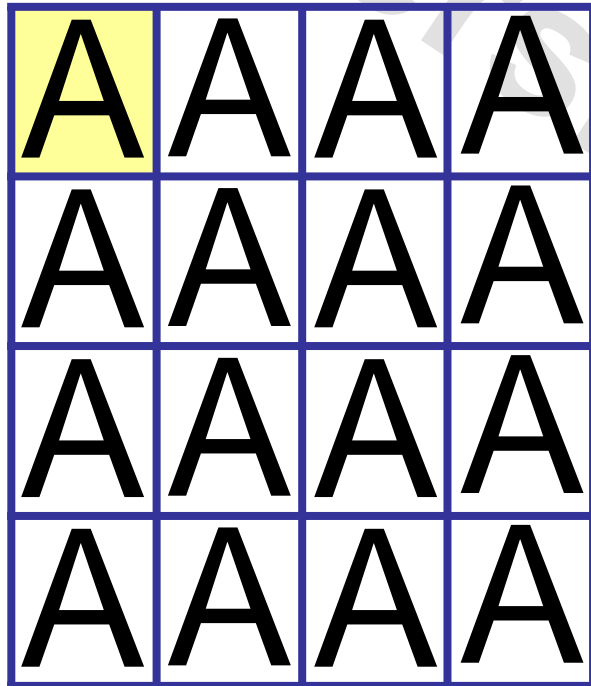


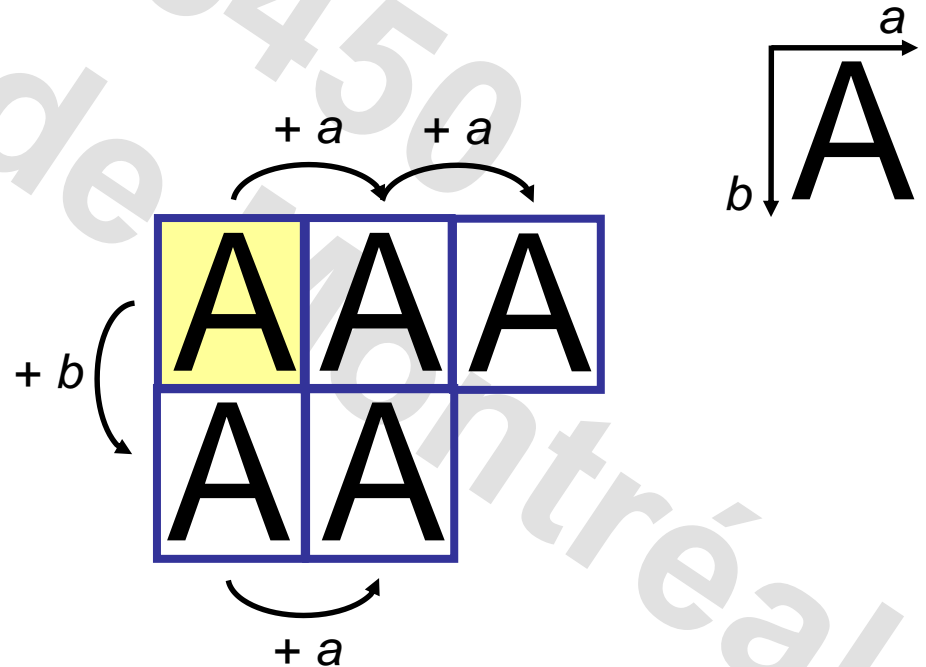
The shortest possible introduction into crystallography

A **crystal** is...

a homogenous solid formed by a **repeating**, three-dimensional pattern of atoms.

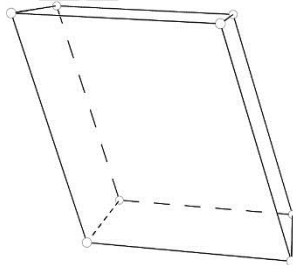
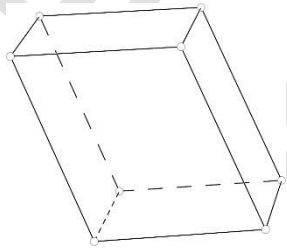


The **unit cell** is the repeating unit with dimensions of a , b , c and angles α , β and γ . A crystal can be described completely by **translations** of the unit cell along the unit cell axes.

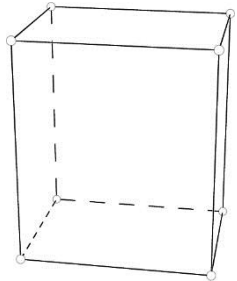


The shortest possible introduction into crystallography

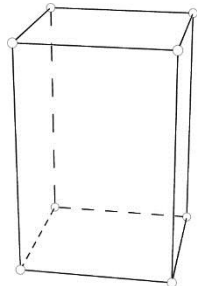
There are seven types of unit cells (**crystal systems**).



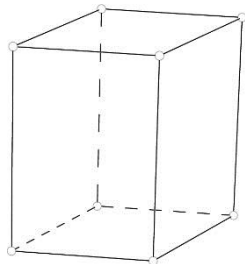
$$\alpha = \gamma = 90^\circ$$



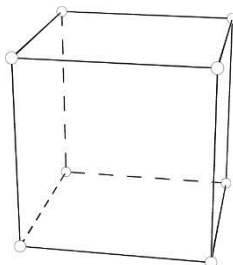
$$\alpha = \beta = \gamma = 90^\circ$$



$$\alpha = \beta = \gamma = 90^\circ$$
$$a = b$$



$$\alpha = \beta = 90^\circ$$
$$\gamma = 120^\circ$$
$$a = b$$



$$\alpha = \beta = \gamma = 90^\circ$$
$$a = b = c$$

Combined with centering, we obtain the 14 **Bravais lattices**.

Crystal systems: **Bravais lattices:**

triclinic

aP

monoclinic

mP, mC

orthorhombic

oP, oA, oI, oF

tetragonal

tP, tI

trigonal/hexagonal

hP, hR

cubic

cP, cI, cF

P : primitive,

A, B, C : face centered

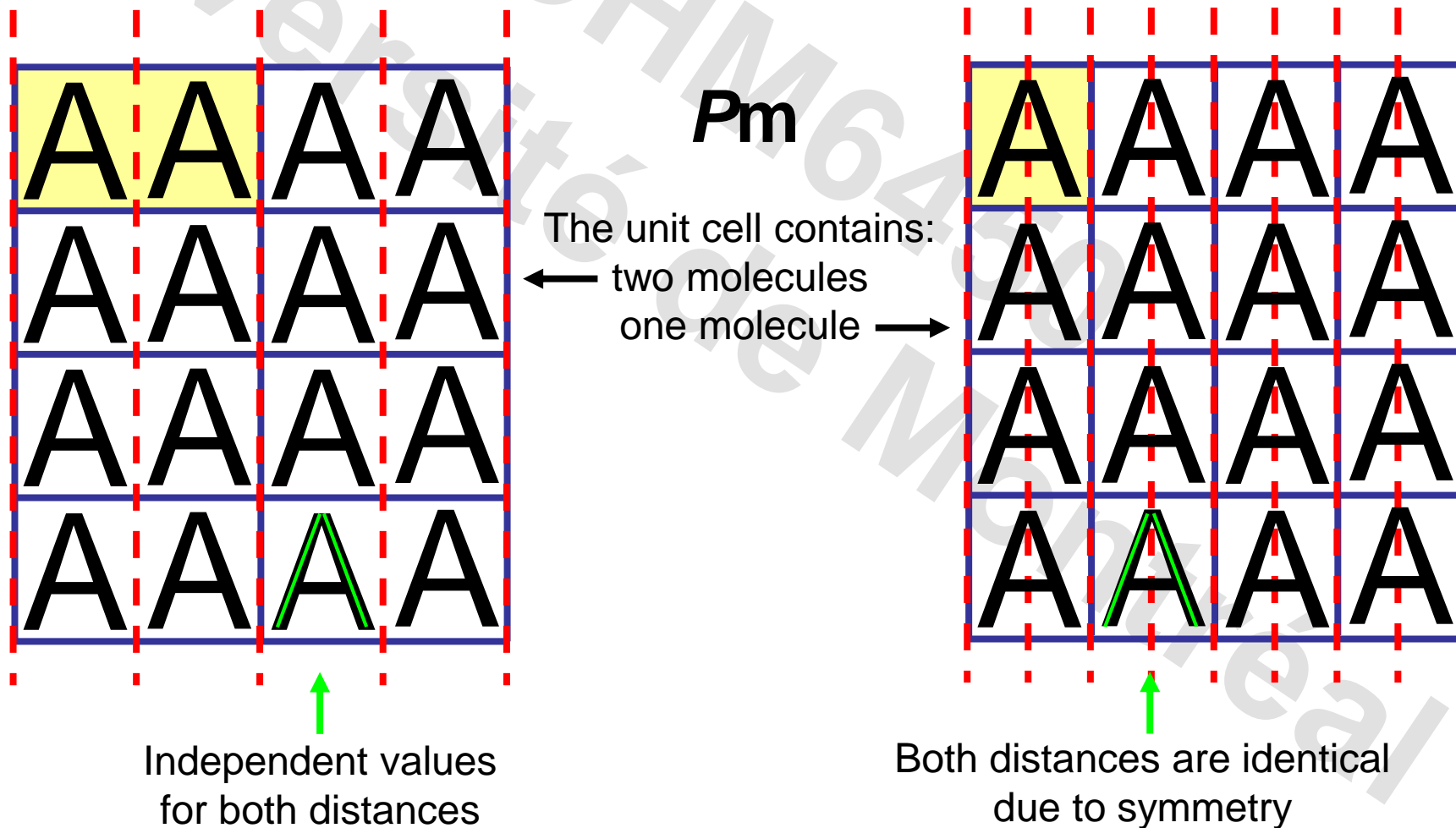
I : body centered

F : (all-)face centered

R : rhombohedral centered

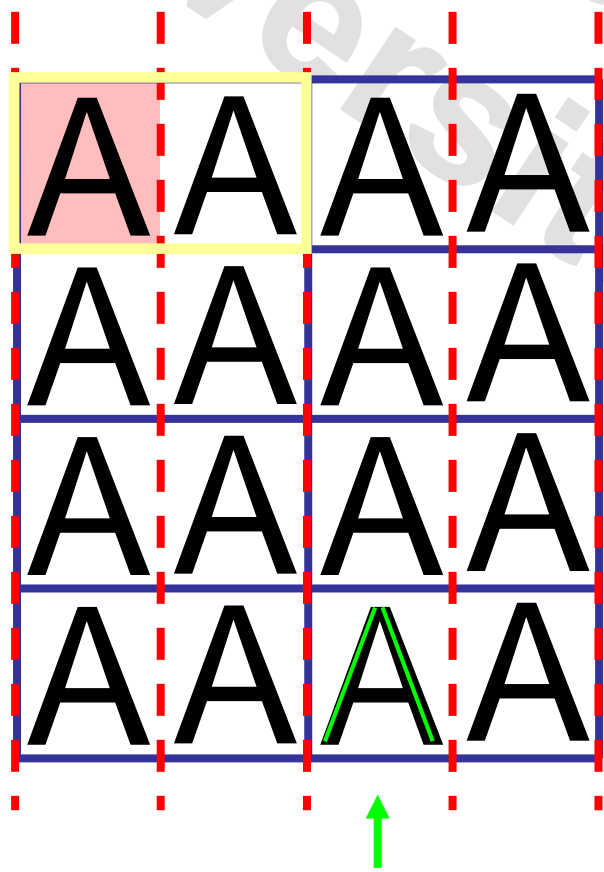
The shortest possible introduction into crystallography

The **space group** is the combination of Bravais lattice + symmetry of the crystal. Point group symmetry of a molecule does not necessarily imply that this symmetry is also present in the crystal.



The shortest possible introduction into crystallography

The **asymmetric unit** is the part of the unit cell, from which the rest of the unit cell is generated using symmetry operations. To build the complete crystal we need only the space group and the atom positions in the asymmetric unit.



Independent values
for both distances

Pm



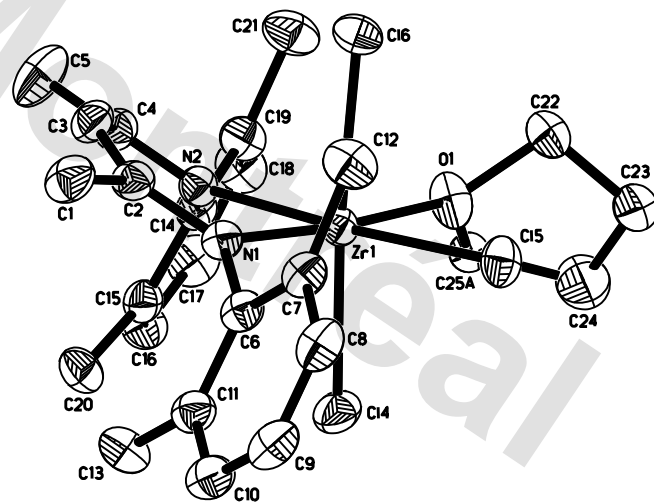
Both distances are identical
due to symmetry



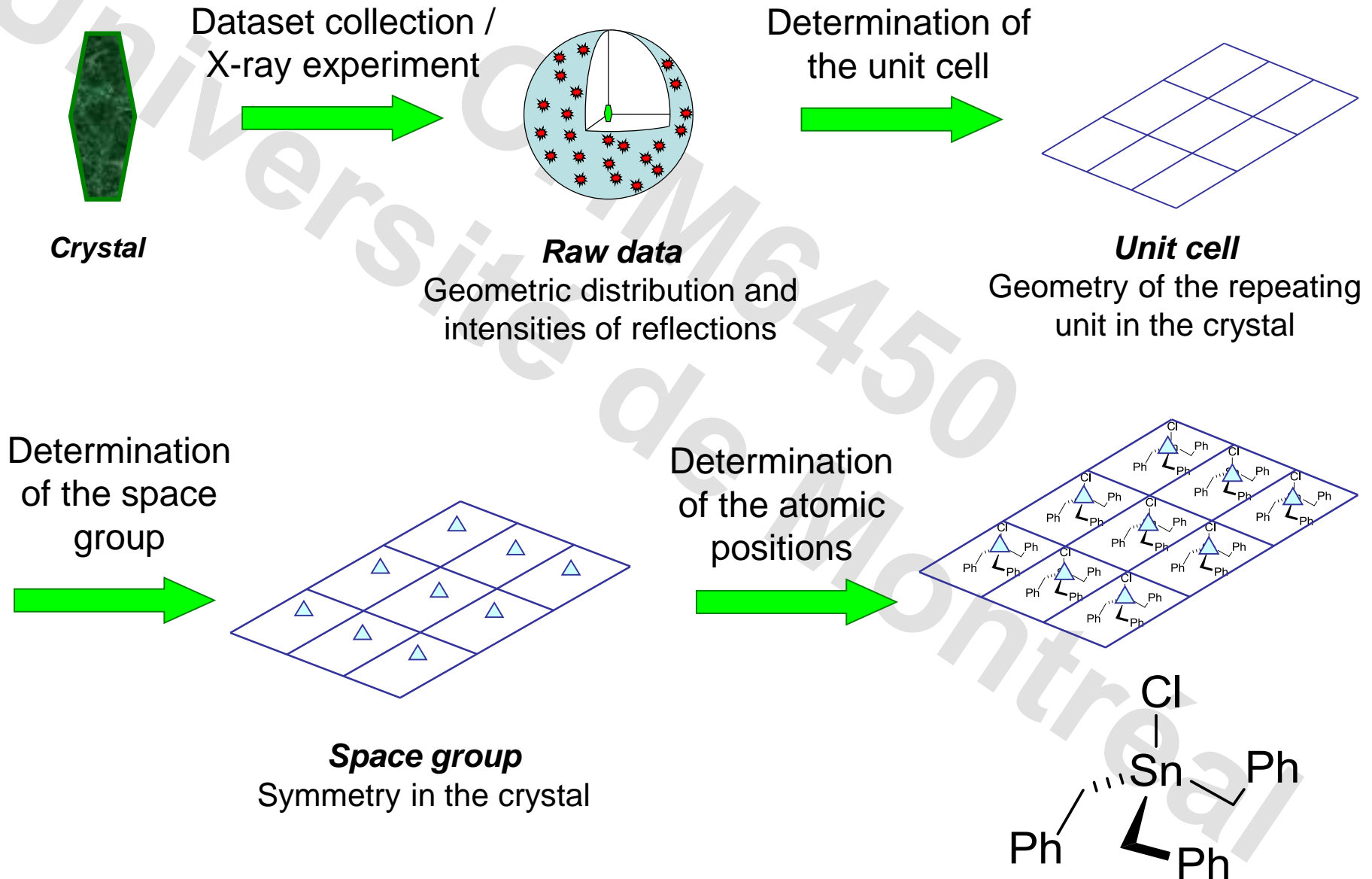
We have a crystal...

How do we get there?

... we want a structure!



Structure determination – a short overview



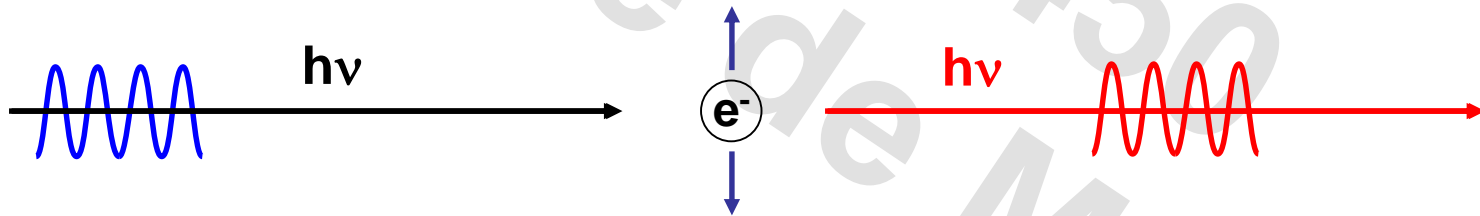
Steps in a single crystal diffraction study

- Grow a crystal
- Choose and mount a single crystal
- **Collect the dataset**
- Determine the unit cell
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- Validation
- Preparation of tables and figures
- Data backup



Interaction of X-rays with matter

- Thomson scattering -

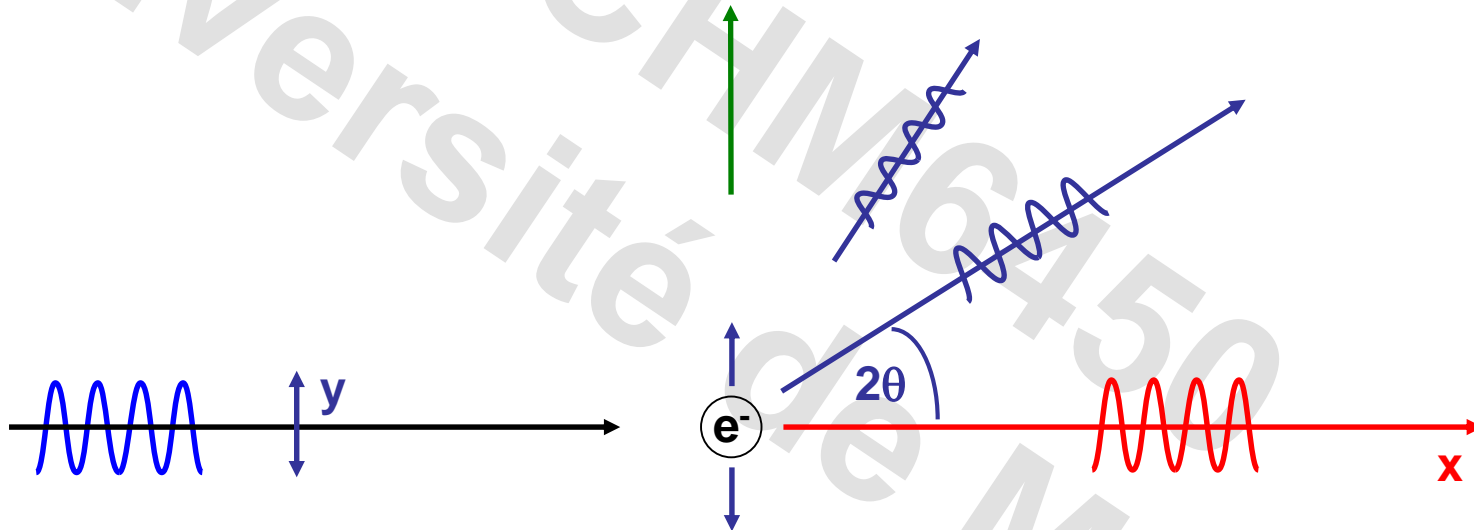


- The interaction with an electromagnetic field induces the oscillation of an electron
- Being an accelerated charged particle, the electron emits another electromagnetic wave.

Interaction of X-rays with matter

- Thomson scattering -

The intensity of the diffracted X-ray beam depends on the diffusion angle.



For polarisation in y- direction:

$$\theta = 0 : I_{Th} = I_i \left(\frac{e^2}{4\pi\epsilon_0 mrc^2} \right)^2$$

$$\theta = 90 : I_{Th} = 0$$

$$I_{Th} = I_i \left(\frac{e^2}{4\pi\epsilon_0 mrc^2} \right)^2 \cos^2 2\theta$$

Thomson scattering

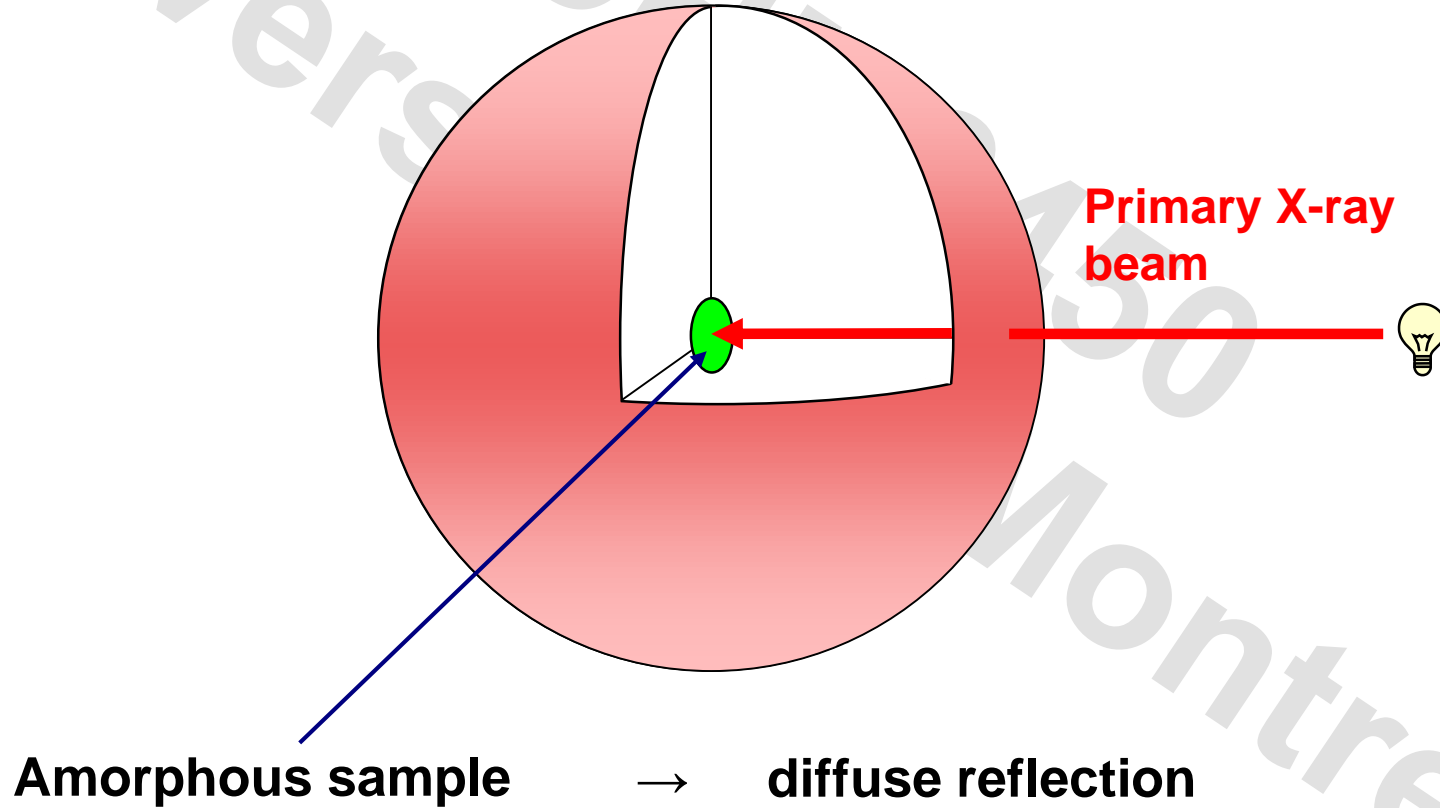
Extension to non-polarised light yields:

$$I_{Th} = I_i \left(\frac{e^2}{4\pi\epsilon_0 m r c^2} \right)^2 \frac{1 + \cos^2 2\theta}{2}$$

- Polarisation factor P (later)
- The total percentage of the scattered light is $I_{Th}/I_i = e^4/6\pi\epsilon_0^2 m^2 c^4 = 10^{-28}$ per electron. Typically, crystals scatter much less than 1% of the incident beam.
- I_{Th} of neutrons is zero
- I_{Th} (protons) = $10^{-6} I_{Th}$ (electrons)
- Thomson scattering is elastic: $\omega_{Th} = \omega_i$
- Thomson scattering is coherent: $\varphi_{Th} = \varphi_i + \alpha$ ($\alpha = 180^\circ$ pour e^-)

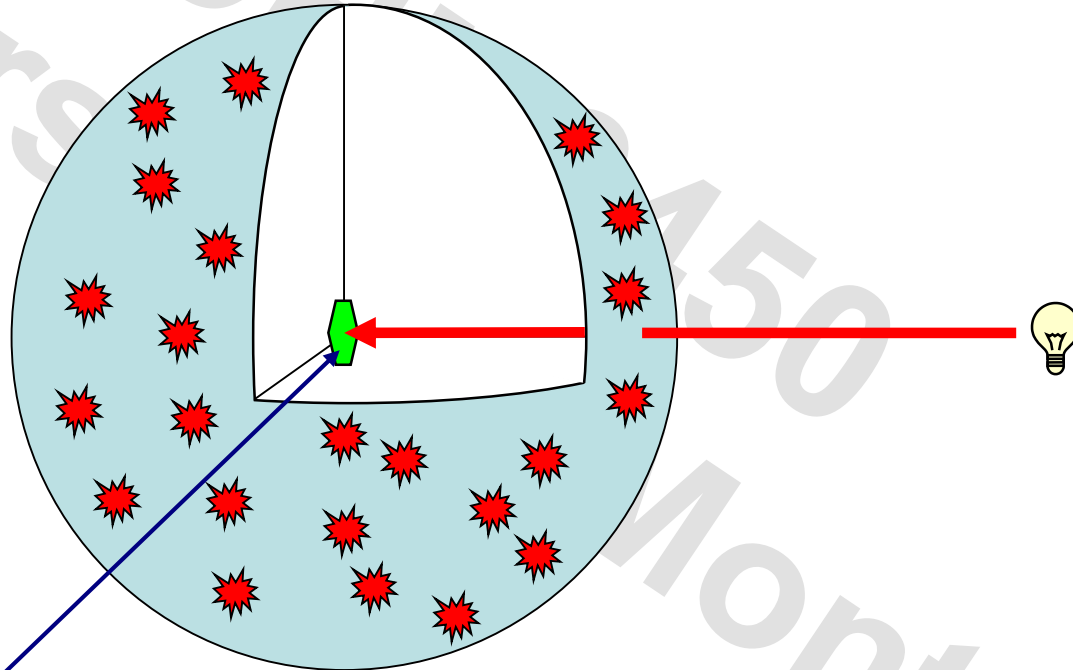
X-ray experiment

Why do we need a single crystal ?



X-ray experiment

Why do we need a single **crystal** ?



Crystalline sample

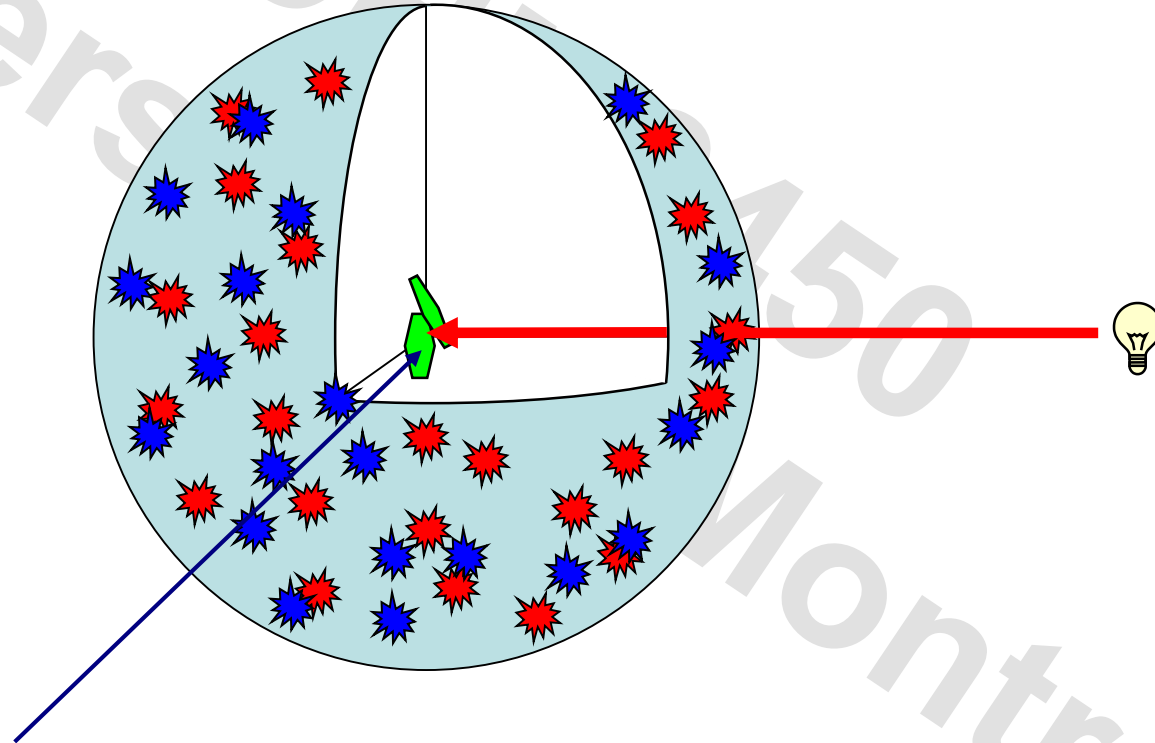
→ **localised reflections**

Amorphous sample

→ **diffuse reflection**

X-ray experiment

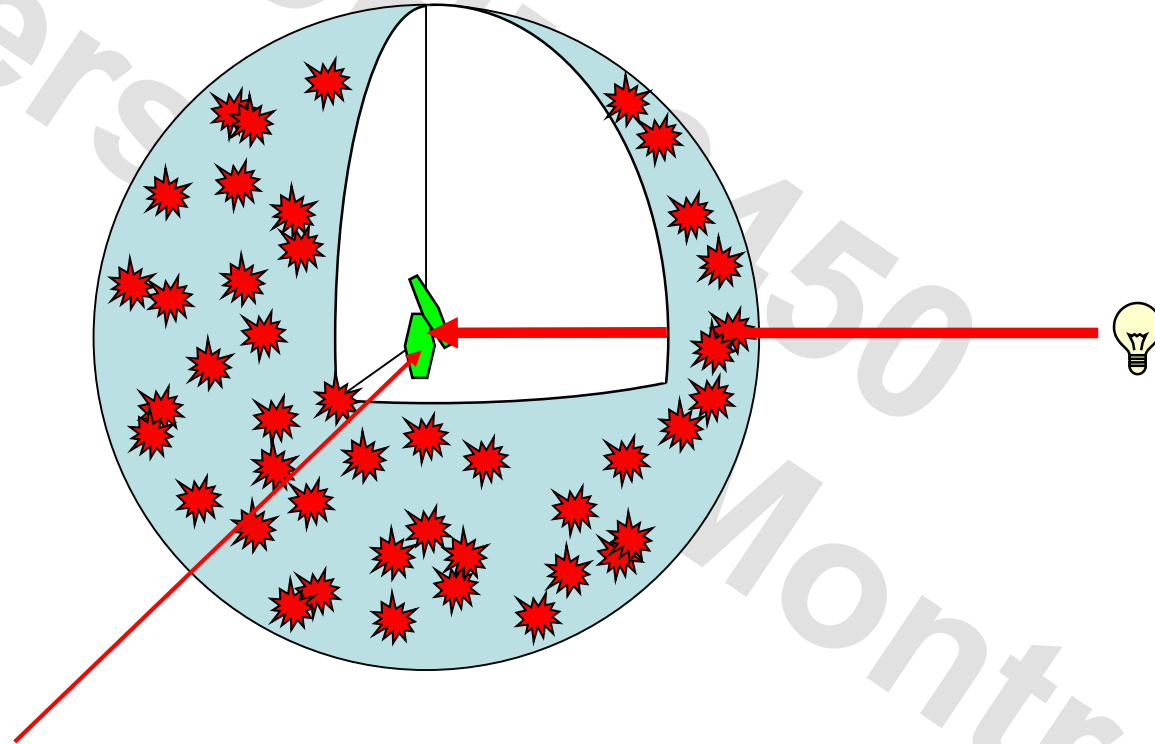
Why do we need a **single** crystal ?



- Polycrystalline sample** → overlapping reflections
- Crystalline sample** → localised reflections
- Amorphous sample** → diffuse reflection

X-ray experiment

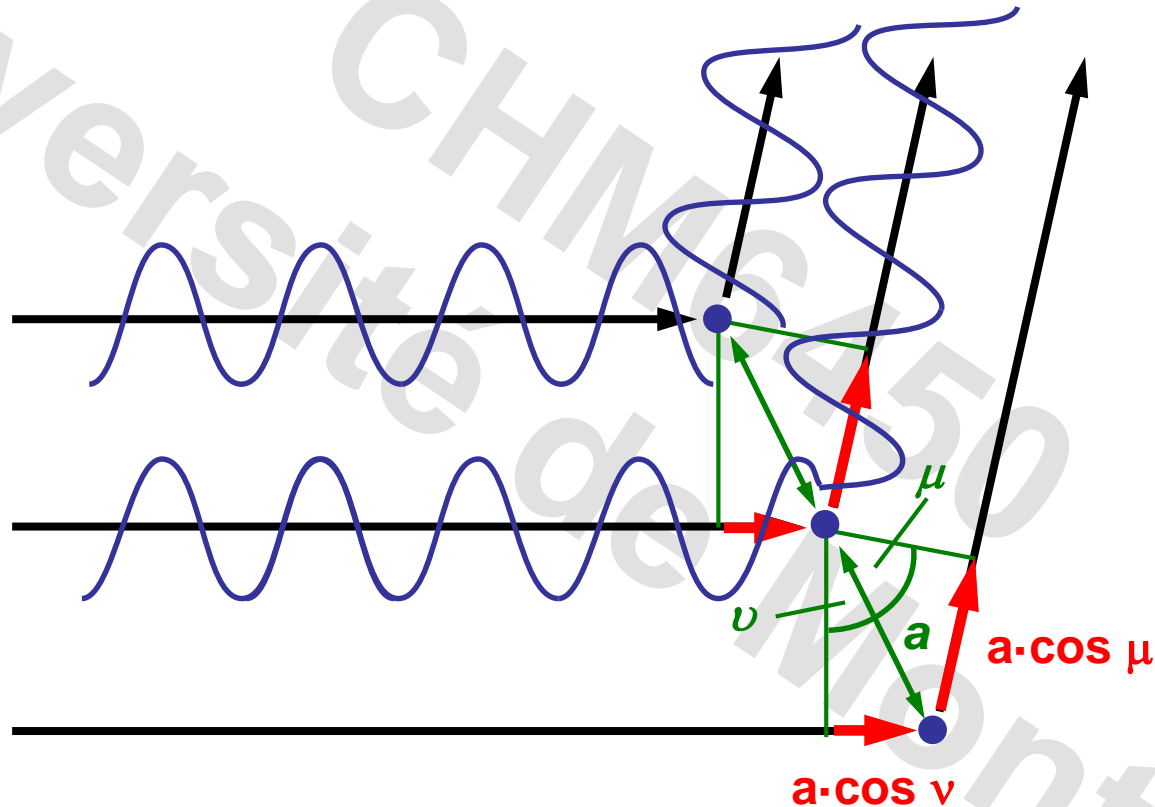
Why do we need a **single** crystal ?



- Polycrystalline sample** → overlapping reflections
- Crystalline sample** → localised reflections
- Amorphous sample** → diffuse reflection

Localised reflections - Laue construction

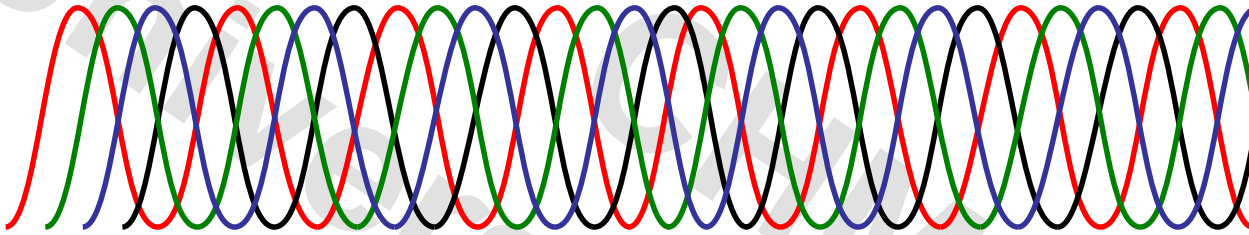
Interactions of an X-ray beam with **ordered** diffracting centers



The intensity is only different from zero, when:

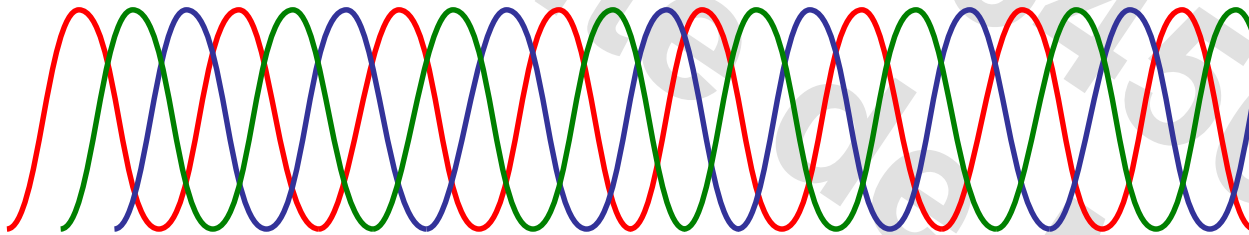
$$\Delta = a \cdot \cos \nu + a \cdot \cos \mu = n \cdot \lambda$$

Why $n \cdot \lambda$?



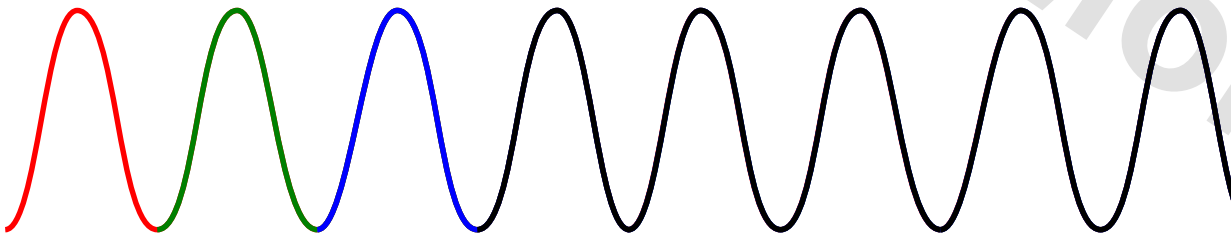
$$\Delta = \frac{1}{4} \lambda$$

$$I = 0$$



$$\Delta = \frac{1}{3} \lambda$$

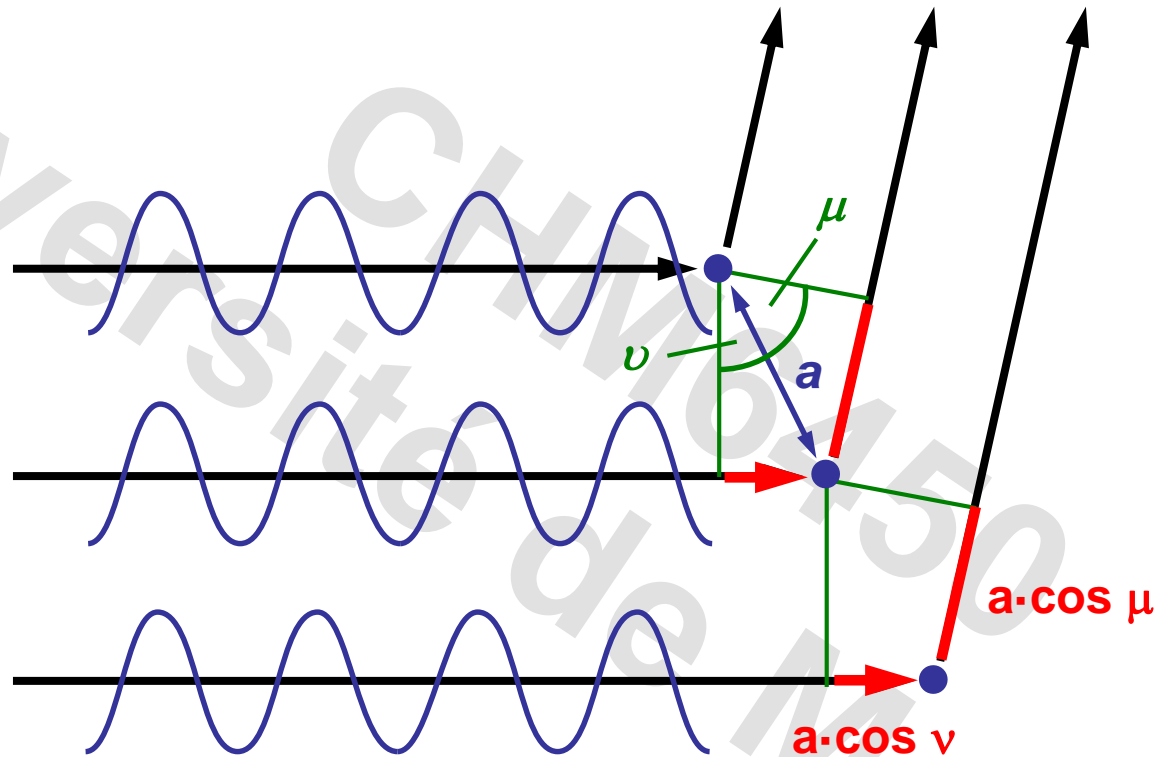
$$I = 0$$



$$\Delta = \lambda$$

$$I = I^0$$

The Laue construction in 3 dimensions



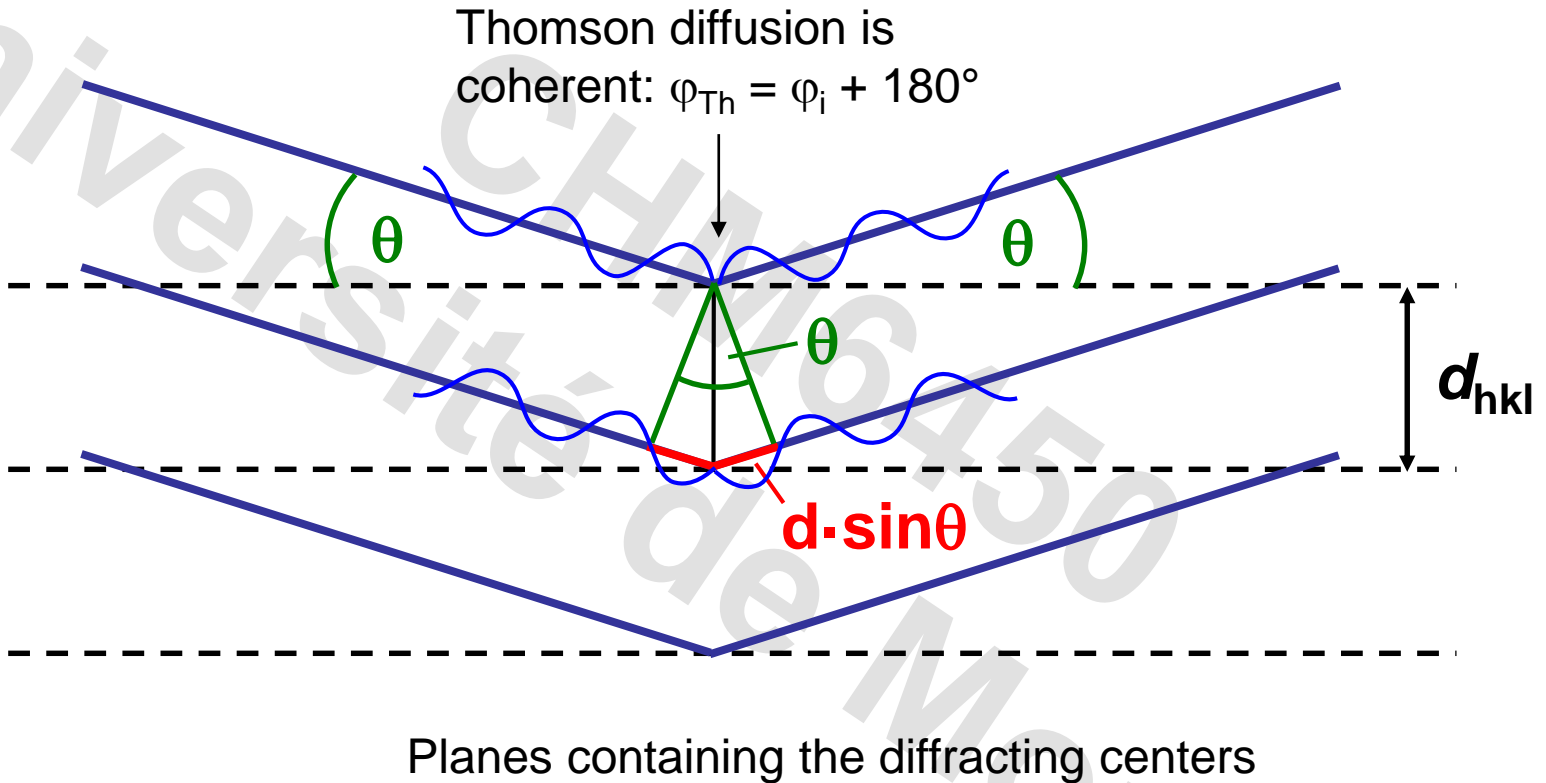
$$a \cdot \cos \mu_a + a \cdot \cos \nu_a = h \cdot \lambda$$

$$b \cdot \cos \mu_b + b \cdot \cos \nu_b = k \cdot \lambda$$

$$c \cdot \cos \mu_c + c \cdot \cos \nu_c = l \cdot \lambda$$

3 equations, 6 angles, 3 distances \Rightarrow too complicated

Bragg construction

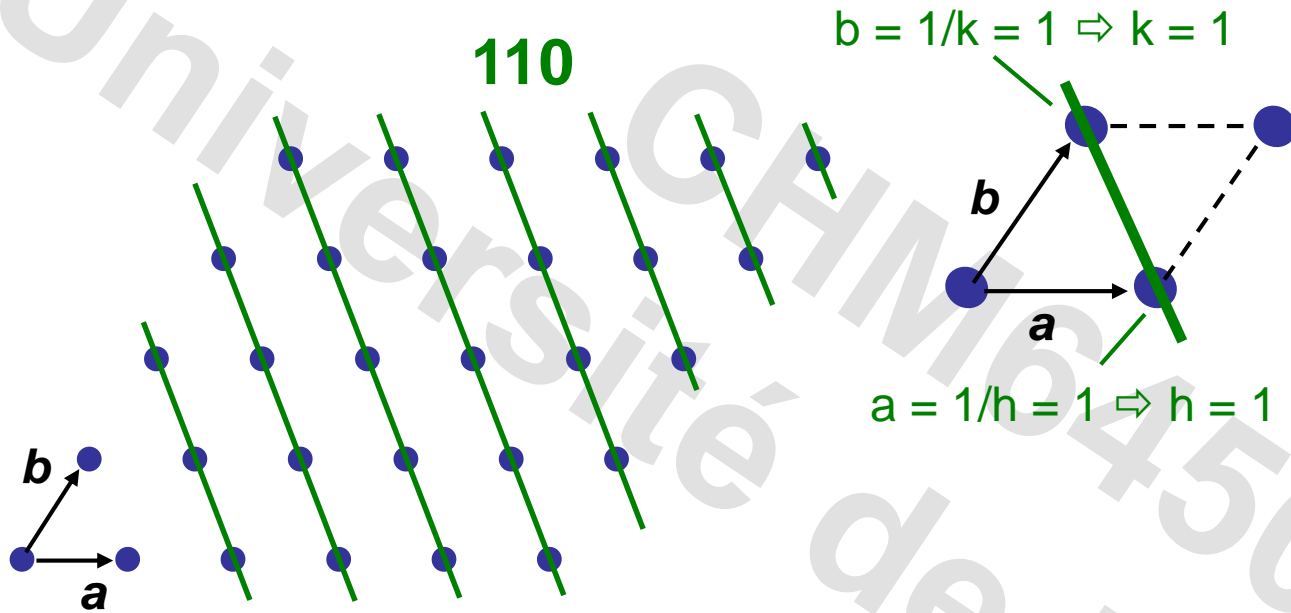


Glancing reflections at the **lattice planes hkl** of the crystal, which obey the Laue condition. The difference in pathlength is $2d_{hkl} \cdot \sin\theta$.

Bragg law: $2d_{hkl} \cdot \sin\theta = n \cdot \lambda \quad (n = 1, 2, 3 \dots)$

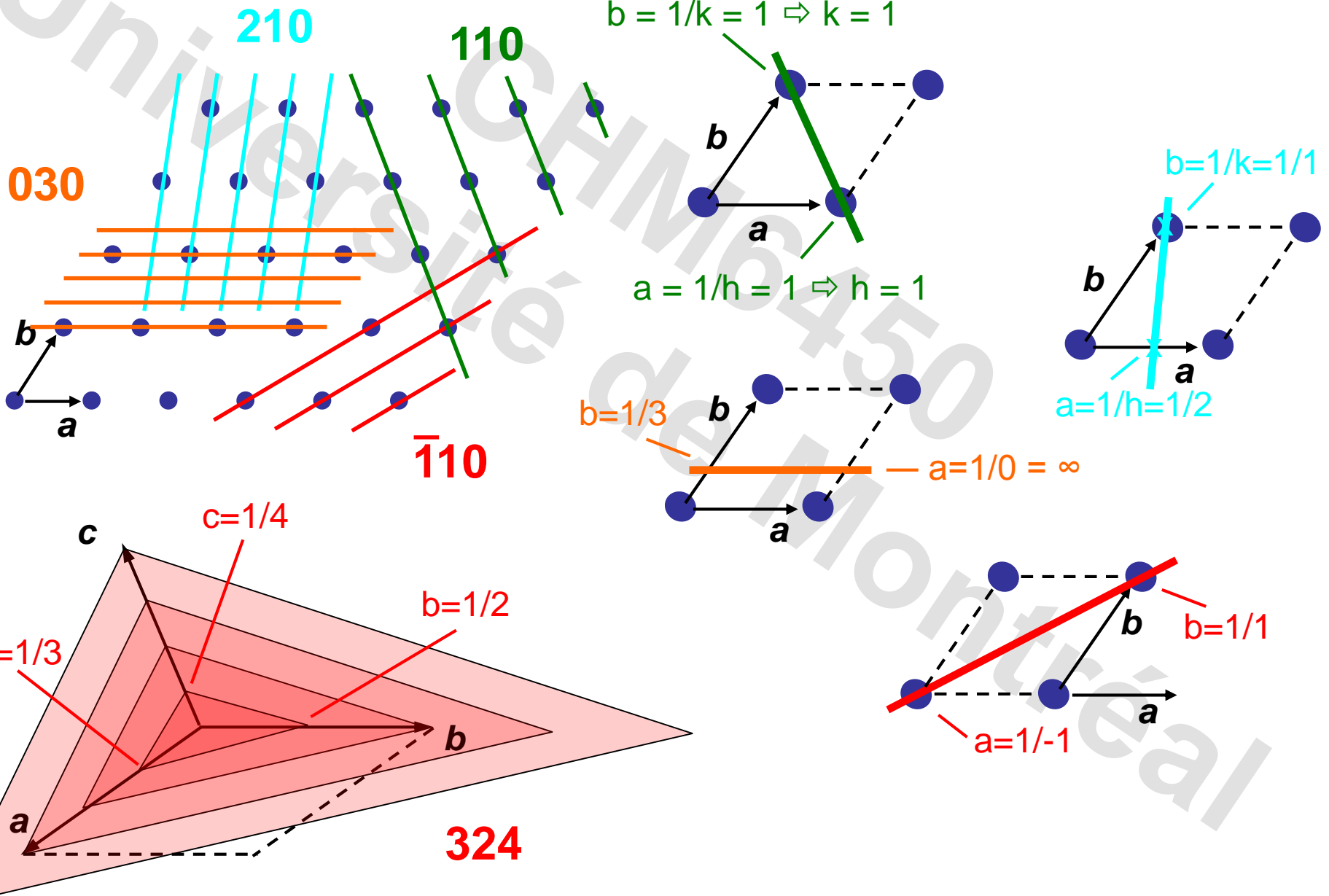
The intensity of a reflection is non-zero if the Bragg condition is fulfilled.

Miller indices of lattice planes

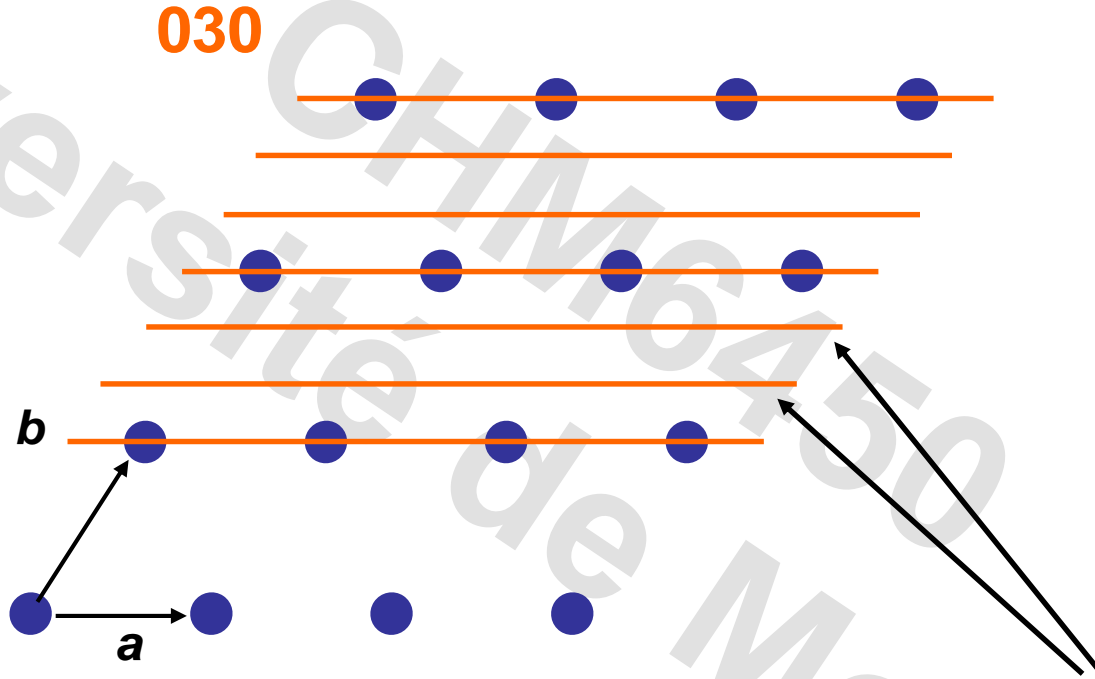


- The plane nearest to the origin (not the plane through the origin), intersects the axes a , b and c at $1/h$, $1/k$ and $1/l$.
- An index of 0 indicates a plane parallel to an axis.
- hkl are the “Miller indices” of the lattice planes
- The higher the indices, the smaller the lattice spacing d_{hkl} .

Miller indices of lattice planes

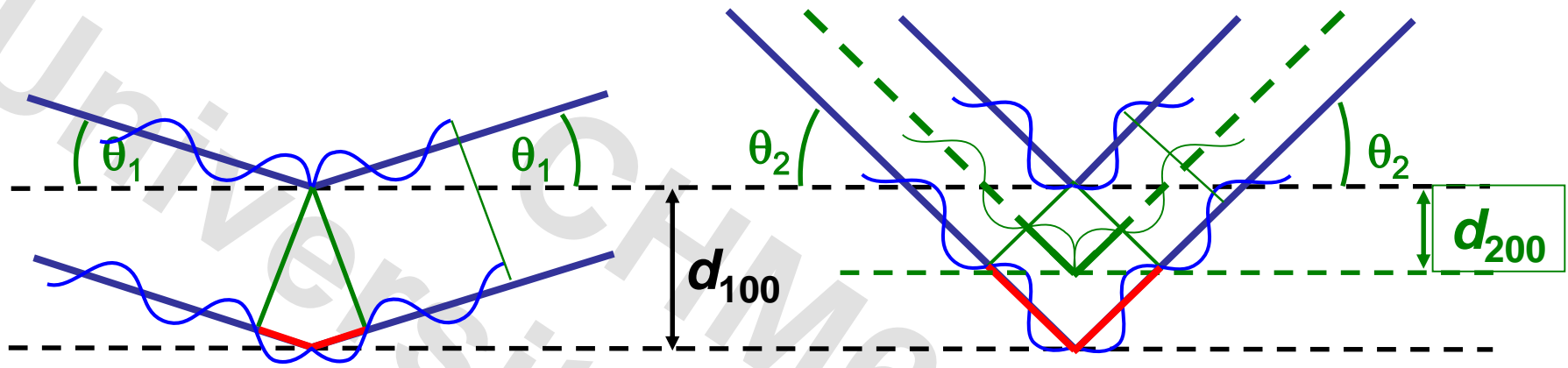


What is 030 ?



There are no atoms in these planes. Why do we see reflections with them?

What is 030 ?



$$2d_{100} \cdot \sin\theta_1 = \lambda$$

$$2d_{100} \cdot \sin\theta_2 = 2\lambda$$

$$2d_{100} \cdot \sin\theta_3 = 3\lambda$$



$$2d_{100} \cdot \sin\theta_n = n \cdot \lambda$$

n reflections for each plane

$$2d_{200} \cdot \sin\theta_2 = \lambda, \quad d_{200} = d_{100}/2$$

$$2d_{300} \cdot \sin\theta_3 = \lambda, \quad d_{300} = d_{100}/3$$



$$2d_{n00} \cdot \sin\theta = \lambda, \quad d_{n00} = d_{100}/n$$

1 reflection for each plane, but additional planes

Thus, we have only first order reflections, but we have to add additional virtual hkl-planes.

Steps in a single crystal diffraction study

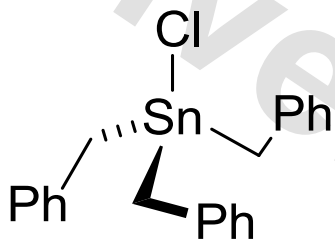
- Grow a crystal
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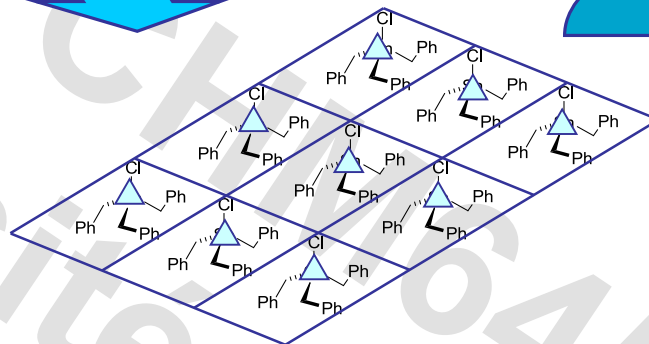
Structure determination

Crystallisation

Single crystal selection



Molecular structure:
Atomic positions



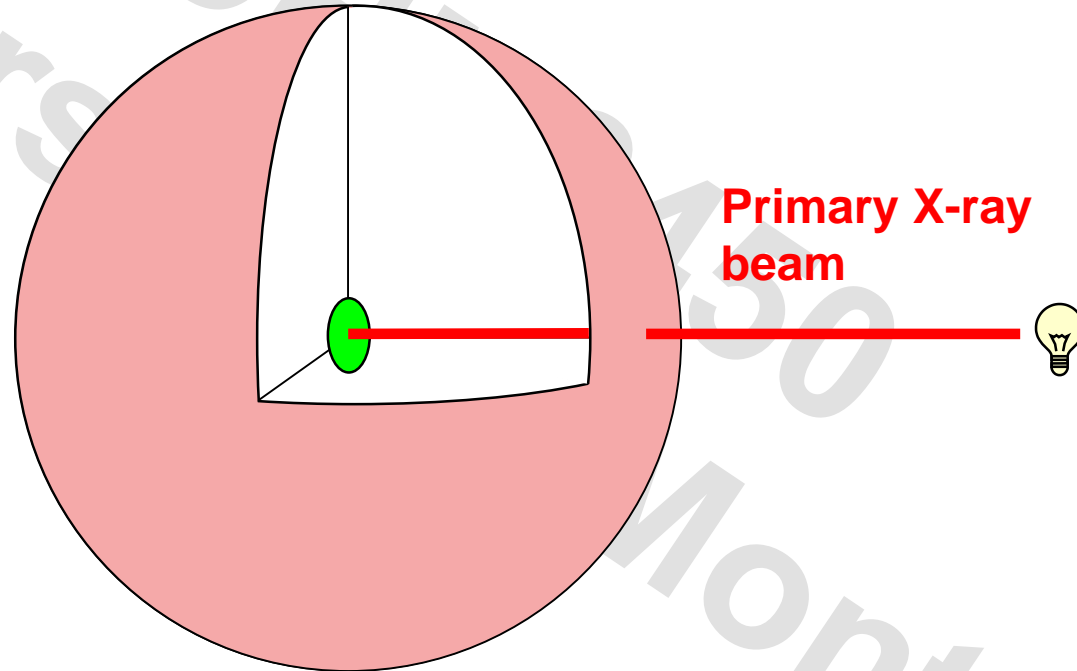
Crystalline structure:
Unit cell and space group



Crystal:
Macroscopic dimensions

↓ Dataset collection

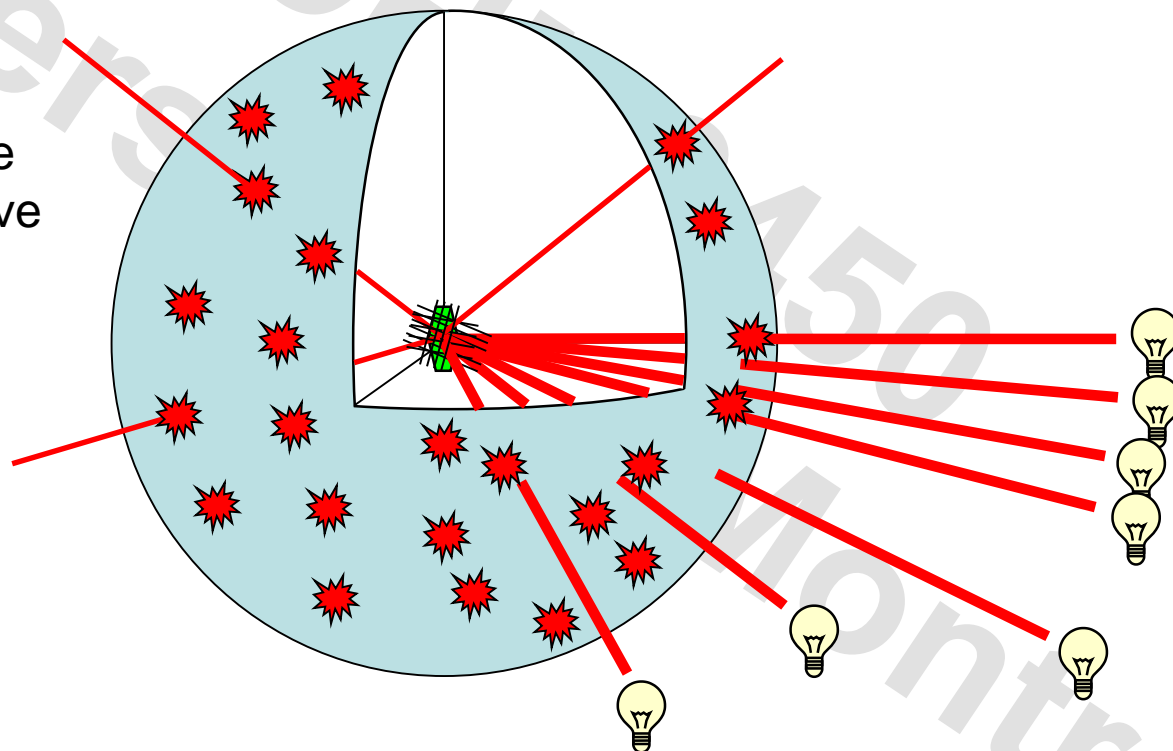
X-ray experiment



Amorphous sample → **diffuse reflexion**

X-ray experiment

In reality it is more convenient to move the crystal and to keep the X-ray source fixed.



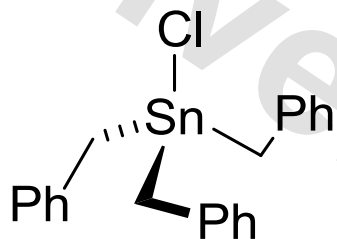
Amorphous sample
Crystalline sample

→ **diffuse reflexion**
→ **reflection only if the Bragg condition is fulfilled.**

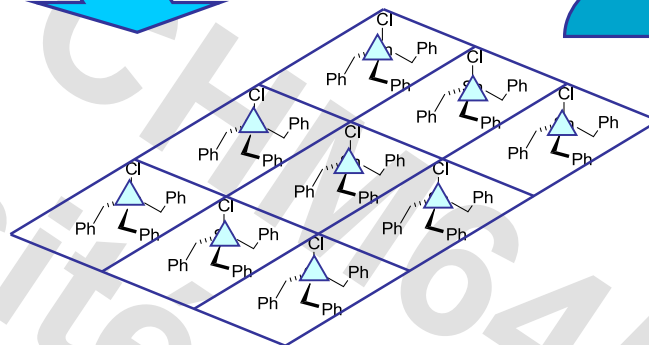
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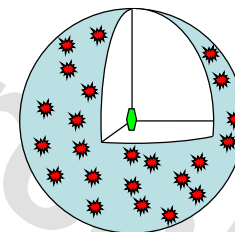


Crystalline structure:
Unit cell and space group



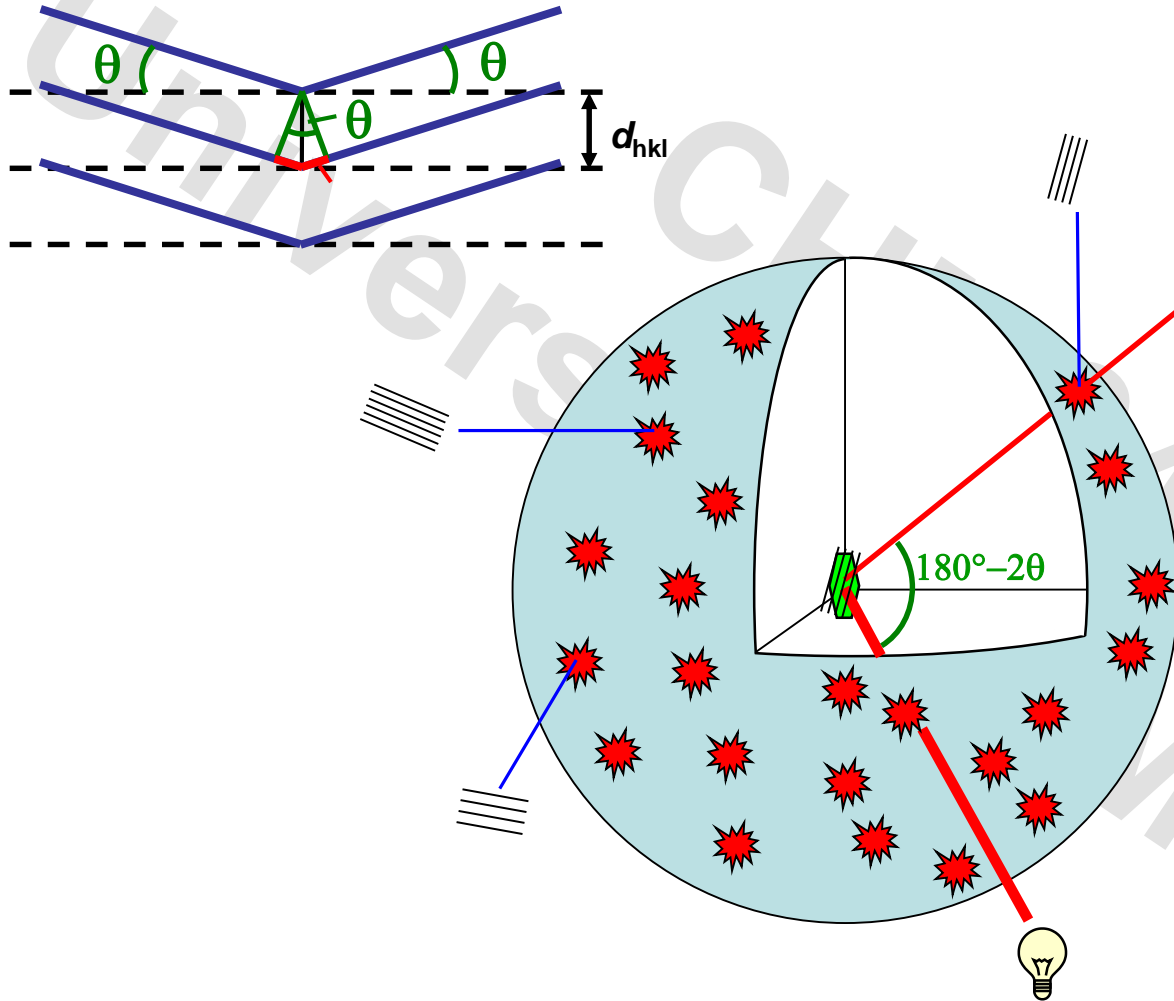
Crystal:
Macroscopic dimensions

↓ Dataset collection



Raw data

X-ray experiment



From the **position** of primary and diffracted beam:

→ **Orientation** of the lattice planes in the crystal (perpendicular to the bisecting of the two beams)

Reflection angle θ :
→ **Distance** between lattice planes

Knowing the **distances** between lattice planes (d_{hkl}) and their **orientations**, we obtain the **unit cell**.

Very fast: the reciprocal lattice

The distance d (d_{hkl}) between lattice planes can be calculated from the unit cell parameters:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

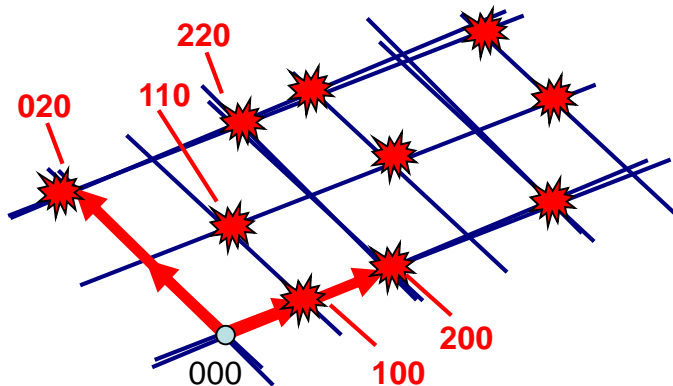
(orthorhombic system)

With the reciprocal values $d^* = 1/d$, $a^* = 1/a$, $b^* = 1/b$, $c^* = 1/c$ we obtain:

$$d^{*2} = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2}$$

Each reflection hkl can thus be described as a vector $d^* = (h \ k \ l)$ in the reciprocal space formed by the basis vectors a^* , b^* and c^* .

From the orientation of the primary and reflected beams, we obtain the direction of d^* for each reflection, from the reflection angle θ the lattice spacing d and thus $d^* = 1/d$. “Indexing” is the art to find a set of basis vectors a^* , b^* , c^* which allow the description of each reflection with integer values of h , k and l .

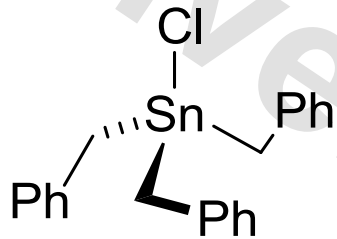


- Finding the longest vectors which can describe all reflections
- A certain error must be allowed
- If necessary, move to shorter basis vectors
- From a^* , b^* and c^* , the unit cell parameters and the Miller indices are known.

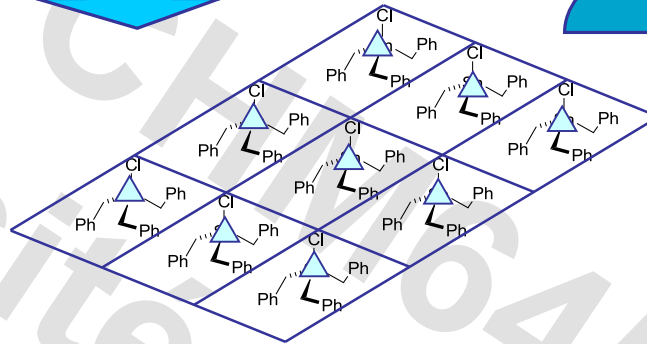
Structure determination

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Molecular structure:
Atomic positions



Crystalline structure:
Unit cell and space group

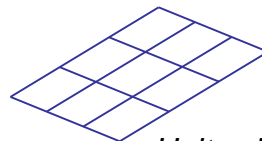


Crystal:
Macroscopic dimensions

Dataset collection

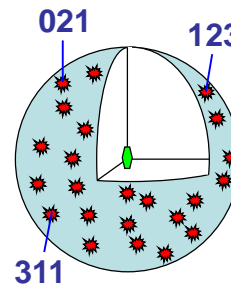
The spatial distribution of the reflections provide information about the unit cell, **but not on the atomic positions.**

These can be obtained from the **reflection intensities.**

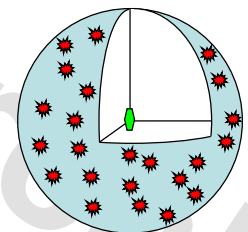


Unit cell

H	K	L	I	σ
0	0	1	134.4	12.5
0	0	2	0.2	1.2
1	1	4	52.4	2.2



Détermination of the unit cell

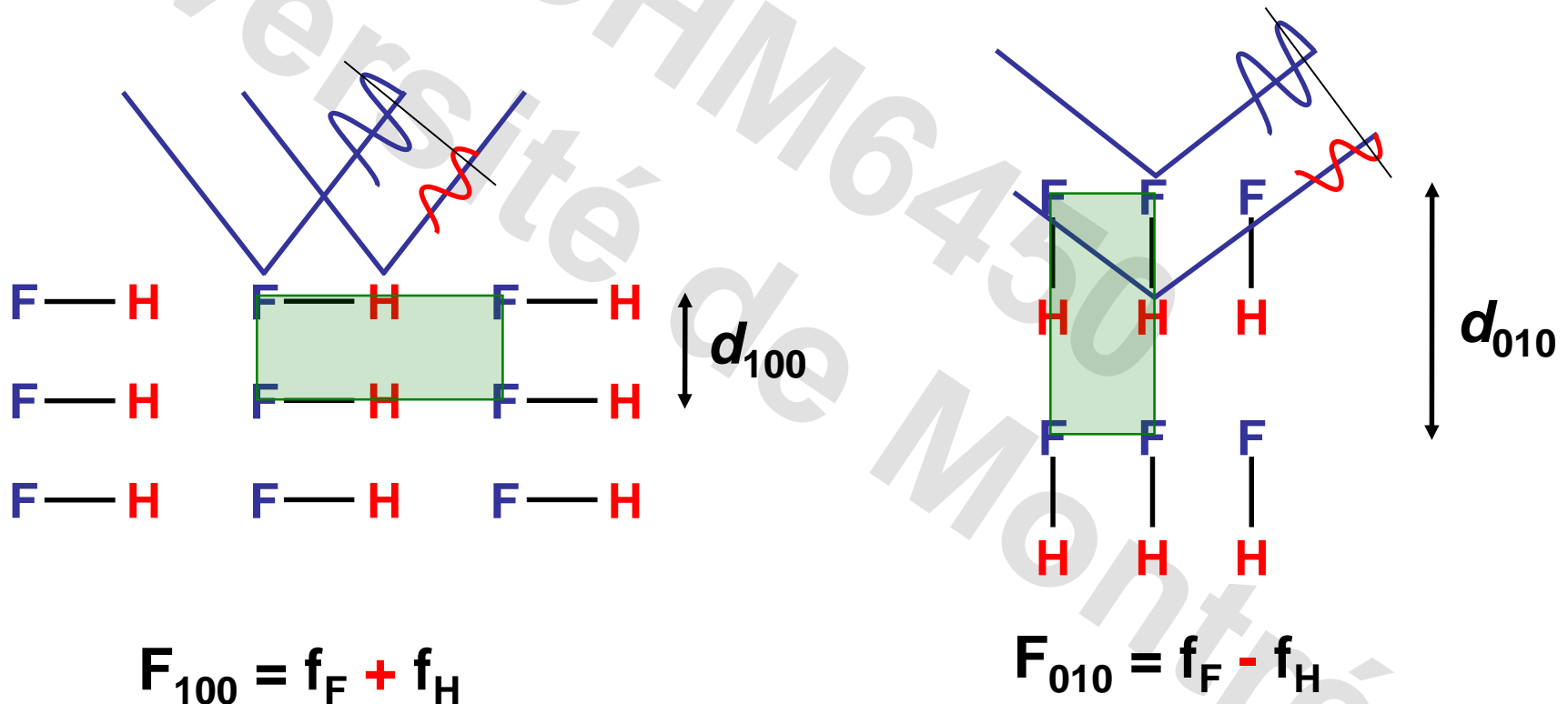


Raw data



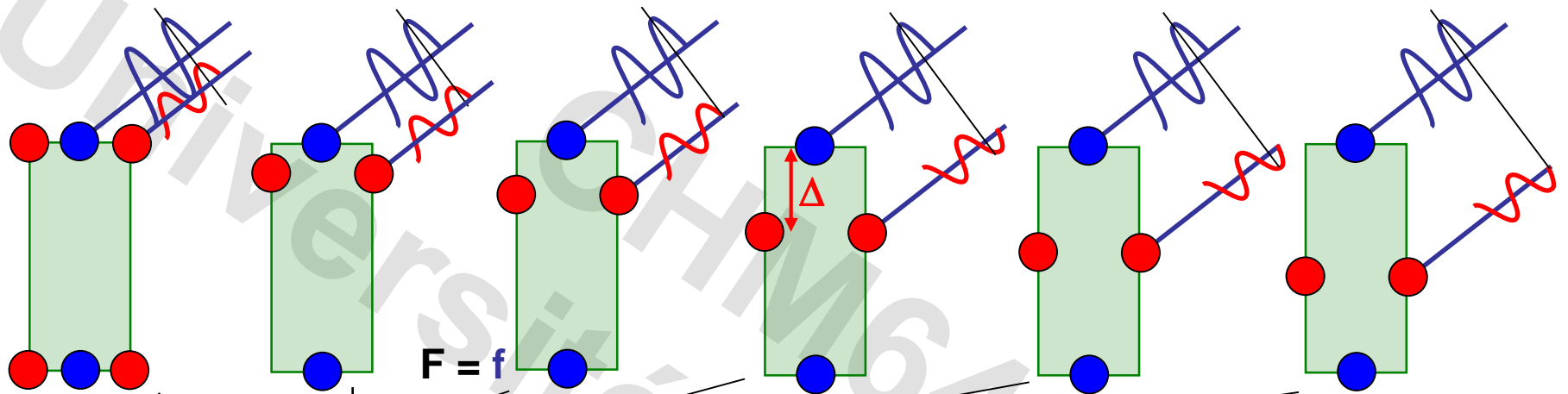
The structure factor F

The intensity of an X-ray beam diffracted at an hkl -plane depends on the **structure factor** F_{hkl} for this reflection. The structure factor is the sum of all the formfactors (atomic scattering factors) in the unit cell.



The structure factor F_{hkl} thus contains information on the spatial distribution of atoms.

The structure factor F

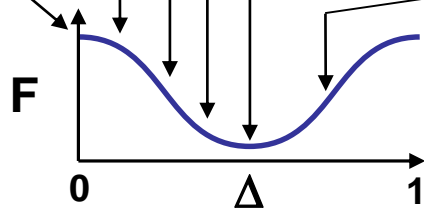


$$F = f + f$$

$$F = f$$

$$F = f - f$$

Δ for lattice plane hkl



$$F = f_1 + \cos 2\pi\Delta \cdot f_2$$

$$= f_1 \cdot e^{2\pi i \cdot \Delta_1} + f_2 \cdot e^{2\pi i \cdot \Delta_2}$$

Structure factor

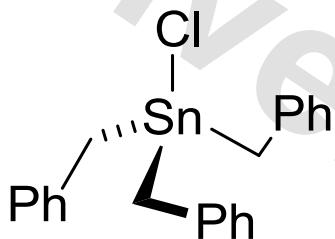
$$F_{hkl} = \sum_{j=1}^N f_j \cdot e^{2\pi i(h \cdot x_j + k \cdot y_j + l \cdot z_j)}$$

The structure factor F_{hkl} depends on the spatial distribution of the atoms or, more specifically, on their distance to the reflection plane.

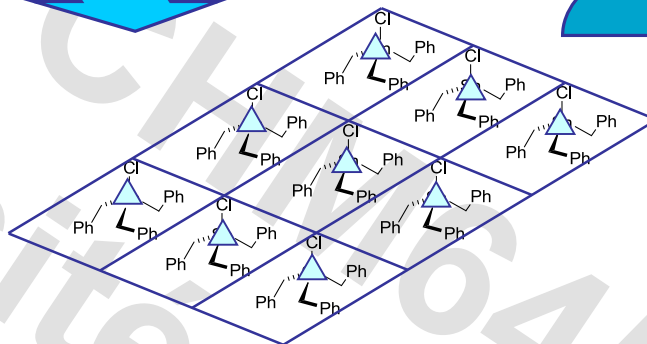
Structure determination

Crystallisation

Single crystal selection



Molecular structure:
Atomic positions



Crystalline structure:
Unit cell and space group



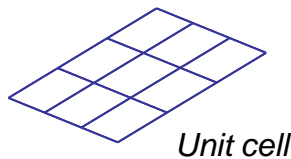
Crystal:
Macroscopic dimensions

Dataset collection

How to find F_{hkl} ?

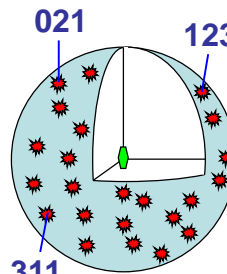
The intensities of the reflections are proportional to the square of the **amplitude** of the structure factor:

$$I \sim |F_{hkl}|^2$$

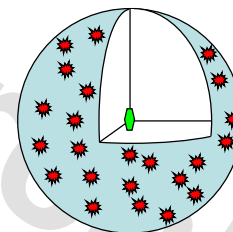


Unit cell

H	K	L	I	σ
0	0	1	134.4	12.5
0	0	2	0.2	1.2
1	1	4	52.4	2.2



Détermination of the elemental cell



Raw data

The phase problem

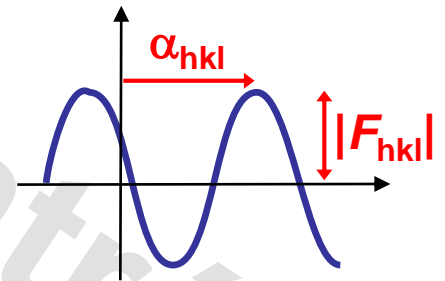
The value of each structure factor F_{hkl} depends on the distribution of the atoms in the unit cell (i. e. the electronic density). We can thus obtain this electronic density, from the combination of all structural factors using a Fourier transformation

$$\rho(x, y, z) = \frac{1}{V} \sum_{hkl} F_{hkl} \cdot e^{-2\pi i(hx+ky+lz)}$$

$$F_{hkl} = \sum_{j=1}^N f_j \cdot e^{2\pi i(h \cdot x_j + k \cdot y_j + l \cdot z_j)} = |F_{hkl}| \cdot e^{i\alpha_{hkl}}$$

The only formula you have to know by heart!

The factor F_{hkl} takes the **form of a cosinus function** with an **amplitude** $|F_{hkl}|$ and a **phase** α_{hkl} . These two, $|F_{hkl}|$ and α_{hkl} , vary for each reflection hkl and depend on the atomic positions relative to the hkl plane.

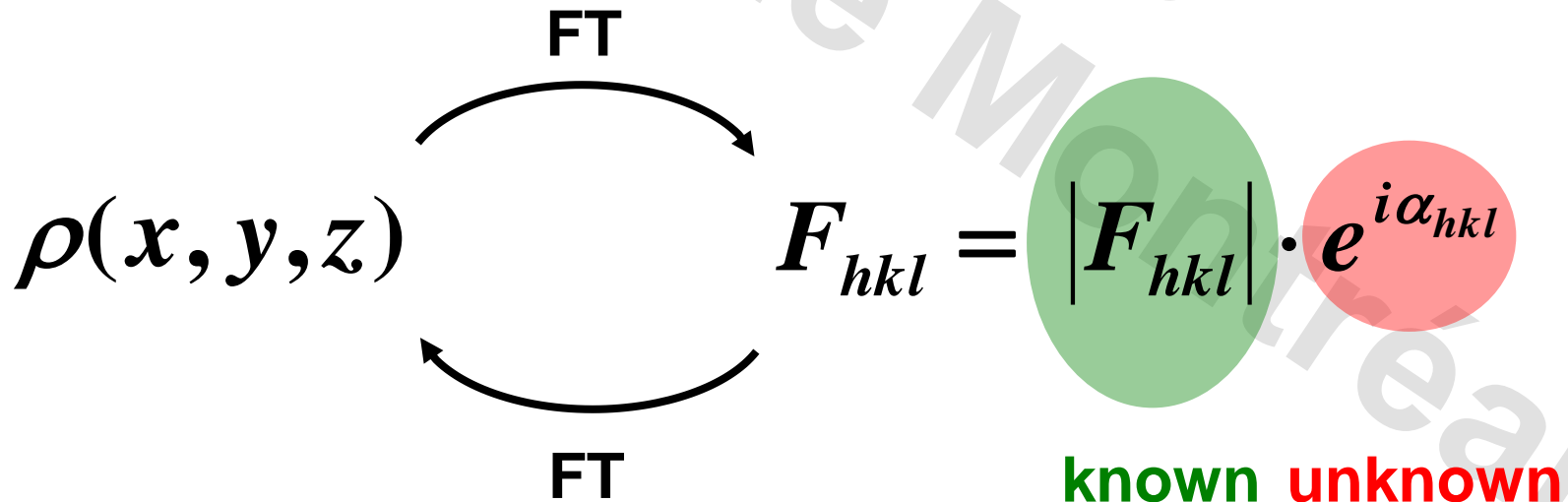


$$\rho(x, y, z) = \frac{1}{V} \sum_{hkl} |F_{hkl}| \cdot e^{i\alpha_{hkl}} \cdot e^{-2\pi i(hx+ky+lz)}$$

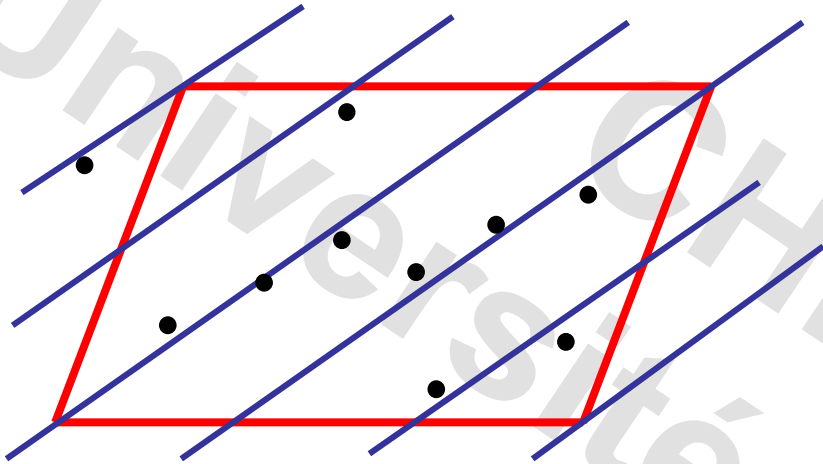
The phase problem

$$\rho(x, y, z) = \frac{1}{V} \sum_{hkl} |F_{hkl}| \cdot e^{i\alpha_{hkl}} \cdot e^{-2\pi i(hx+ky+lz)}$$

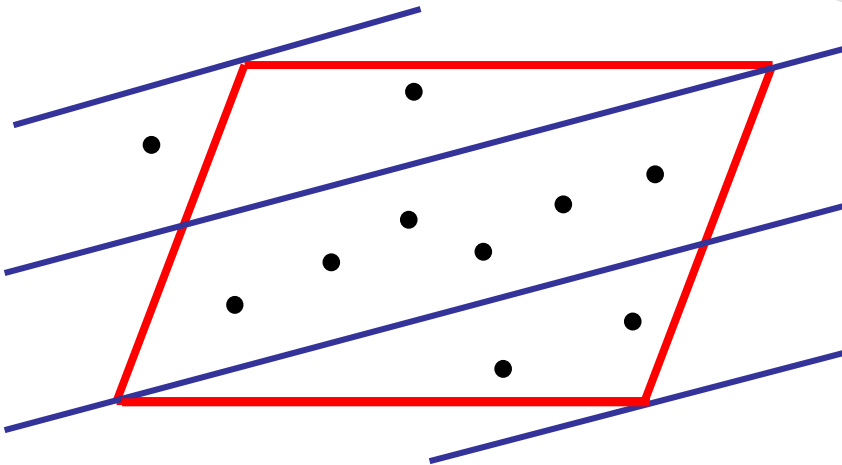
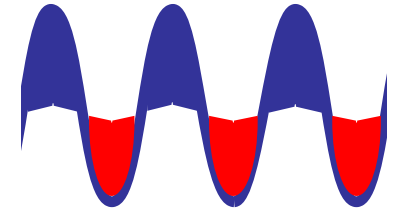
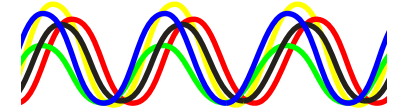
One small problem: We can determine $|F_{hkl}| = \sqrt{I_{hkl}}$,
but we do not know the phases α_{hkl} !



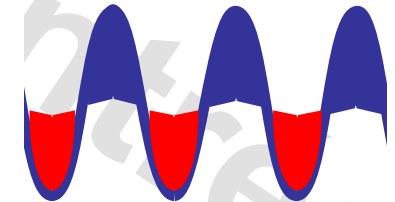
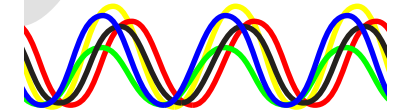
A (very) short introduction to phases



$h,k,l = 2,3,0$; Centers on planes, $\alpha_{230} = 0^\circ$, strong reflection

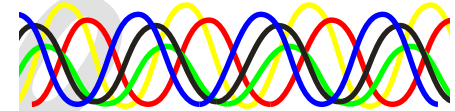
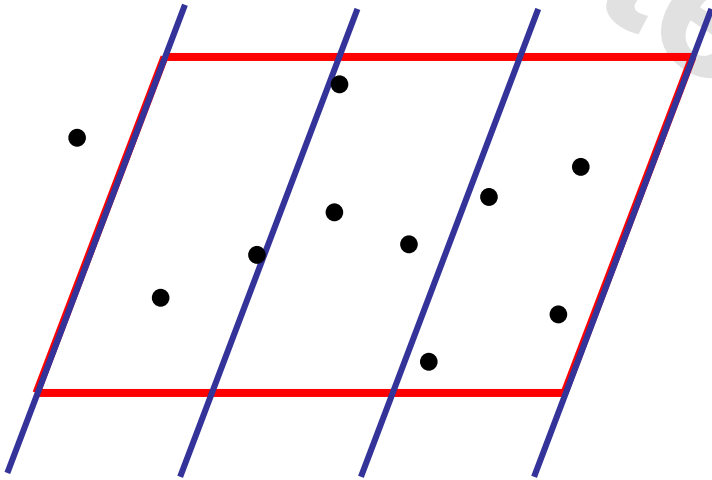


$h,k,l = 2,1,0$; centers between planes, $\alpha_{210} = 180^\circ$, strong reflection



A (very) short introduction to phases

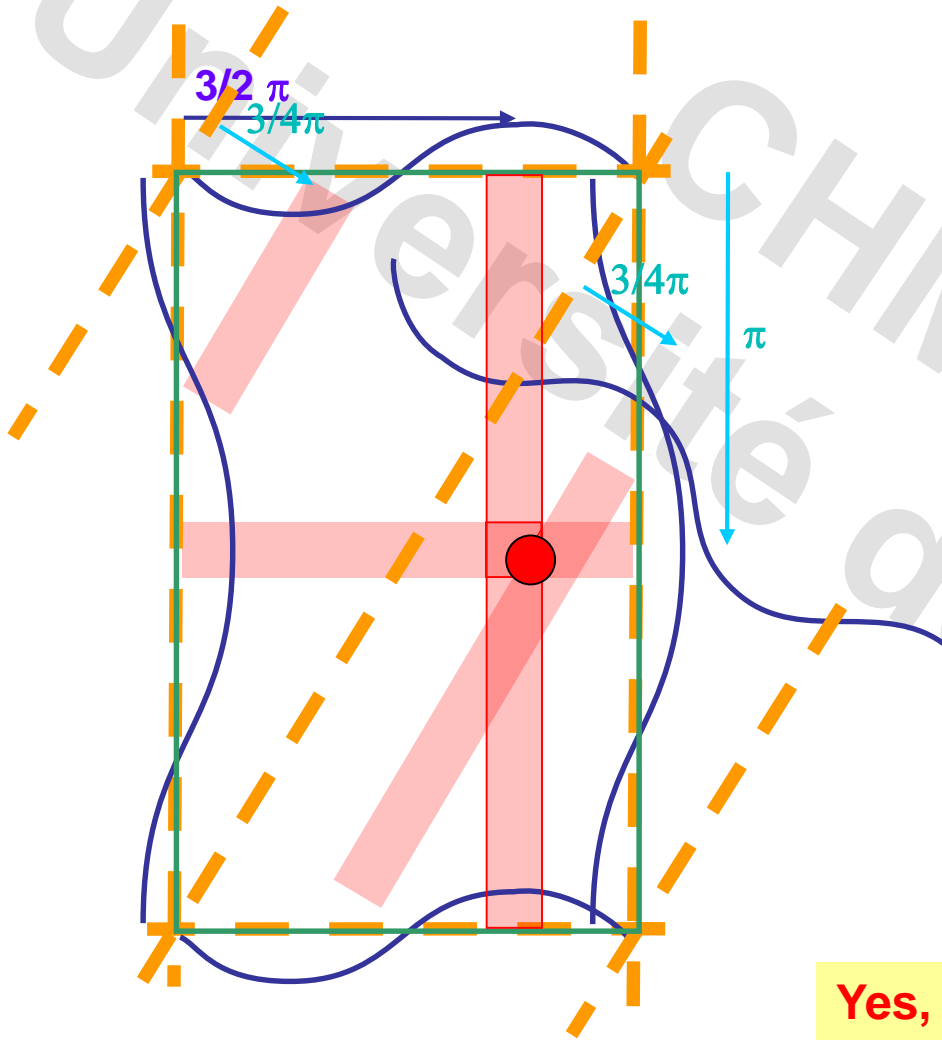
The phase ϕ of a reflection where the atoms are situated on the hkl planes has a phase of approximately 0° ; if the atoms are found between the planes the phase is approximately 180° . For randomly distributed atoms, we cannot predict the phase and the reflection is weak due to strong destructive interference.



$h,k,l = 0,3,0$; weak reflection, $\alpha_{030} = ?$

Do we really need the phases?

Do we really need the phases...



Where do we find the atom?

Since there is only one atom, $F_{hkl} = f \cdot e^{i\alpha}$.

Reflection on 100:
We find $\alpha = 3/2\pi$

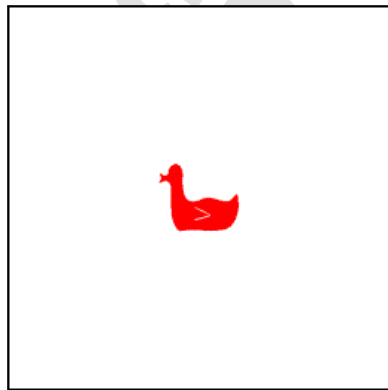
Reflection on 010:
We find $\alpha = \pi$

Reflection on 110:
We find $\alpha = 3/4\pi$

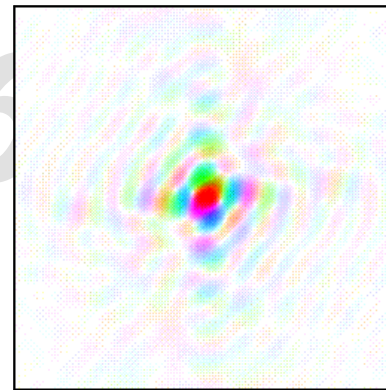
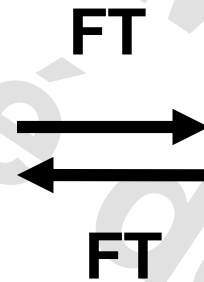
Yes, we need them. Because of the Fourier transformation, the phases are connected with the atom positions!

This is a model. In a structure with only one atom, the atom is always placed at the origin.

A duck in reciprocal space (by Fourier transformation)

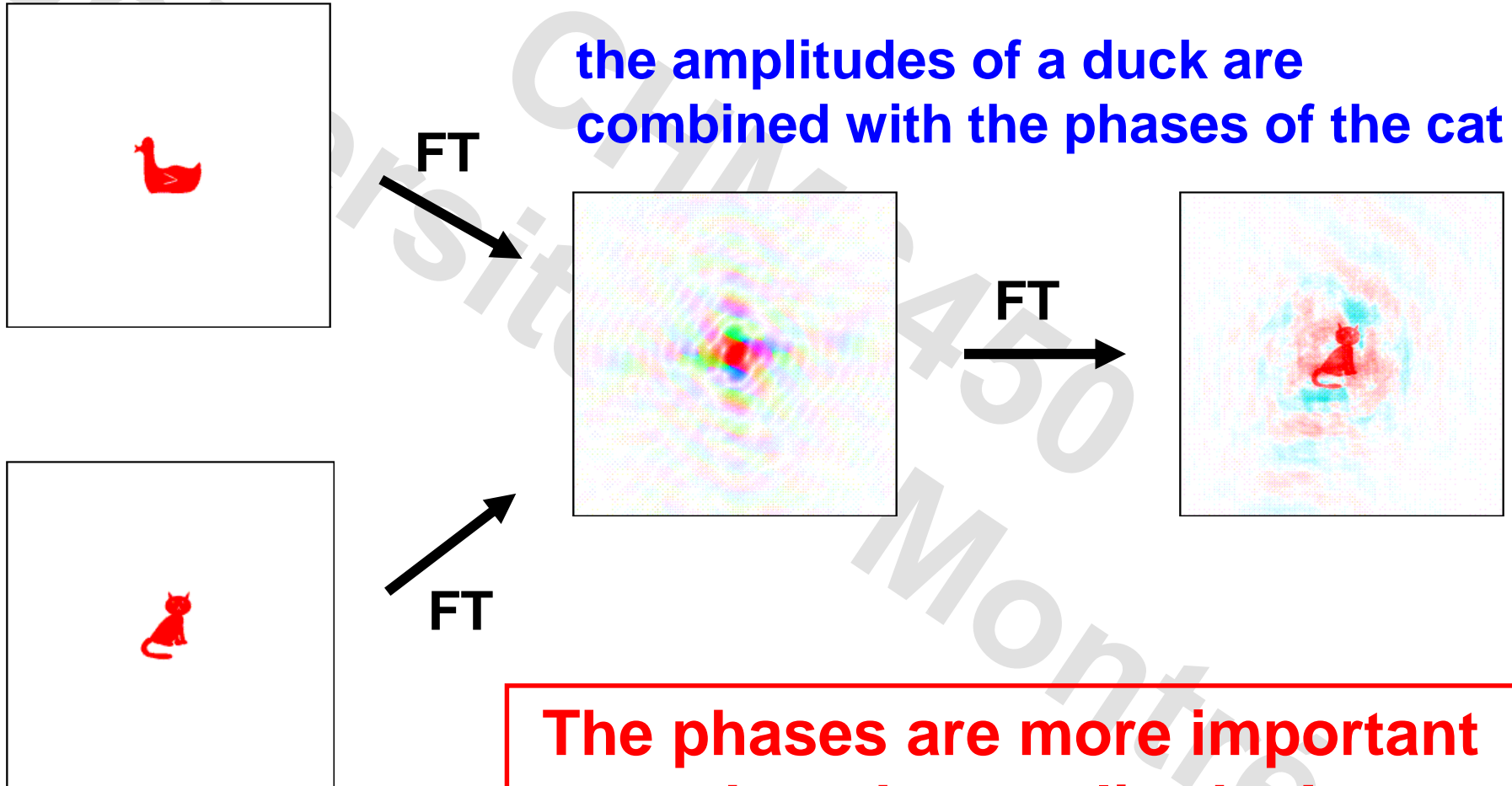


duck



Fourier transform of
a duck

Combination of different amplitudes (F) and phases (ϕ)



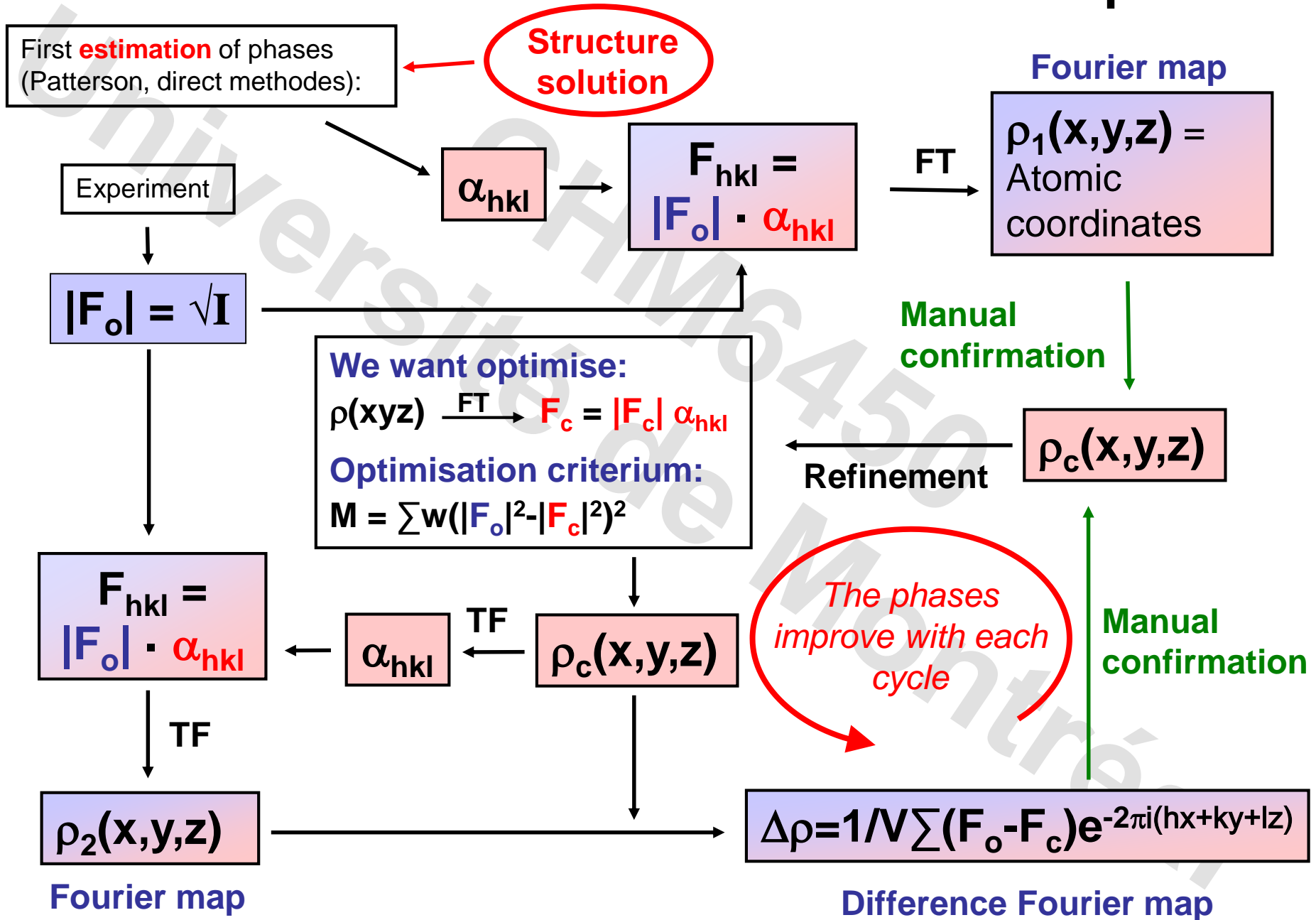
The phases are more important than the amplitudes!

Steps in a single crystal diffraction study



- Grow a crystal
- Choose and mount a single crystal
- Collect the dataset
- Determine the unit cell
- Integration of the image files and data reduction
 - Lorentz correction
 - Polarisation correction
 - Absorption correction
 - Other corrections (twinning etc.)
- Space group determination
- **Structure solution** ← Estimation of a first set of phases
- **Structure refinement** ← Refinement of the phases
- Validation
- Preparation of tables and figures
- Data backup

Solution of a structure = estimation of the phases



Take-home messages

- Phases cannot be determined experimentally (Exception: synchrotron)
- Our structural solution is thus a **model**.
- The first step is the “structure solution”, a first **estimation** of the phases, which we do not know.
- During the refinement we improve our model by matching experimental to calculated intensities. A good model results in phases closer to reality.
- Thus the better the model, the better the phases, the better the resulting electron density map, the better the model, ...
- **Refinement is thus a cyclical process during which our structural model improves more and more.**