X-ray diffraction

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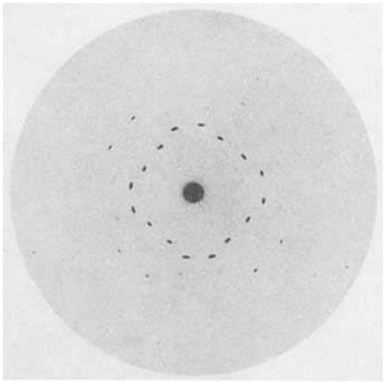
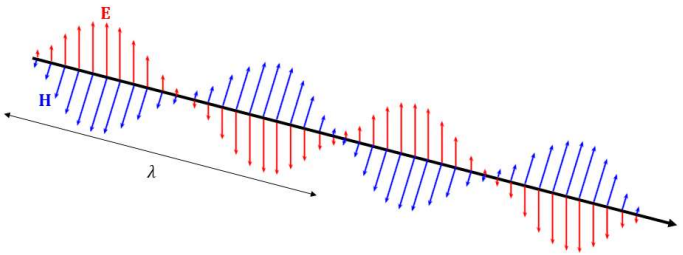
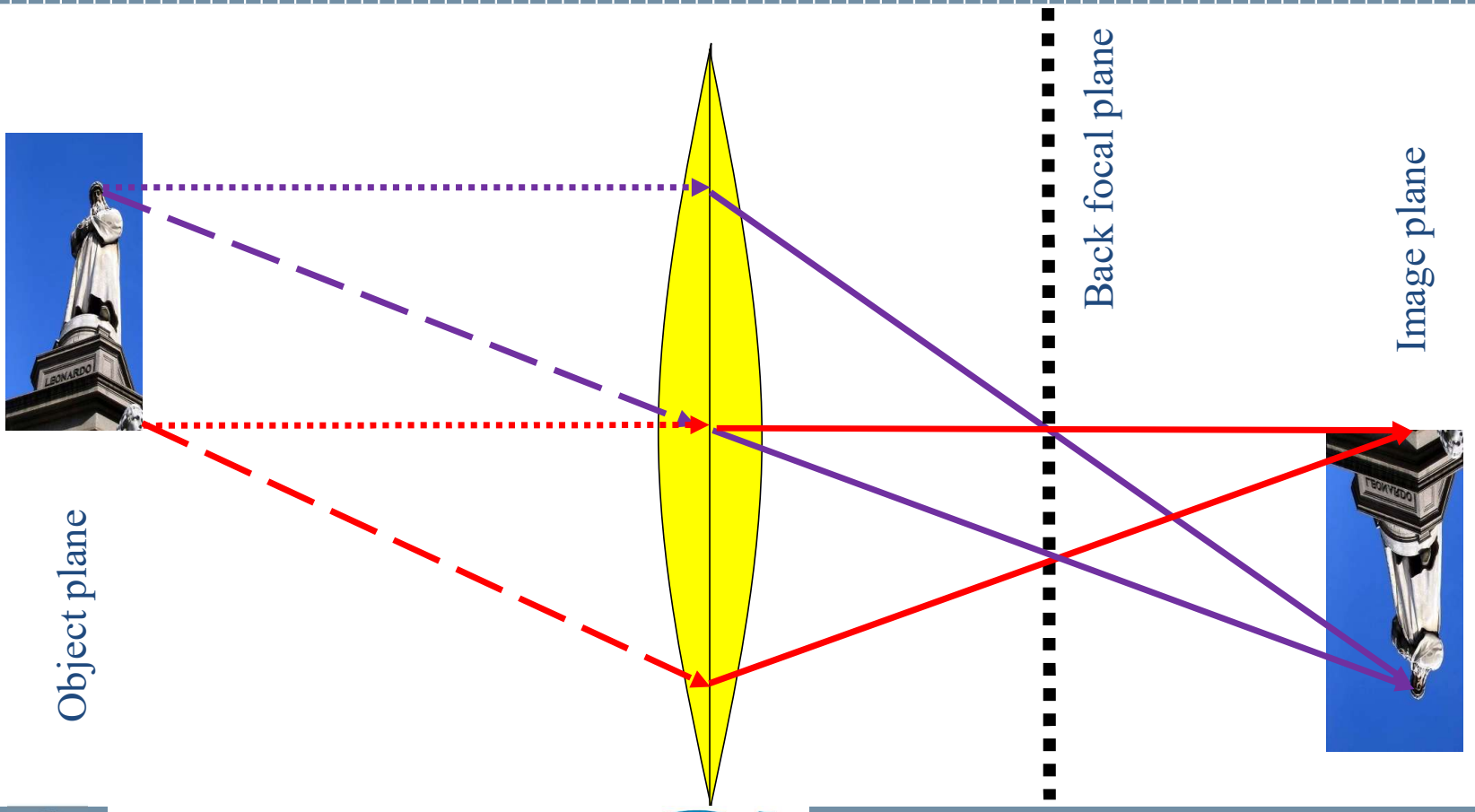
How to see small objects

If we want to see things, we need light.
Depending on the object and the features we want to detail, the radiation must be appropriately selected. Imaging is a vital tool in natural science, but until the XIX century, the only light practicably usable for taking pictures of the objects under investigation, was the light visible by human eye, and the only technique to reconstruct a magnified image of a body was the optical microscopy.
The perspective changed disruptively after the discovery of X-rays at the end of the XIX century. The higher energy of this radiation implied an unprecedented penetration power that enabled to inspect the inside of objects.
Even more, the higher energy meant noticeably short wavelength and therefore the ability to detail smaller particles and inspect that mysterious part of the realm that was puzzling physicists at the turn of the century.
Weiss (1996) provocatively wrote that “if it were not for electrons, photons would leave in a dreary world of nothingness”. Indeed, it is through interaction between photons and electrons that we can do the observations and without this interaction photons would be “useless”.





If we use visible light and a magnifying lens…



With an objective lens, we can magnify 10-1000 times.
That's not enough to see atoms!
What is the limit?

Resolution Limit

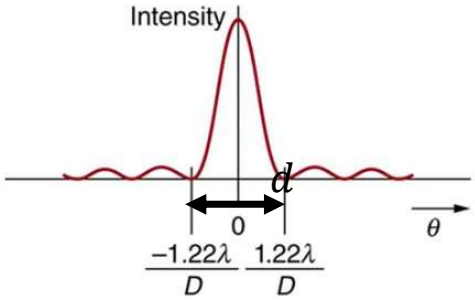
minimal distance that we can resolve

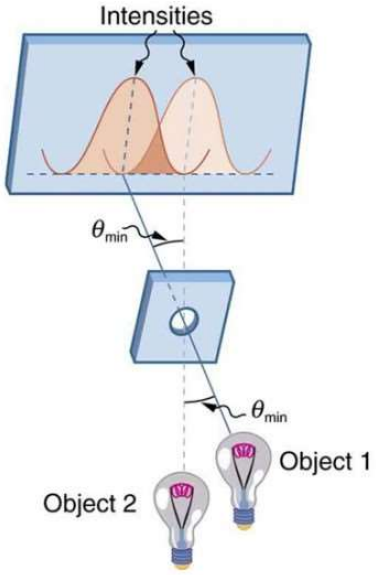
$$r = \frac{d}{2} = \frac{1.22\lambda}{D} = \frac{0.61\lambda}{n \sin \vartheta}$$

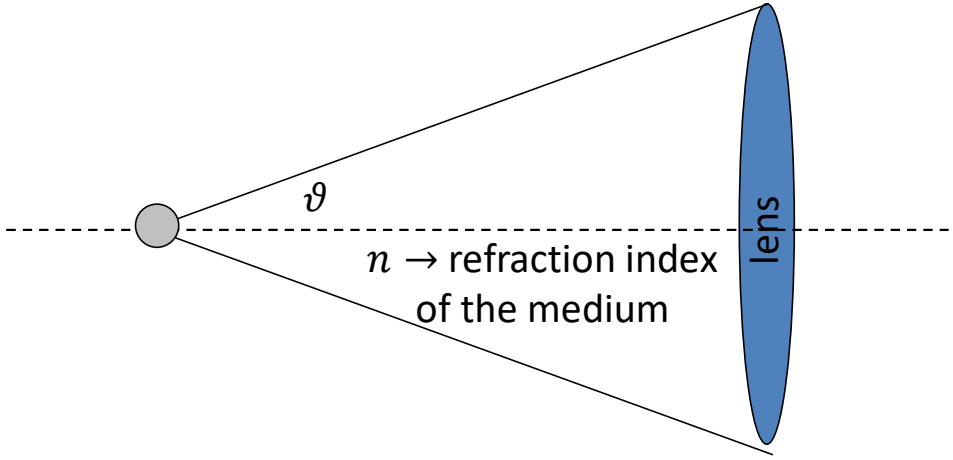
λ wavelength

numerical aperture

Rayleigh criterion







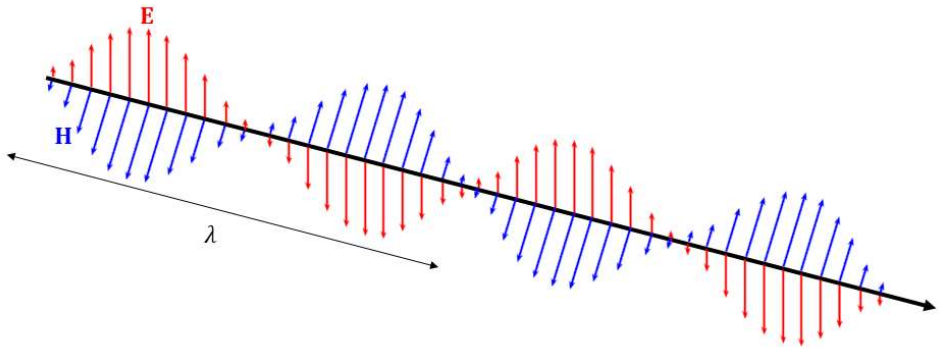
So we need the right wavelength…..

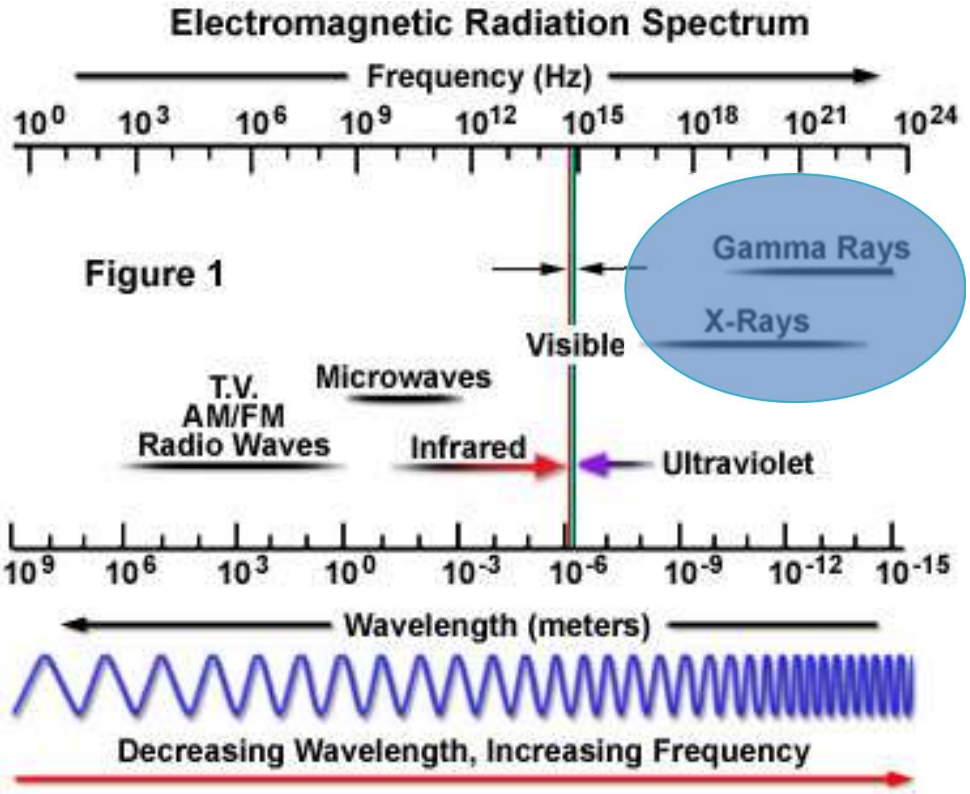
$$E = mc^2 = h\upsilon$$

Dualism particle/wave

$$\lambda = \frac{h}{mv} = \frac{nh}{mc} = \frac{nc}{\upsilon}$$

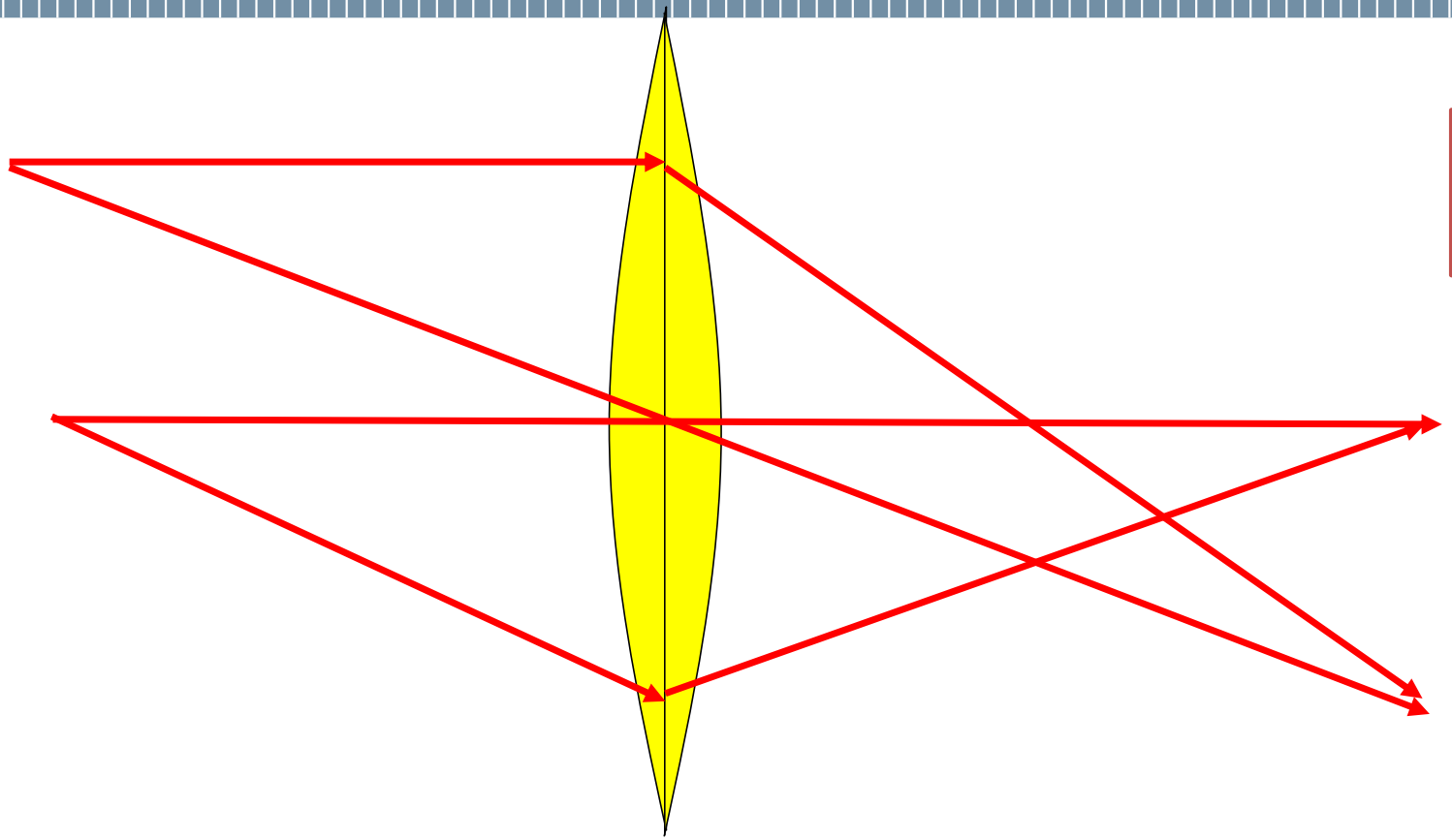
E = **energy**
m = **mass**
h = Plank's constant
υ = **frequency**
λ = **wavelength**
c = speed of light in vacuum
v = speed of light in a medium
n = **refraction index**



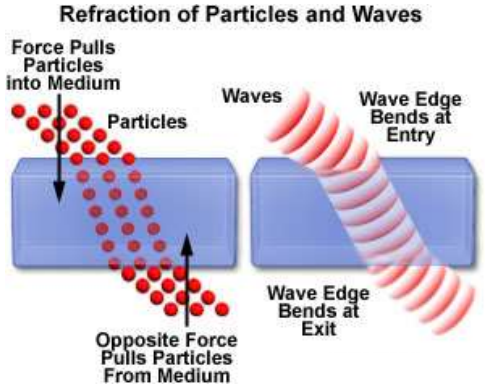


We need a sufficiently high energy radiation: X-ray or γ-ray but also….

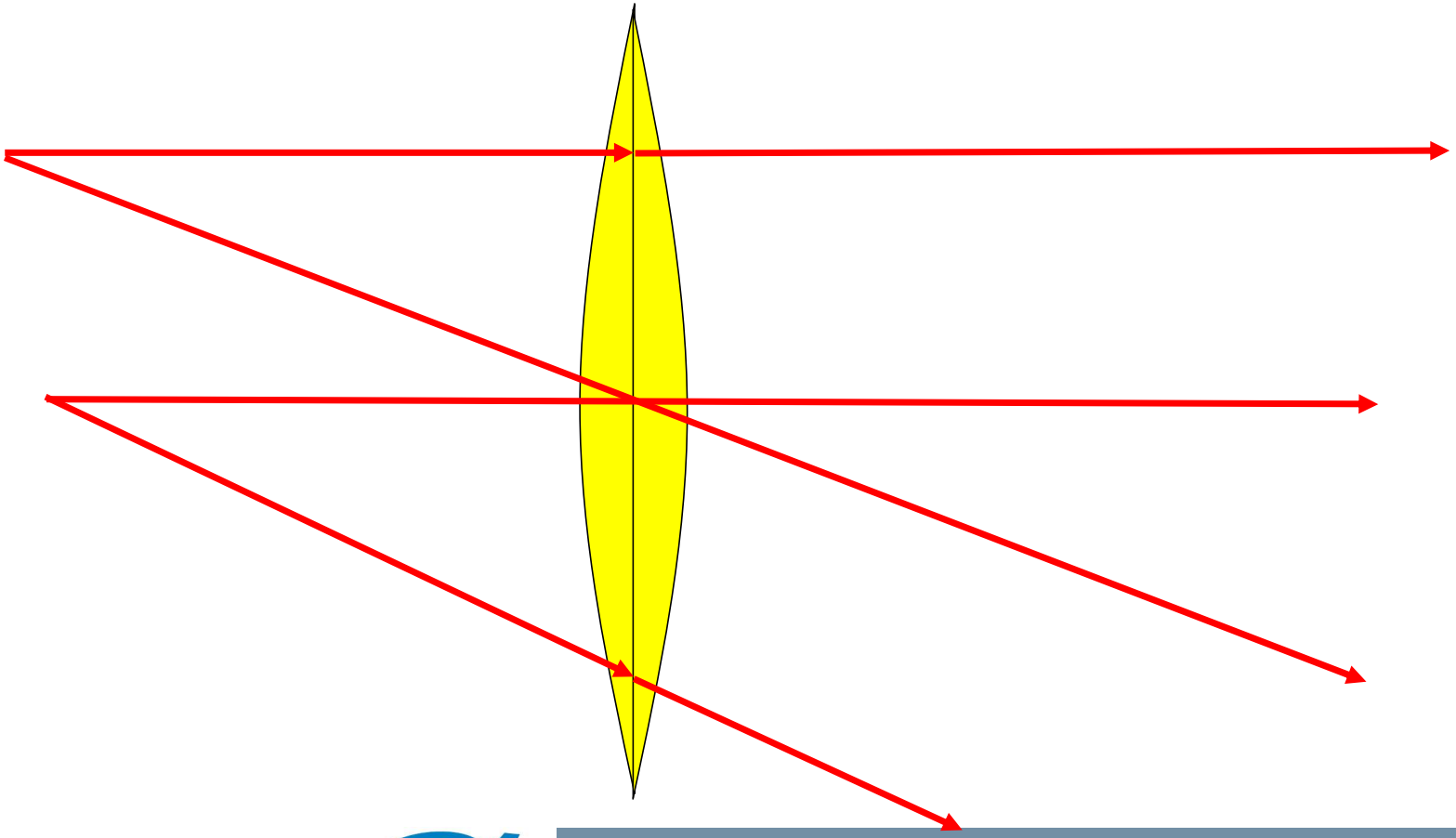
What kind of lens….



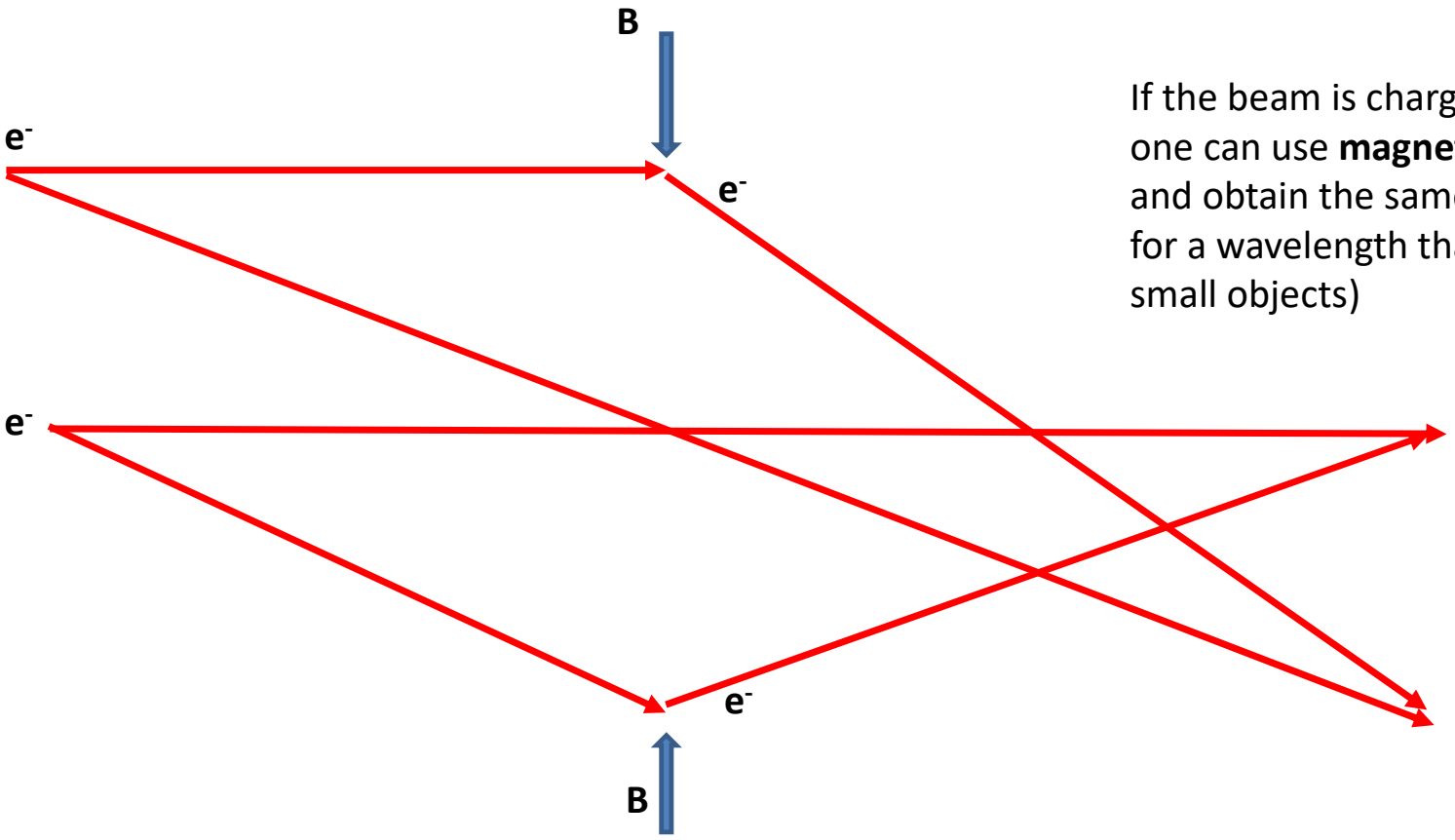
In a conventional, optical microscope, lenses uses refraction of light to focus the rays and form the image



But….. at high Energy, $n \approx 1$

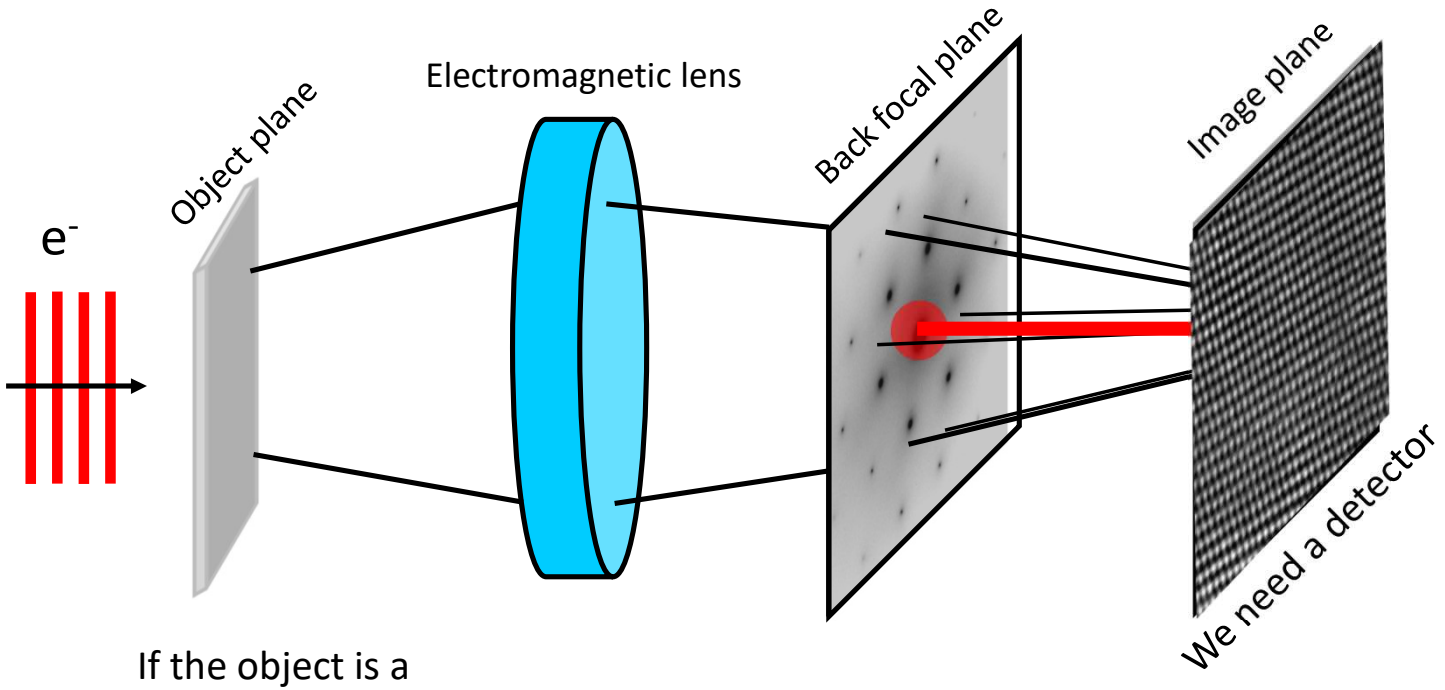


Electromagnetic lenses



If the beam is charged, like a beam of electrons, one can use **magnetic fields** to deflect their paths and obtain the same effect of a glass lens (though for a wavelength that can be appropriate to see small objects)

Electron microscope



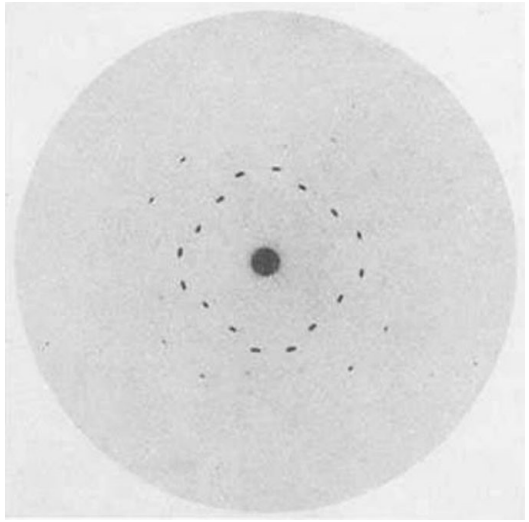
If the object is a crystal

By accelerating electrons to ca. 50-300 kV, hypothetical resolutions of less than 1 nm are achievable

PROBLEM: electrons are charged and therefore extremely sensistive to particles along their path. High vacuum is necessary

What is the back focal plane image?

X-ray crystallography

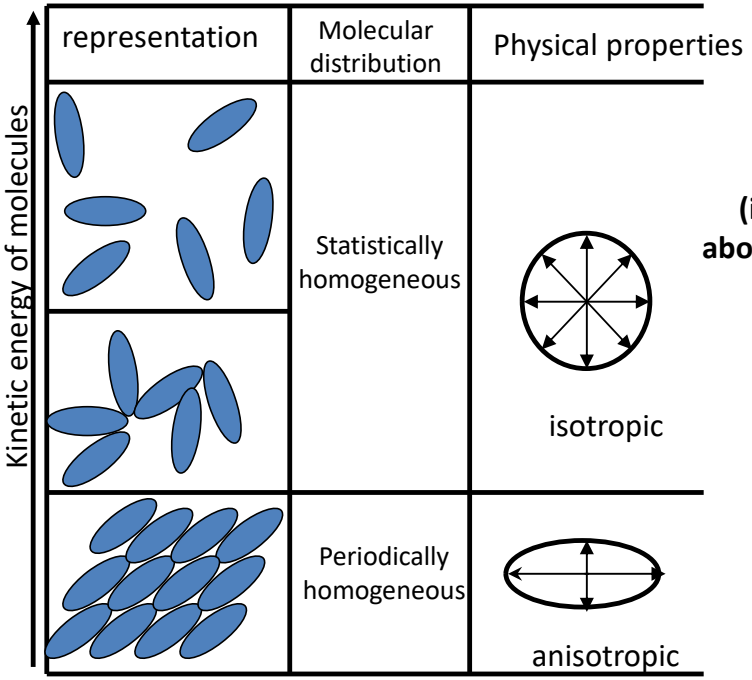


There are two “crystallography”: before and after 1896

The revolution: in 1913 Bragg and von Laue determined crystals structures of NaCl, KCl, KBr, KI, ZnS, Diamond etc. using the diffraction of X-rays produced by crystals.

What is a crystal?

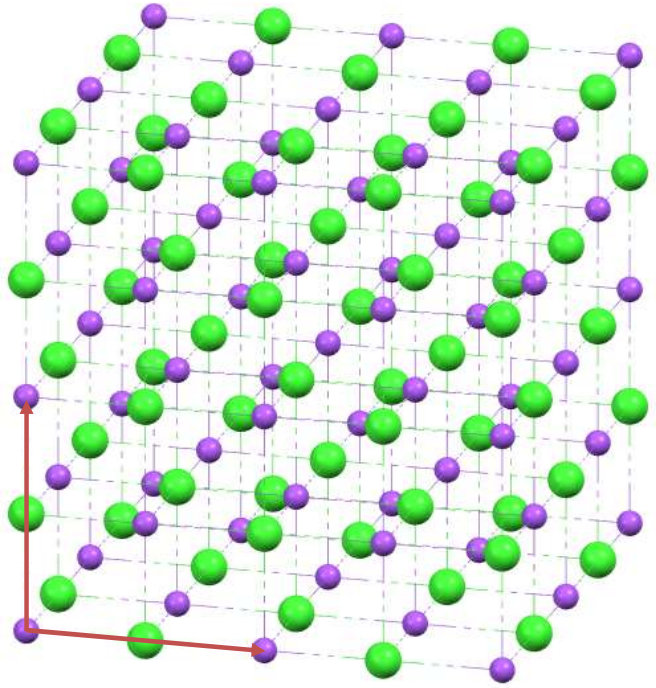
A crystal is an **anisotropic**, **homogeneous** object, that possesses a **three-dimensional** periodic **order** generated by the exact repetition of elementary bricks



Gas / liquid (indistinguishable above the critical point)

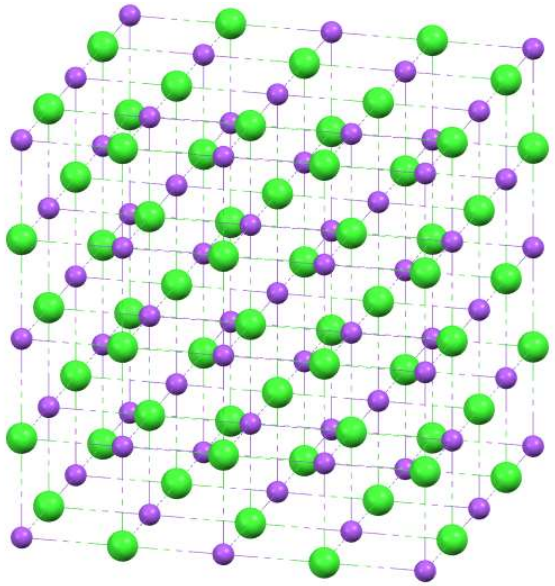
amorphous solids

Crystalline state



The crystal structure

The **crystal structure** is the set of positions occupied by regularly disposed atoms in an ideal crystal.



The crystal lattices

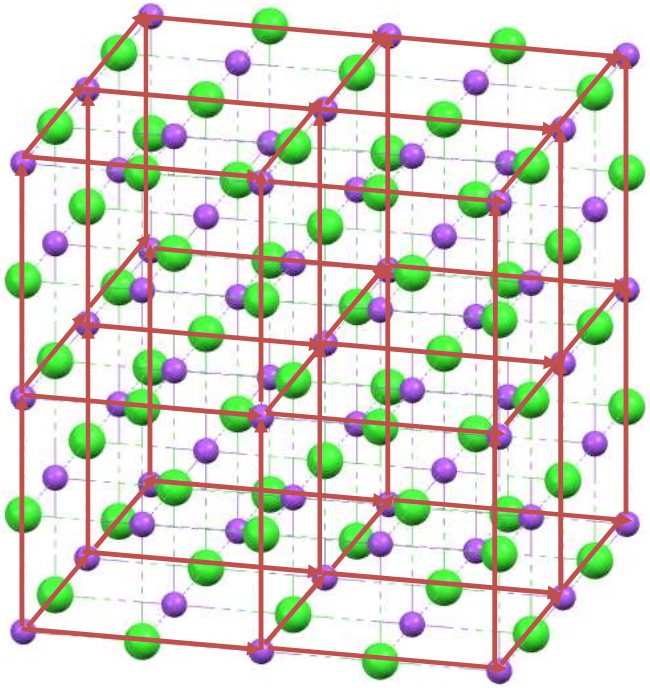
A lattice in the vector space $\mathbf{V}^{\mathrm{n}}$ is the set of all integral linear combinations

$$\mathbf{t} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + \ \ldots + u_k\mathbf{a}_k$$

of a system ($\mathbf{a}_1$, $\mathbf{a}_2$…. $\mathbf{a}_k$) of linearly independent vectors in $\mathbf{V}^{\mathrm{n}}$

If $k = n$, *i.e.* if the linearly independent system is a basis of $\mathbf{V}^{\mathrm{n}}$, the lattice is often called a **full lattice**. In crystallography, lattices are almost always full lattices, therefore the attribute *full* is usually suppressed.

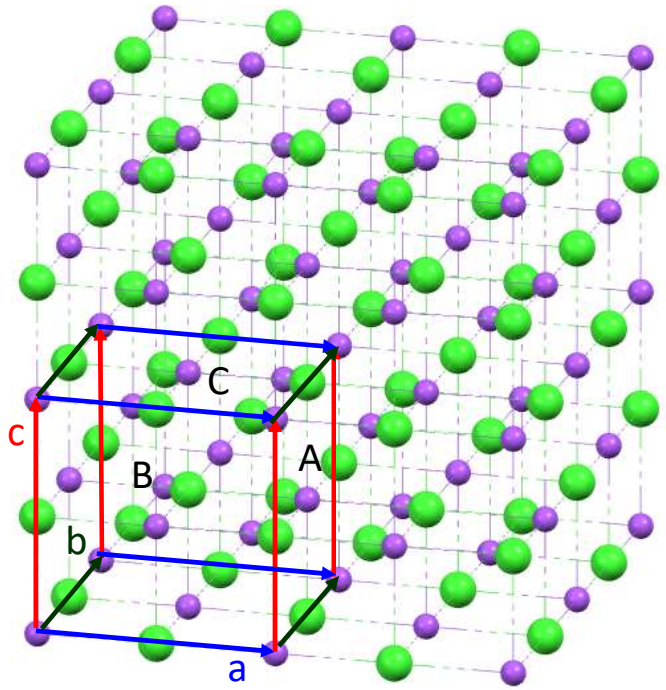
The crystal lattices



The crystal lattices

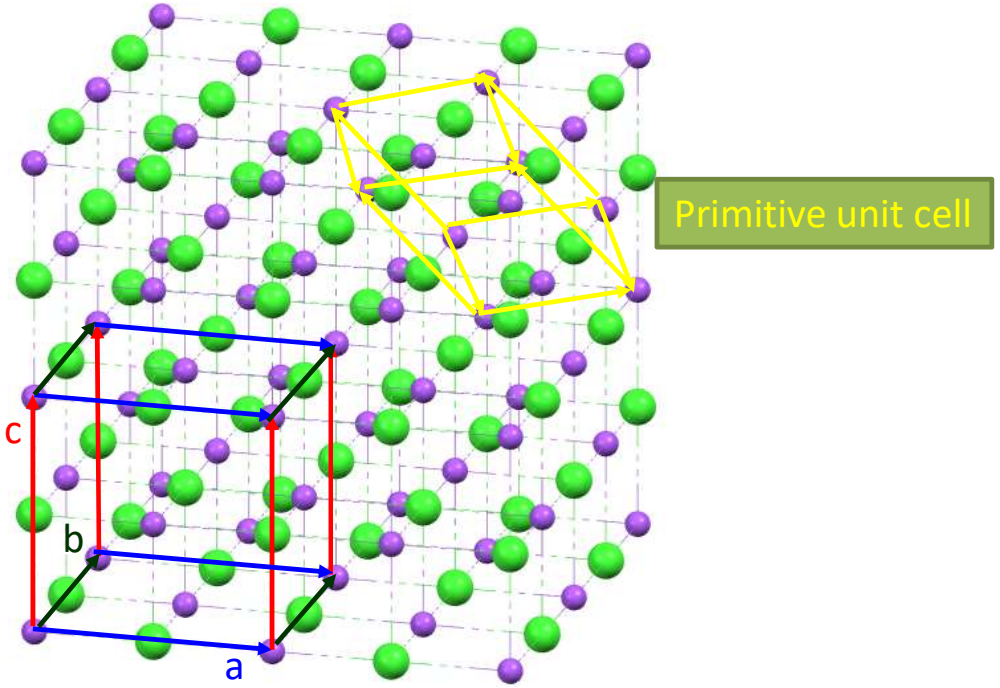
Unit cell

Unit cell vectors



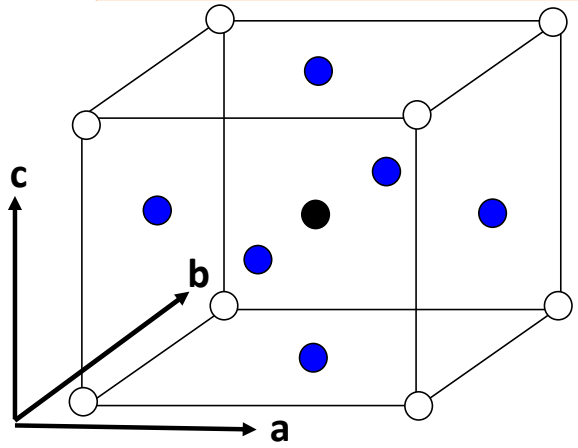
Unit cell faces

The crystal lattices



The crystal lattices

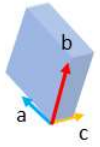
Lattice type	Axis metric	Angular metric	Centering type
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	None
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°, \beta > 90°$	A, C, I
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	A, B, C, F, I
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	I
Trigonal Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma$	None
Hexagonal, Trigonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	R
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	F, I



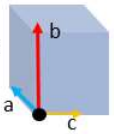
- Lattice node at unit cell vertex
- Lattice node at unit cell centre
- Lattice node at unit cell face centre

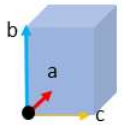
The crystal symmetries: 32 crystallographic point groups

Triclinic: no special direction (e. g. P1, P$\bar{1}$)

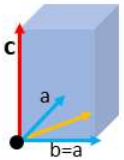


Monoclinic: ac is the monoclinic plane; the 2-fold axis is parallel to b, which is the only relevant direction (e.g. P2/m; extended symbol P12/m1)



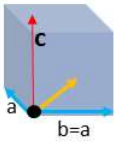


Orthorhombic: all directions a, b, c are relevant and non-equivalent (e.g. $P2_12_12_1$)

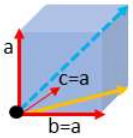


Tetragonal: the four-fold axis is parallel to c, the other two relevant directions are a (=b) and the diagonal a+b (=a-b). (e.g. I4/mmm)

Trigonal/Hexagonal: the 3-fold or 6-fold axis is parallel to c, the other two relevant directions are a+b and a (=b). (e.g. $P6_322$)



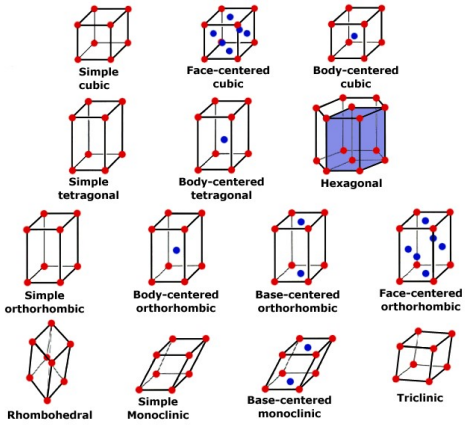
Cubic: 4-fold axis is parallel to a, 3-fold axis is parallel to body diagonal a+b+c, 2-fold axis is parallel to face diagonal (e. g. Fm$\bar{3}$m)



lattice type	centrosymmetric point group (Laue class)	non-centrosymmetric point group	
	achiral	achiral	compatible with chirality
Triclinic	$\bar{1}$		1
Monoclinic	$2/m$	m	2
Orthorhombic	mmm	$mm2$	222
Tetragonal	$4/m$	$\bar{4}$	4
	$4/mmm$	$\bar{4}m2$	422
		$4mm$	
Trigonal Rhombohedral	$\bar{3}$		3
	$\bar{3}m$	$3m$	32
Hexagonal	$6/m$	$\bar{6}$	6
	$6/mmm$	$\bar{6}2m$	622
		$6mm$	
Cubic	$m3$		23
	$m3m$	$\bar{4}3m$	432

The crystal symmetries: 230 crystallographic space groups

14 lattice types (lattice systems)
describe the combinations of translational vectors allowed in 3D

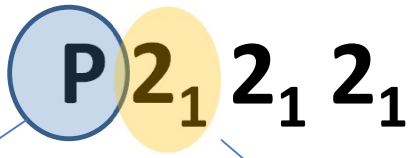


+ symmetry elements including partial translations (glide planes and helical axes)

32 point group classes
Describe symmetry of the periodic system as a whole object

230 space groups
Describe completely the structure

The crystal symmetries: 230 crystallographic space groups



Centered or primitive lattice
P = primitive
A = face A (formed by b and c vectors) is centered
B = face B (formed by a and c vectors) is centered
C = face C (formed by a and b vectors) is centered
F = all faces are centered
I = body centered

Contracted form of the symmetry along a specific directions
Sometime the space group symbol is also contracted, removing directions having only identity (for example **$P2_1/c$** (the extended symbol would be **P** 1 **$2_1/c$** 1)

The crystal symmetries: properties

Neumann's principle:
If a crystal structure is invariant with respect to certain symmetry operations, any of its physical properties must also be invariant with respect to the same symmetry operations.

The crystal symmetries: properties

Crystal system	Piezoelectric point groups	Pyroelectric (polar) point groups
Triclinic	1	1
Monoclinic	$2, m$	2
Orthorhombic	$222, mm2$	222
Tetragonal	$4, \bar{4}, 422, 4mm, 42m$	$4, 4mm$
Trigonal	$3, 32, 3m$	$3, 3m$
Hexagonal	$6, \bar{6}, 6mm, 622, 62m$	$6, 6mm$
Cubic	$23, \bar{4}3m$	

The crystal symmetries: diffraction

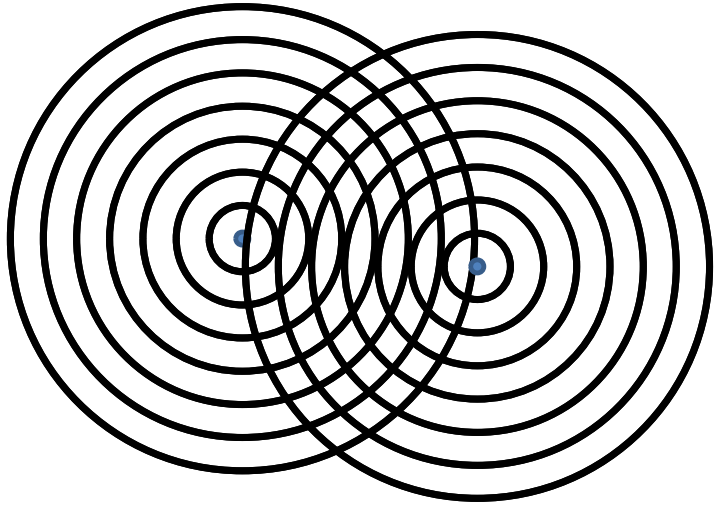
lattice type	centrosymmetric point group (Laue class)	non-centrosymmetric point group	
	achiral	achiral	compatible with chirality
Triclinic	$\bar{1}$		1
Monoclinic	$2/m$	m	2
Orthorhombic	mmm	$mm2$	222
Tetragonal	$4/m$	$\bar{4}$	4
	$4/mmm$	$\bar{4}m2$	422
		$4mm$	
Trigonal	$\bar{3}$		3
Rhombohedral	$\bar{3}m$	$3m$	32
Hexagonal	$6/m$	$\bar{6}$	6
	$6/mmm$	$\bar{6}2m$	622
		$6mm$	
Cubic	$m3$		23
	$m3m$	$\bar{4}3m$	432

What is a crystal in X-ray diffraction experiments?

A crystal is like a **magnifying tool** that enables the visualization of its microscopic (sub-nanometric) constituents and the enhancement of their properties

Diffraction of light: Huygens principle

Any wave can be thought of as spreading spherically at every point along its wave front. All these little spherical 'wavelets' are constantly interacting, so can maintain a planar (or flat) wave front. But if this wave front is interrupted by an obstacle the wave spreads spherically at the points where it has been broken.



Diffraction from one slit

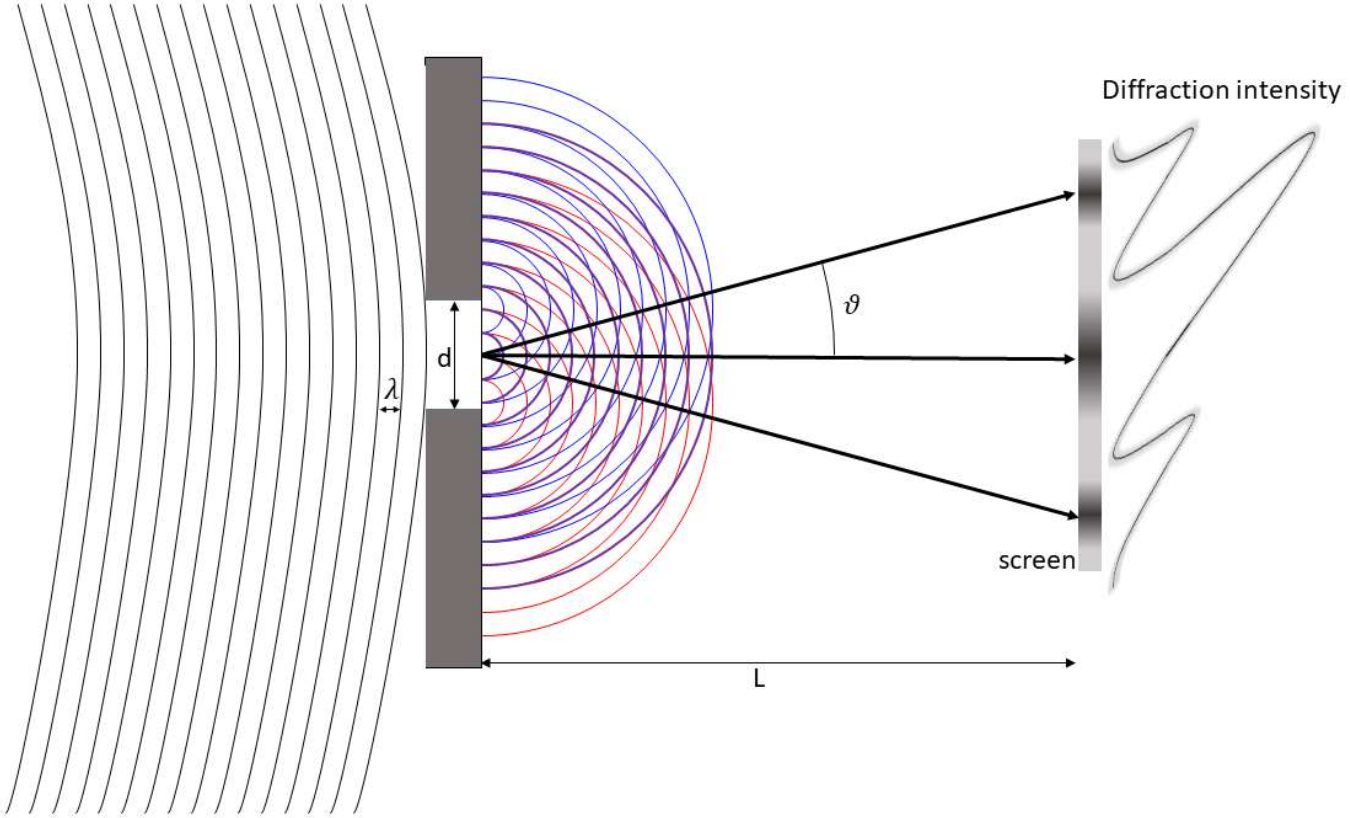
Two rays will form **destructive interference** if

$$r = (d/2 \sin\vartheta) = n\,\lambda/2$$

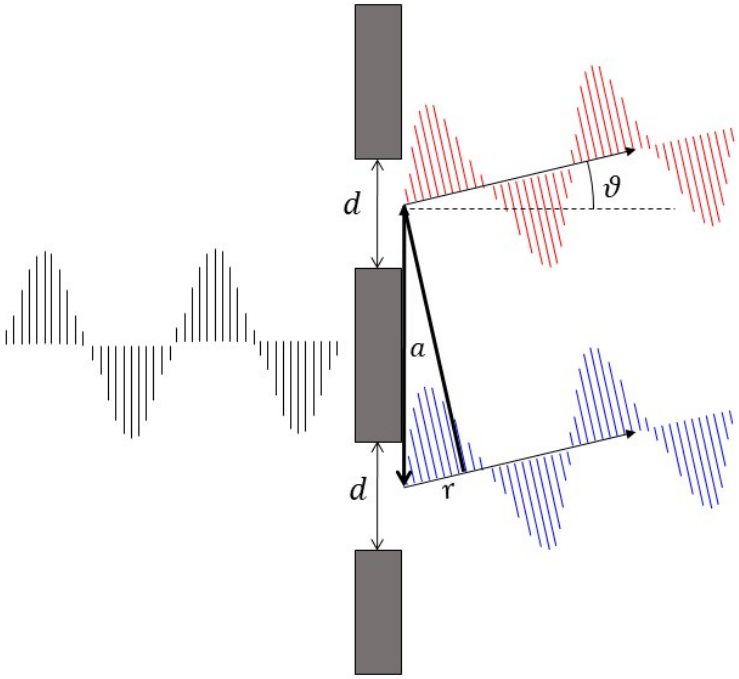
Thus, destructive interference is present if

$$d\ sin\,\vartheta = n\,\lambda$$

Everywhere else there is some non-destructive interference



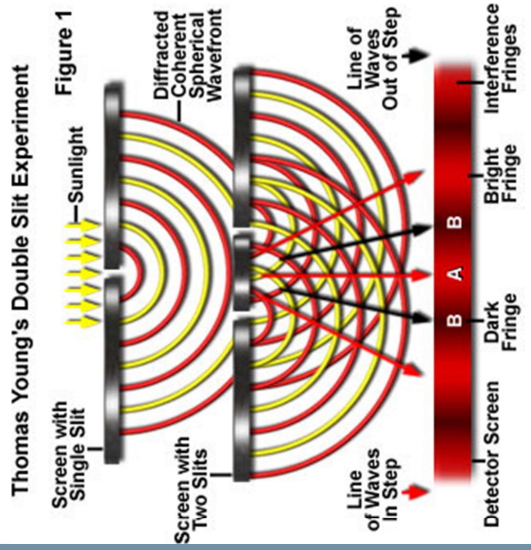
Diffraction from two slits



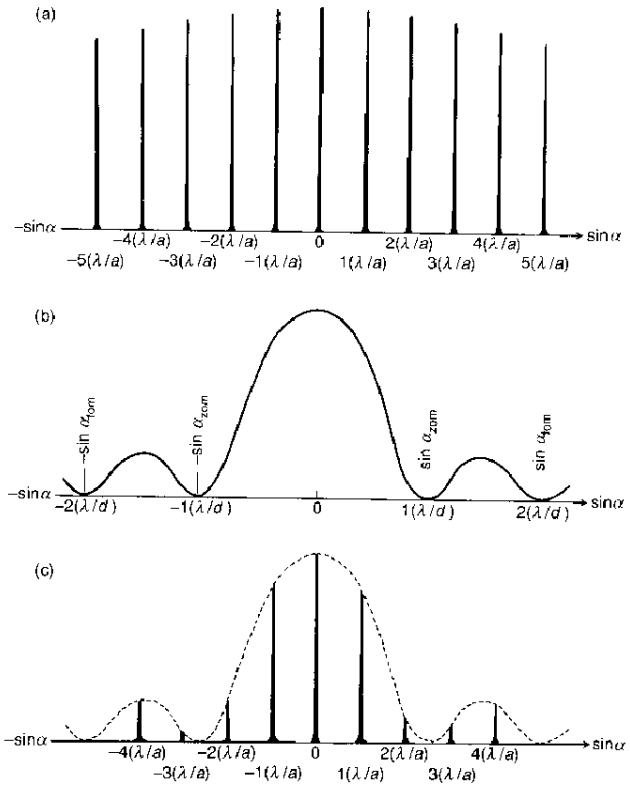
These two rays will form **constructive interference** if

$$r = (a \sin\vartheta) = n\,\lambda$$

Everywhere else there will be destructive interference



Diffraction from two slits

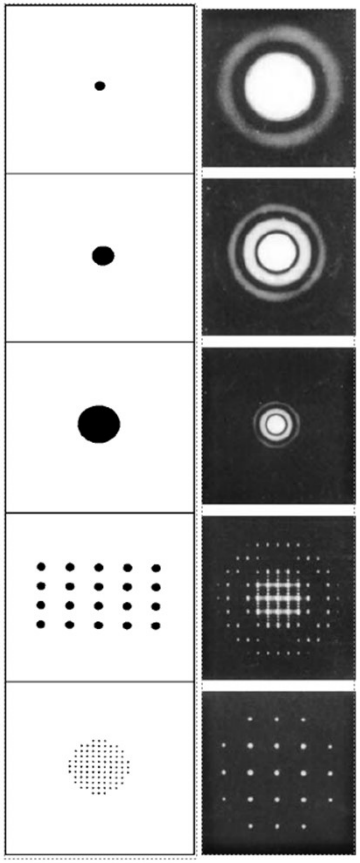


Conditions imposed by the slit separation

Diffraction from a single slit

Diffraction from two slits

Diffraction images



If we take a metal slit with a micrometric aperture and irradiate with a visible light (nanometric wavelength) we observe a scattering that depends on:

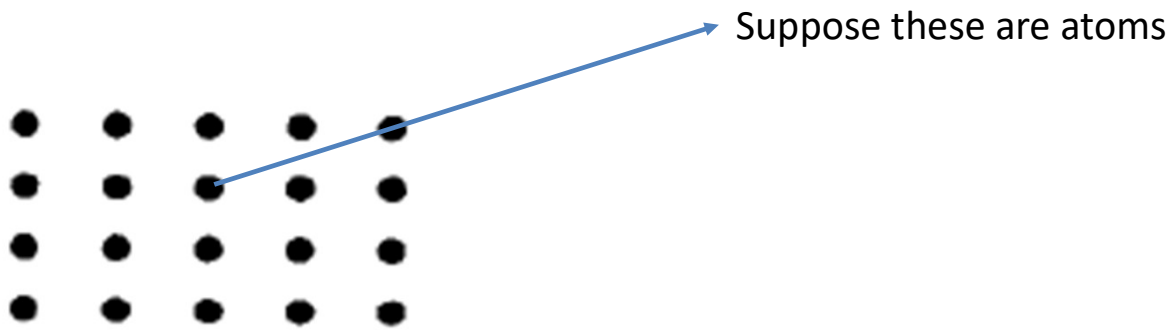
a) Shape and size of the aperture
b) Wavelength of the radiation

If we take a slit with a periodic distribution of apertures, the diffraction pattern depends also on the lattice

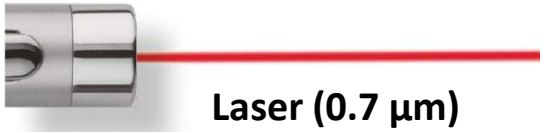
Interference of waves

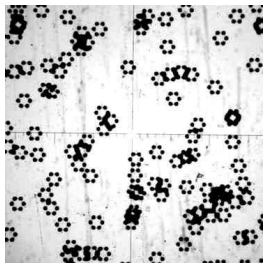
The analogy between X-ray and visible light is clear if we think of atoms like “slits” or obstacles that deviate the waves with a specific “form factor”

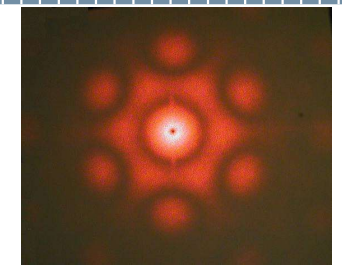
If atoms are arranged periodically, then the diffraction pattern will resemble that of a grid put in visible light

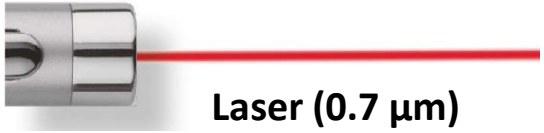


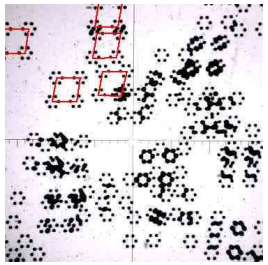
Diffraction Images

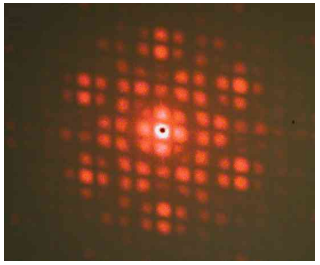


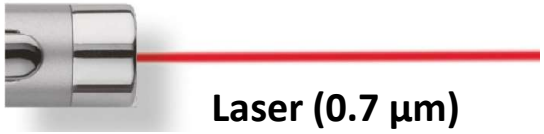


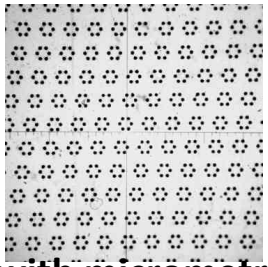


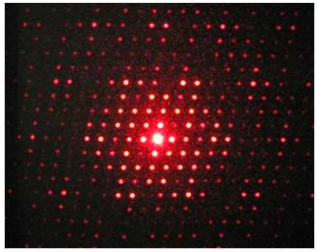








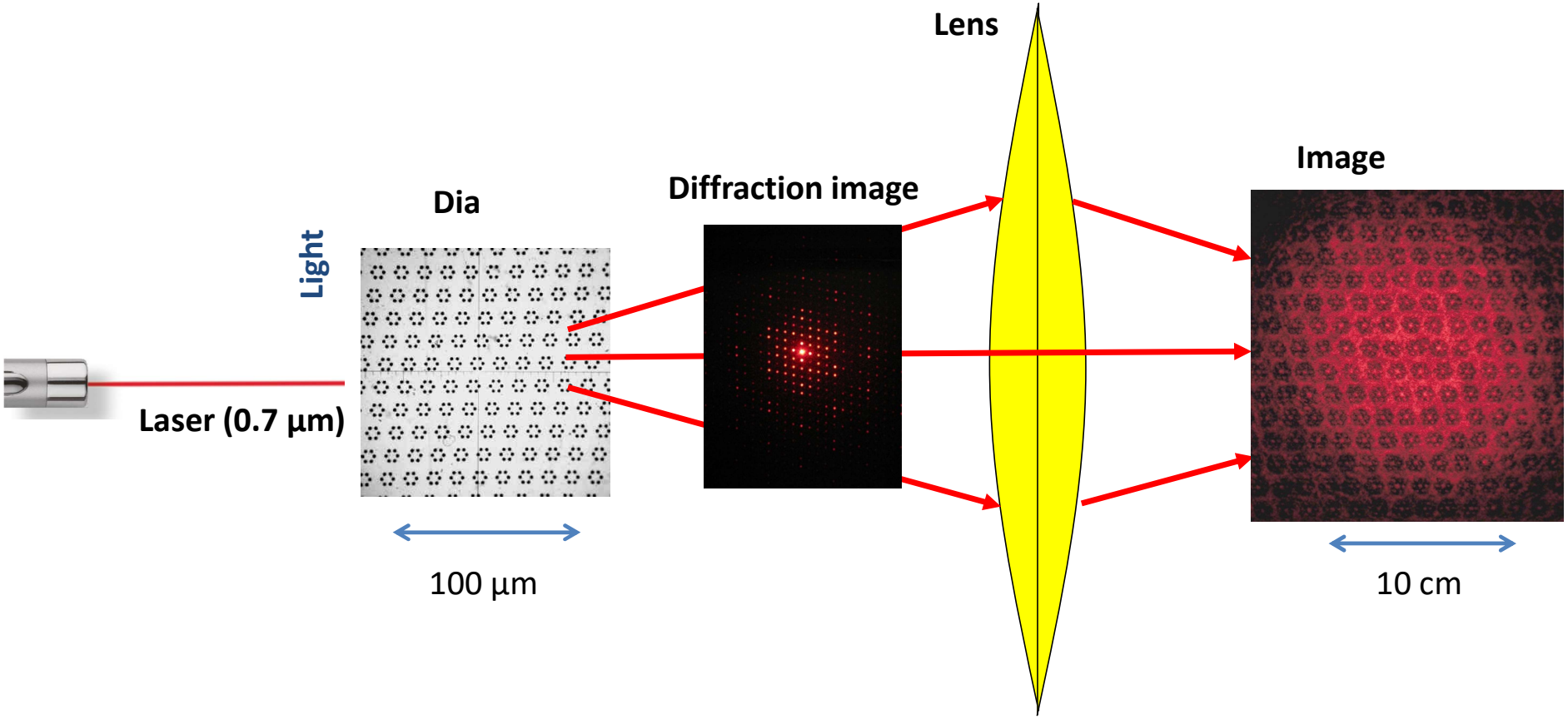




Slides with micrometric dots

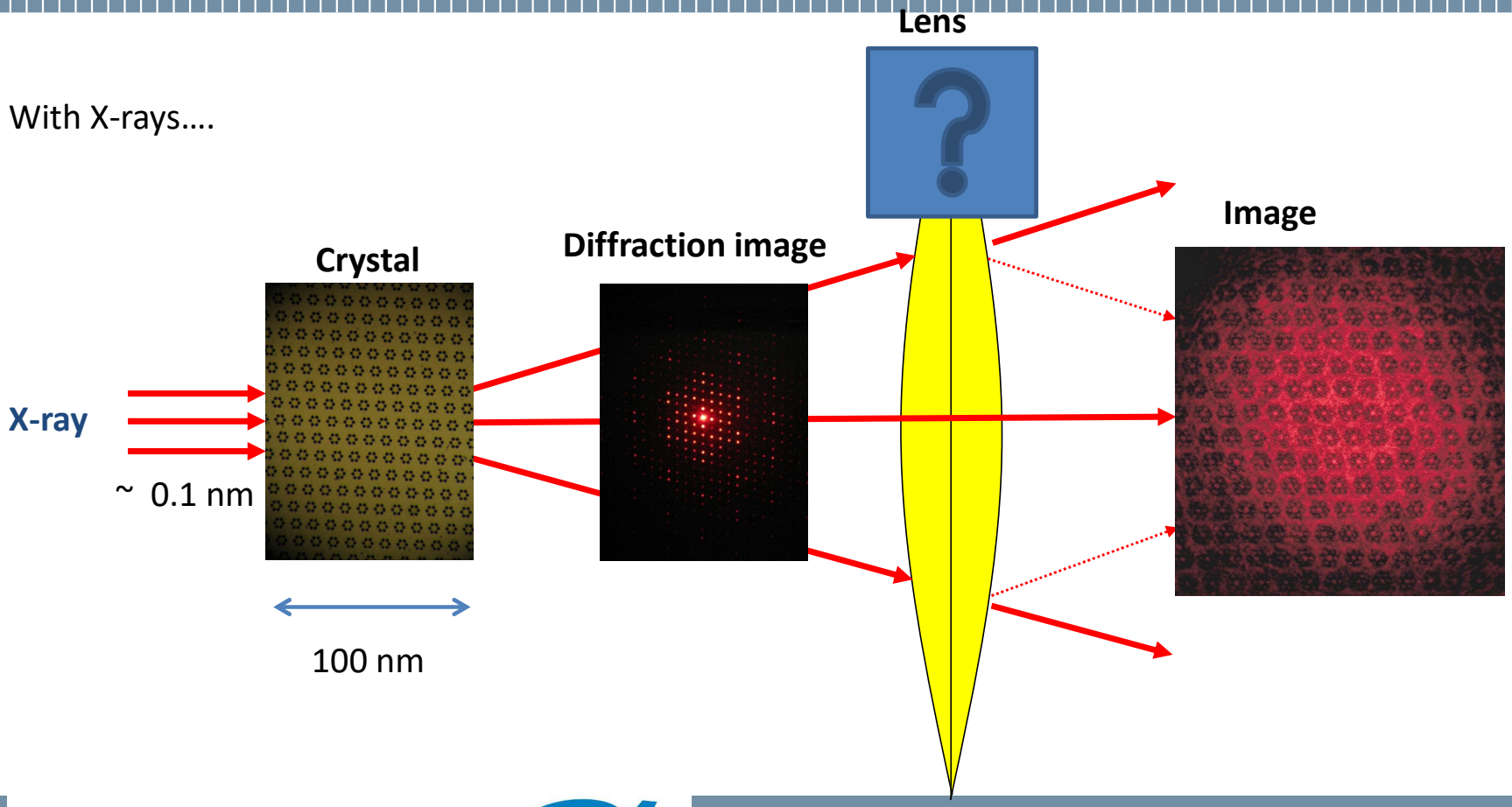
Diffraction images

Microscopy/Diffraction two sides of the same coin

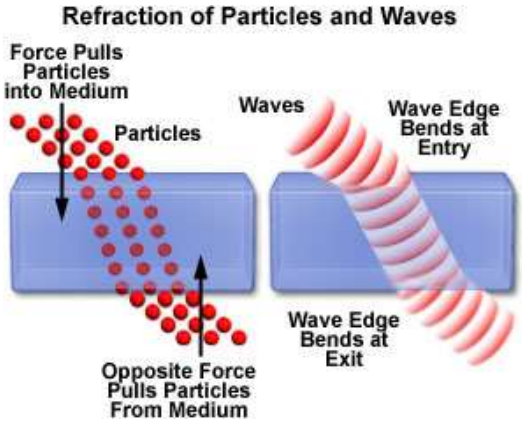


Microscopy/Diffraction two sides of the same coin

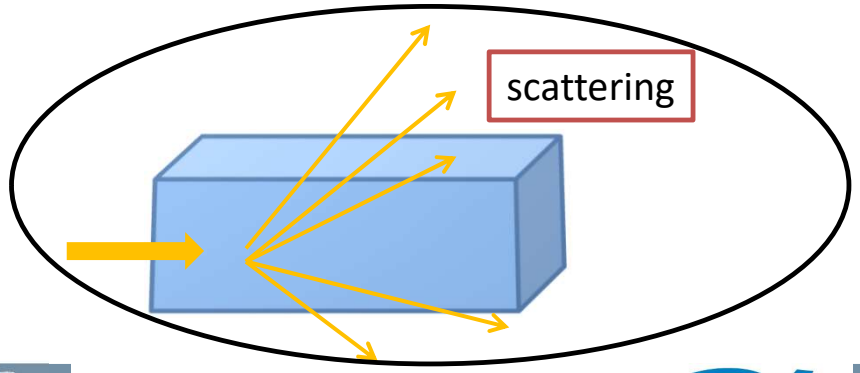
With X-rays….



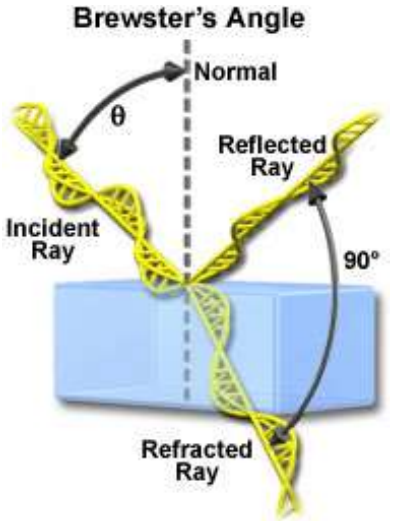
Interaction of X-rays with matter



refraction



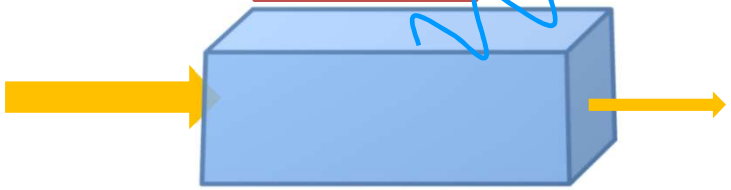
scattering



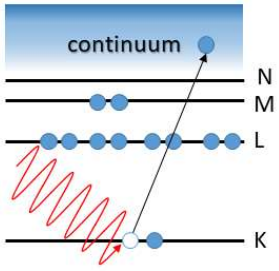
Reflection

fluorescence

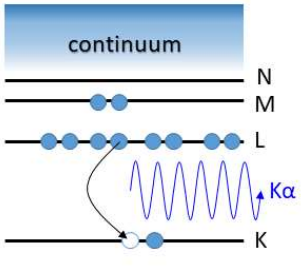
absorption



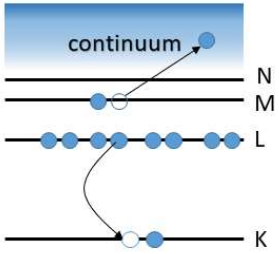
Interaction of X-rays with matter



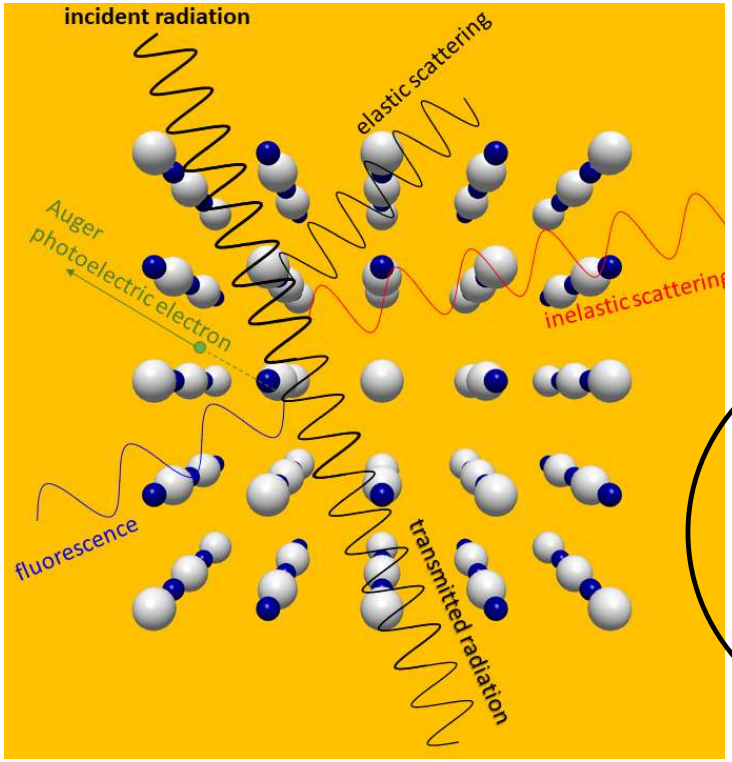
Photoelectric effect

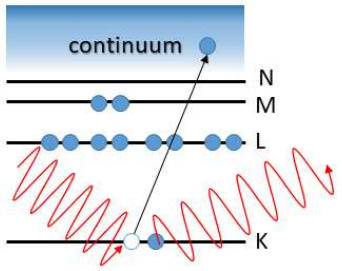


Fluorescence

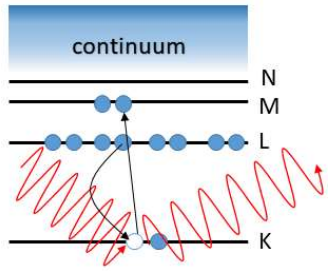


Auger electron

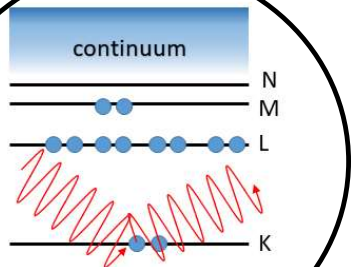




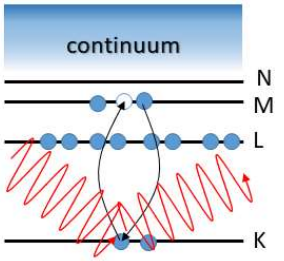
inelastic scattering



resonant inelastic scattering

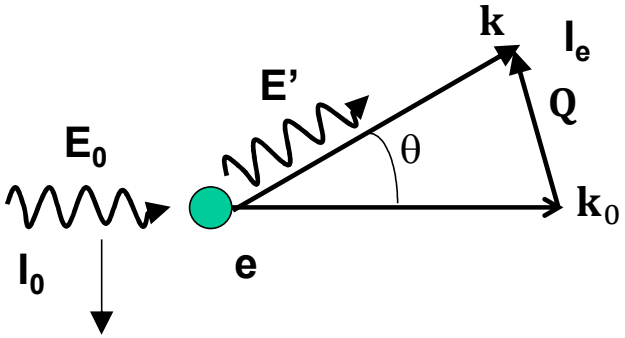


Elastic scattering



resonant elastic scattering

The scattering



X photon, wavelength λ, energy **E**

$$Q = |\mathbf{Q}| = |\mathbf{k} - \mathbf{k_0}| = \frac{4\pi sin\theta}{\lambda}$$

Momentum transfer

Thomson scattering

- elastic scattering (E_0-E' = 0) ⇒ $I_e \div \frac{1 + \cos^2(\vartheta)}{2} I_0$

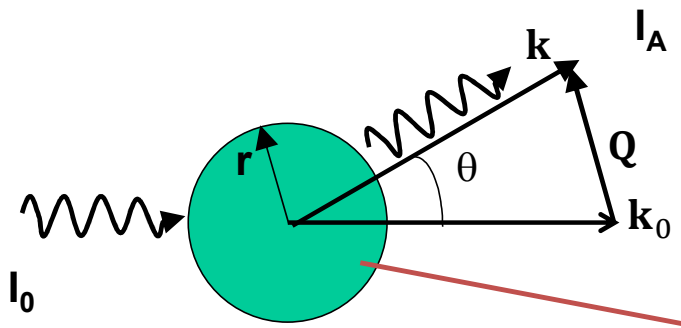
- inelastic scattering (E_0-E' ≠ 0) ⇒ $\Delta\lambda = \frac{h}{m_e c}(1 - cos\vartheta)$

Compton scattering

The momentum transfer: notations

Symbol	Modulus	Remark
$\mathbf{k}, \mathbf{k_0}$	$2\pi/\lambda$	Wave vectors for scattering and incident directions, respectively
$\mathbf{s}, \mathbf{s_0}$	$1/\lambda$	Wave vectors for scattering and incident directions, respectively
$\mathbf{H} = \mathbf{h} = \mathbf{s} - \mathbf{s_0} = (\mathbf{k} - \mathbf{k_0})/2\pi$	$2sin\vartheta/\lambda$	Scattering vector (Bragg condition)
$\mathbf{S} = \mathbf{s} - \mathbf{s_0} = (\mathbf{k} - \mathbf{k_0})/2\pi$	$2sin\vartheta/\lambda$	Scattering vector (general)
$\mathbf{Q} = \mathbf{q} = \mathbf{k} - \mathbf{k_0}$	$4\pi sin\vartheta/\lambda$	Scattering vector (typically used for small angle scattering or total scattering)
$\mathbf{K} = \mathbf{k} - \mathbf{k_0}$	$4\pi sin\vartheta/\lambda$	Scattering vector

The atomic scattering

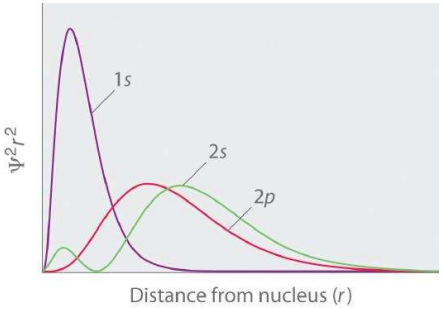


$I_A \div |f_A|^2$ (atomic form factor)

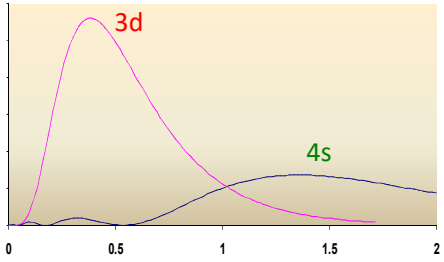
one atom (n electrons)

The ***atomic form factor*** is the sum of the elastic contribution of all its electrons, taking into account the different shapes of the electron clouds around an atom (core/valence electrons, for example)

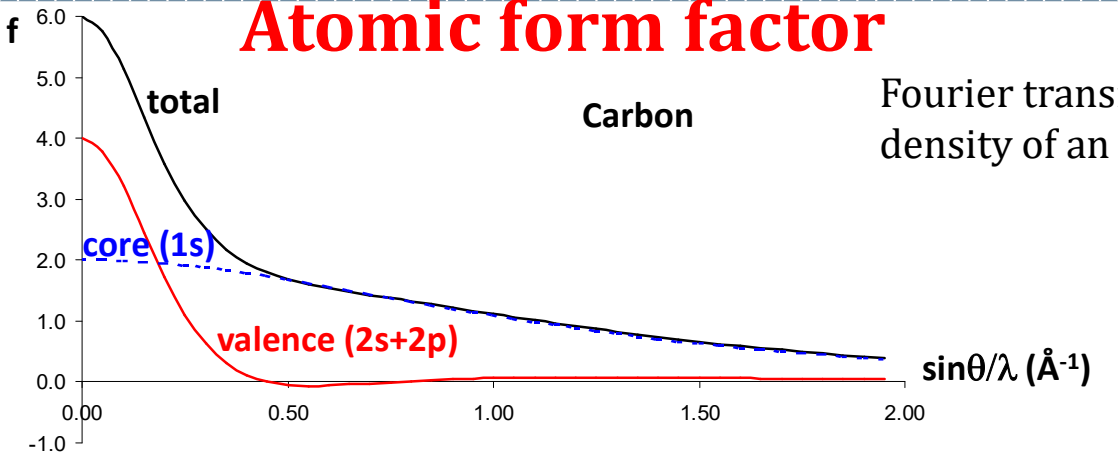
The scattering of one atom

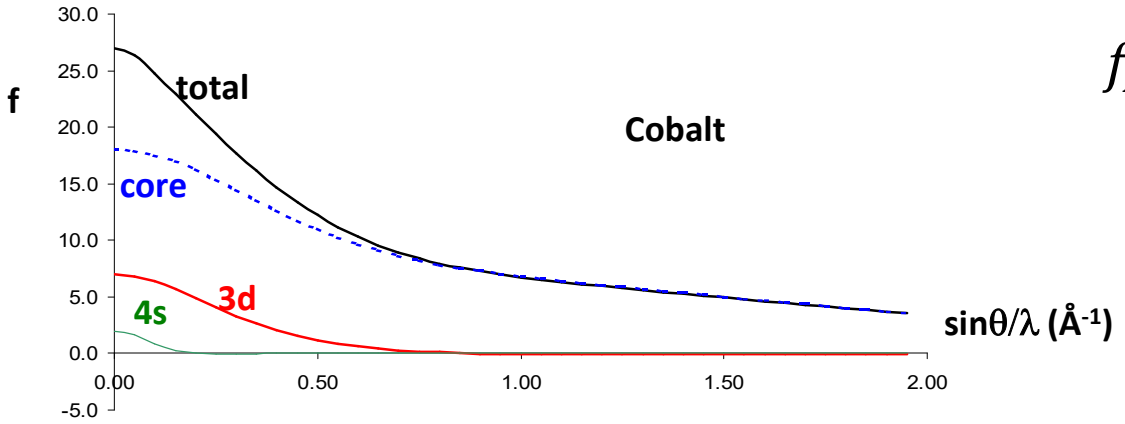


atomic riadial electron density



Atomic form factor





Fourier transform of the electron density of an isolated atom

Form factor

$$f_A(Q) = \int_V \rho(\mathbf{r})\, e^{i\mathbf{Q}\mathbf{r}}\, d\mathbf{r}$$

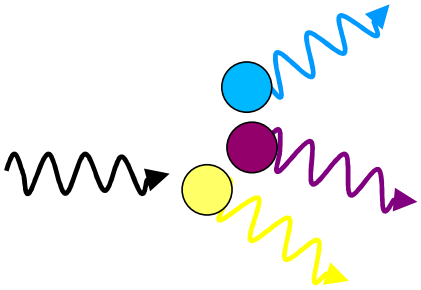
The scattering by N atoms

Interference function

$$\psi(\mathbf{s}) = \frac{I(\boldsymbol{Q})}{F^2(\boldsymbol{Q})} = \frac{I_N(\boldsymbol{Q})}{NF^2(\boldsymbol{Q})}$$

$$I(\boldsymbol{Q}) = \frac{I_N(\boldsymbol{Q})}{N}$$

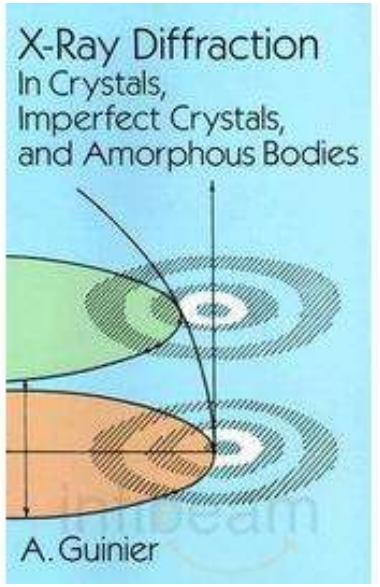
Unit scattering power



The waves generated by each atom produce interference because they are within the **coherence domain**.
The interference only depends on the relative position of the atoms (**atomic distances**) and on the diffusive power of each atom (**atomic form factors**).

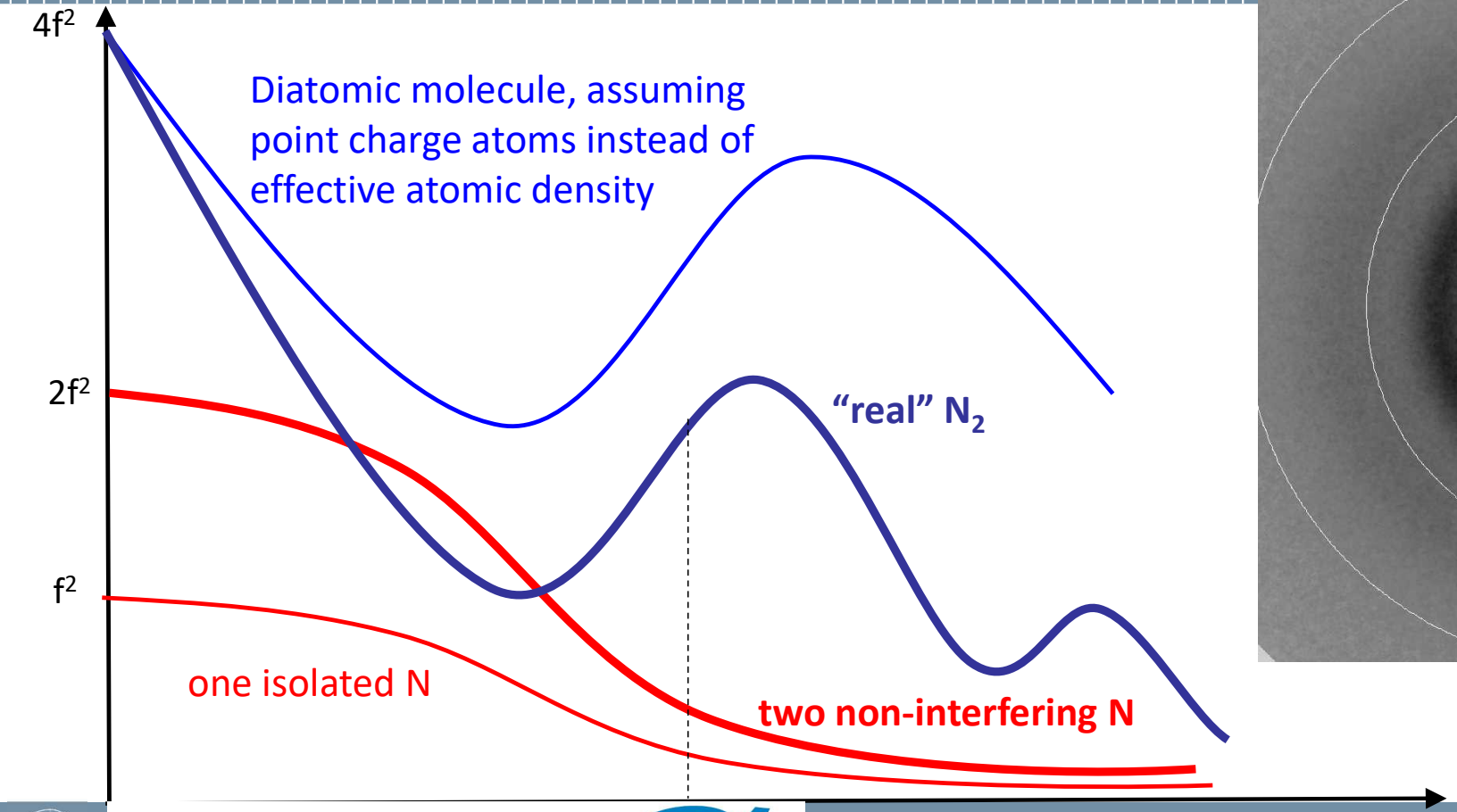
If all the diffusers (atoms) are randomly distributed **the interference function** $\psi(\mathbf{s})$ is 1.0 (average between 0.0 in case of destructive interference and 2.0 in case of constructive interference). This in case of "ideal amorphous".

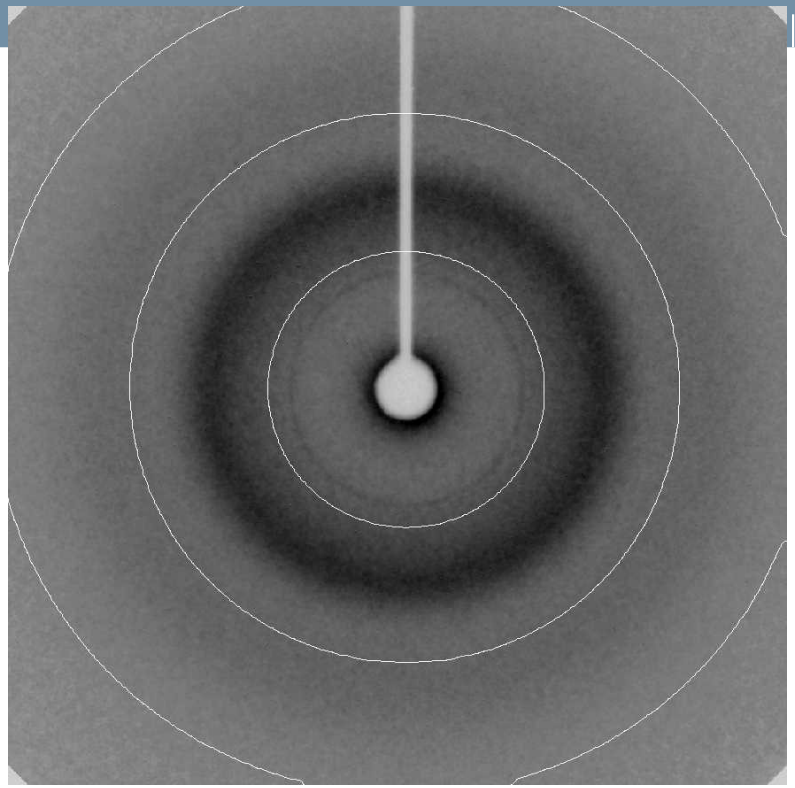
This determines the **phase**, which is lost when measuring $I_N(\boldsymbol{Q})$



$$I_1(\boldsymbol{Q}) = |A(\boldsymbol{Q})|^2$$

The scattering by N atoms

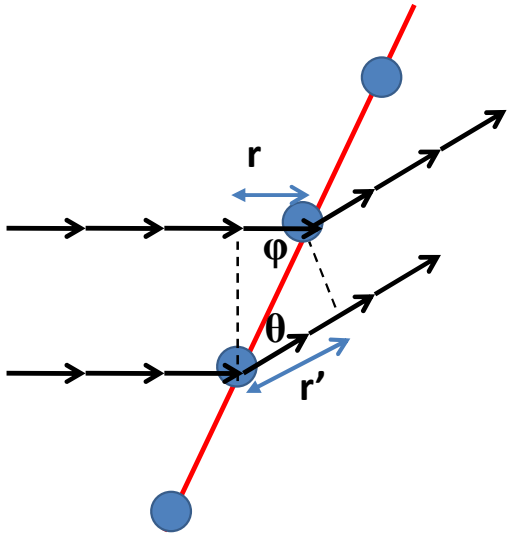




Diffraction from crystals

Infinite Periodic crystals

von Laue described the X-ray diffraction of crystals by modelling a crystal as a combination of three one-dimensional atomic nets.



In order to avoid destructive interference it is necessary that all pairs of atom have constructive interference.
This means that the waves diffused by any two atoms have a phase difference of 0 ± nλ

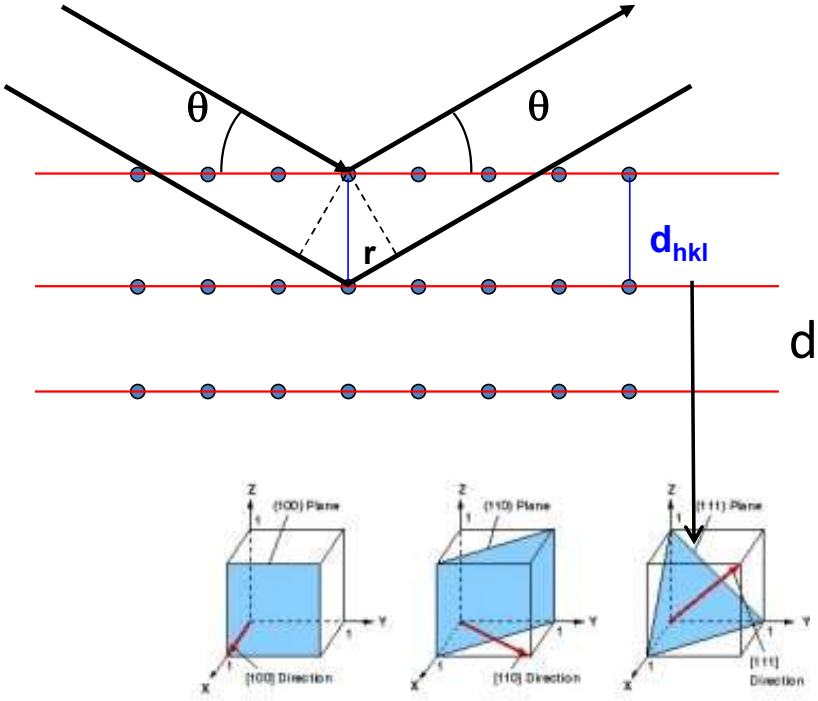
$$r' - r = a\cos(\theta) - a\cos(\varphi) = h\lambda$$

$$r' - r = a \cdot (S - S_0) = h\lambda$$

Extending in three dimensions, diffraction occurs when the difference between scattered and incident wave vectors satisfies the condition along each of the three directions, thus with a “triplet” of integers (h, k , l)

Diffraction from crystals

A different viewpoint of the same phenomenon is given by Bragg. Diffraction is regarded as a simple reflection of the photon on a given surface of the crystal. However, we must consider that the X-ray beam “penetrates” the surface and therefore contribution from inner layers must also be accounted for.

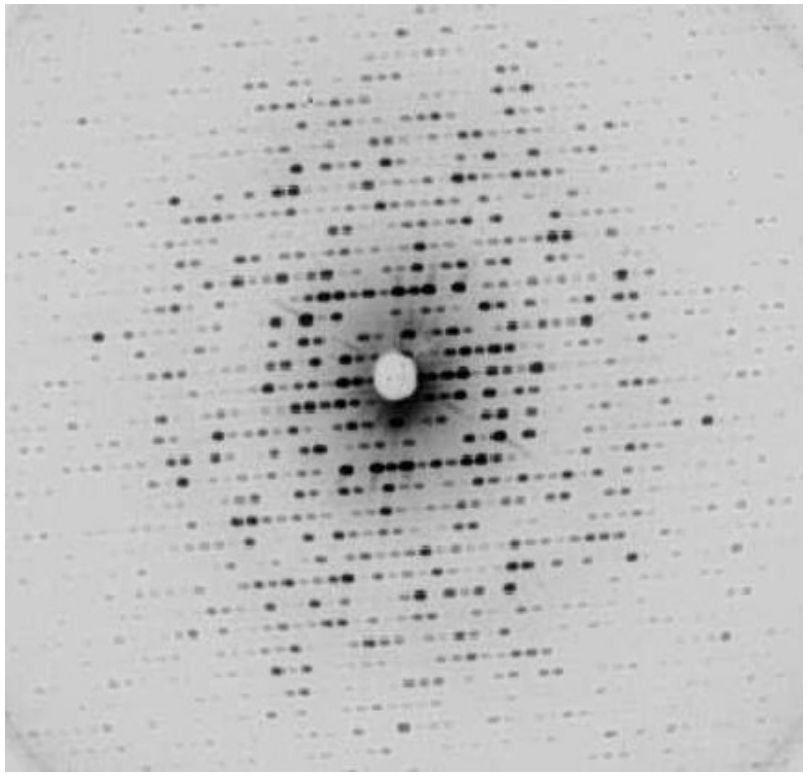


Miller indexes

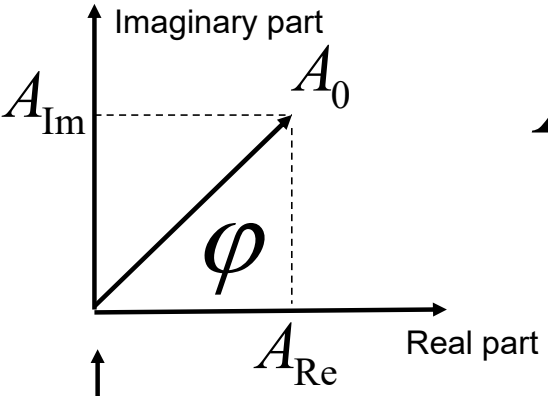
$$r + r =$$

$$d_{hkl} \sin(\theta) + d_{hkl} \sin(\theta) = n \lambda$$

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



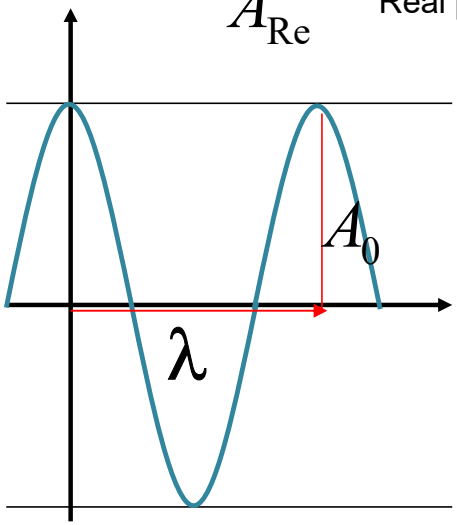
Diffraction from crystals

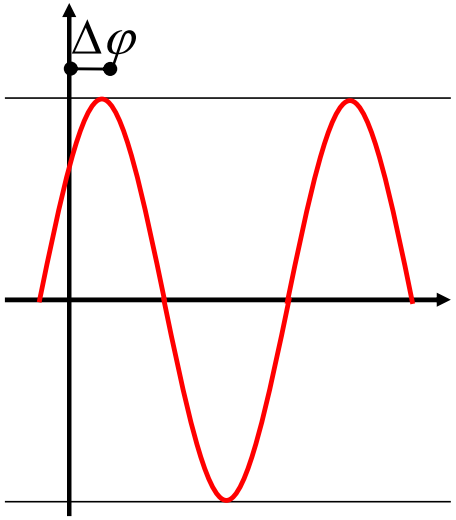


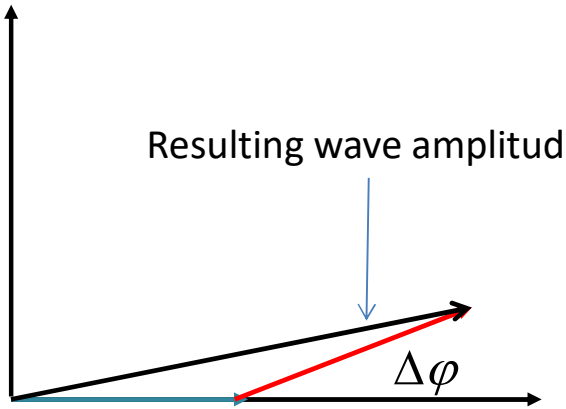
$$A = A_0 e^{i\varphi}$$

Phase (distance from the origin)

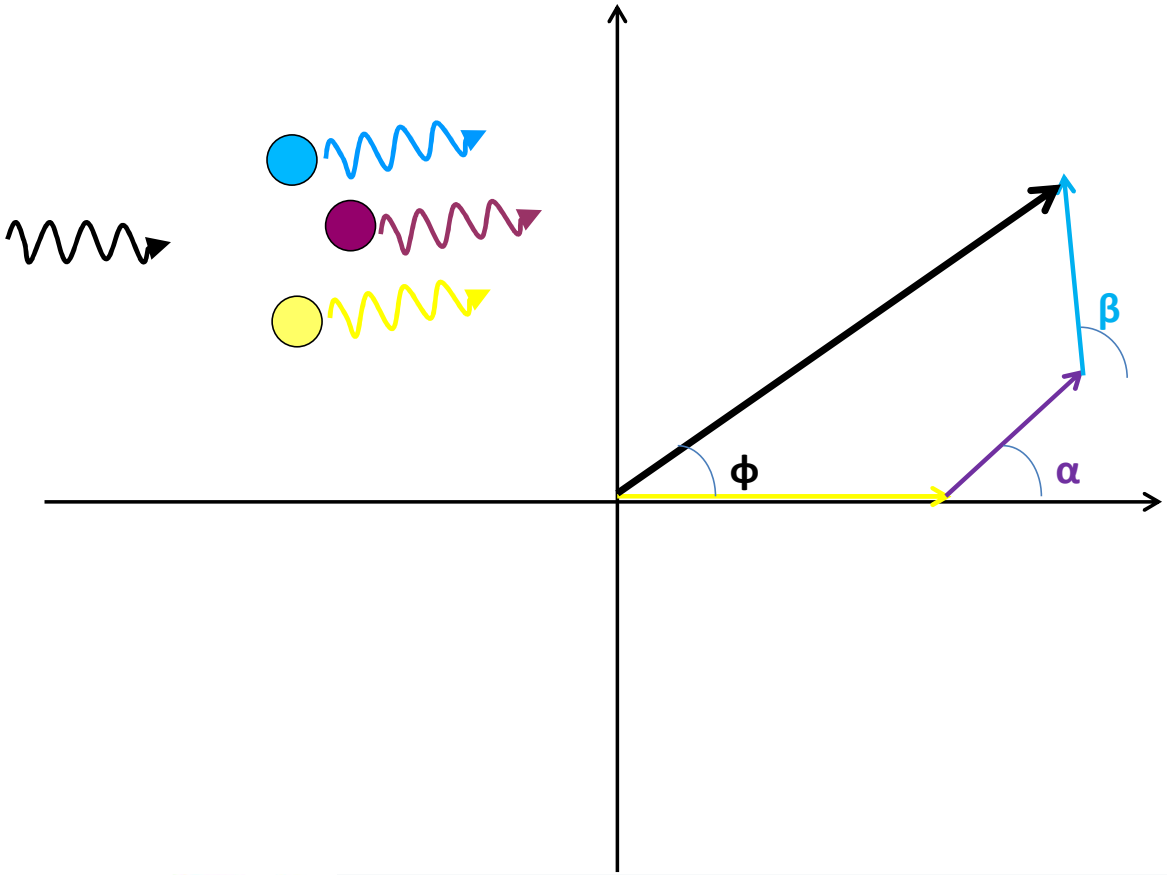
amplitude



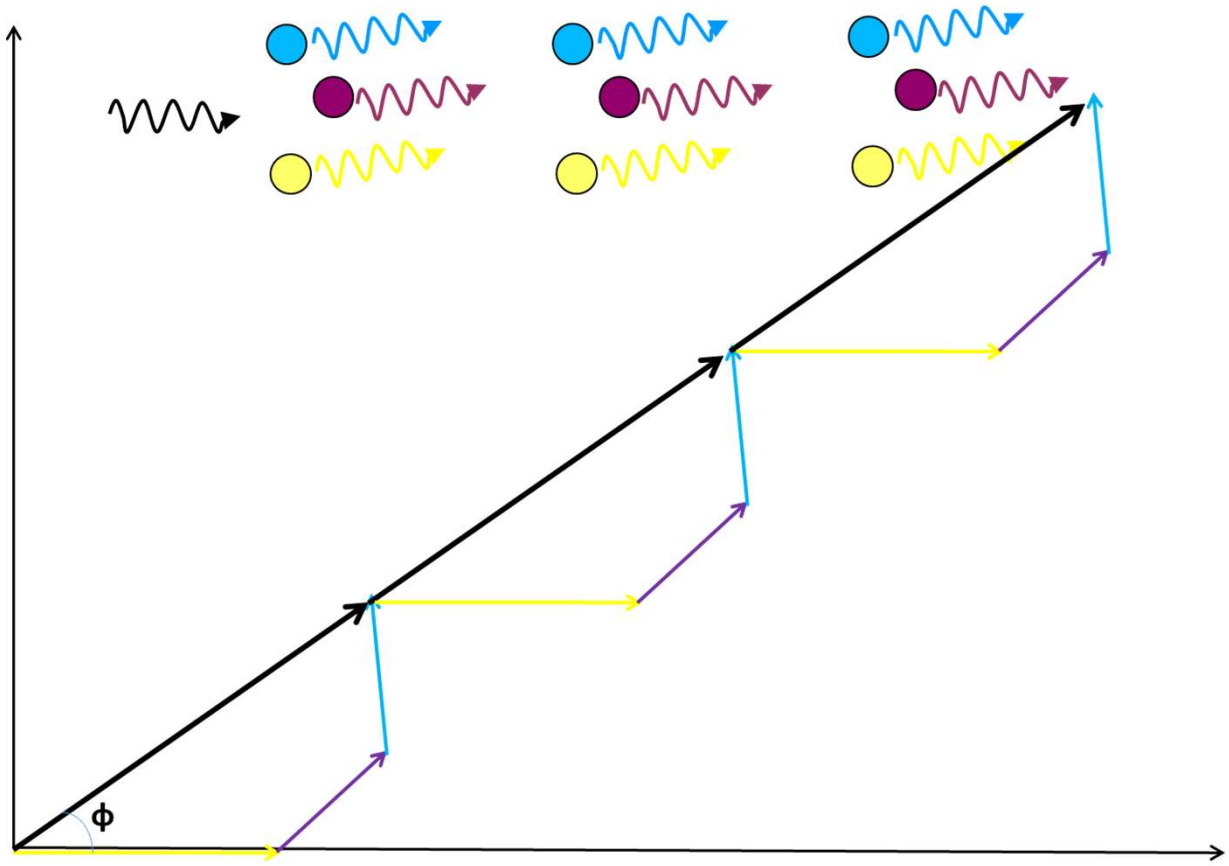




Polyatomic system



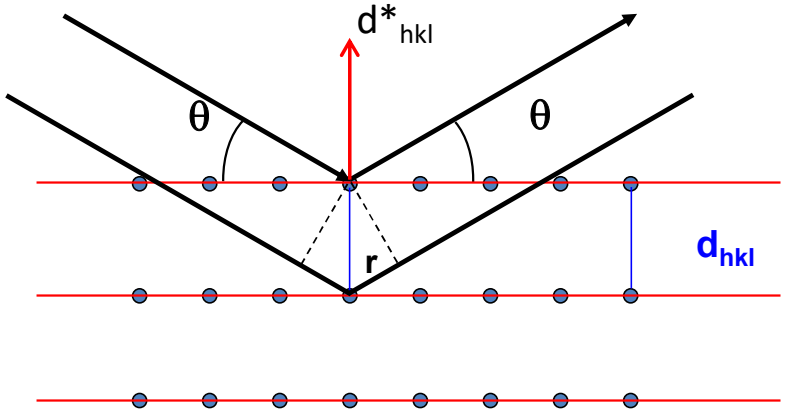
Periodic system



The reciprocal space

We need a simplified way to handle planes in order to describe diffraction phenomena from crystals (having in mind Bragg formalism) and predict diffraction conditions

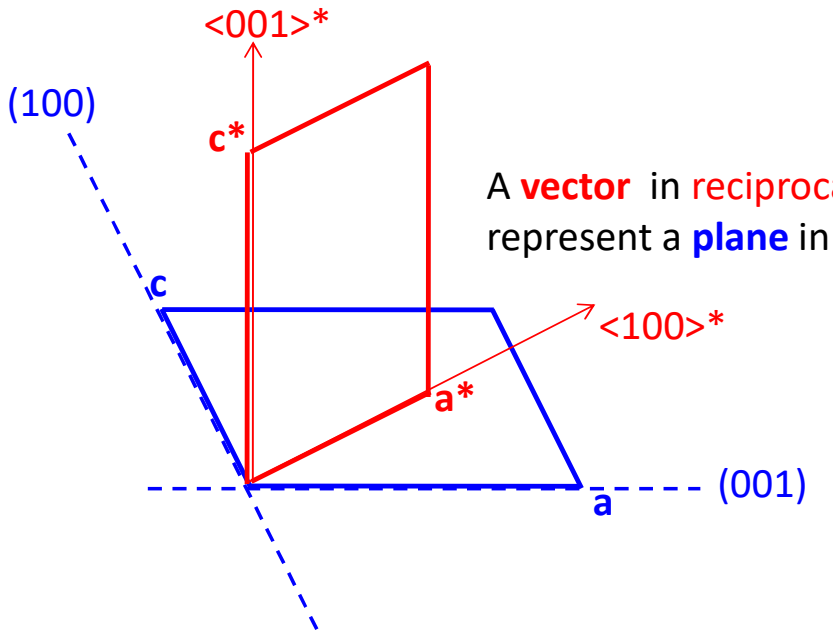
A family of planes can be simply represented by its normal



A reciprocal lattice vector d* is perpendicular to a plane and its length is inversely proportional to d_{hkl} spacing

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

The reciprocal space



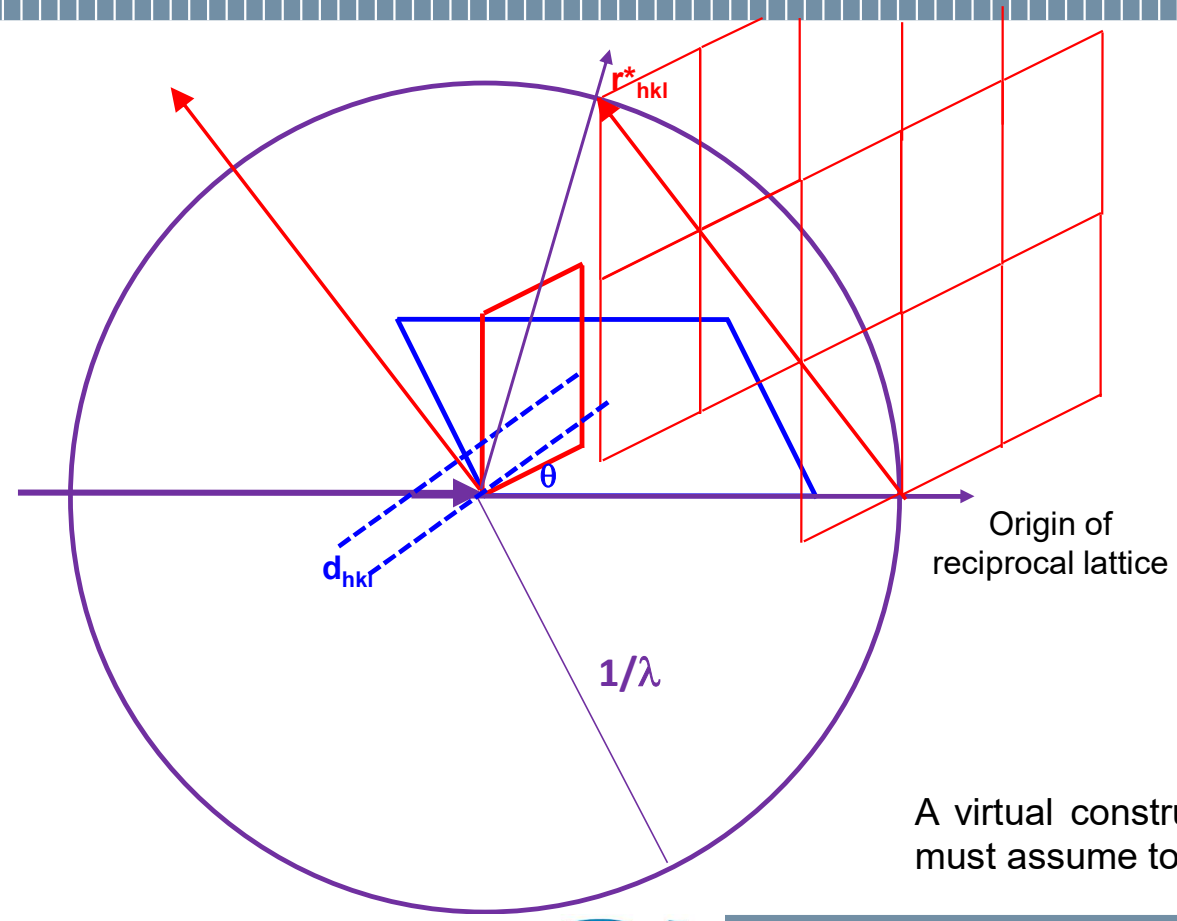
A **vector** in reciprocal space
represent a **plane** in direct space

Conditions:

a · **a*** = **1.0**	**b** · **a*** = 0.0	**c** · **a*** = 0.0
a · **b*** = 0.0	**b** · **b*** = **1.0**	**c** · **b*** = 0.0
a · **c*** = 0.0	**b** · **c*** = 0.0	**c** · **c*** = **1.0**

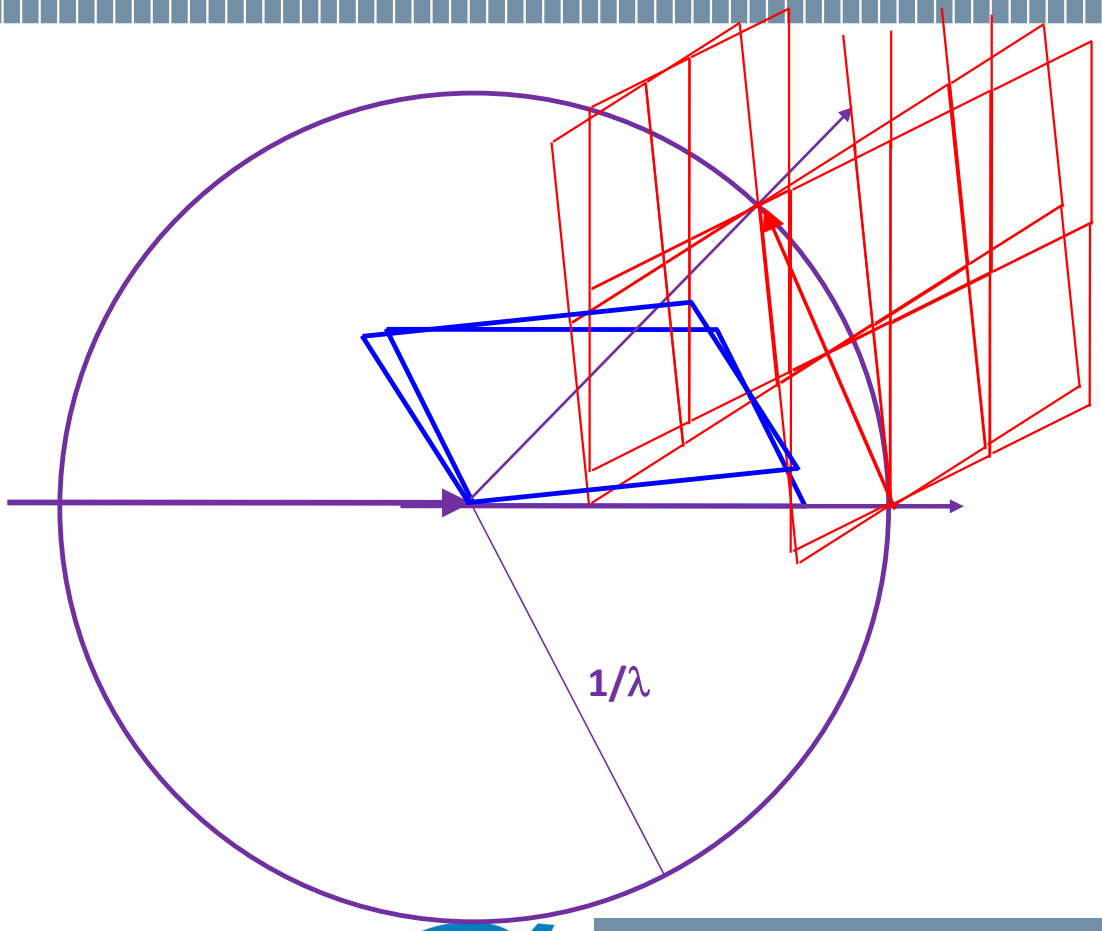
It follows that: **V = 1/V***

The Ewald sphere

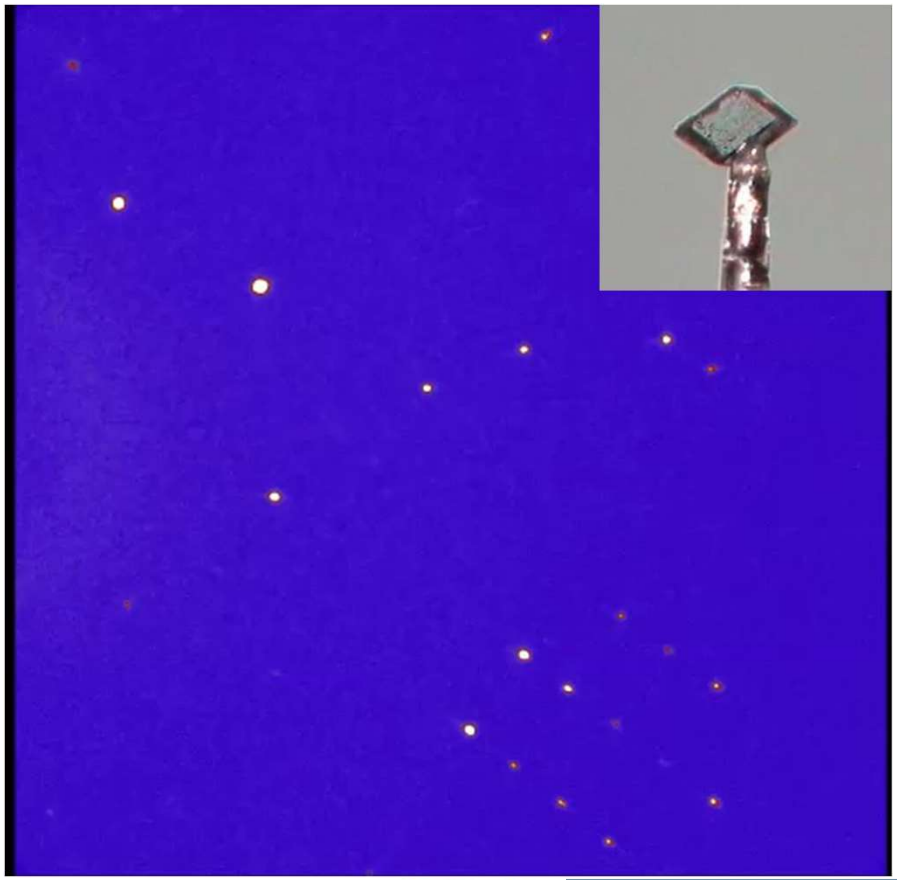


A virtual construction to predict the necessary orientation a crystal must assume to give diffraction from a given family of planes

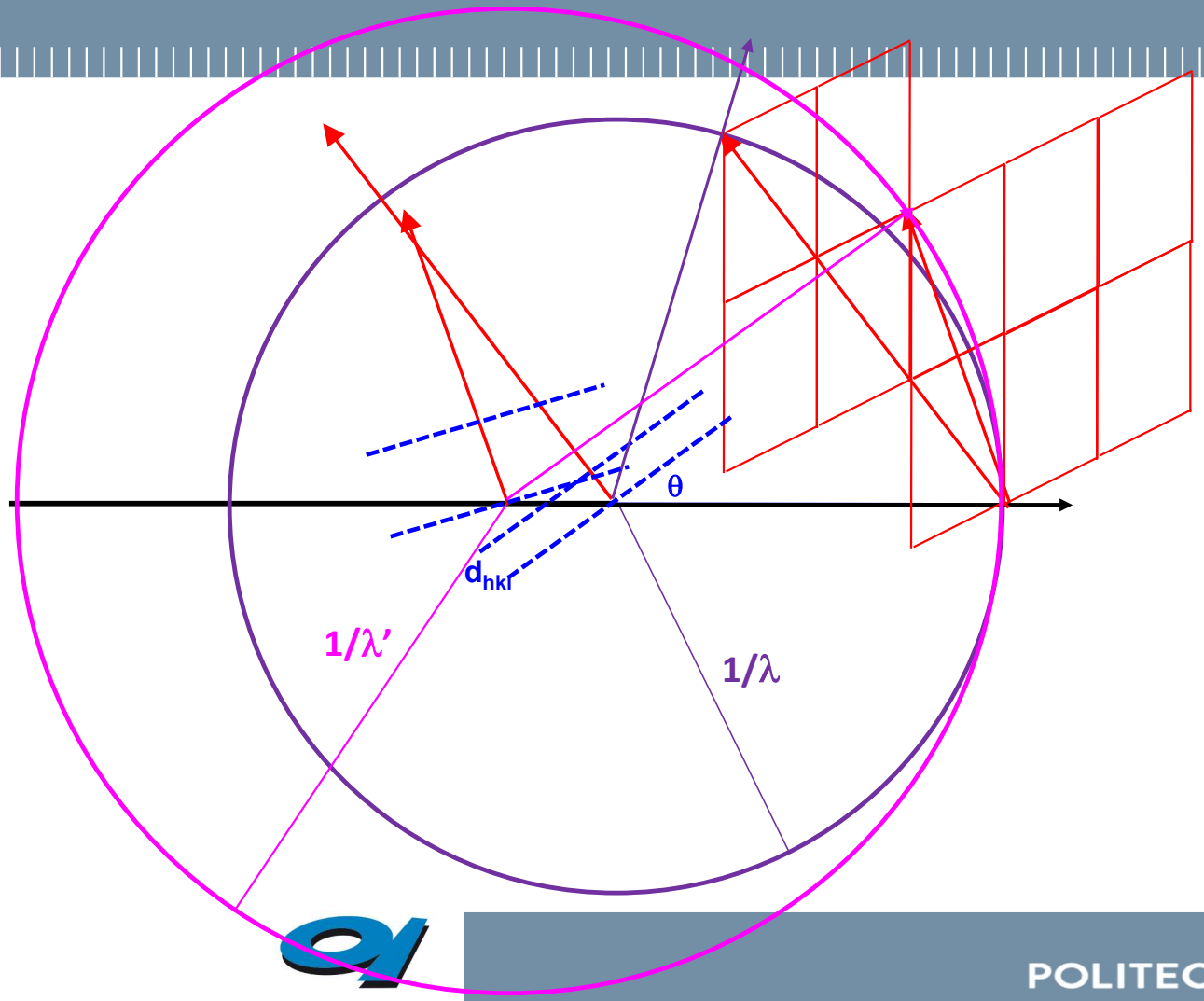
The Ewald sphere: Bragg technique



The Ewald sphere: Bragg technique

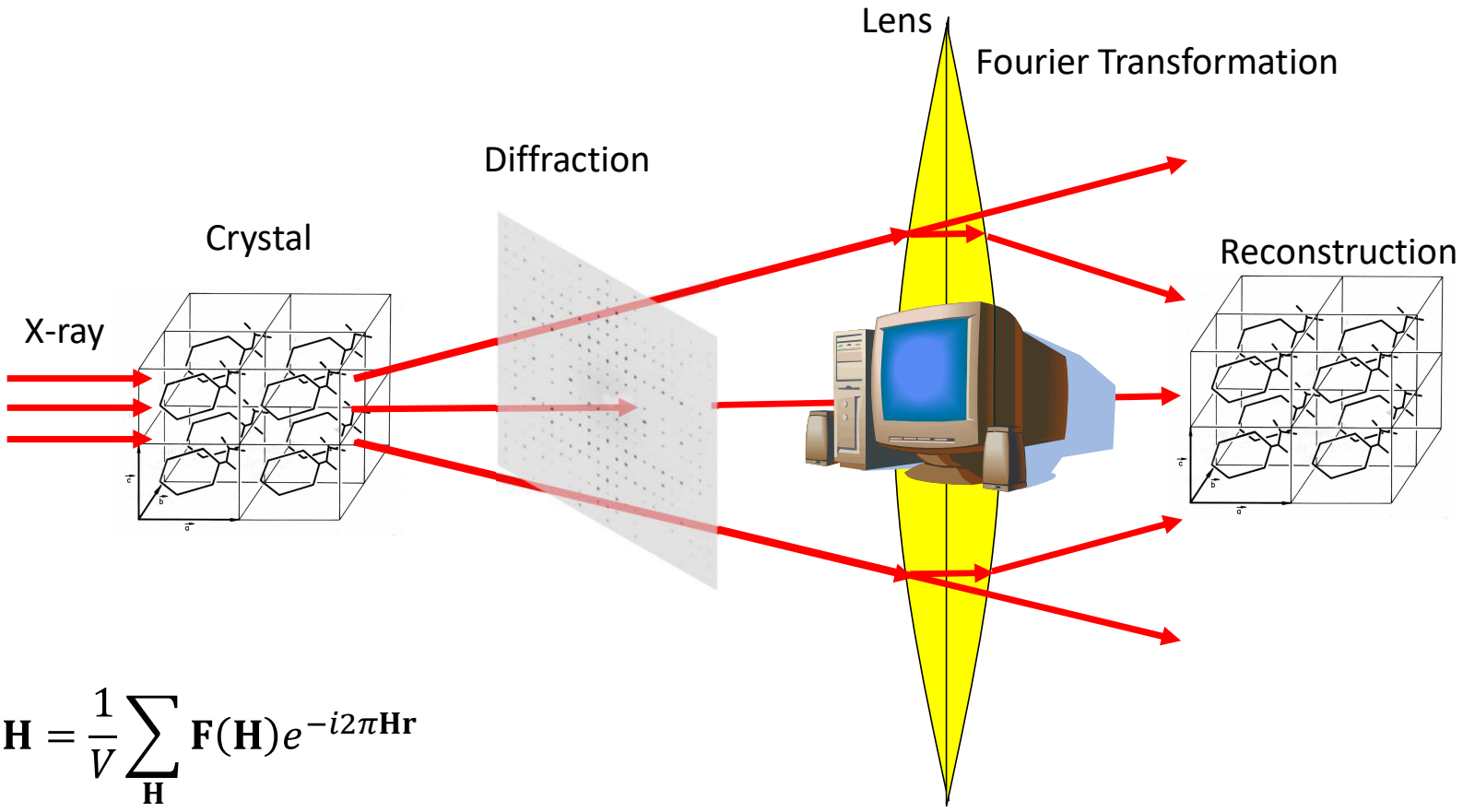


The Ewald sphere: Laue technique



The “lens”

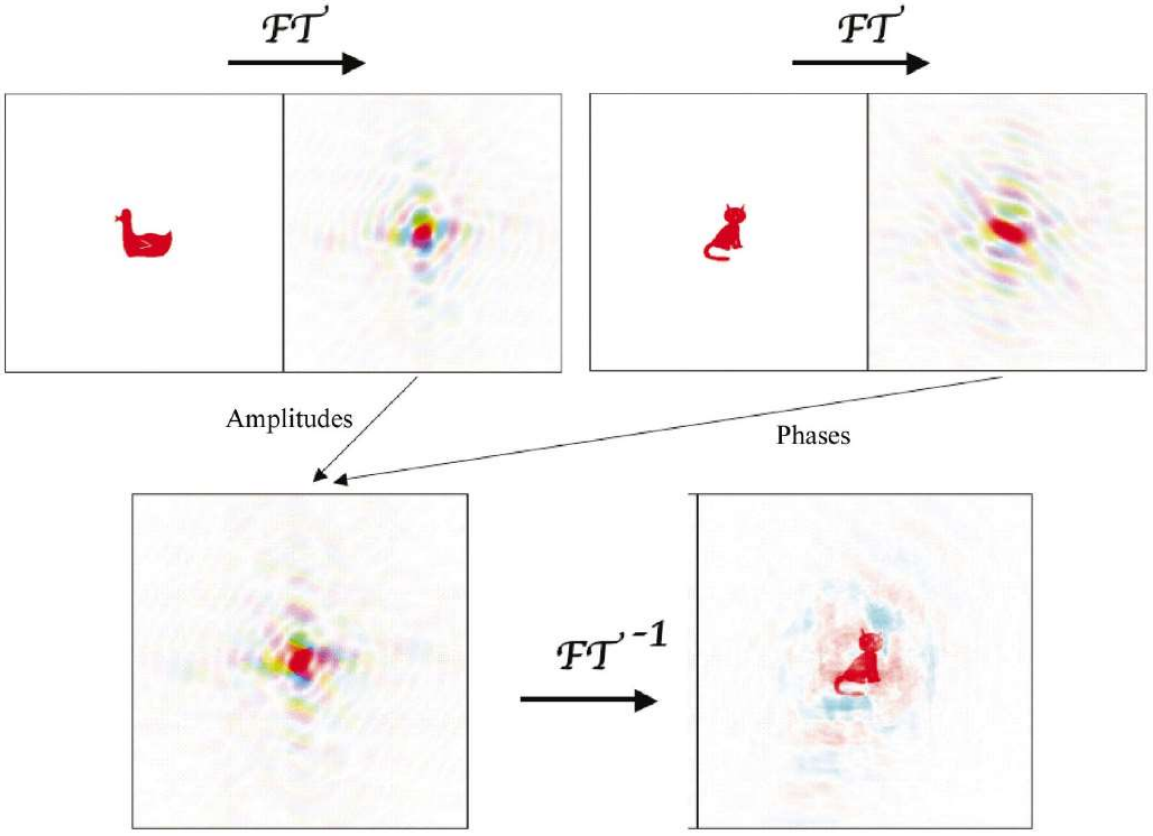
$$|\mathbf{H}| = H = \frac{2sin\theta}{\lambda} = \frac{Q}{2\pi}$$



$$\mathbf{F}(\mathbf{H}) = \int \rho(\mathbf{r}) e^{i2\pi \mathbf{H}\mathbf{r}}\, d\mathbf{r}$$

$$\rho(\mathbf{r}) = \int \mathbf{F}(\mathbf{H}) e^{-i2\pi \mathbf{H}\mathbf{r}}\, d\mathbf{H} = \frac{1}{V}\sum_{\mathbf{H}} \mathbf{F}(\mathbf{H}) e^{-i2\pi \mathbf{H}\mathbf{r}}$$

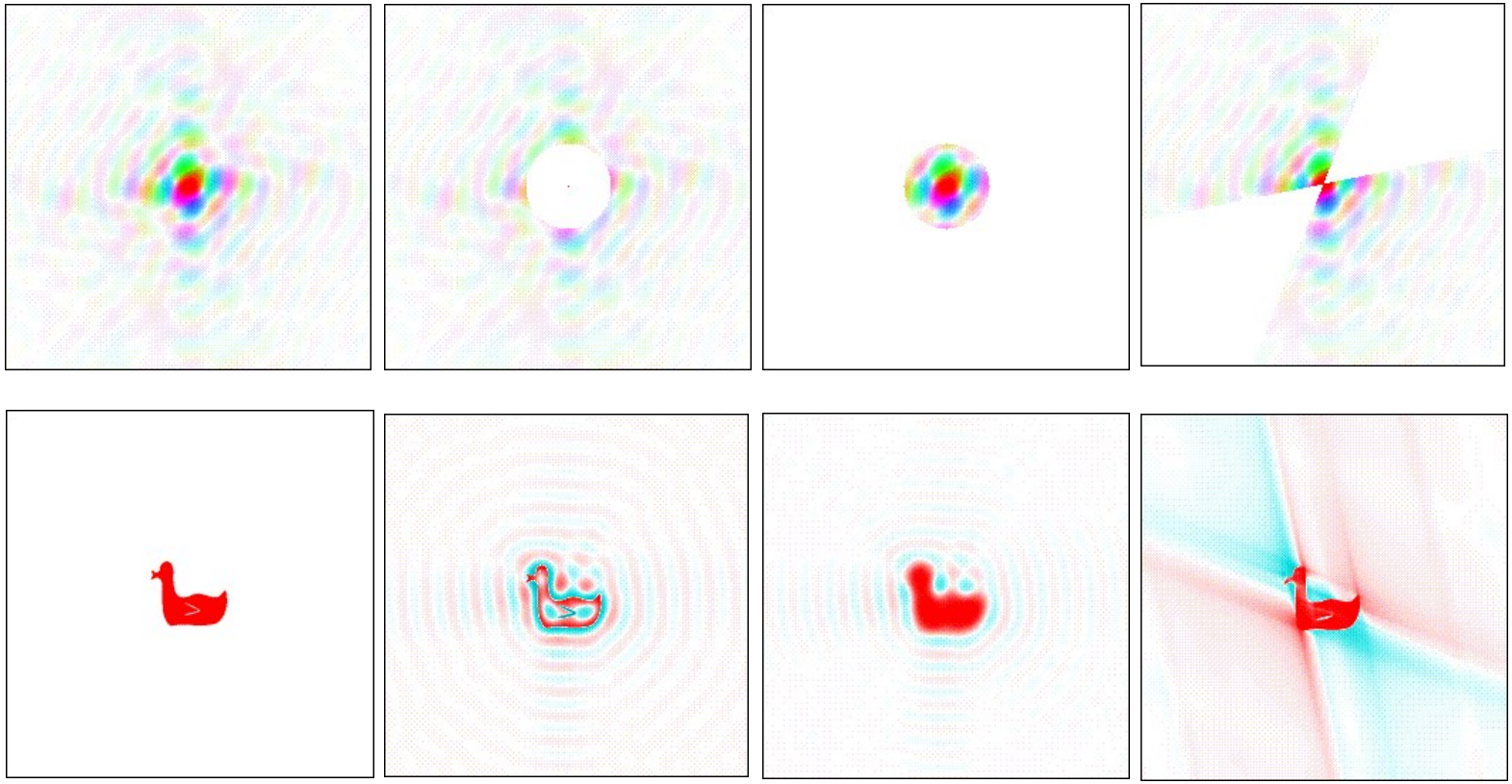
The phase problem



Phasing the reflections is the main problem of a crystal structure solution

$$\rho(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{H}} |\mathbf{F}(\mathbf{H})| e^{2\pi i \varphi_H} e^{-i2\pi \mathbf{H}\mathbf{r}}$$

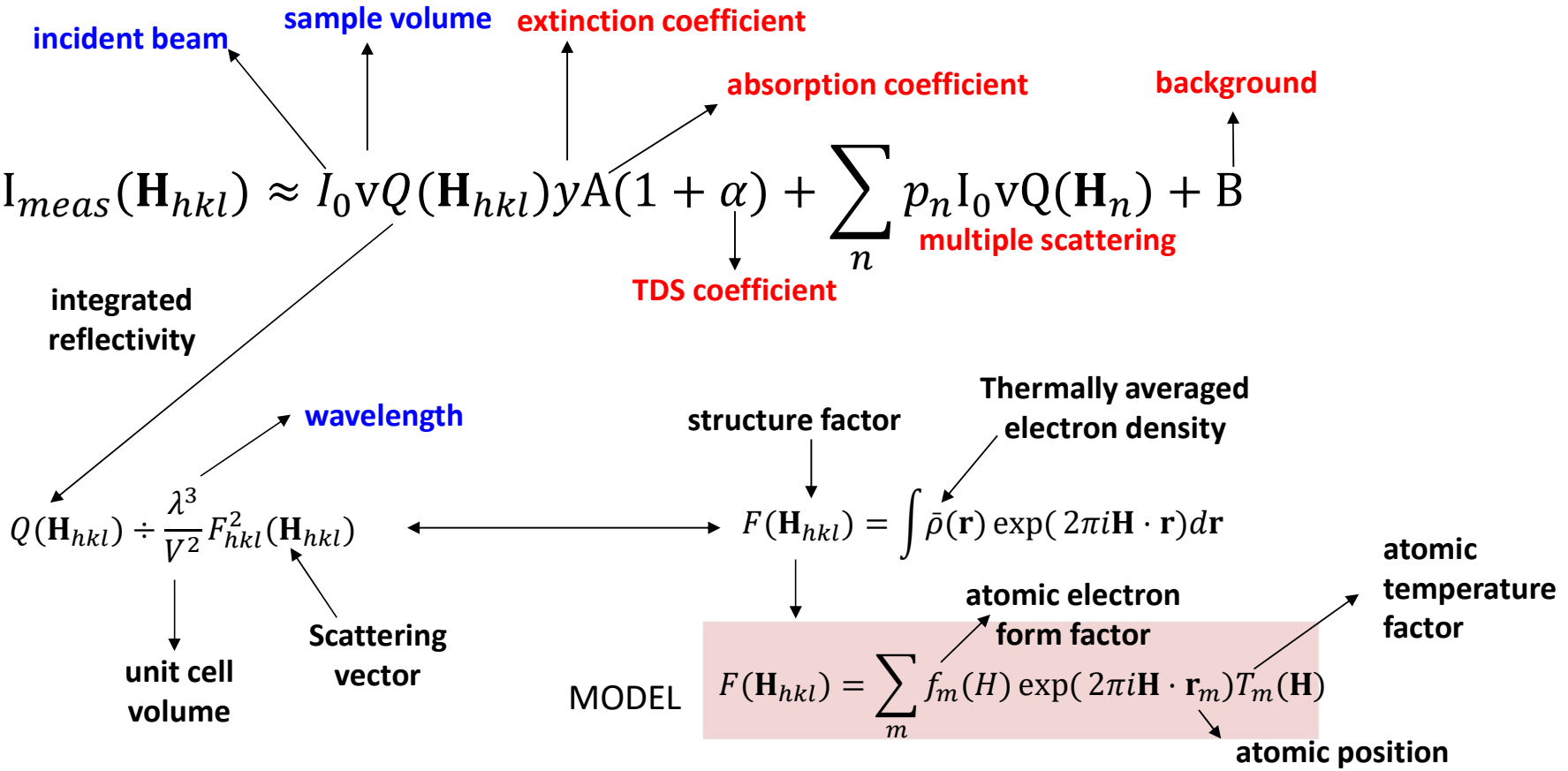
The truncation problem



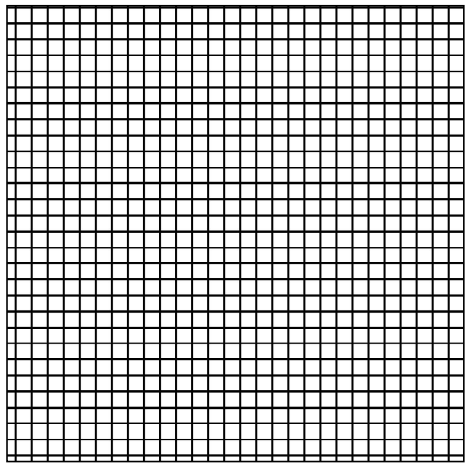
The series termination and data incompleteness is also a problem

$$\rho(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{H}} |\mathbf{F}(\mathbf{H})| e^{2\pi i \varphi_H} e^{-i2\pi \mathbf{Hr}}$$

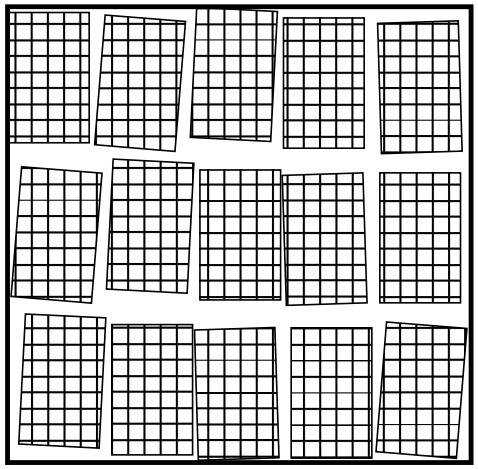
The diffracted intensity



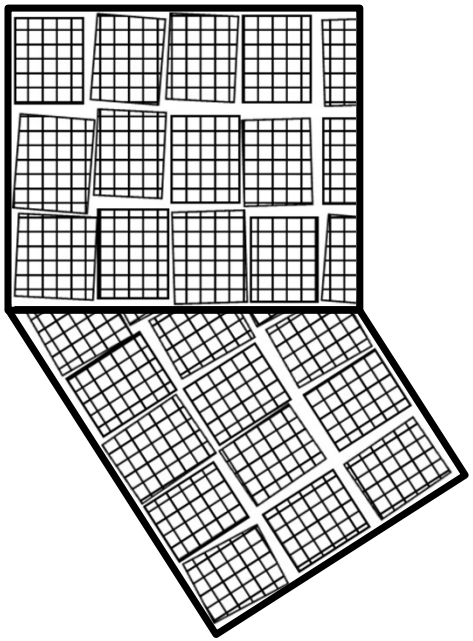
Ideal, real, twin and powder crystals



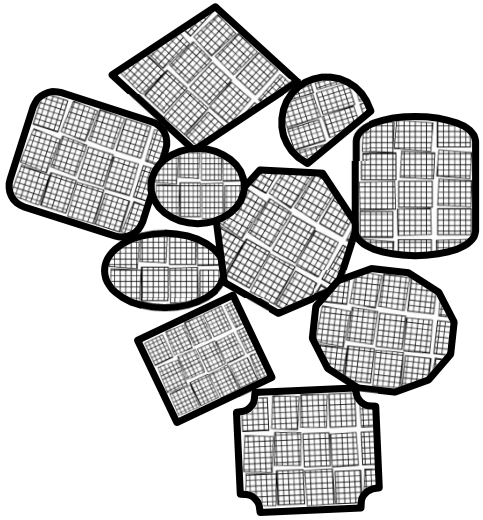
Ideal single Crystal
(**perfect**, without boundaries)



Real (imperfect) single crystal:
composed of domains (approx. radius 10^{-4} cm);
The **ideally imperfect** crystal has a statistically distributed mosaicity

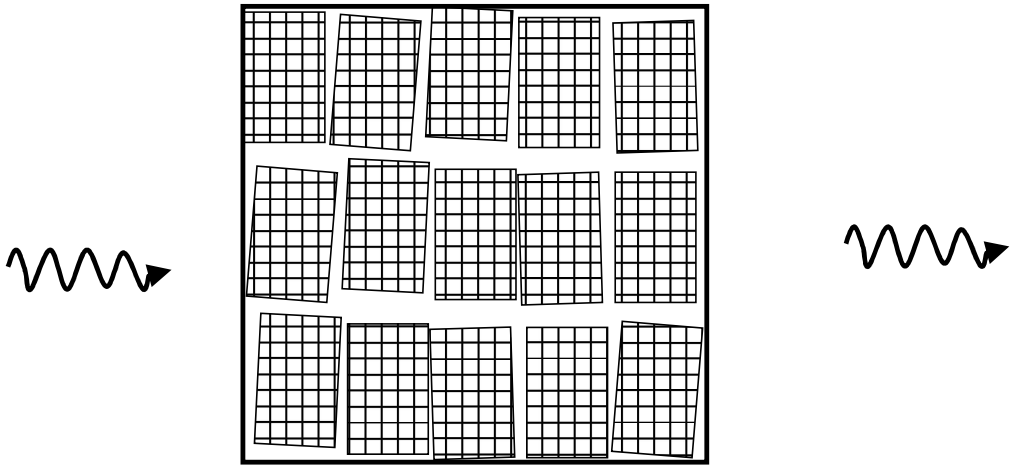


The **twinned** crystal consist of more than one real crystals fused in a single particle
(intergrowth or contact twins are possible)



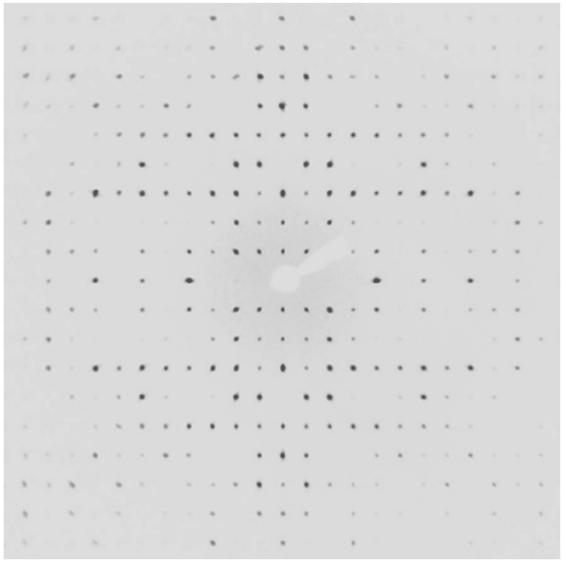
A **powder sample** consists of several (small) real crystals (separated from each other)

Diffraction from real single crystals

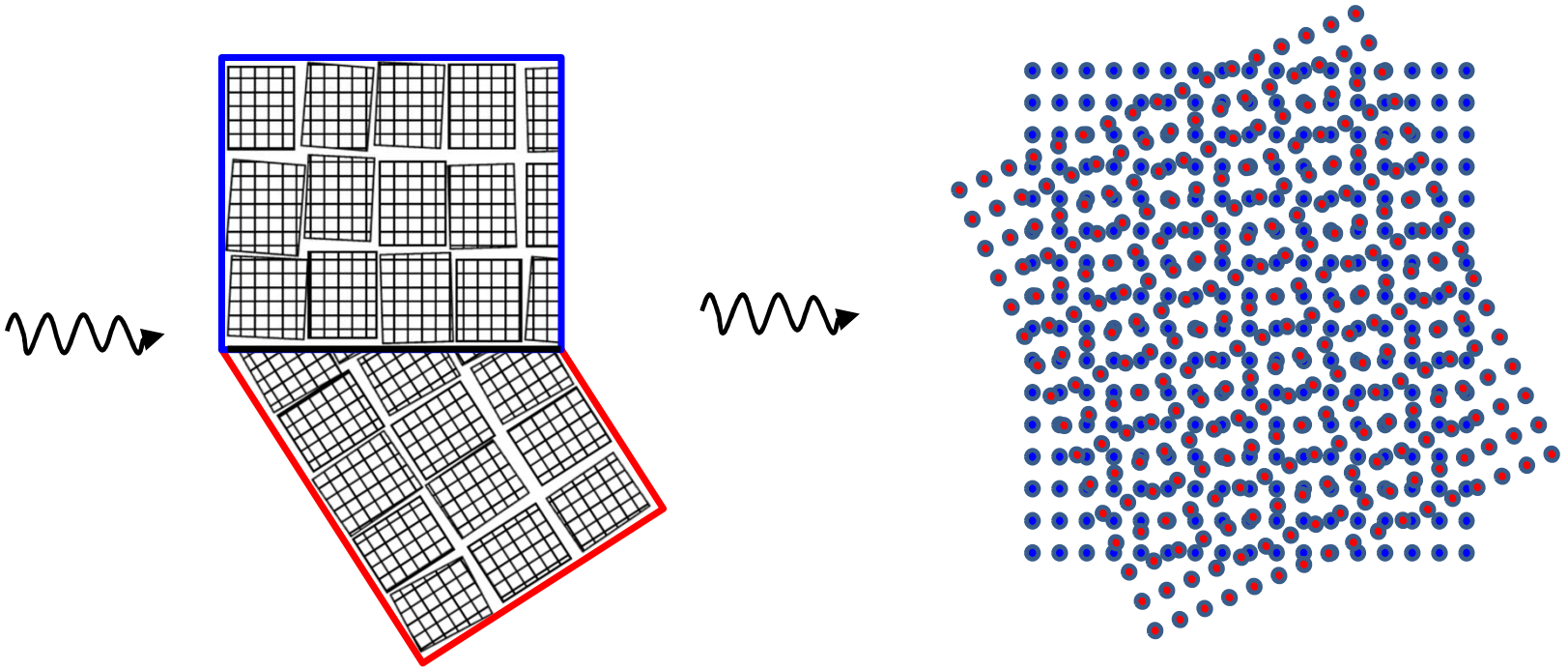


Single crystal

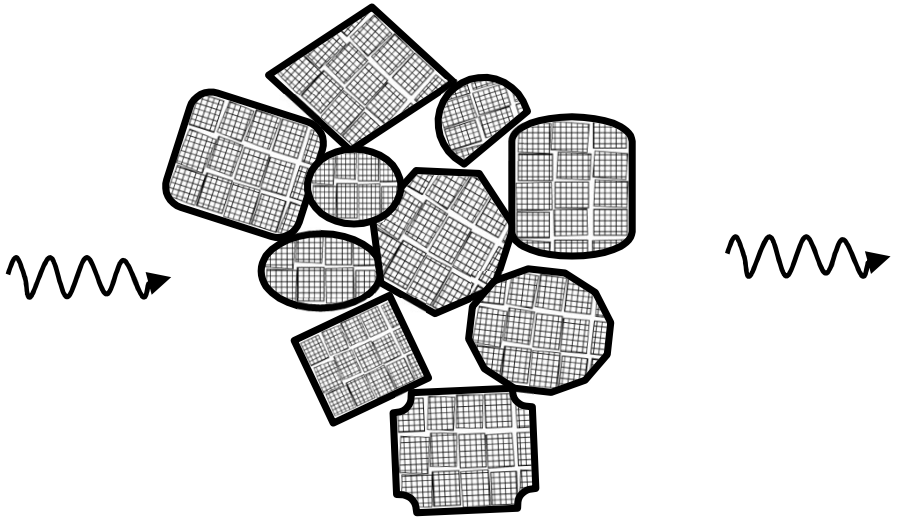
The *mosaicity* causes the broadening of diffraction spots



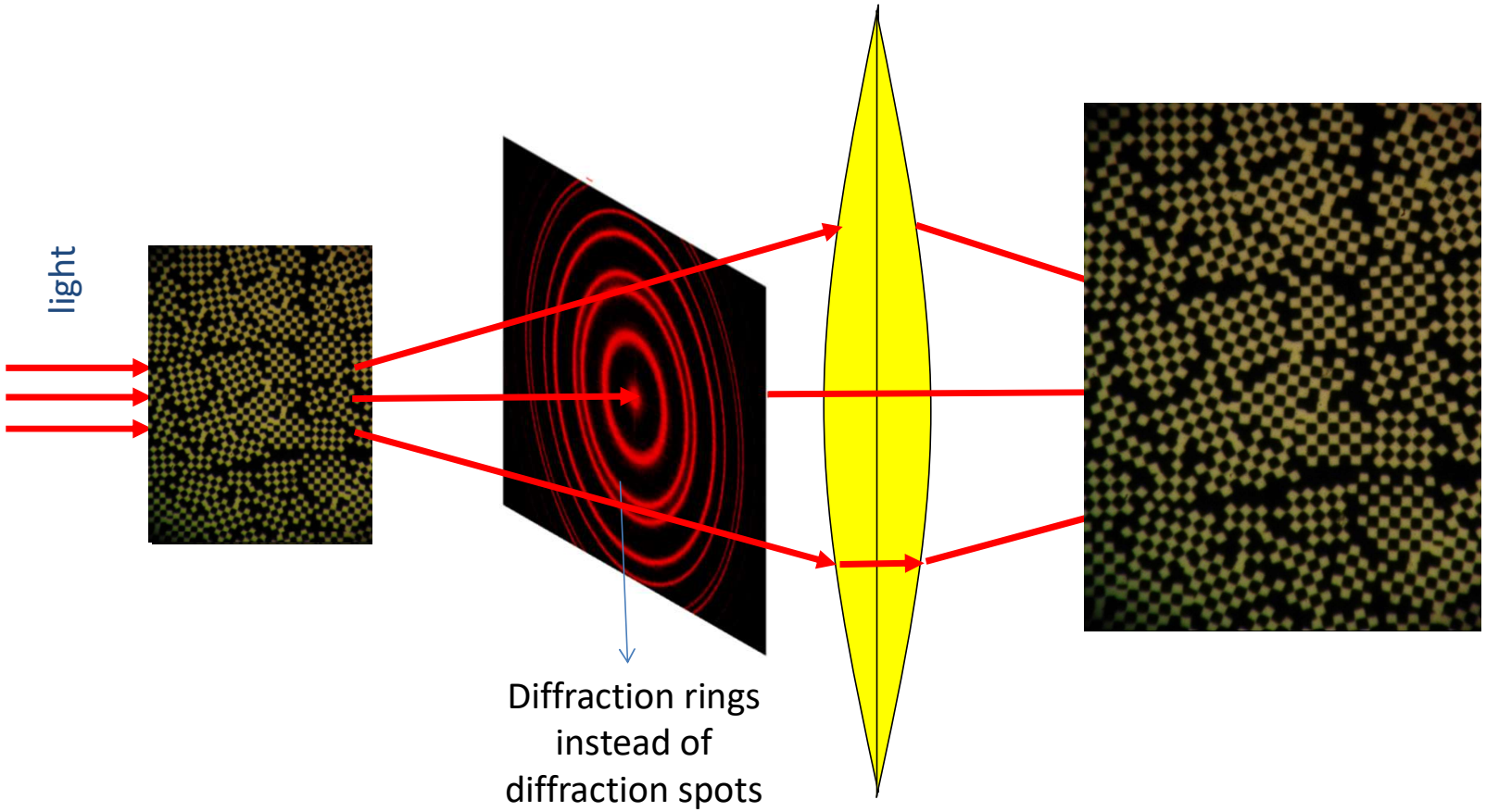
Diffraction from twin crystals



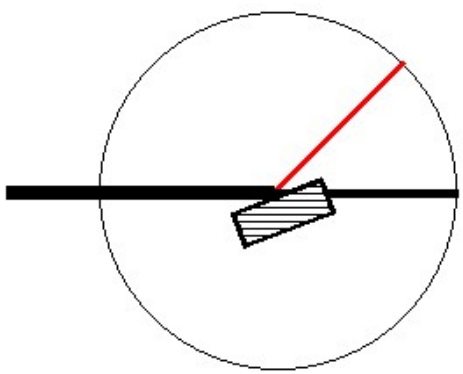
Diffraction from powders

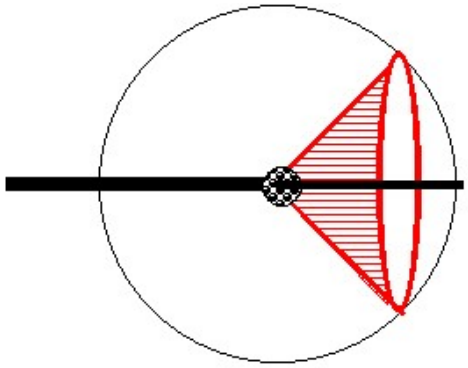


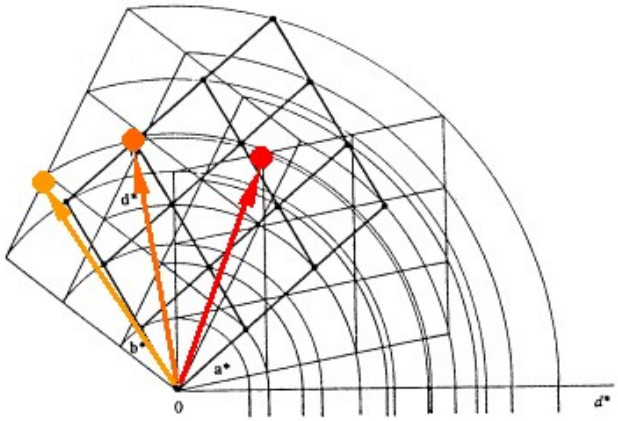
Diffraction from powders

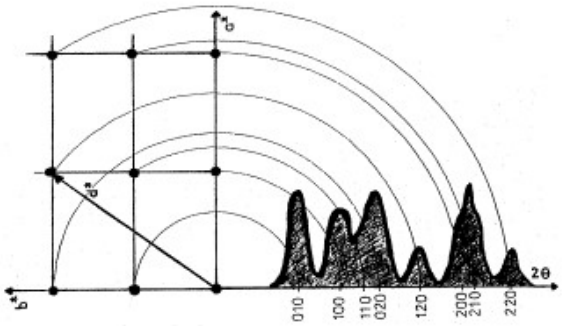


Diffraction from powders

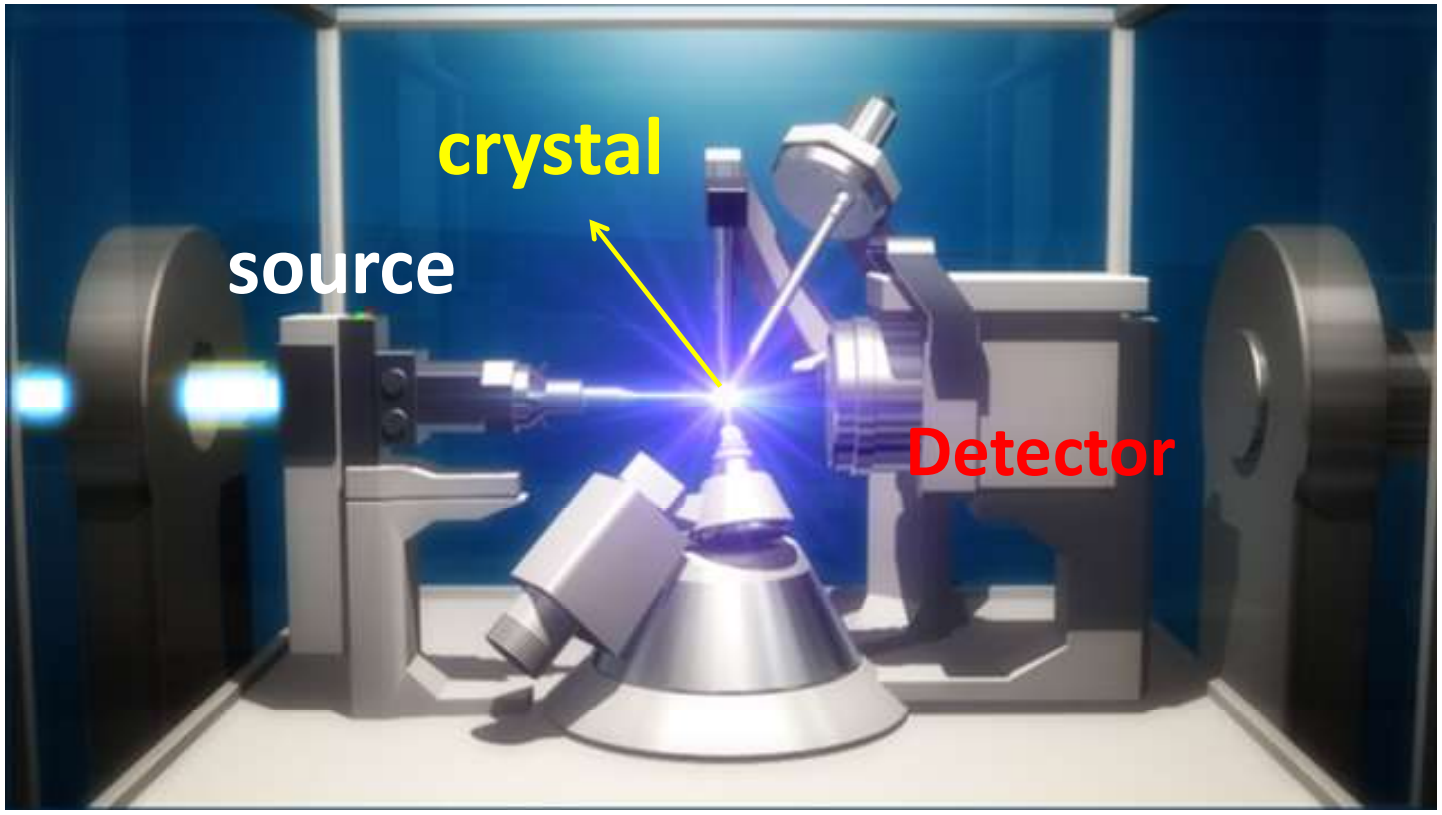




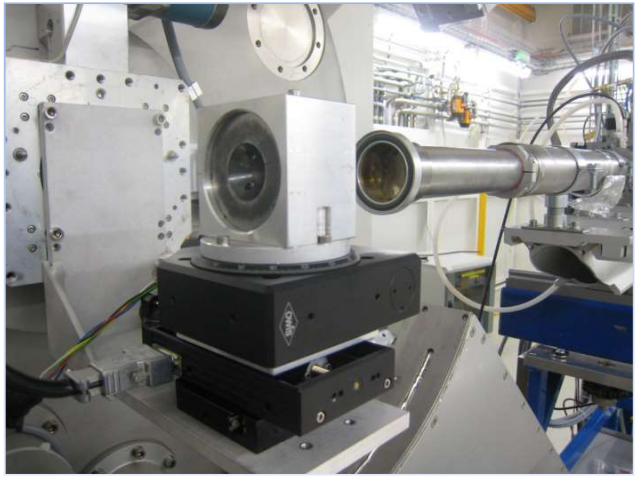




Laboratory single crystal diffractometer

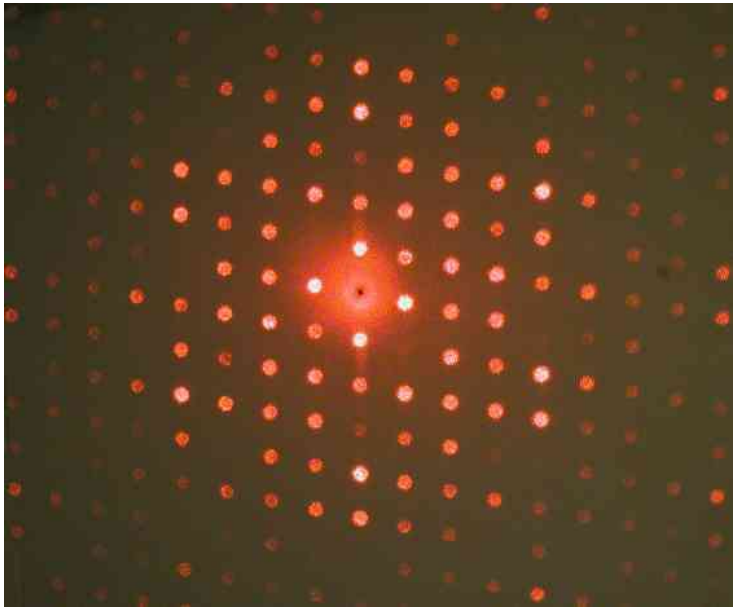


Large scale source diffractometer

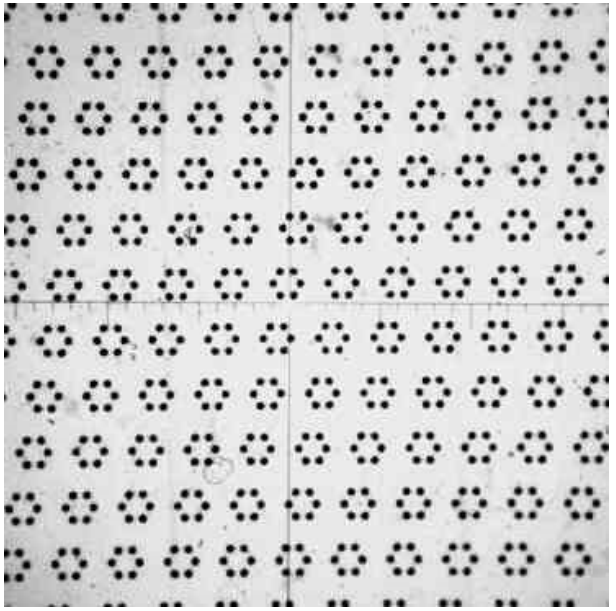


Brighter sources
Tunable radiation energies
Micro-focusing

How to solve a crystal structure?



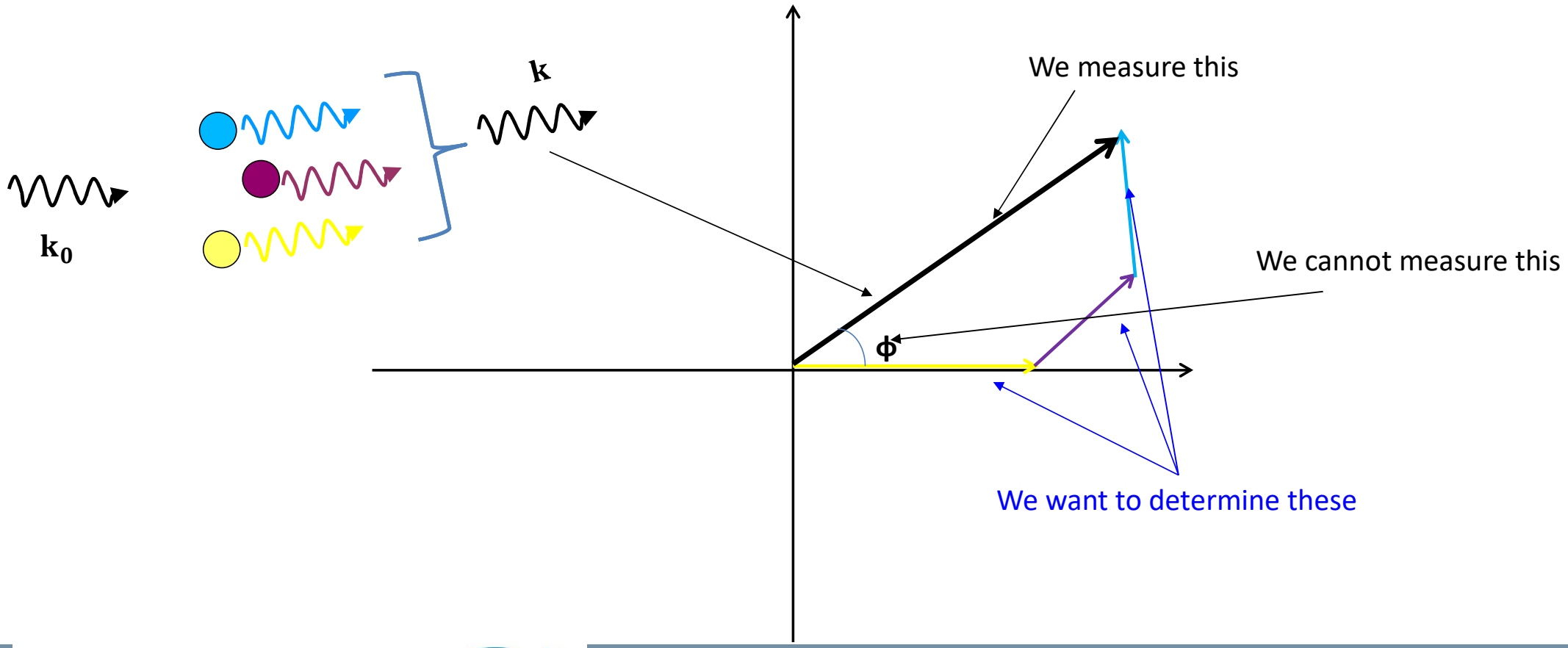
?



We measure this

We want to obtain this

How to solve a crystal structure?

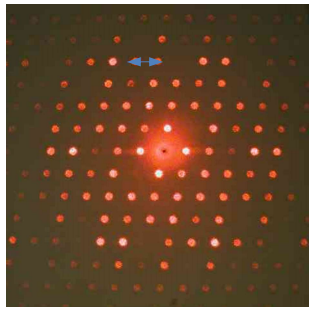


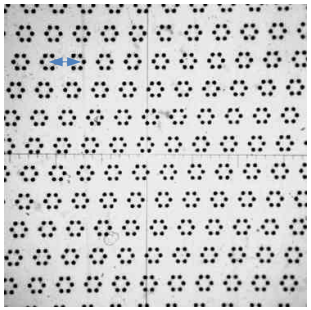
How to solve a crystal structure?

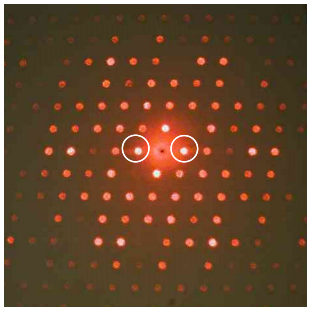
Screening of crystals and analysis of linear optical properties

Collection of few diffraction images to detect lattice parameters

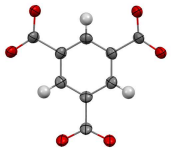
Data Collection of a full set of reflection intensities; Laue class; Space group determination







Structure solution: Patterson or Direct methods (or other methods)



$$\rho(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{H}} |\mathbf{F}(\mathbf{H})| e^{2\pi i \varphi_H} e^{-i2\pi \mathbf{H}\mathbf{r}}$$

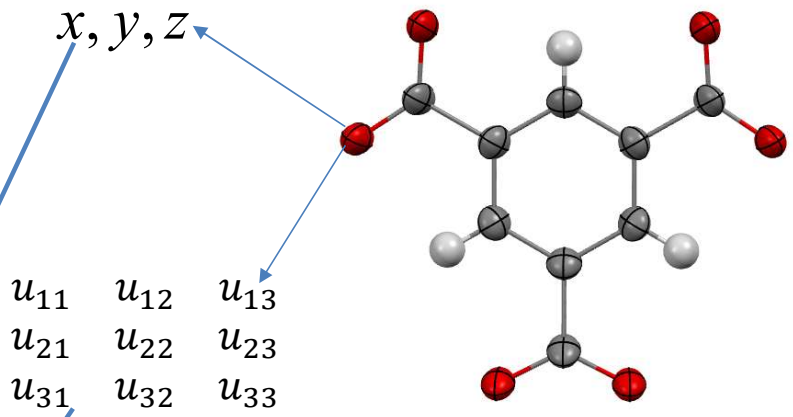
(least squares) Refinement of a structural model

The structural model

Using structure solution methods like *Direct methods* or *Patterson method* combined with *Fourier synthesis* we are able to get an approximate model for a crystal structure.

This model consists of the fractional coordinates x, y, z of each atom in the unit cell, at which its spherical electron density distribution is centered, and a description of the movement of the atom about its mean position as a harmonic oscillator characterized by the displacement parameters u_{ij}.

Based on this model we may calculate the structure factors $F_{model}(\mathbf{H})$ associated to each scattering vector H as

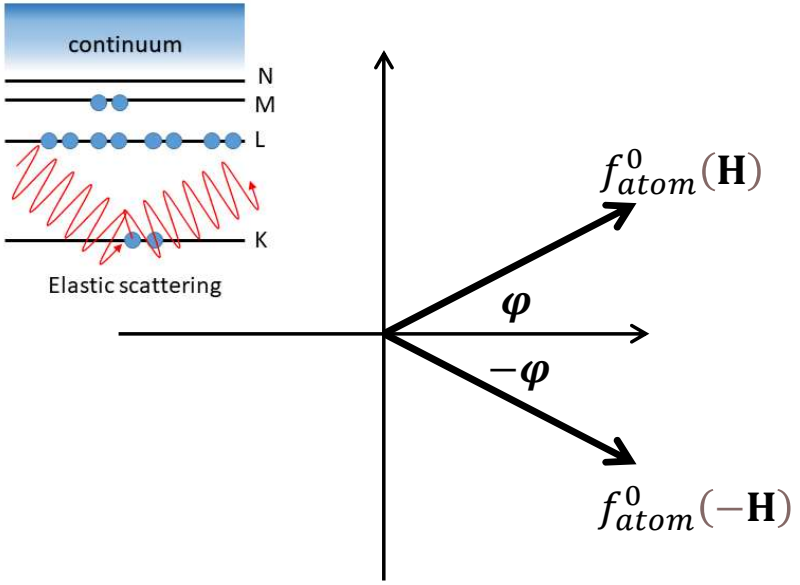


$$F(\mathbf{H}) = \sum_m f_m(H) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_m) T_m(\mathbf{H})$$

Friedel's law and its violation

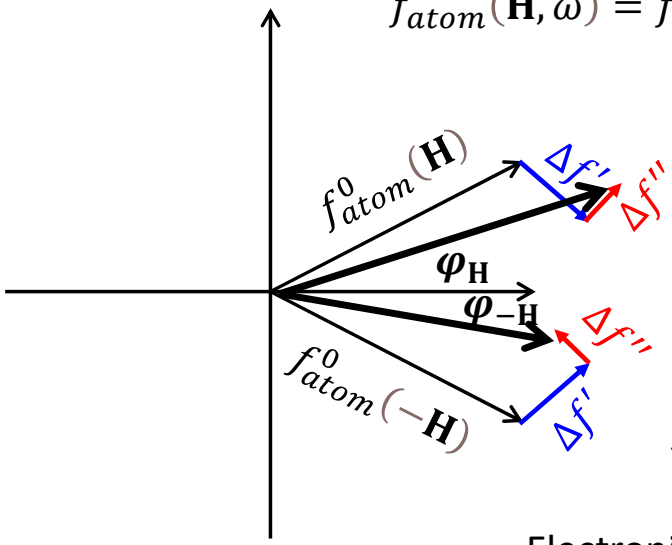
$$|F(\mathbf{H})|^2 = F(\mathbf{H})\mathrm{F}^*(\mathbf{H}) = \left(\int \bar{\rho}(\mathbf{r}) \exp(2\pi i \mathbf{H}\cdot\mathbf{r}) d\mathbf{r}\right)\left(\int \bar{\rho}(\mathbf{r}) \exp(-2\pi i \mathbf{H}\cdot\mathbf{r}) d\mathbf{r}\right) = |F(-\mathbf{H})|^2$$

Friedel, G. (1913). *C.R. Acad. Sci. Paris*, **157**, 1533-1536



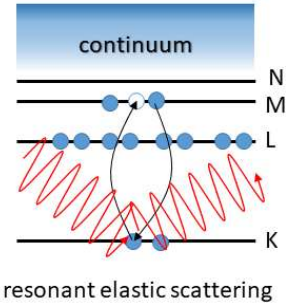
Without considering the frequency of the X-rays
Friedel's law is valid

$$f_{atom}(\mathbf{H},\omega) = f^0_{atom}(\mathbf{H}) + \Delta f'(\mathbf{H},\omega) + i\Delta f''(\mathbf{H},\omega)$$



$$|\varphi_{\mathbf{H}}| \neq |\varphi_{-\mathbf{H}}|$$

$$f_{atom}(\mathbf{H}) \neq f_{atom}(-\mathbf{H})$$

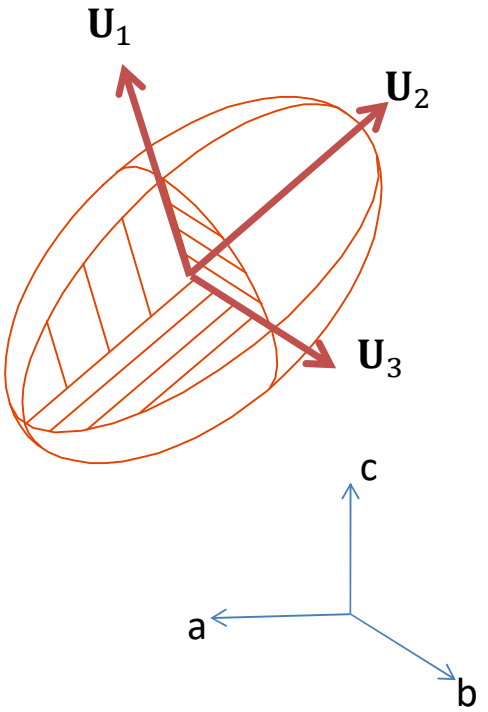


Electronic contribution and resonant electron
Friedel's law is not valid

The structural model

The term T_i accounts for the fact that the scattering of an atom at rest is affected by its thermally induced motion about its mean position.
For an anisotropic motion T_i becomes more complicated

$$T_m(\mathbf{H}) = e^{-2\pi^2 \mathbf{H}^T \mathbf{u}_m \mathbf{H}}$$



The so called *anisotropic displacement parameters* u_{ij} are the elements of a symmetrical tensor, i.e. a quantity which is defined by the length and direction of three mutually perpendicular vectors. It's usual graphical representation is a so called vibration or displacement ellipsoid with the three principal axes U_1, U_2 and U_3.

The structural model: refinement

The model coming out from structure solution, as already mentioned, is approximate. How could we improve it?

In crystallography this model is improved by the so-called least squares technique.

We may calculate from our approximate model the intensities I_{model}

$$I_{model}(\mathbf{H}) = \frac{1}{k}\left(F_{model}(\mathbf{H})\right)^2$$

The scale factor k is needed to scale our model intensities to the measured intensities which depend on many things as e.g. the volume of the crystal.

The quantity which we minimize in least squares is *S*, the sum over all weighted squared deviations between I_{obs} and I_{model}

$$S\sum_{\mathbf{H}} w(\mathbf{H})\left[I_{obs}(\mathbf{H}) - \frac{1}{k}|F_{model}(\mathbf{H})|^2\right]^2 \qquad w(\mathbf{H}) = \frac{1}{\sigma^2(I(\mathbf{H}))}$$

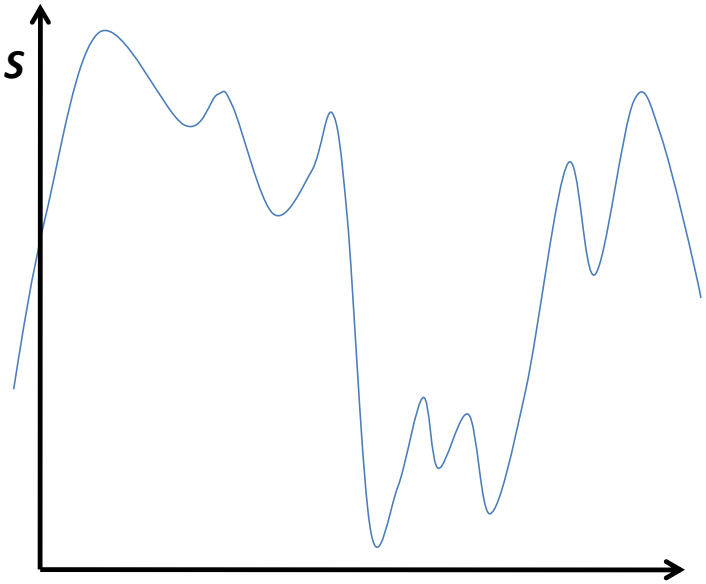
The structural model: refinement

The function S(model parameters) is a complicated hyper surface in n-dimensional space, where n = number of parameters. It has an absolute minimum, which corresponds to the best solution, and many relative minima. If our structure model is far away from the correct solution, our shifts in the parameters will be big and thus the linear approximation will not be valid anymore.

One possible consequence of this is that we may end up in a false relative minimum. We somehow have to find a better model.

Another possible consequence is that our refinement never goes to a minimum but keeps jumping around in hyperspace, possibly with increasing parameter shifts: The refinement does not converge or even explodes.
In such a situation it may help to damp the parameter shifts

As shifts will be small for high damping we have to calculate much more least squares cycles to eventually reach convergence.



$\{x_j\}$ (variables of the model)

Model quality measurement

The goodness of fit (GOF or GOOF) is the variance of an observation of unit weight

$$G.o.F. = \sqrt{\frac{\sum_{\mathbf{H}} w_{\mathbf{H}}(F_{obs}^2 - F_c^2)^2}{n_{obs} - n_{par}}}$$

Its expectation value is 1.0.

$G.o.F.$ should be close to 1 for all reflections grouped either in ranges of resolution or in ranges of F^2

$$wR_2 = \sqrt{\frac{\sum_{\mathbf{H}} w_{\mathbf{H}}(F_{obs}^2 - F_c^2)^2}{\sum_{\mathbf{H}} w_{\mathbf{H}}(F_{obs}^2)^2}}$$

Typical values for wR_2 are 0.1+/-0.09

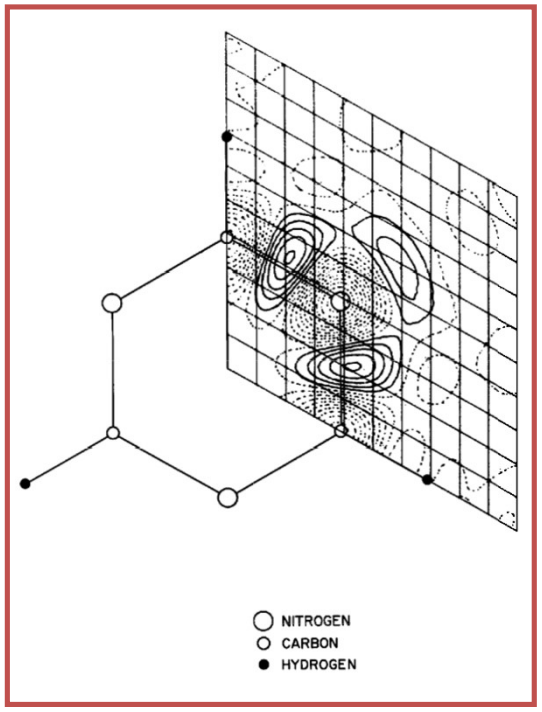
Model quality measurement

Another often used quality measure is

$$R_1 = \frac{\sum_H \left| |F_o| - |F_c| \right|}{\sum_H |F_o|}$$

R_1 does not have any relation to the theory of least squares and has a not well defined relation to statistical theory.
As a rule of thumb: $wR_2 \sim 2\ R_1$
Other criteria:
wR_2 >> R_{int} : model probably not complete
R_{int} >> wR_2 : model may be over-parameterised

Beyond conventional models: visualization of the chemical bond through the deformation density



Coppens, P. *Science*, **1967**, *158*, 1577–1579.

Comparative X-Ray and Neutron Diffraction Study of Bonding Effects in s-Triazine

Abstract. *X-ray and neutron-diffraction data were combined for study of deviations from spherical symmetry of the atomic charge distributions in the small organic molecule* s-*triazine. The results indicate that density has migrated from the atomic regions into the bonds and into the nitrogen lone-pair region. Refinement procedures for x-ray data, which do not take these bonding effects into account, give parameters containing small but measurable errors.*

$$\Delta\rho(\mathbf{r}) = \frac{1}{V}\sum_{|\mathbf{k}|\leq k_{max}} \left(\mathbf{F}_{X-ray,obs}(\mathbf{k}) - \mathbf{F}_{calc,spher}(\mathbf{k})\right) e^{i\mathbf{kr}}$$

Based on a model refined from neutron diffraction

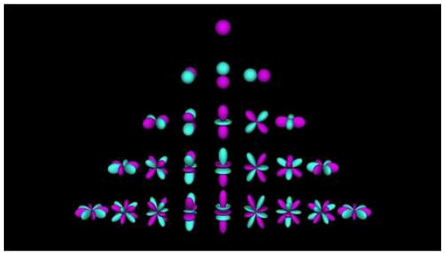
Beyond conventional models: The multipolar model

Conventional crystal structure refinement

$$\rho_{unit\ cell}(\mathbf{r}) = \sum_{m=1}^{\substack{Nat \in \\ unit\ cell}} \rho_i(\mathbf{r} - \mathbf{r}_i)$$

Atom centred multipolar expansion with adjustable coefficients against Bragg intensities

$$\rho_i(\mathbf{r}) = \rho_{i,core}(\mathbf{r}) + P_{i,val}\kappa^3_{i,valence}\rho_{i,valence}(\kappa\mathbf{r}) + \sum_{l=0,}^{l_{max}}\left[\kappa'^3_i R_{i,l}(\kappa'_l\mathbf{r})\sum_{m=0,l} P_{i,lm\pm}y_{lm\pm}(\boldsymbol{r}/r)\right]$$



$$\mathcal{F}(\overline{\rho_i}(\mathbf{r})) \rightarrow f_i(\mathbf{k}) \longrightarrow \sum_{i=1}^{Nat} f_i(\mathbf{k})\, e^{-i\varphi} \longrightarrow \boldsymbol{F}(\mathbf{k}) \longrightarrow \mathrm{I}(\mathbf{k}) \div |\boldsymbol{F}(\mathbf{k})|^2$$

$$\rho_{i,deformation-valence}(\boldsymbol{r})$$

Kurki-Suonio K., Meisalo V. *J. Phys. Soc. Jap.* **1966**, *21*, 122–126. Stewart R. F. *Acta Cryst.*,**1976**, *A32,* 565-574. Hirshfeld F. L. *Isr. J. Chem.* **1977**, *16*, 226-229. Hansen NK, Coppens P. *Acta Cryst.* **1978**, *A34*, 909-921.

Beyond conventional models: The multipolar model

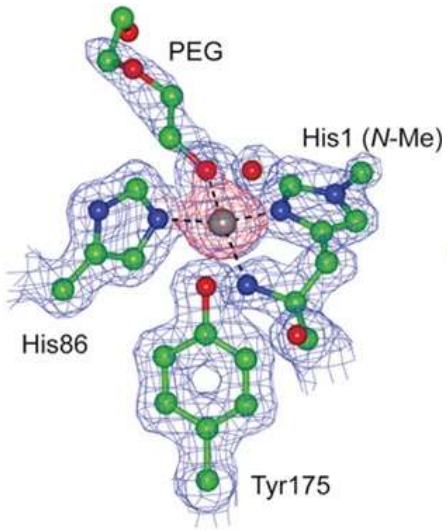
Molecular structure

Resolution $d = \frac{\lambda}{2\sin\vartheta}$

d → space resolution
λ → X-ray wavelength

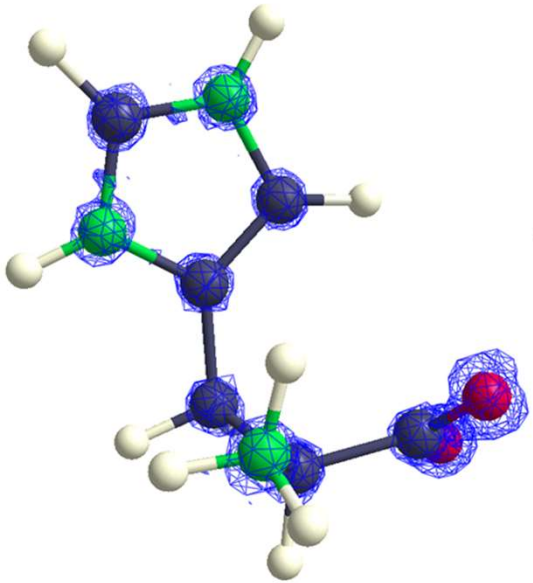
Chemical Bonding

1 Å



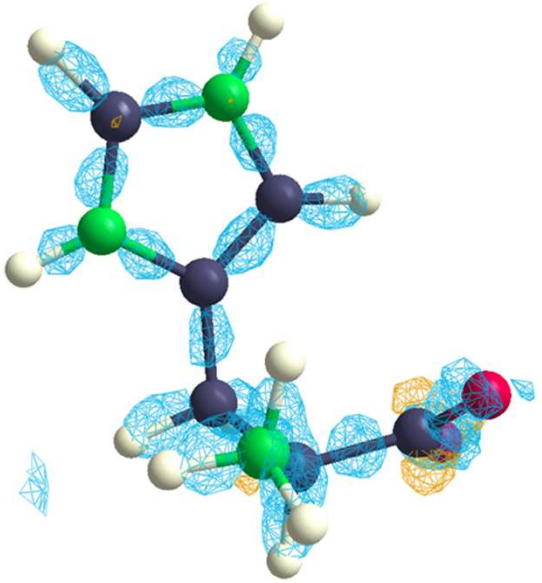
An Enzyme consisting of amino acids (N-methyl histidine)

0.8 Å



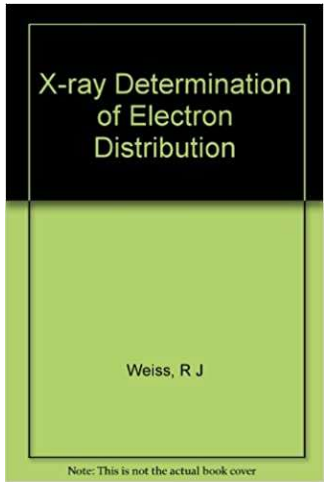
L-Histidinium cation in a oxalate salt
2 e/Å^3 isosurface

0.5 Å



Deformation density of the L-Histidinium cation
blue-positive, orange -negative; 0.12e/Å^3 isosurface

Beyond conventional models: Wavefunctions from X-ray diffraction



Weiss RJ. X-ray determination of Electron Distributions. North-Holland Publishing Company. Amsterdam. **1966**.

Wavefunction models: a molecular wavefunctions adjusted to reproduce the measured X-ray diffraction

$$\hat{H}\psi = E\psi \qquad \rho(\mathbf{r}) \div \left|\psi(\mathbf{r})\right|^2$$

Approximated Hamiltonian (e.g. Hartree-Fock)

$$\hat{H}^{HF}\psi^{HF} = E\psi^{HF}$$

Perturbative approach

$$\hat{H} = \hat{H}^{HF} + \hat{H}_{err=X-ray-HF}$$

Richard J. Weiss (1923-2008)

Beyond conventional models: Wavefunctions from X-ray diffraction

Wavefunction models: a molecular wavefunctions adjusted to reproduce close enough the measured X-ray diffraction

Jayatilaka D. *Phys. Rev. Lett.* **1998**, *80*, 798–801.

$$\hat{J}\psi_{XRW} = L\psi_{XRW} \qquad \hat{J} = \hat{H}^0[\psi^0] + \lambda(\chi^2[\psi^0] - \Delta)$$

$$\chi^2 = \frac{1}{N_r - N_p}\sum_{\mathbf{H}} \frac{\left|\eta\left(F_{\mathbf{H}}^0\right)^2 - \left(F_{\mathbf{H}}^{\text{X-ra}}\right)^2\right|}{\left[\sigma\left(F_{\mathbf{H}}^{\text{X-ray}}\right)\right]^2}$$

Dylan Jayatilaka

Density matrix from X-ray diffraction experiments. N-representability problem

Clinton W, Massa L. *Phys. Rev. Lett.* **1972**, *29*, 1363-1366.

Density matrix models: Refinement of atomic expansion against Compton profiles

$$\Gamma(\mathbf{r}',\mathbf{r}) = \sum_a \Gamma_a(\mathbf{r}',\mathbf{r}) + \sum_{a,b} \Gamma_{ab}(\mathbf{r}',\mathbf{r})$$

Gillet J-M. *Acta Cryst.* **2007**, *A63*, 234-238.

Jean Michel Gillet

Lou Massa

William L. Clinton

Take home message

- Diffraction is the other side of the coin of microscopy
- X-ray diffraction is the manifestation of the elastic scattering of photons by electrons of periodically ordered (crystalline) solids
- The result of X-ray diffraction is not a direct image of the inner structure of the material. The outcome is a model, with parameters refined in order to minimize the discrepancies with respect to observations.
- The model can go well beyond the simple positions of atoms in the structure. One can refine the average distribution of electrons or even compute a wavefunction restrained to the experimental observations.