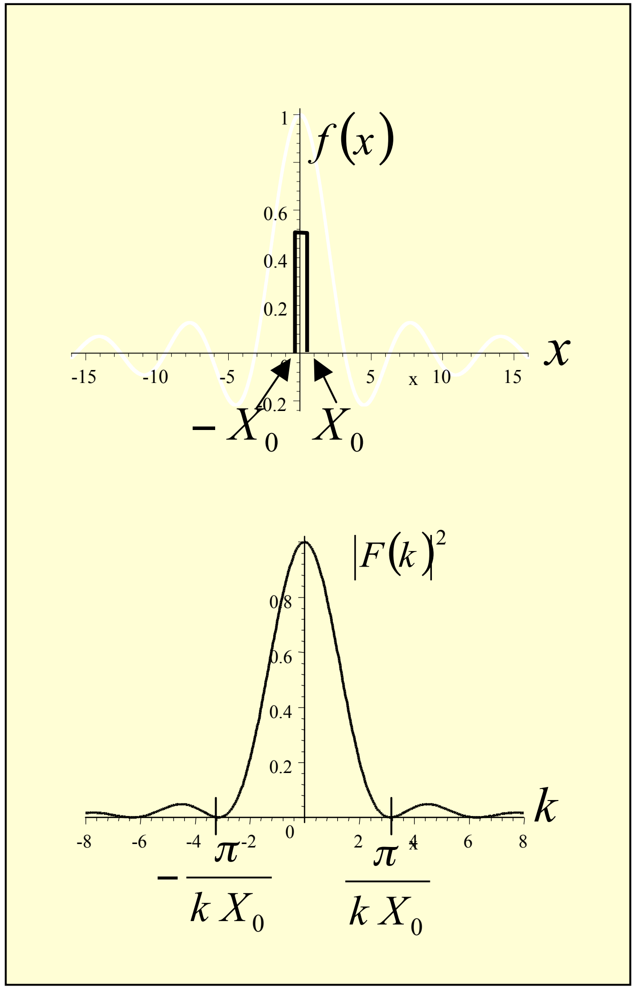
⇨ $F(k) = Tf(x)$



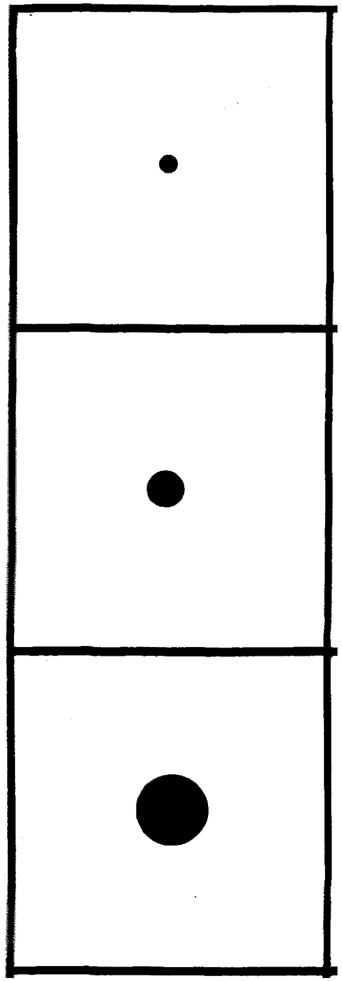
$\Delta k = \frac{2\pi}{X_0}$

The more extended f(x) the narrower F(k)

Diffraction by one wide slit



Real space



Holes on black paper

Reciprocal space

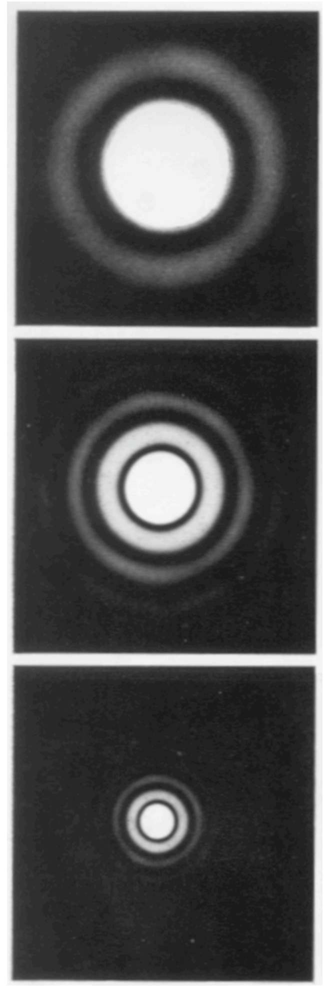
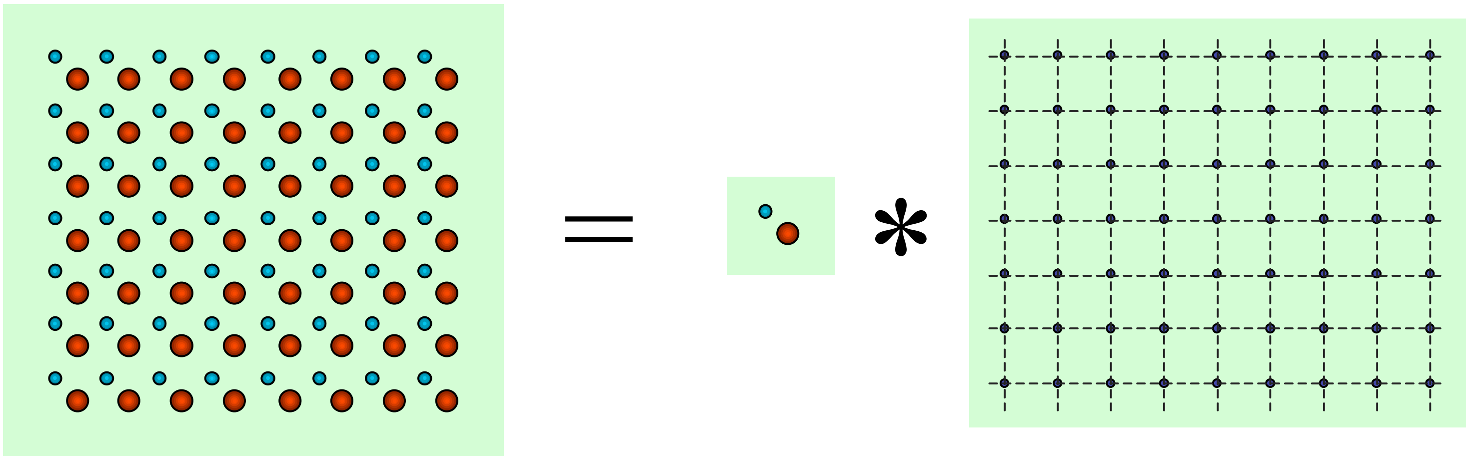


Image on film

Crystalline Structure

as a convolution



Crystal = Base * Lattice

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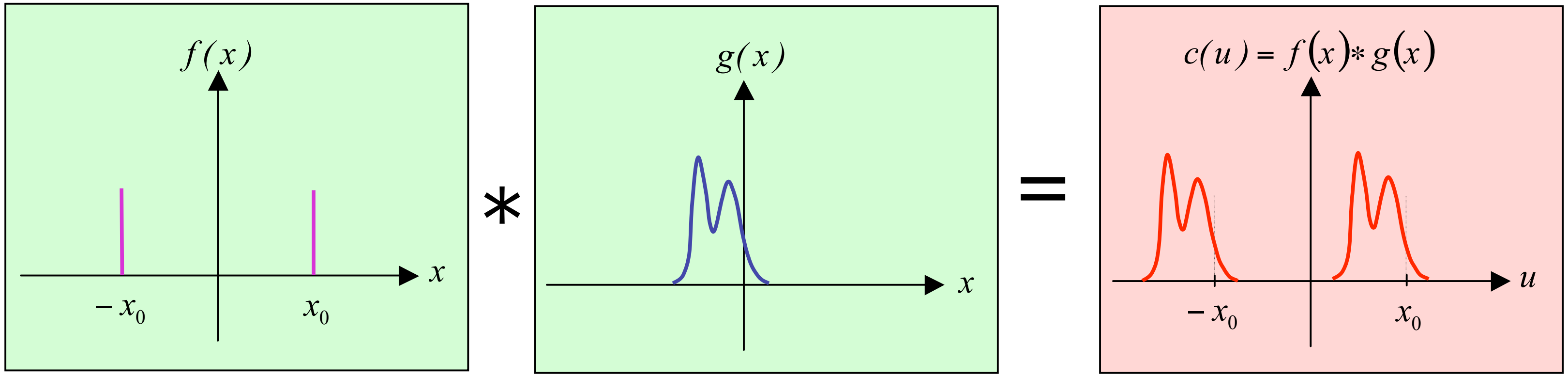
Convolution Integral

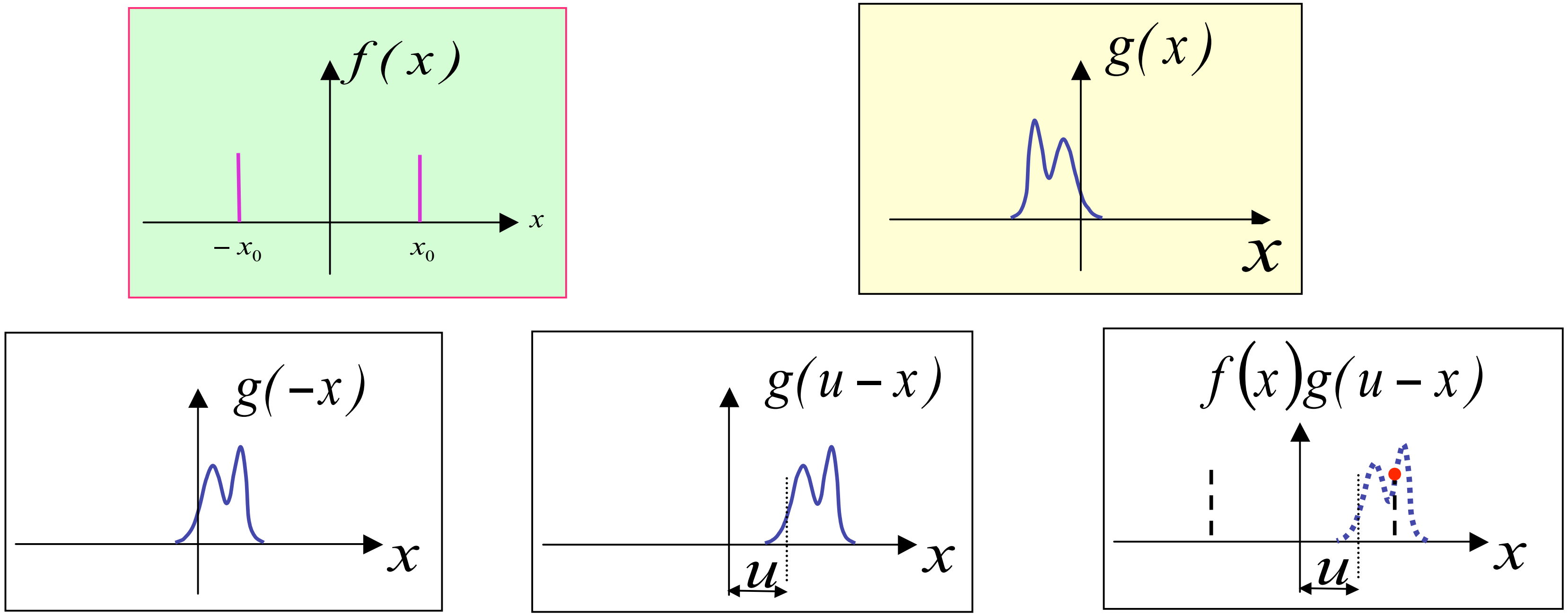


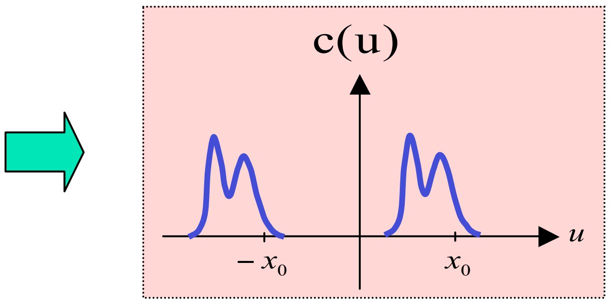
$$c(u) = \int_x f(x)\, g(u - x)\, dx$$

c(**u**) is the convolution integral of f(x) e g(x)

Convolution function

$$c(u) = \int_x f(x)\, g(u-x)\, dx$$



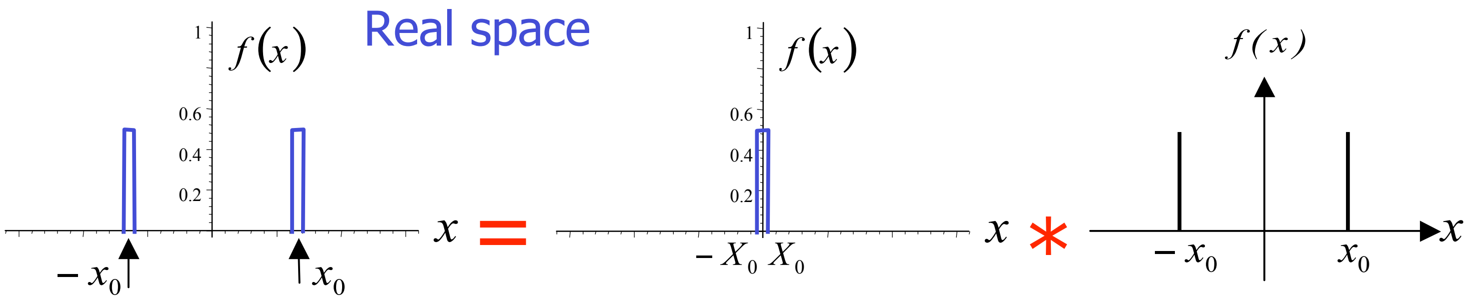


$$c(u) = f(x) * g(x)$$

a theorem about convolution

$$T\big(f(x) * g(x)\big) = T\big(f(x)\big) \times T\big(g(x)\big)$$

Diffraction by two wide slits



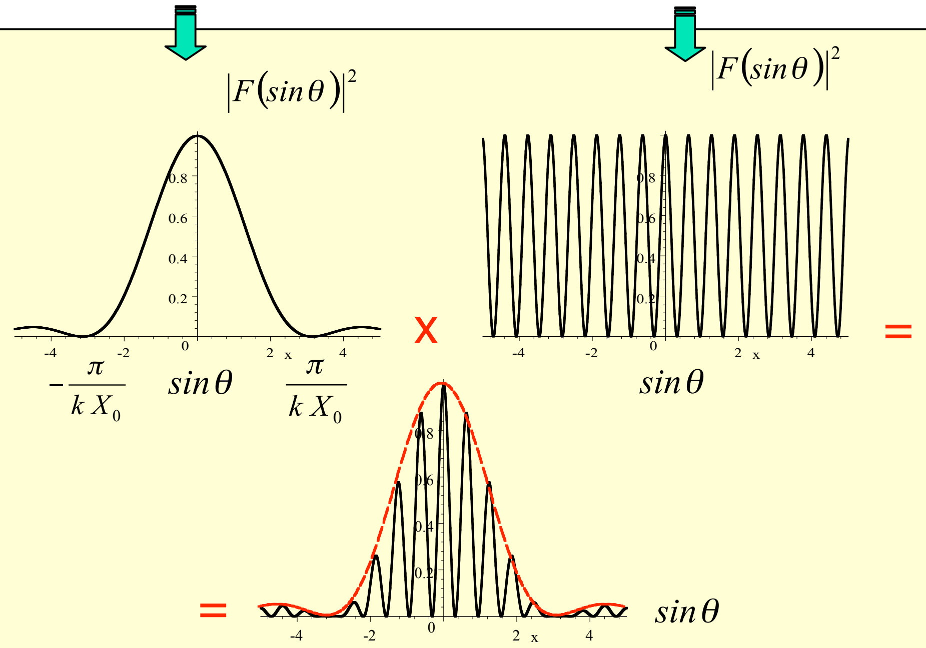
f(2 wide slits) = f(1 wide slit) * f(2 narrow slits)

Reciprocal space

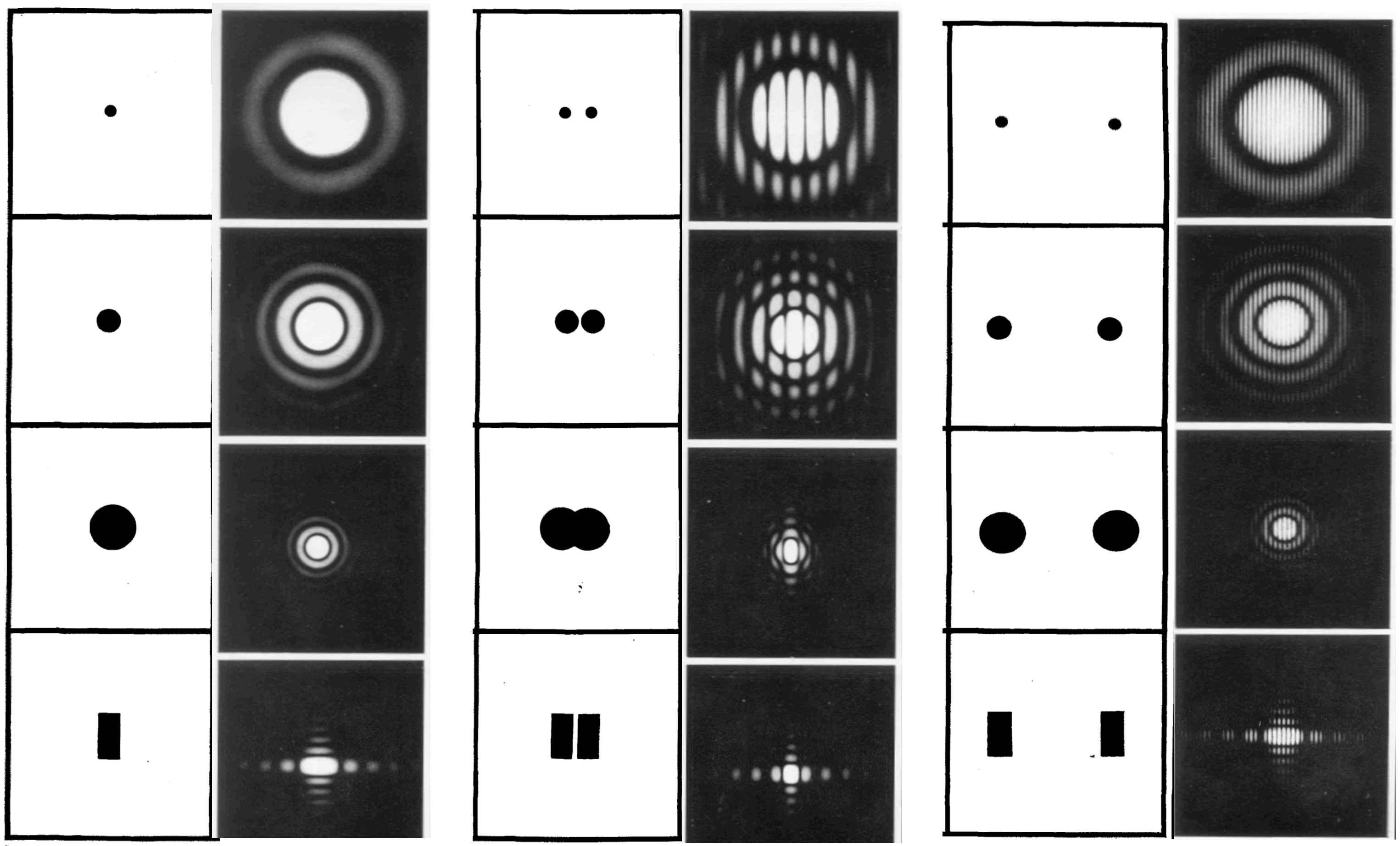
T f(2 wide slits) =

= T [f(1 wide slit)*Tf(2 narrow slits)]=

= T f(1 wide slit) x T f(3 narrow slit)



Two slits diffraction



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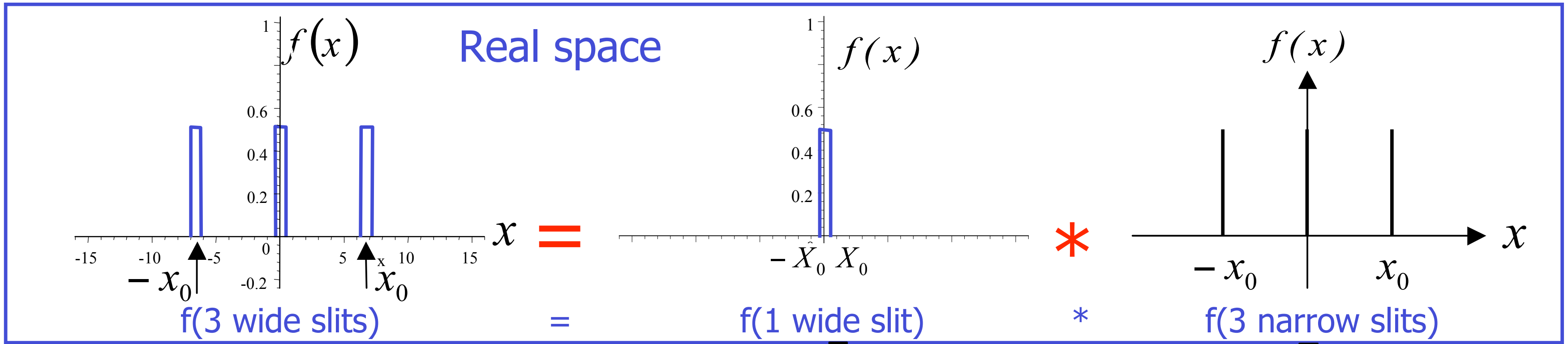
Diffraction by three wide slits

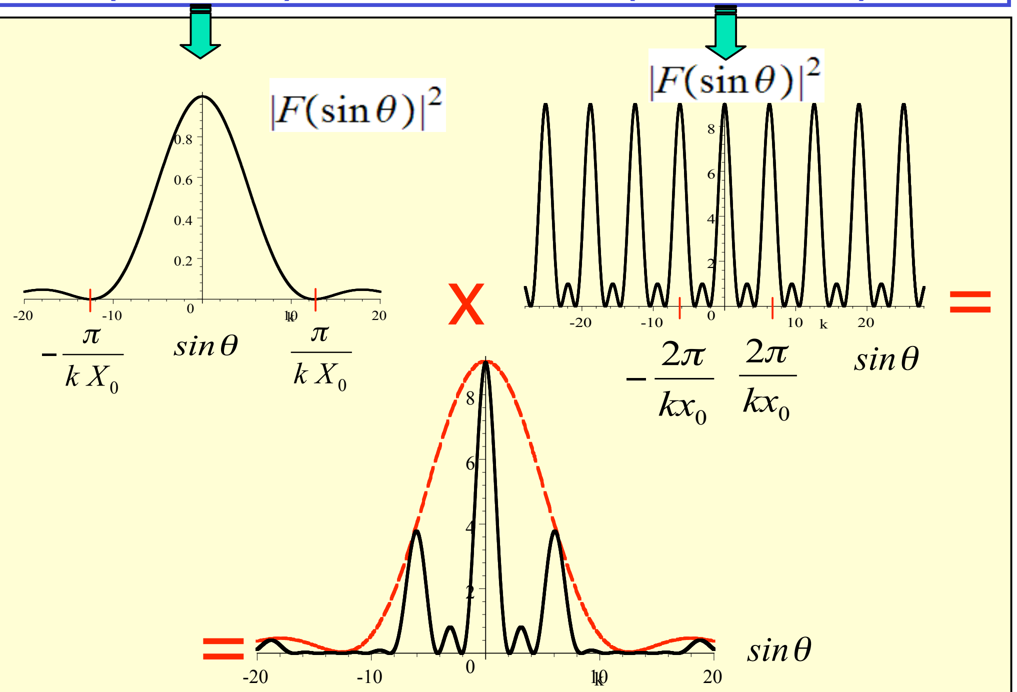


Reciprocal space

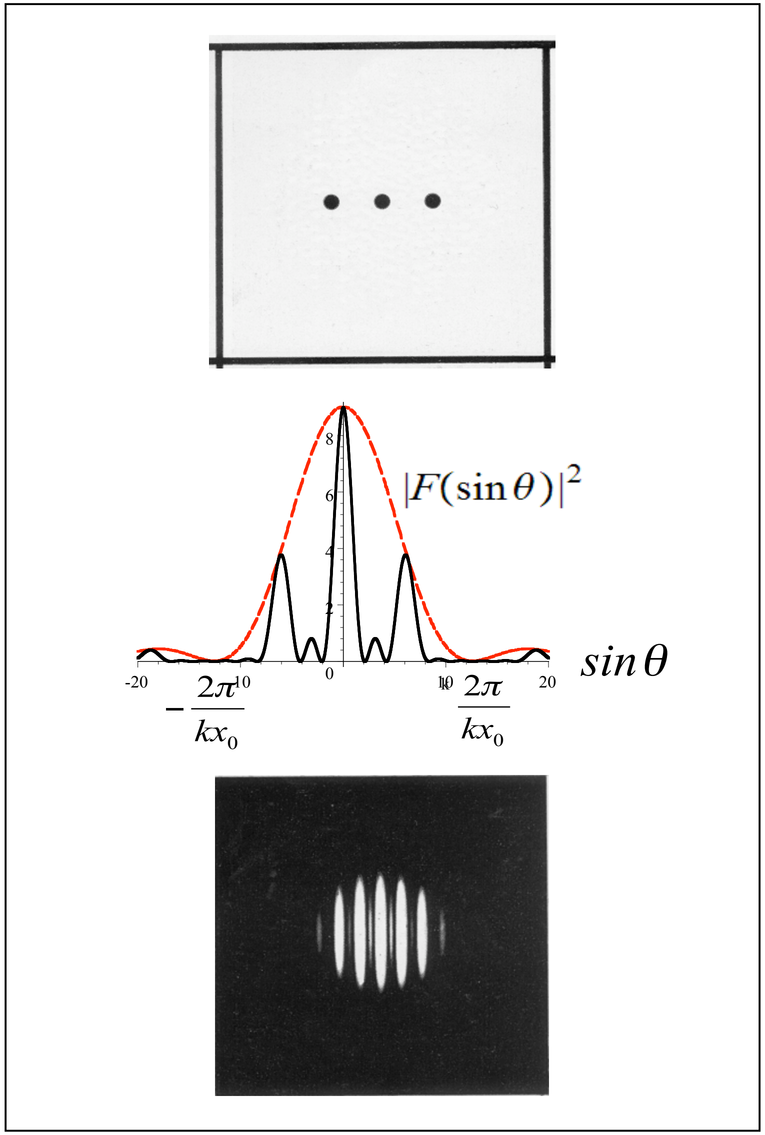
T f(3 wide slits) =

= T [f(1 wide slit) * f(3 narrow slit)]=

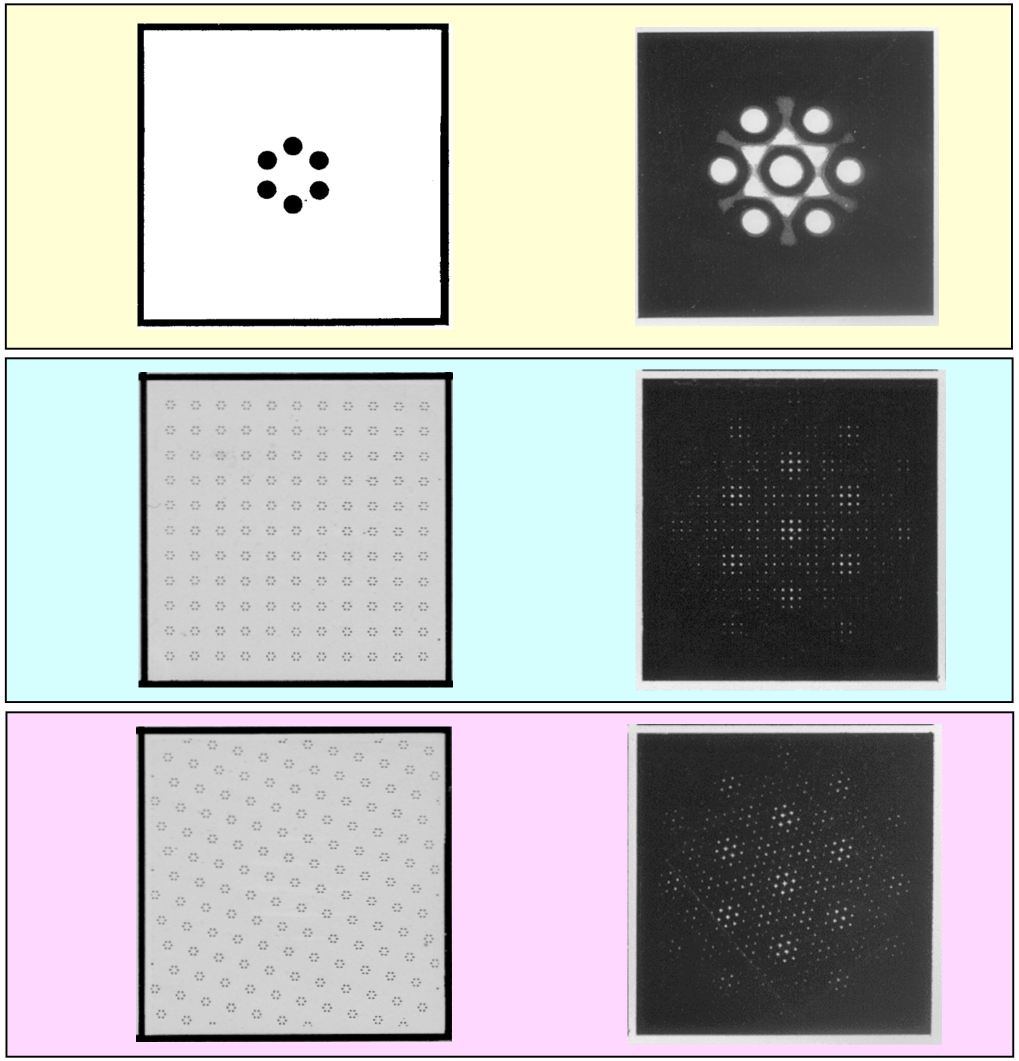
= T f(1 wide slit) x T f(3 narrow slit)



Three slits diffraction



Hypothetical benzene molecular crystals



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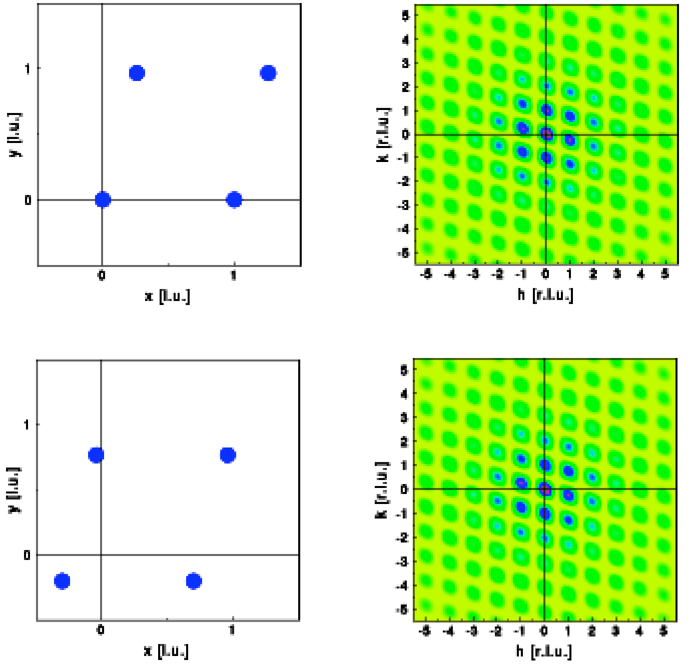
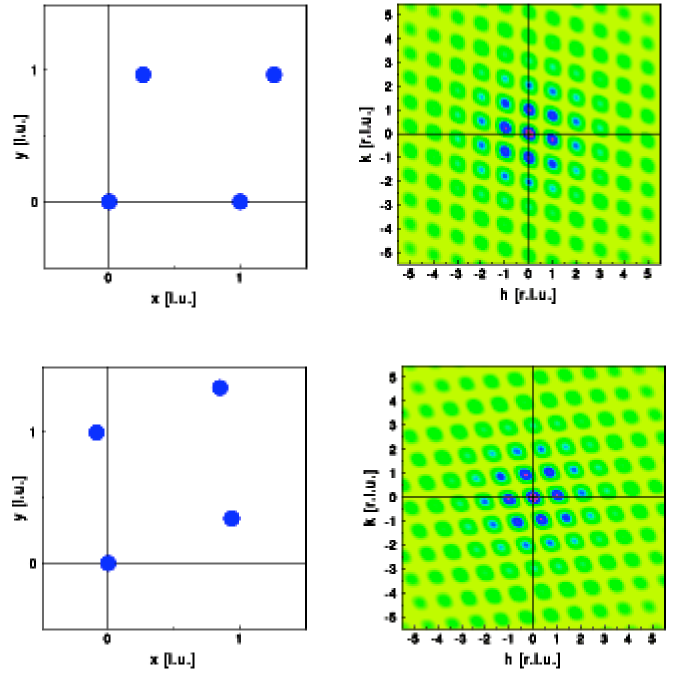
Traslation and Rotation

TRANSLATION



Any translation in the real space is not observed in the reciprocal Space.

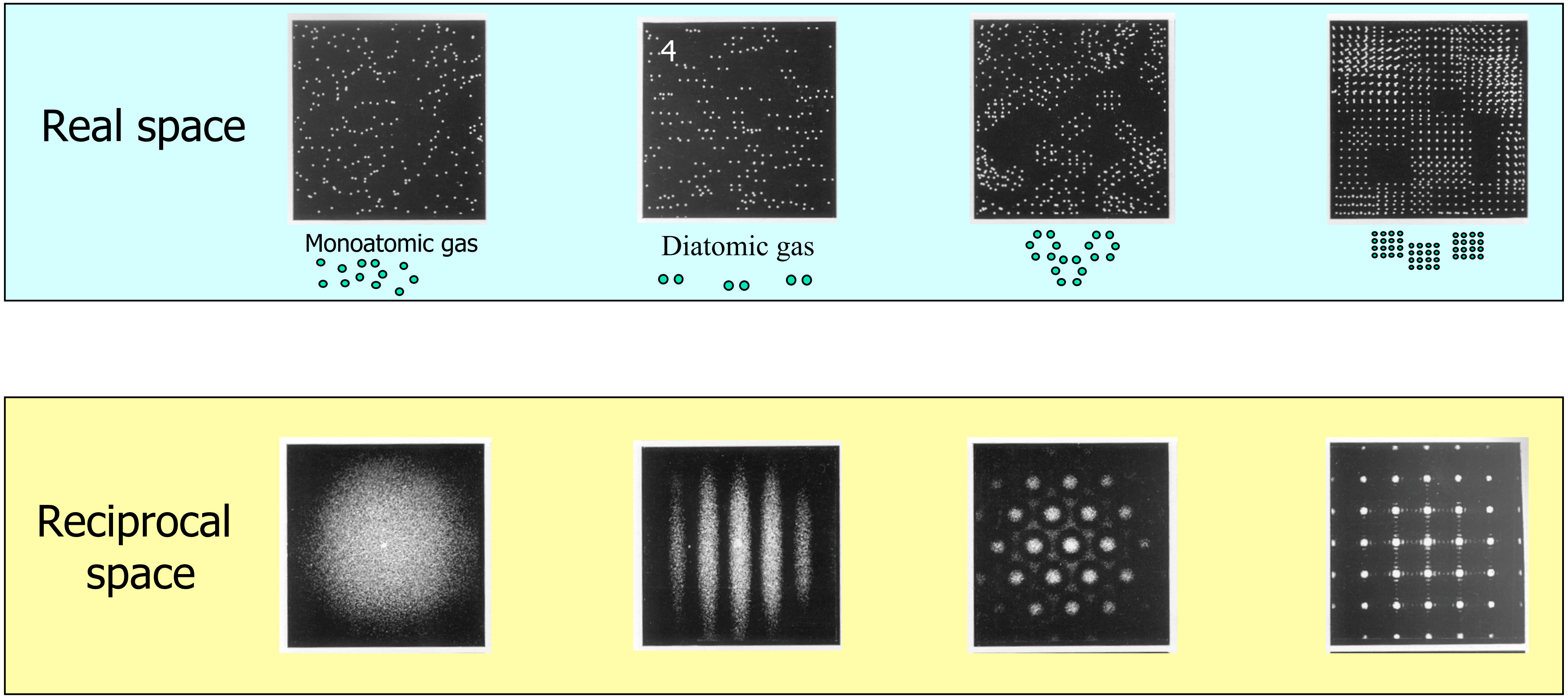
ROTATION



A rotation in direct space causes an identical rotation in reciprocal space.

Gas and powder patterns

TRANSLATION



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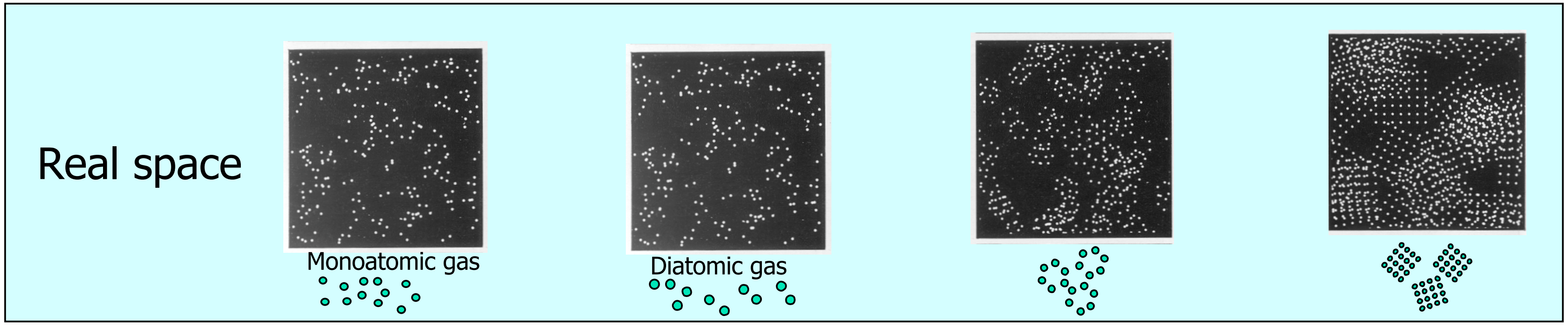
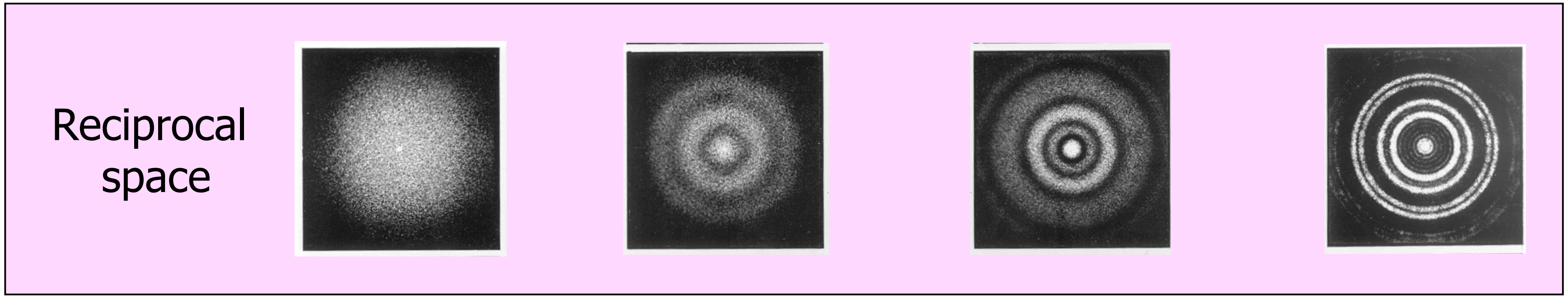
Gas and powder patterns

ROTATION





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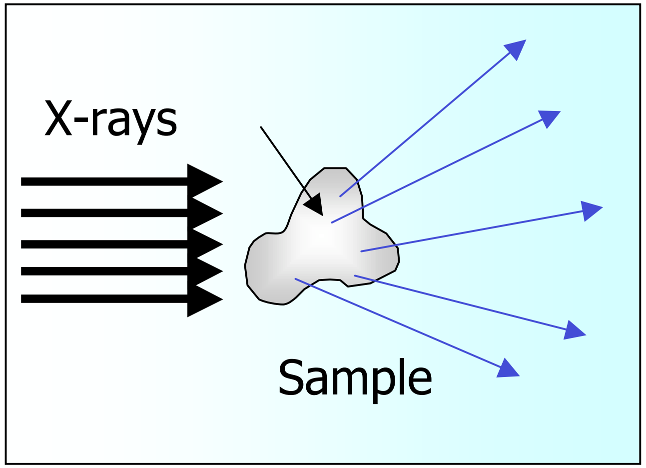
Rotating crystal method, Powder method, Laue method
The temperature effect

Mathematical Fourier-backtransform

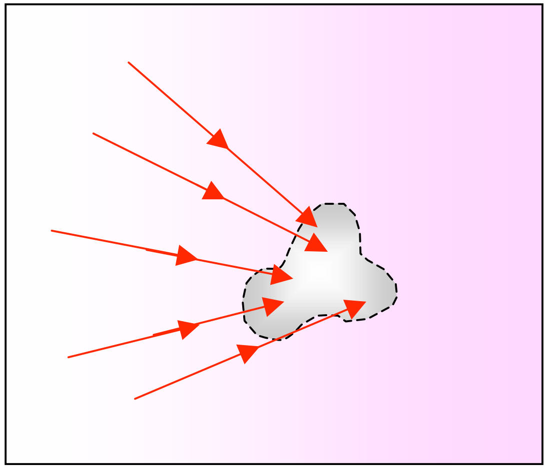
…still no lenses for atomic X-rays "microscopy"



Data collection

+

Back-Fourier transformation



Data collection

$$F(\mathbf{k}) = \int_{\mathbf{k}} f(\mathbf{r})\, e^{i\,\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}$$

⇩

X-ray diffractometer

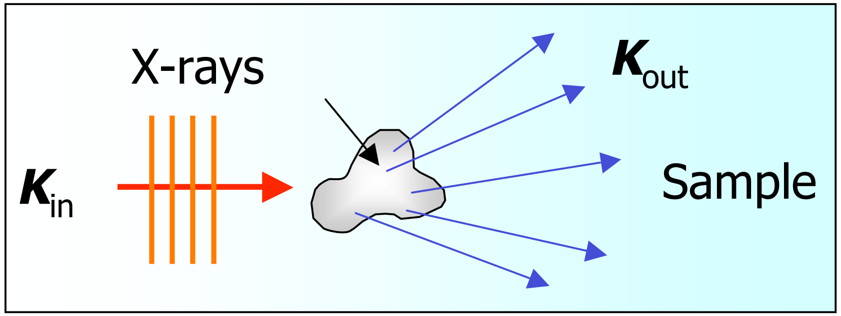
Back-Fourier transformation

$$f(\mathbf{r}) = \int_{\mathbf{r}} F(\mathbf{k})\, e^{-i\,\mathbf{k}\cdot\mathbf{r}} d\mathbf{k}$$

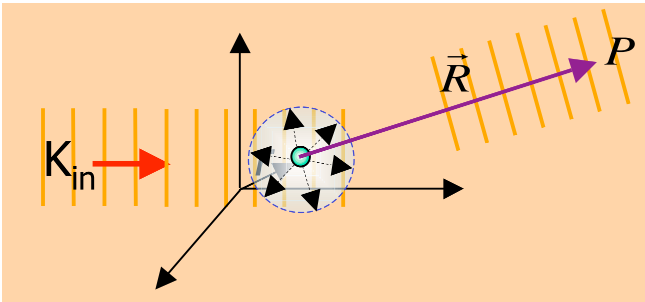
⇩

Computer

Scattering amplitude of electrons



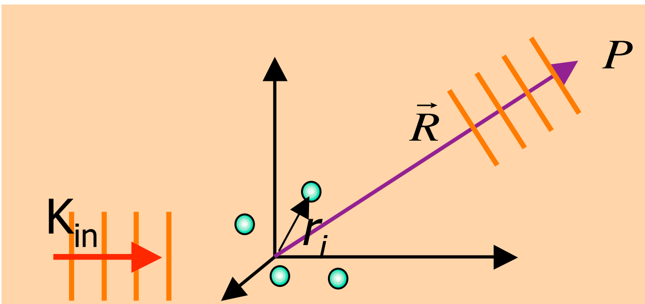
Sample = 1 electron



$$A(\vec{K}) = -E_0 r_e \frac{e^{-ik_{out}R}}{R} e^{i\omega t} e^{i\vec{K}\cdot\vec{r}}$$

$$= A_{el}\, e^{i\vec{K}\cdot\vec{r}}$$

Sample = n electrons



$$A(\vec{K}) = A_{el} \sum_i e^{i\vec{K}\cdot\vec{r}_i}$$

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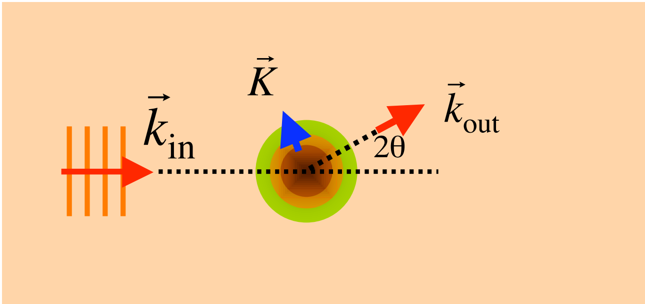
Scattering from an atom

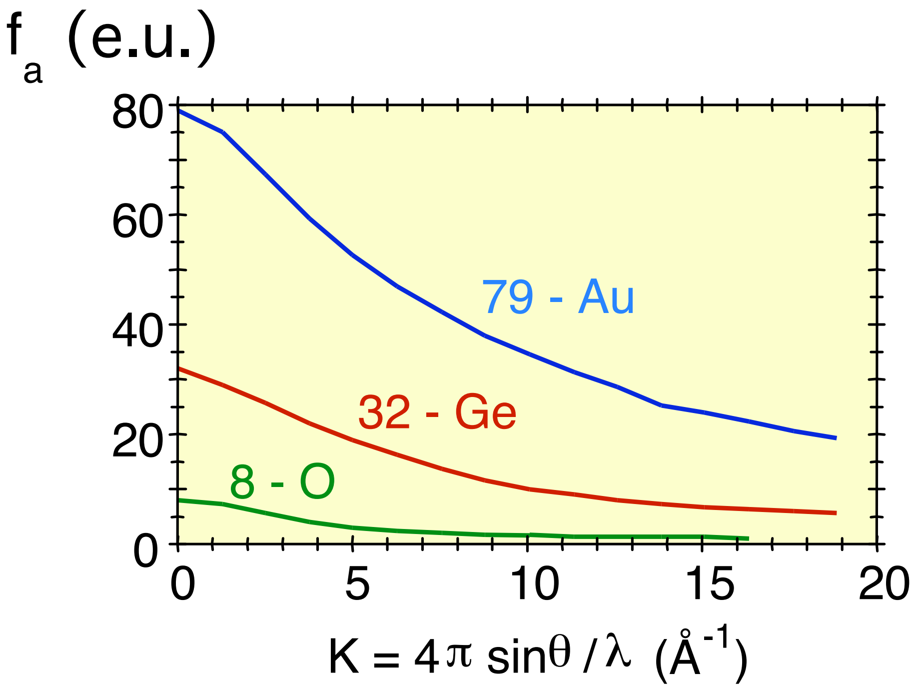
Sample = 1 atom



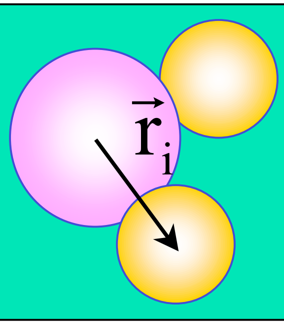
$$f_a(\vec{K}) = \int \rho(\vec{r})\, e^{i\vec{K}\cdot\vec{r}} dV$$

Atomic form function

$$f_a = \begin{cases} Z & \text{for } K \to 0 \\ 0 & \text{for } K \to \infty \end{cases}$$



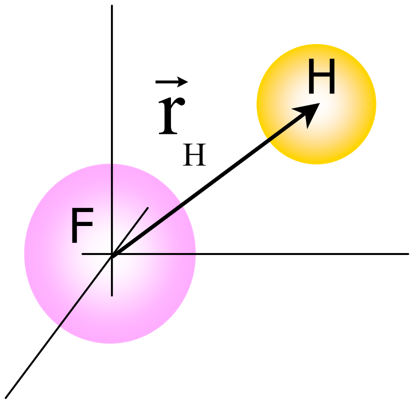
Diffraction from a molecule



Molecular form factor

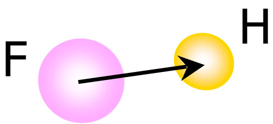
$$F_{mol} = \sum_{r_i} f_{ai}\left(\vec{K}\right) e^{i\vec{K}\vec{r}_i}$$

Diatomic molecule



$$F_{HF}\left(\vec{K}\right) = f_F\ e^{i\vec{K}\cdot\vec{r}_F} + f_H\ e^{i\vec{K}\cdot\vec{r}_H} = f_F + f_H\ e^{i\vec{K}\cdot\vec{r}_H}$$

Orientational averaging

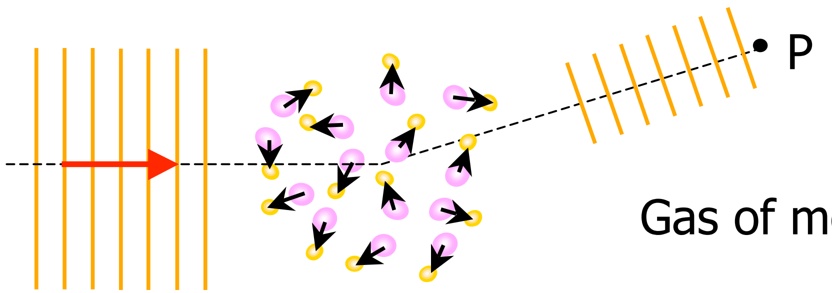


$\vec{r}_H$ = constant

Spatial orientation = random

$$F_{HF}(\vec{K}) = f_F + f_H\, e^{i\vec{K}\cdot\vec{r}_H}$$

$$I(\vec{K}) = F_{HF}(\vec{K})F_{HF}^{*}(\vec{K}) =$$
$$= f_F^{\,2} + f_H^{\,2} + f_F f_H e^{i\vec{K}\cdot\vec{r}_H} + f_F f_H e^{-i\vec{K}\cdot\vec{r}_H}$$

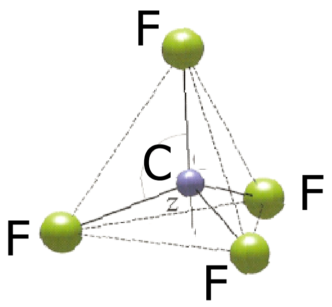


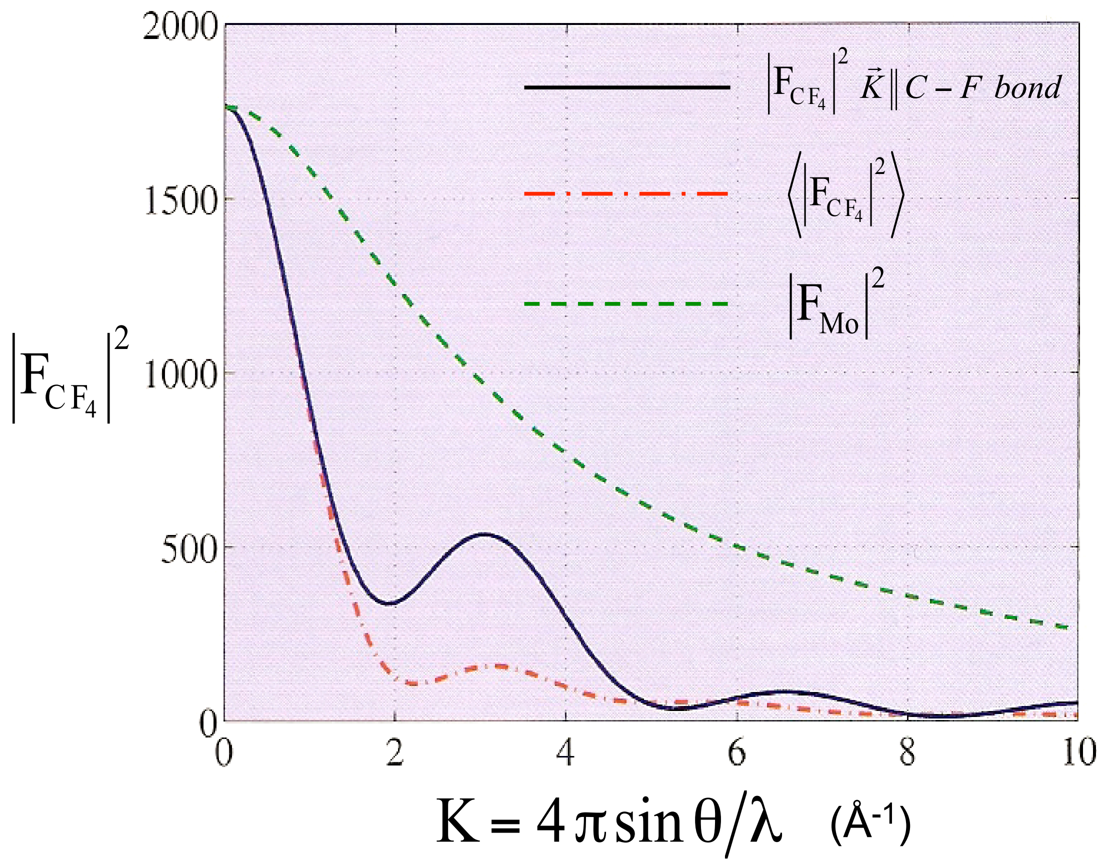
Gas of molecules

$$\left\langle I(\vec{K})\right\rangle_{Orientational\ average} = f_F^{\,2} + f_H^{\,2} + 2 f_F f_H \left\langle e^{-i\vec{K}\cdot\vec{r}_H}\right\rangle_{orientational\ average}$$

$$= f_F^{\,2} + f_H^{\,2} + 2 f_F f_H \frac{\sin \vec{K}\cdot\vec{r}_H}{\vec{K}\cdot\vec{r}_H}$$

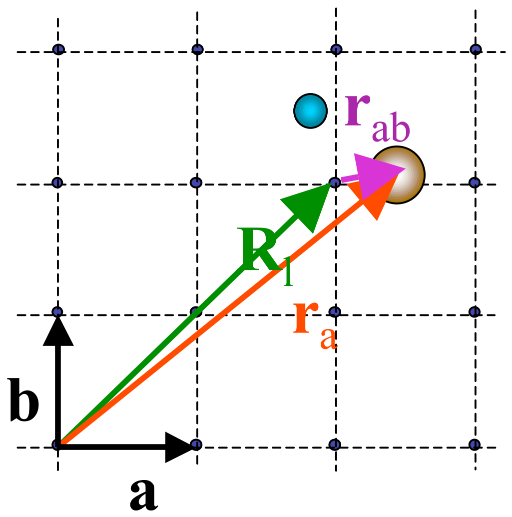
The case of CF_4 molecules





Mo has the same number of electrons of the CF_4 molecule

Scattering factor of a crystal



$\mathbf{r}_a$ locates each atom of the crystal,
$\mathbf{R}_l$ locates a generic lattice point,
$\mathbf{r}_{ab}$ locates the position of each atom within the base

$\mathbf{r}_a = \mathbf{R}_l + \mathbf{r}_{ab}$ $\quad\quad$ $\mathbf{R}_l = l_1\mathbf{a}+l_2\mathbf{b}+l_3\mathbf{c}$

$$f_{CR} = \sum_{\text{elettrons}} e^{i\vec{K}\vec{r}_l} = \sum_{r_a} e^{i\vec{K}\vec{r}_a} = \sum_{R_l} e^{i\vec{K}\left(\vec{R}_l+\vec{r}_{ab}\right)} = \sum_{R_l} e^{i\vec{K}\vec{R}_l} \sum_{r_{ab}} e^{i\vec{K}\vec{r}_{ab}} = L\cdot F$$

$$f_{CR} = \sum_{R_l} e^{i\vec{K}\vec{R}_l} \sum_{r_{ab}} e^{i\vec{K}\vec{r}_{ab}} = L\cdot F$$

$$L = \sum_{R_l} e^{i\vec{K}\vec{R}_l} \quad\quad F = \sum_{r_{ab}} e^{i\vec{K}\vec{r}_{ab}}$$

The atomic structure factor

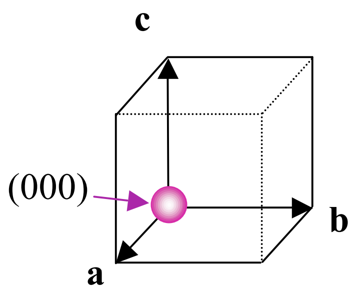
$$F = \sum_{r_{ab}} e^{i\vec{K}\vec{r}_{ab}} = \sum_j f_j e^{2\pi i\left(h x_j + k y_j + l z_j\right)}$$

x_j, y_j, z_j = fractional positions in the unit cell

F is independent on the shape and size of the unit cell.

Simple cubic structure (a-Polonium)

One atom per cell located at: $(x_j, y_j, z_j) = (0,0,0)$



$$F = f\, e^{2\pi i\left(h0 + k0 + l0\right)} = f$$

All the reflections are allowed

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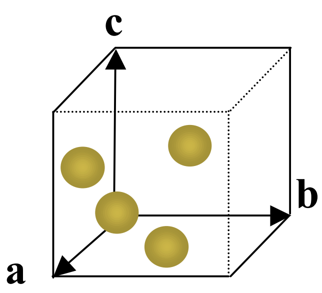
The structure factor (fcc)

Face-centered cubic (Cu structure)



4 atoms per cell located at:

$(x_j, y_j, z_j) =$ (000), (_ _ 0), (0 _ _), (_ 0 _)

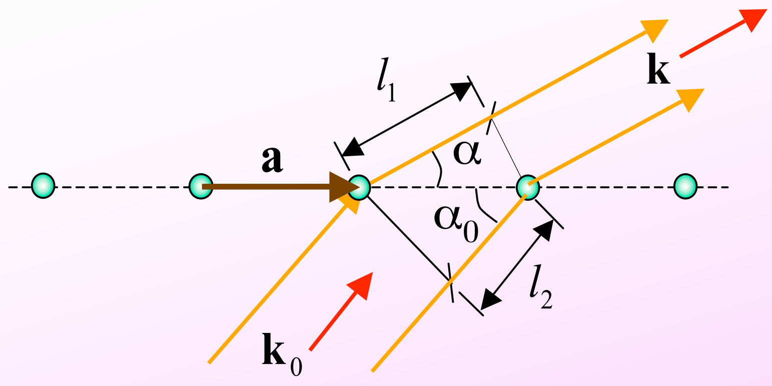
$$F = f\left[1 + f\,e^{\pi i(h+k)} + f\,e^{\pi i(h+l)} + f\,e^{\pi i(k+l)}\right]$$

- *h, k, l* all even or all odd (unmixed) _ F=4 *f*
- *h, k, l* mixed _ F=0

Allowed reflections: the unmixed ones, i.e. (111), (200), (220), …

Forbidden reflections: (100), (110), (311), (210),

Linear array of atoms

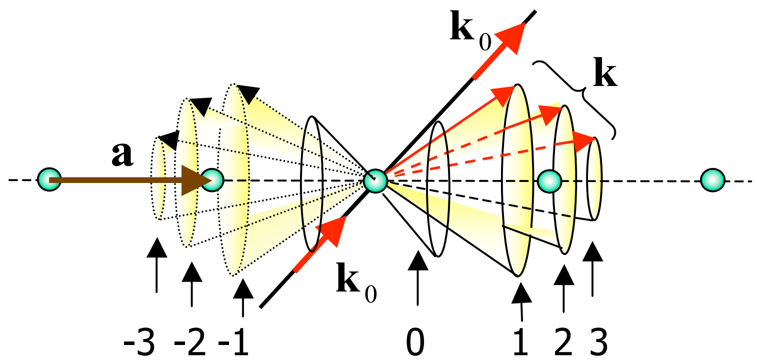


Constructive interference

$$l_1 - l_2 = n_1 \lambda$$

$$a\left(\cos\alpha_0 - \cos\alpha\right) = \pm h\lambda$$

$$h = 0, 1, 2, \ldots$$

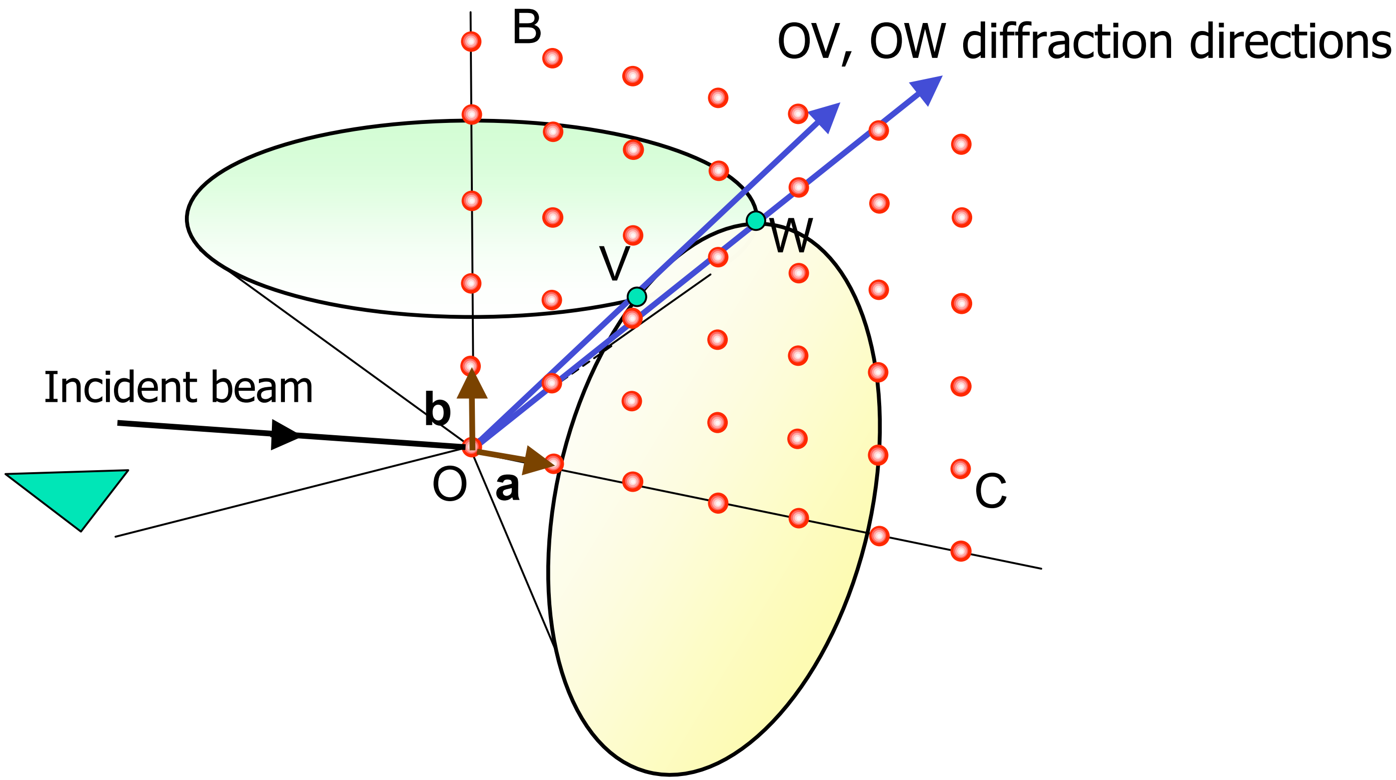


How many Laue cones?

$$\text{max value of } \left(\cos\alpha_0 - \cos\alpha a\right) = 2$$

$$\Rightarrow\ 2a = h_{max}\lambda \ \Rightarrow\ h_{max} = 2a/\lambda$$

Diffraction by a plane array of atoms

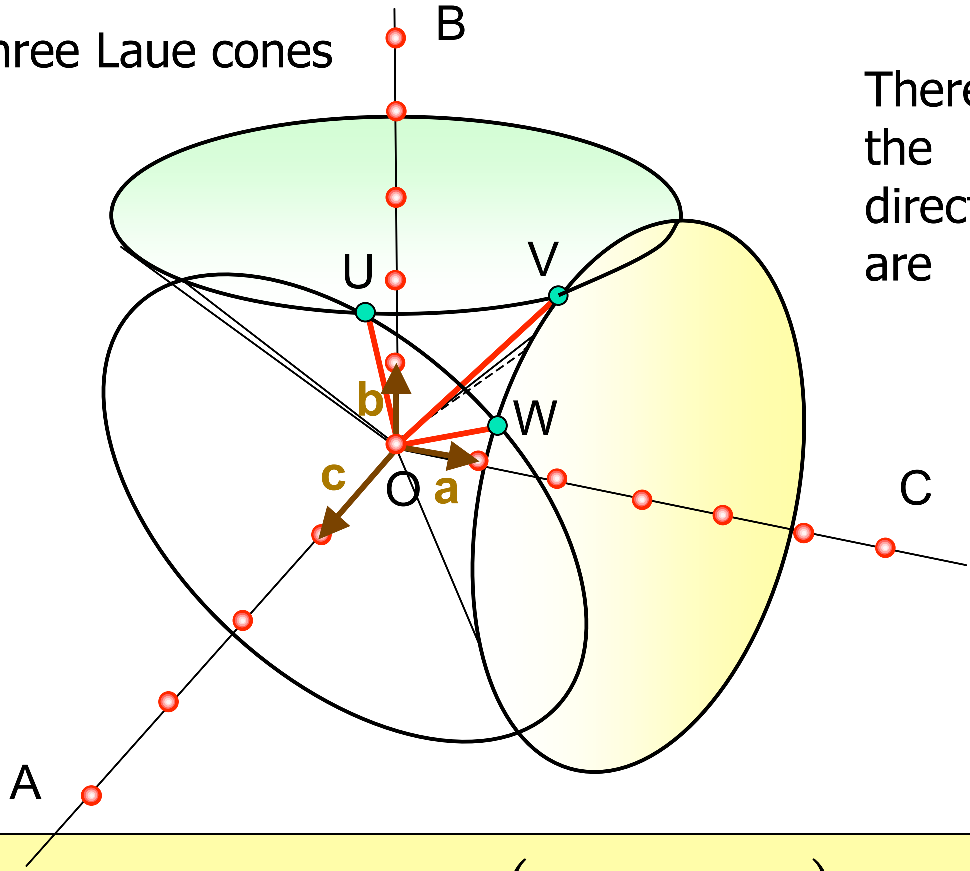


Laue conditions:

$$\begin{cases} a(\cos\alpha_0 - \cos\alpha) = \pm h\lambda & h = 0,1,2,\ldots \\ b(\cos\beta_0 - \cos\beta) = \pm k\lambda & k = 0,1,2,\ldots \end{cases}$$

Diffraction by a 3 dimensional lattice array of atoms

The three Laue cones

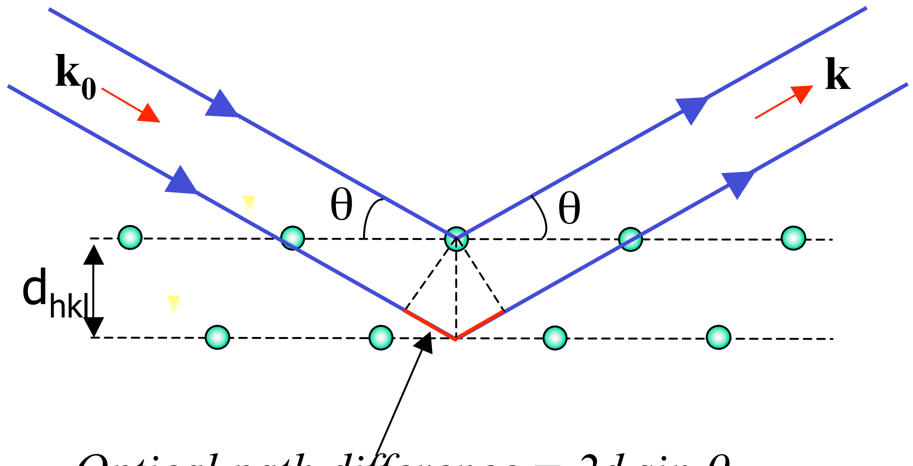


There will be diffraction only under the special condition that the directions O-U. O-V and O-W are coincident

Laue conditions:

$$\begin{cases} a\left(\cos\alpha_0 - \cos\alpha\right) = \pm h\lambda & h = 0,1,2,\ldots \\ b\left(\cos\beta_0 - \cos\beta\right) = \pm k\lambda & k = 0,1,2,\ldots \\ c\left(\cos\chi_0 - \cos\chi\right) = \pm l\,\lambda & l = 0,1,2,\ldots \end{cases}$$

Bragg Law



Optical path difference = 2d sin θ

Constructive interference: *Optical path difference* $= n\,\lambda$, $n \in \mathbf{N}$

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

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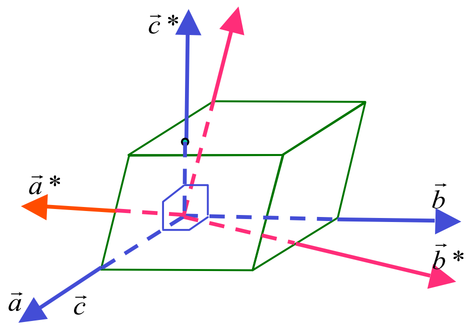
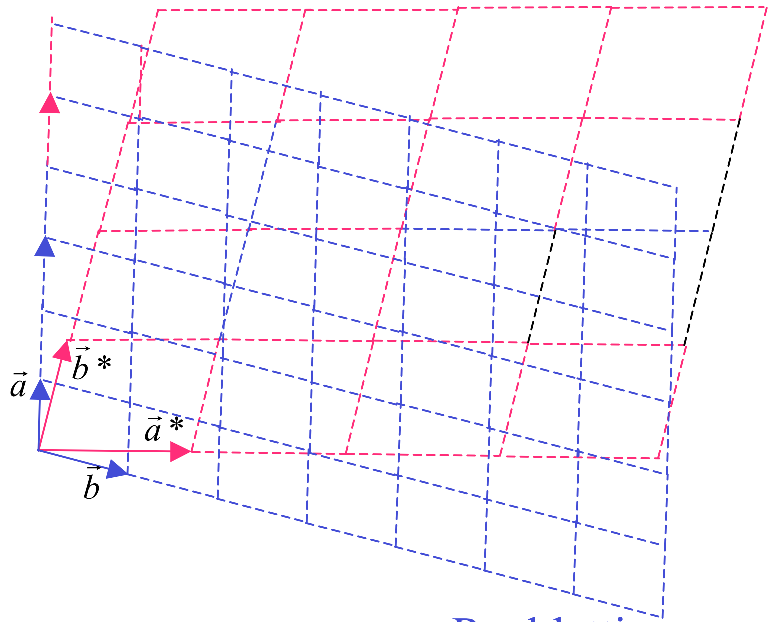
Reciprocal lattice

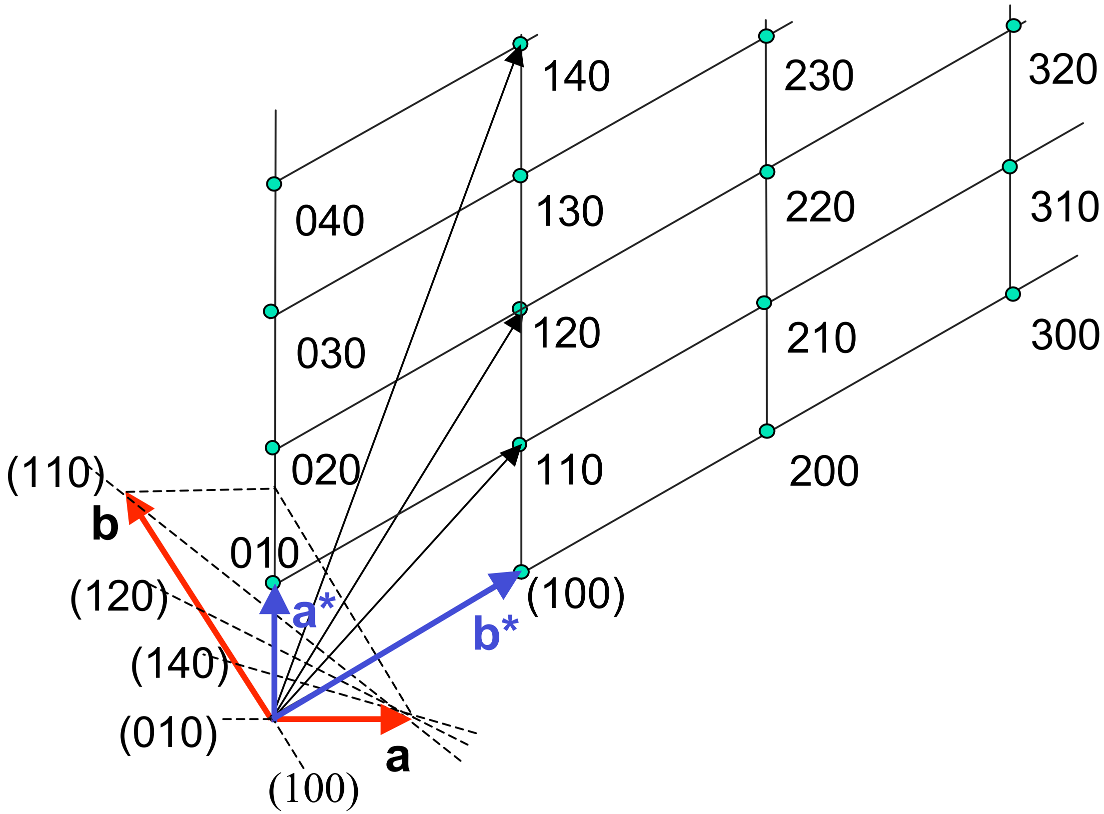
Every real lattice has its own reciprocal lattice

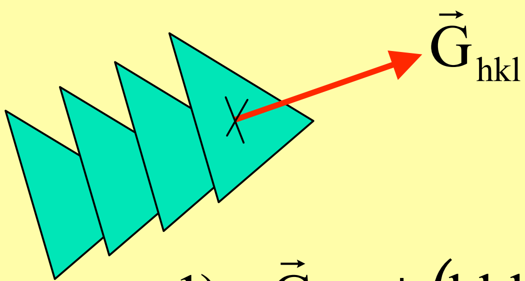
$$\vec{a}^* = 2\pi \frac{\vec{b}\times\vec{c}}{\vec{a}\cdot\vec{b}\times\vec{c}}, \quad \vec{b}^* = 2\pi \frac{\vec{c}\times\vec{a}}{\vec{a}\cdot\vec{b}\times\vec{c}} \quad \vec{c}^* = 2\pi \frac{\vec{a}\times\vec{b}}{\vec{a}\cdot\vec{b}\times\vec{c}}$$



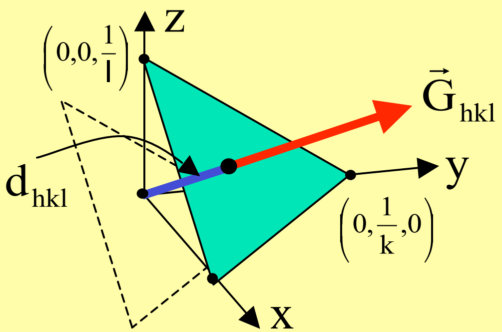


Reciprocal lattice construction and properties





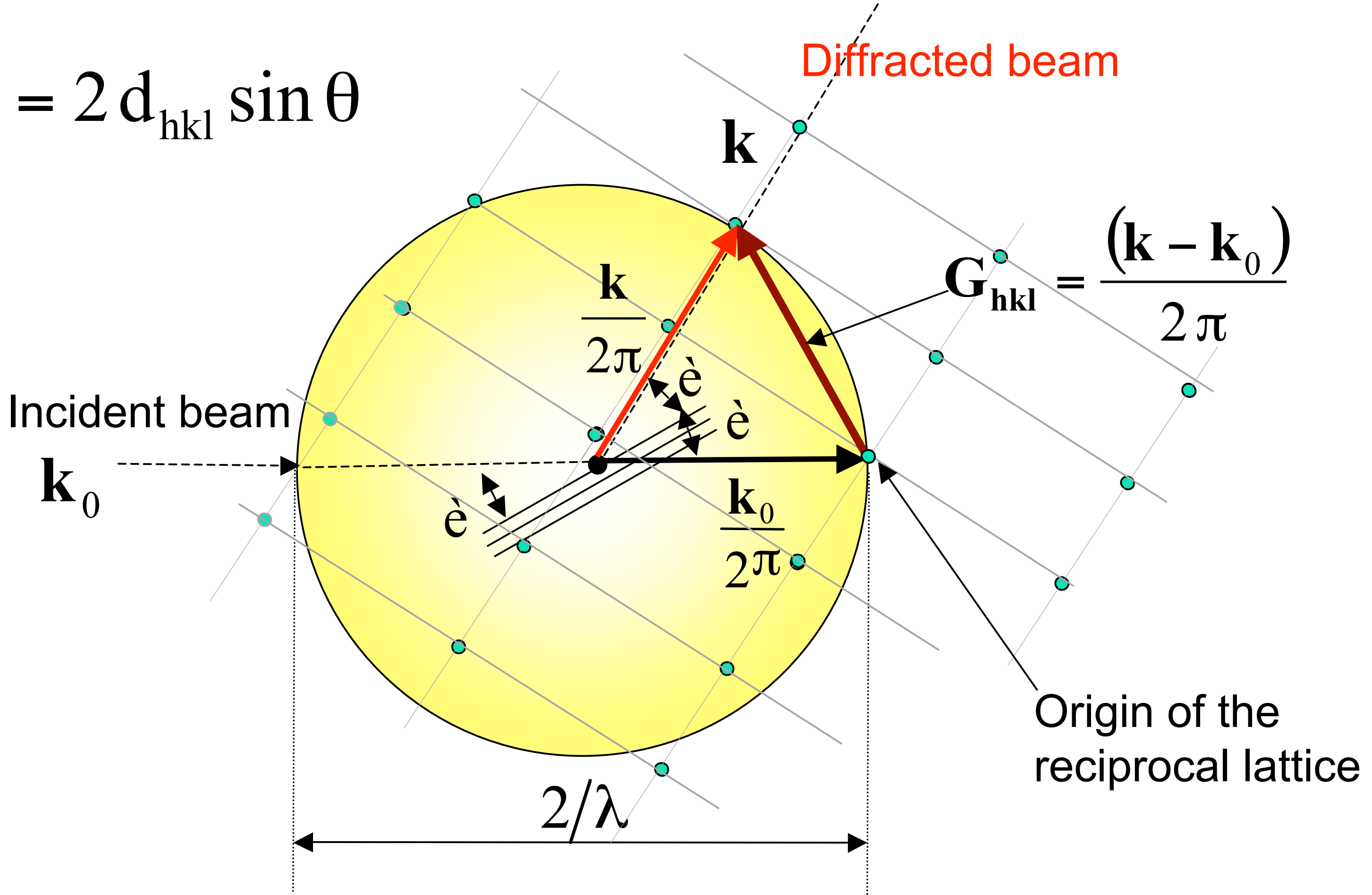
1) $\vec{G}_{hkl} \perp (hkl)$ planes



2) $G_{hkl} = \frac{1}{d_{hkl}}$

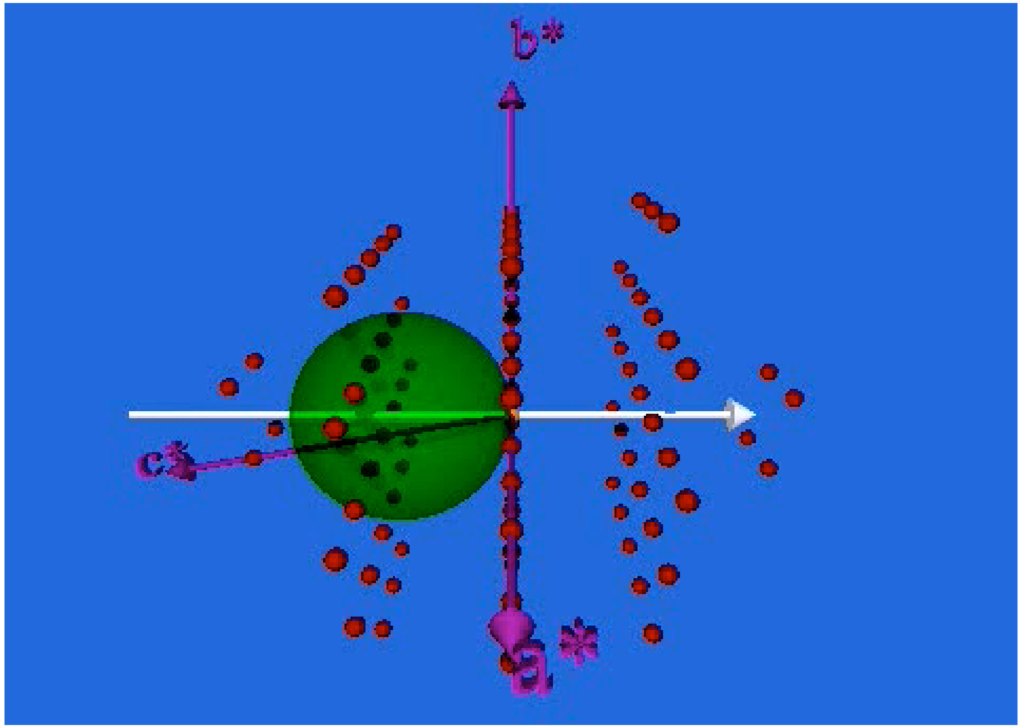
Ewald Sphere

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

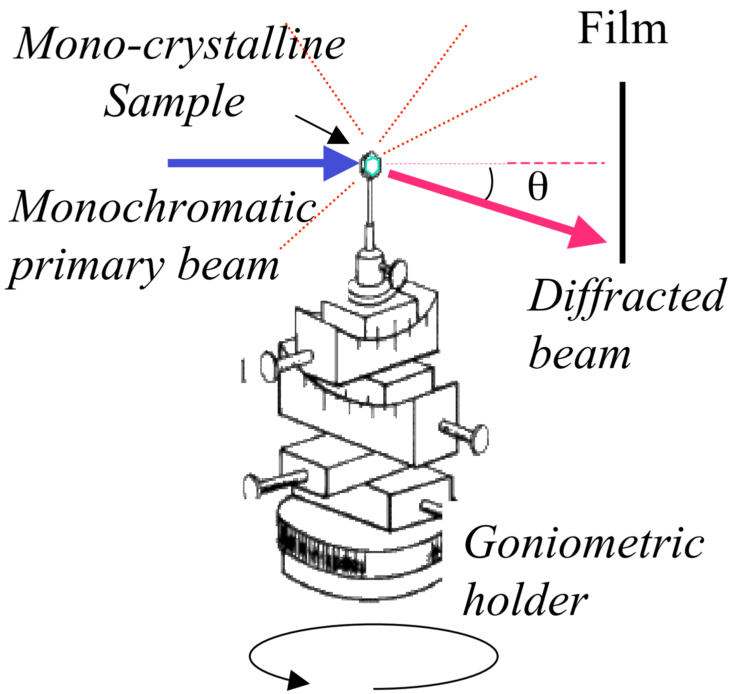


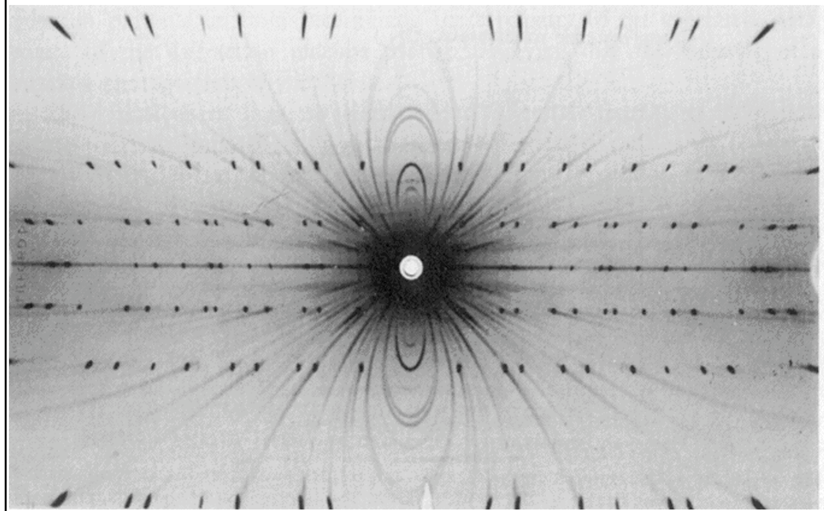
$$\mathbf{G}_{hkl} = \frac{(\mathbf{k}-\mathbf{k}_0)}{2\pi} \Rightarrow \frac{1}{d_{hkl}} = \frac{1}{2\pi}\frac{4\pi\sin\theta}{\lambda} \Rightarrow \lambda = 2\, d_{hkl}\sin\theta$$

Ewald Sphere



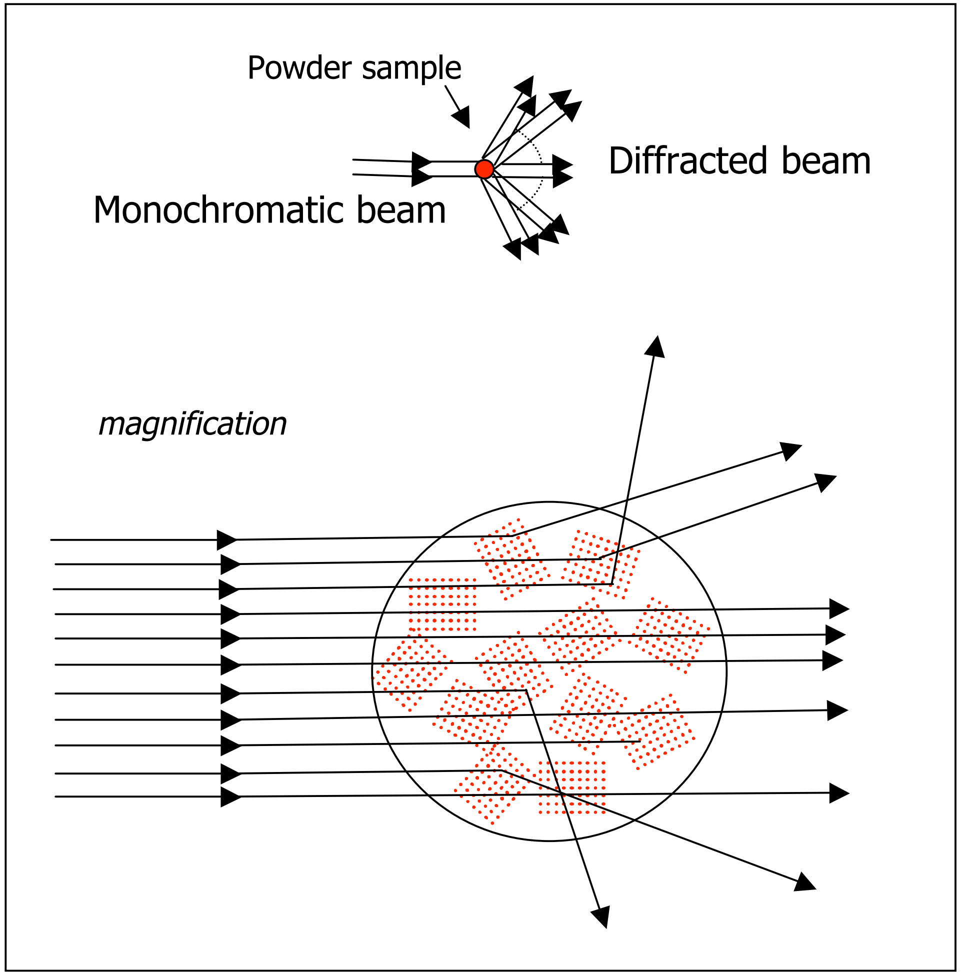
Rotating crystal method



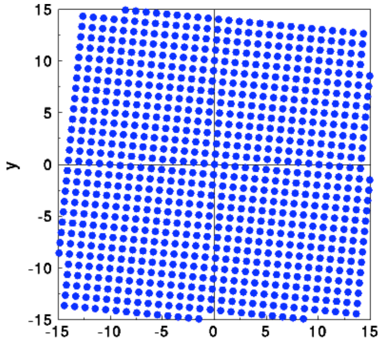


Quartz crystal rotating around an axis

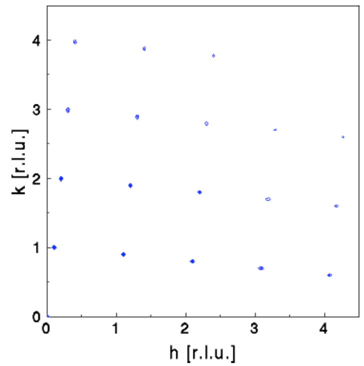
Diffraction of crystalline powders



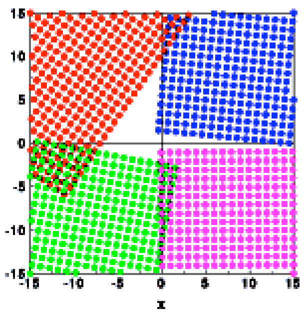
Translations and Rotations of crystallites



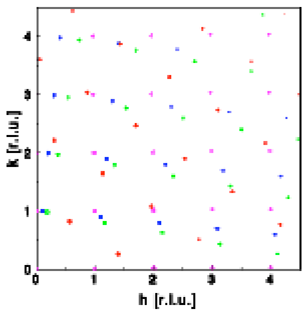
4 identical single crystallites
with the same orientation…



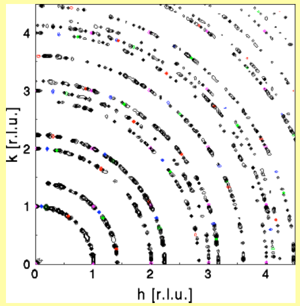
…their diffraction patterns overlap



Random orientation of
the 4 crystallites…

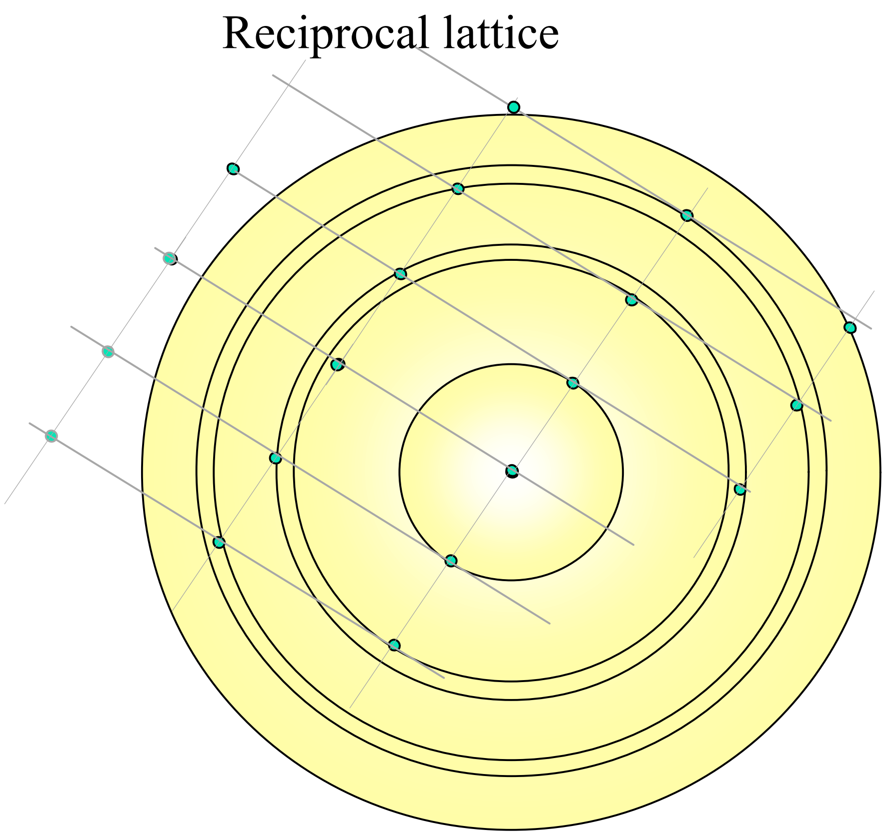


…each diffraction pattern rotates
assuming the same orientation of
the corresponding crystallite



40 identical crystallites
randomly oriented

Crystalline powder reciprocal lattice

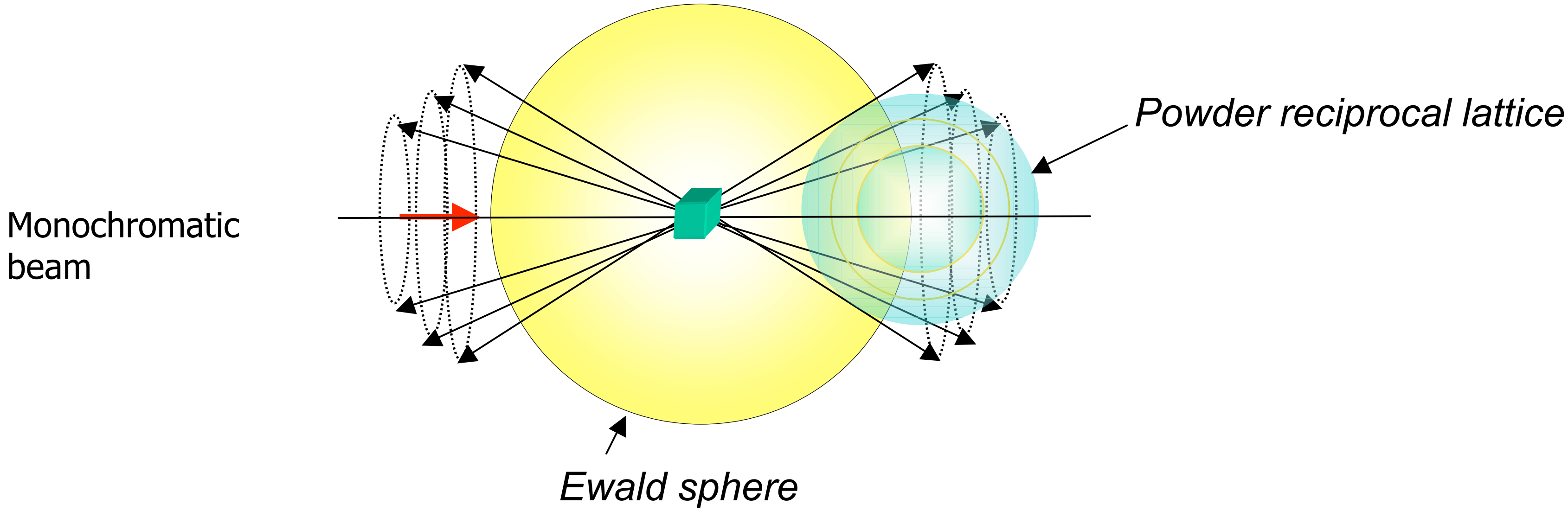


The crystallites are randomly oriented as well as their reciprocal lattices which, however, share a common origin.

The spheres are described by the points of the reciprocal lattices as if single crystallites rotate.

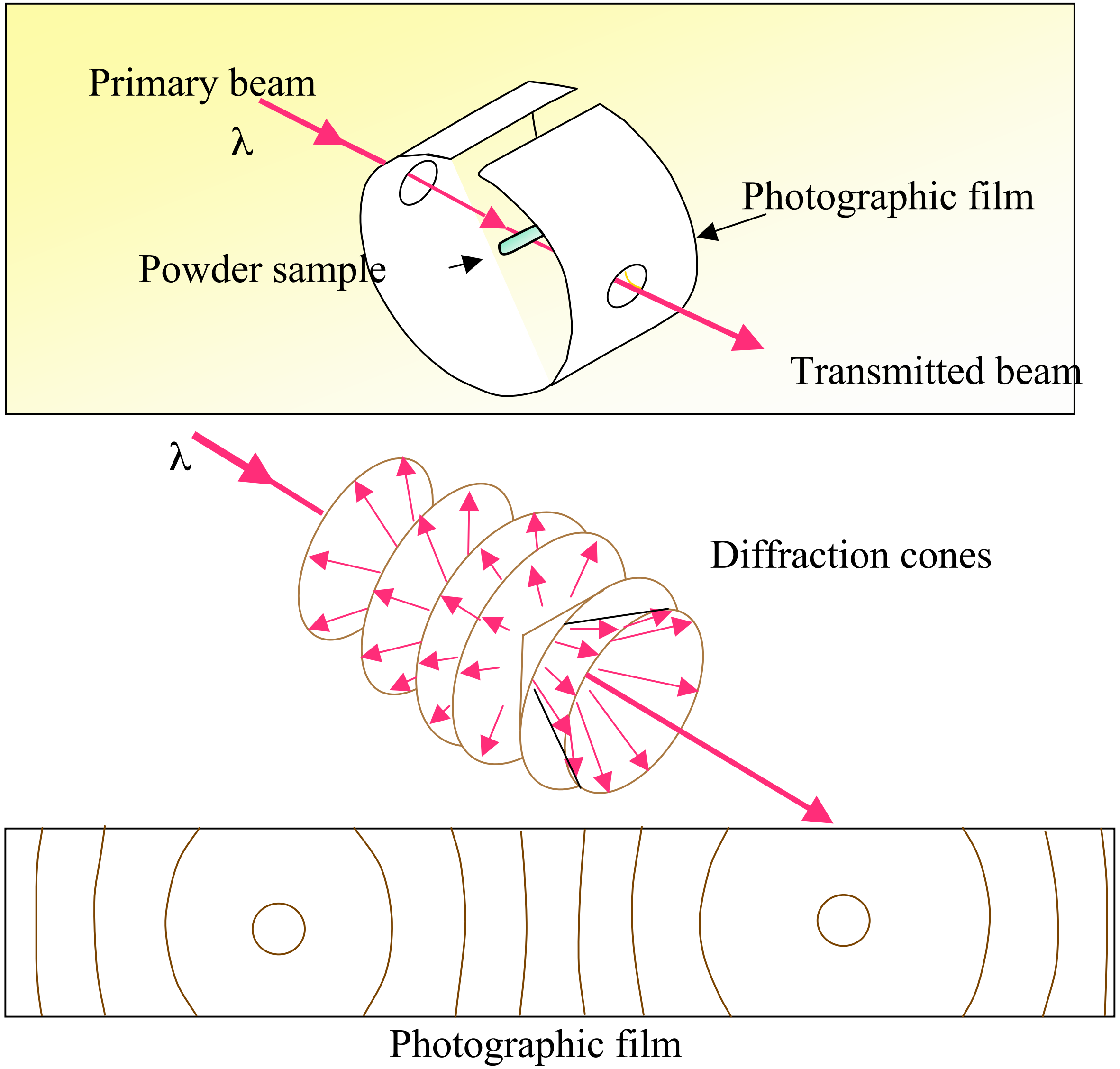
The reciprocal lattice of a crystalline powder is done by concentric spheres.

Ewald sphere for powder diffraction

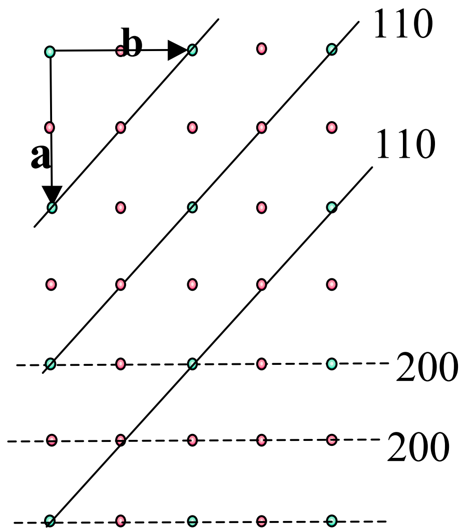


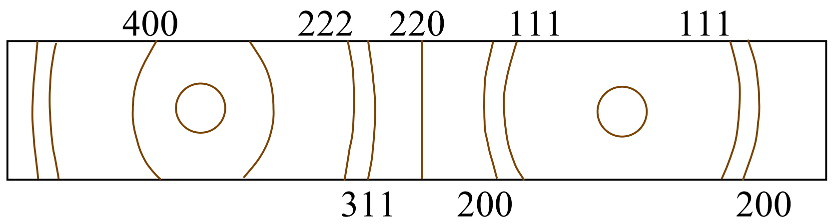
These spheres intersect the Ewald sphere in a set of circles. The diffracted beams generate a set of cones.

The powder method



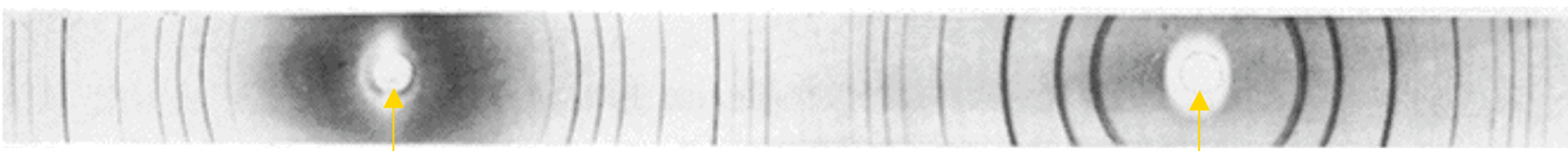
Diffraction Pattern of a fcc lattice





h k l all odds or all o all even

All the diffraction patterns relative to the crystalline planes containing atoms in the lattice points are present; i.e the planes 220 but not the 110.



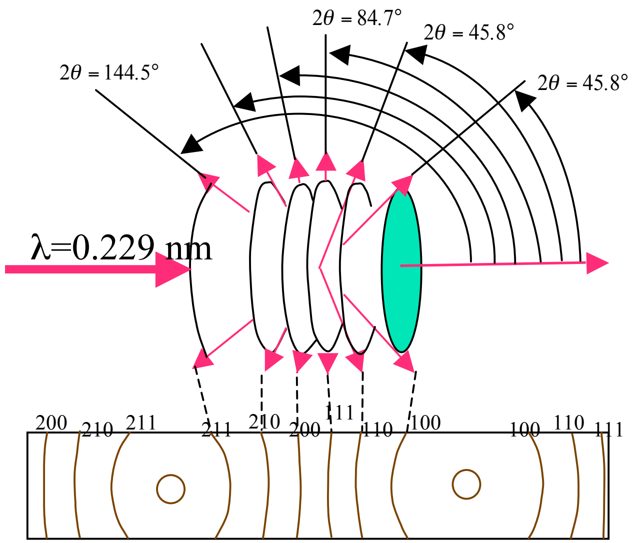
è = 0°

Ahead reflection

è = 90°

Back reflection

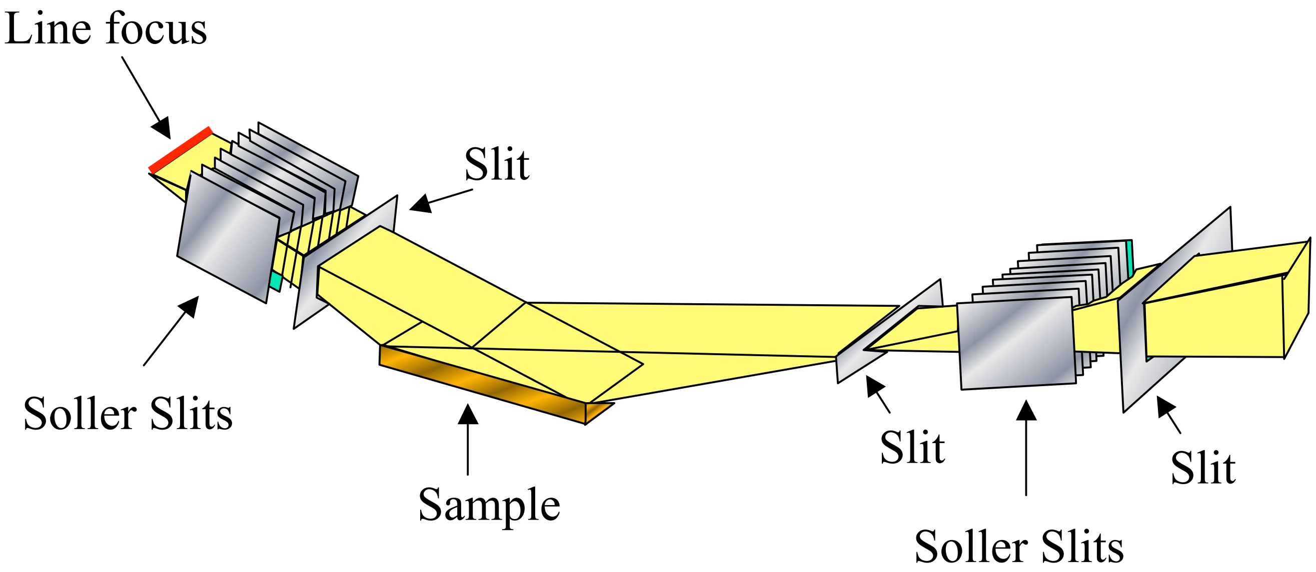
Lattice parameter calculation



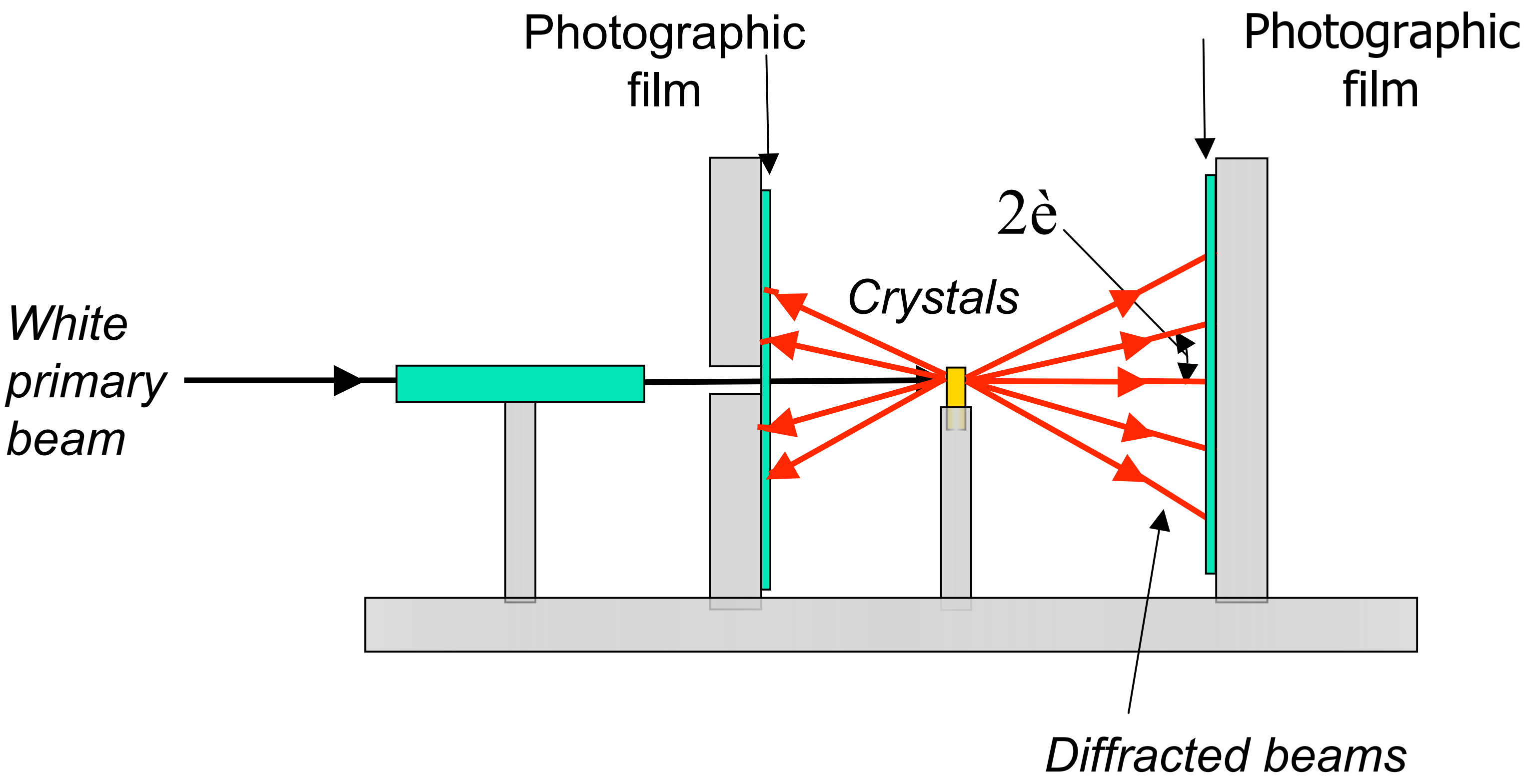
$$a = d_{hkl}\sqrt{h^2+k^2+l^2}$$

hkl	2θ	$d_{hkl} = \lambda/\sin\theta$	$a = d_{hkl}\sqrt{h^2+k^2+l^2}$
100	45.8°	0.294	$a = d_{hkl}\sqrt{1+0+0} = 0.294\,nm$
110	66.7°	0.208	$a = d_{hkl}\sqrt{1+1+0} = 0.208\sqrt{2} = 0.295\,nm$
111	84.7°		$a = d_{hkl}\sqrt{1+1+1} = 0.294\,nm$
200	102°		$a = d_{hkl}\sqrt{2+0+0}$
210	120.8°		$a = d_{hkl}\sqrt{2+1+0}$
211	144.5°		$a = d_{hkl}\sqrt{2+1+1}$

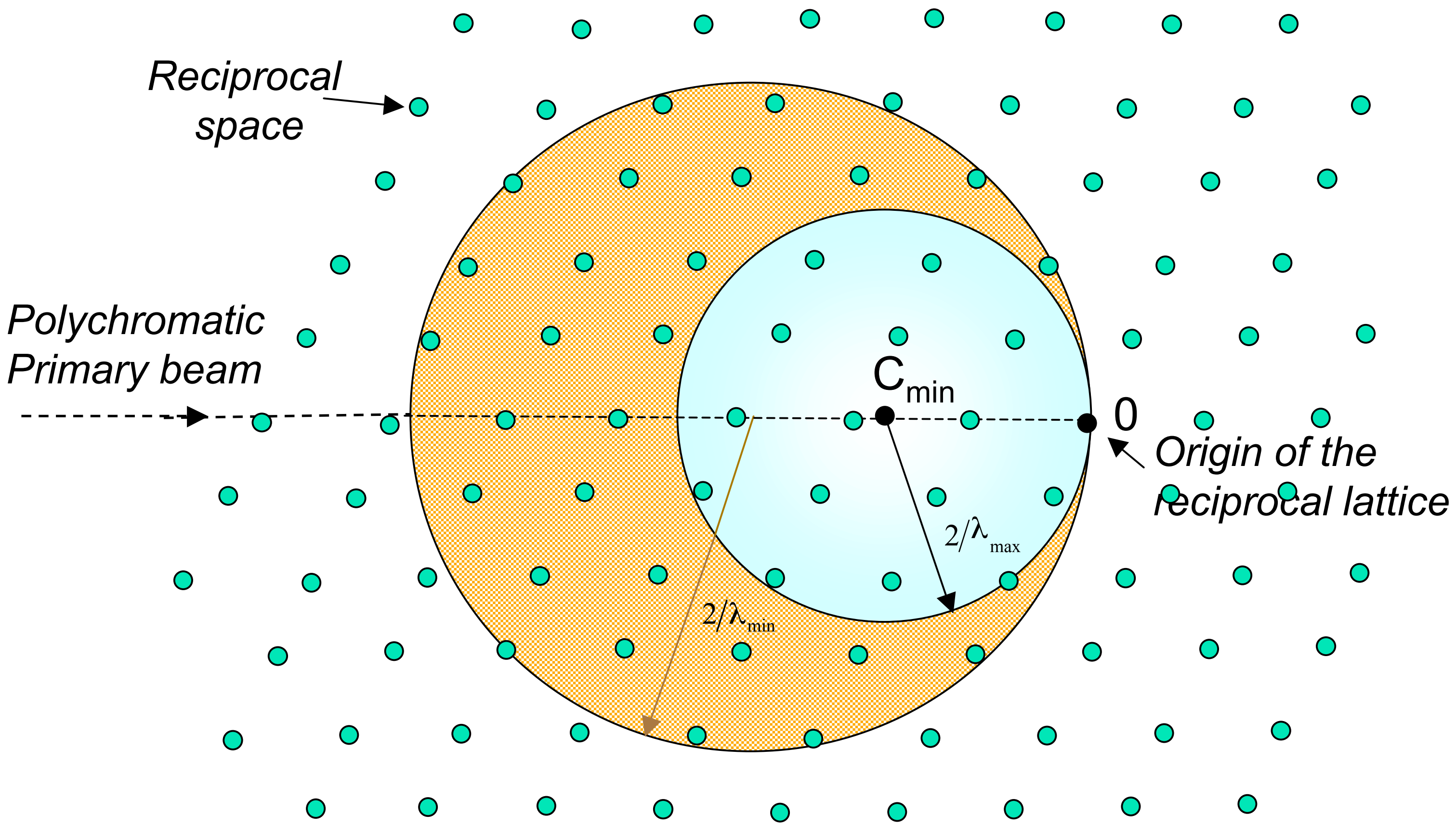
Bragg Brentano diffractometer



Laue Apparatus



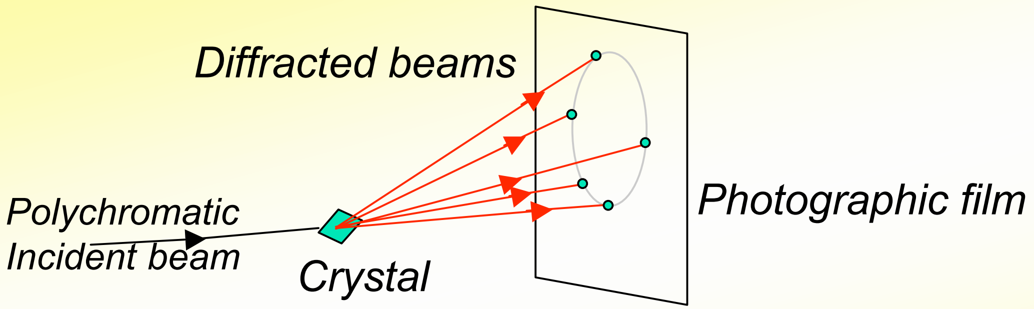
Planes satisfying the Bragg condition

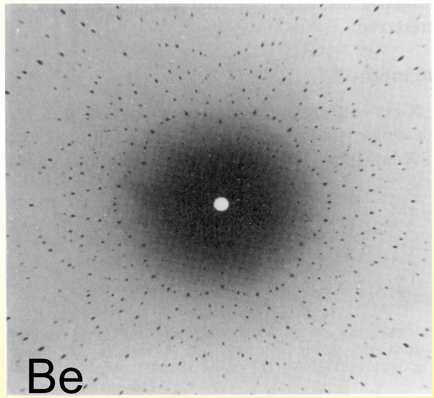


All reciprocal lattice points belonging to the greater sphere and not belonging to the smaller sphere satisfy the Bragg condition.

Laue immages

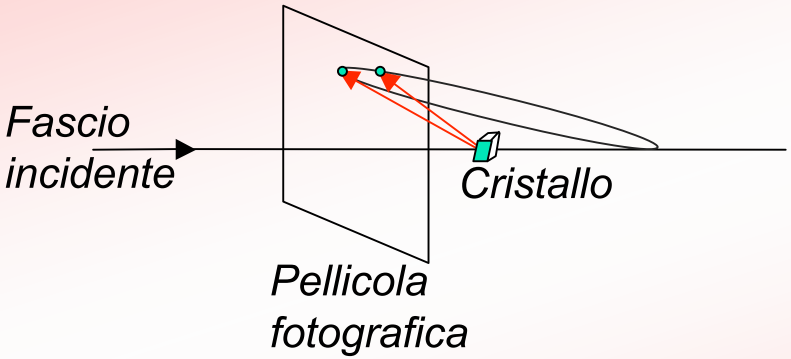
Transmission mode

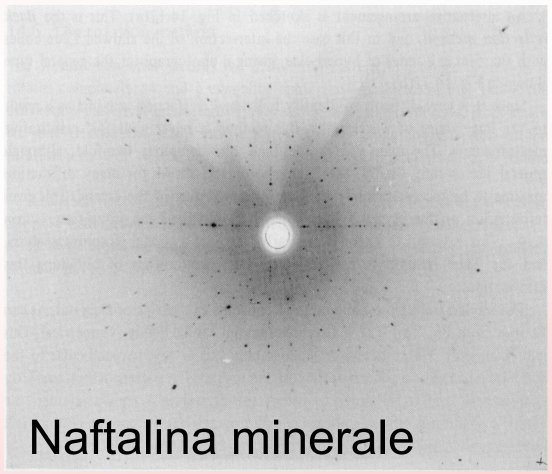




The Laue cones intersect the photographic film in ellipses

Back-reflection mode





Temperature effect

The increase of temperature has 3 effects:

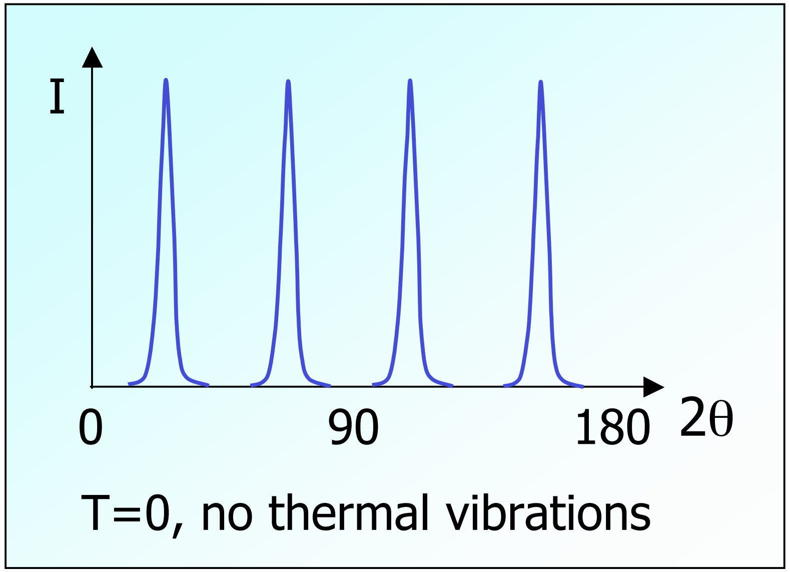
1 The unit cell expands ⇨ The plane spacing d changes ⇨ 2 θ positions change

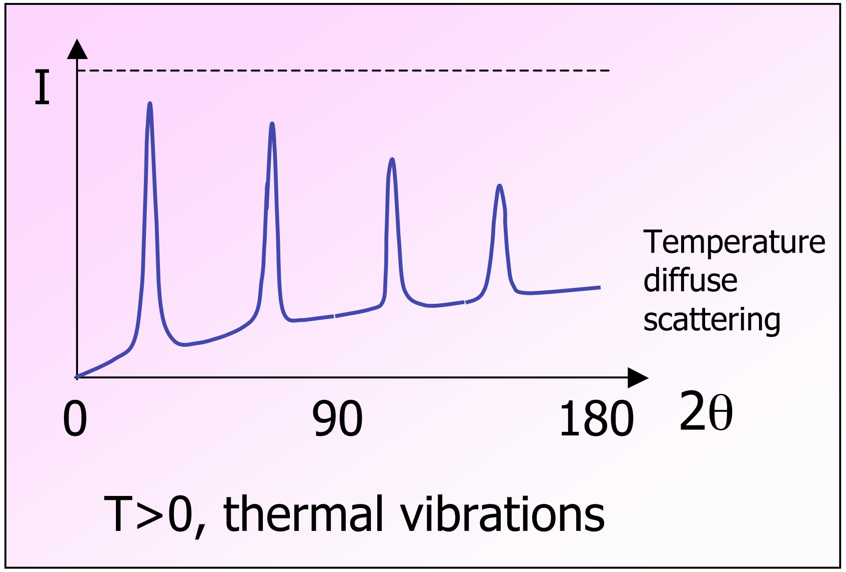
2 The intensities of the diffraction lines decrease

3 The intensity of the background scattering between lines increases

Temperature effect

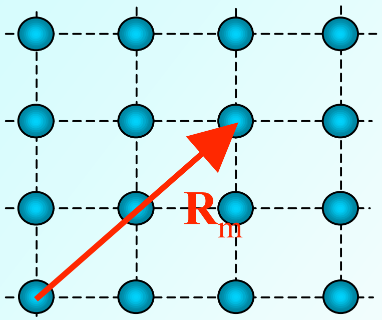
Hypotetivcal pattern





Temperature Factor

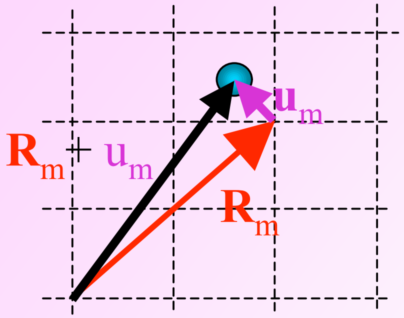
T = 0 K



$$F(\vec{K}) = \sum_m f_a(\vec{K}) e^{i\vec{K}\cdot\vec{R}_m}$$

$$I = \left|F(\vec{K})\right|^2$$

T > 0 K



$$F(\vec{K}) = \sum_m f_{atom}(\vec{K}) e^{i\vec{K}\cdot\vec{R}_m}$$

$$f_{atom} = f_a(\vec{K})\, e^{-\frac{1}{2}\left(K^2\langle u_K^2\rangle\right)} = f_a(\vec{K})\, e^{-M}$$

$$I = \left|F(\vec{K})\right|^2 \cdot e^{-2M}$$

u_K is the component of the atomic displacement parallel to **K**

The exponential term is called Debye Waller

Bibliography

- Sherwood
  - Introduction to X-ray diffraction
- Lypson
  - Optical diffraction
- G. Harburn, C. A. Taylor T. R. Welberry
  Optical Transforms" G. Bell& Sons Ltd, Plate 16
- C.A. Taylor
  - Atlas of optical transforms
- Cullity
  - X-ray diffraction