POWDER X-RAY DIFFRACTION
II – DIFFRACTION

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Outline of the course

I – CRISTALLOGRAPHY

II – X-RAY DIFFRACTION

III – POWDER DIFFRACTOMETRY

Outline of the course

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3. - DIFFRACTION BY A PERIODIC LATTICE

    3.1. - Diffraction condition

    3.2. – Ewald's sphere

    3.3. – Bragg's relation

    3.4. - Structure Factor

    3.5. – Systematic absences

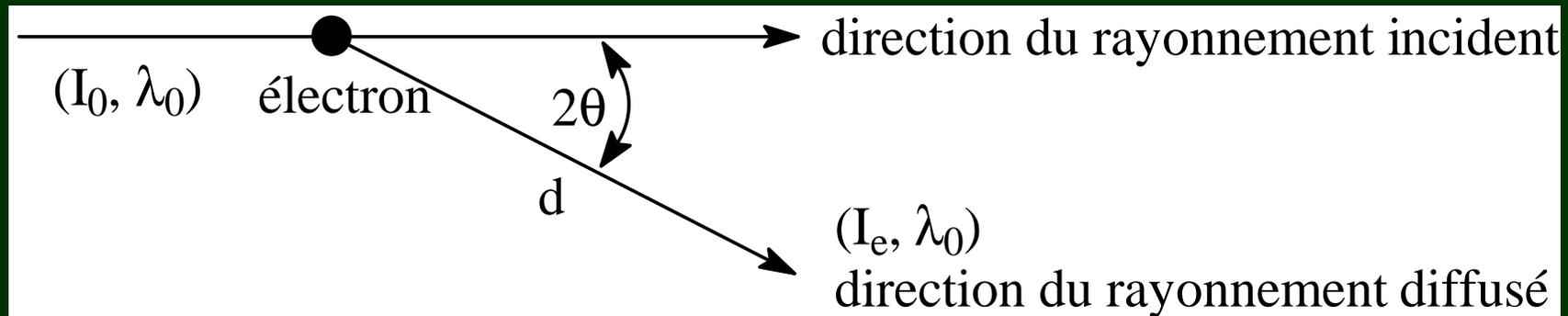   *3.6. - Lorentz-polarization Factor Lp*

    3.7. - Debye-Waller factor DW

    3.8. - Multiplicity factor M_{hkl}

    3.9. – General relation

    3.10. – Peak width – Scherrer's relation

2.3. - Thomson coherent diffusion
2.3.1. – Scattering by a single electron

$$I_e = I_0 \left(\frac{R^2}{d^2} \right) \left(\frac{1 + \cos^2 2\theta}{2} \right)$$
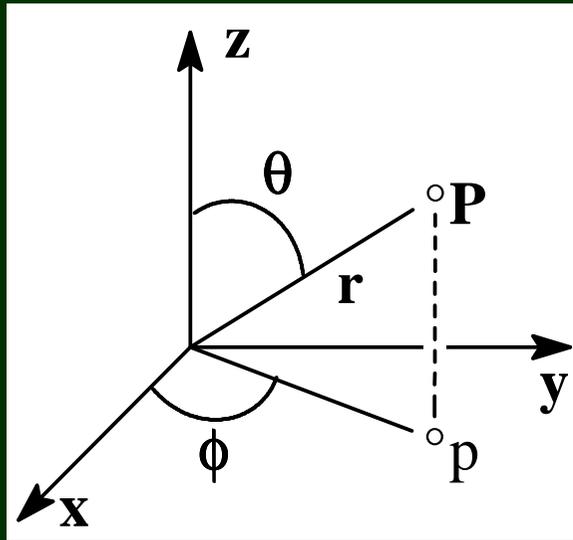
$$R = \left(\frac{1}{4\pi\varepsilon_0} \right) \left(\frac{e^2}{mc^2} \right)$$

Neutral atom (atomic number Z):
- positive point charge Z^+ (nucleus) surrounded by an electronic cloud.
- the electronic cloud extents from the nucleus up to several Å
- it can be characterized by the local electron density $\rho(x,y,z)$
- the cartesian coordinates can be transform into polar coordinates ➜ $\rho(r, \theta, \varphi)$

For a neutral atom

$$\iiint_V \rho(x, y, z)\, dx\, dy\, dz = \iiint_V \rho(r, \theta, \varphi)\, 4\pi r^2 \sin\theta\, dr\, d\theta\, d\varphi = Z$$

The integration is performaed over the whole space.

For an atom we take into account the volume of the electronic cloud.
An elemental volume dV with electron density ρ works as a charged point for the primary photon. The charge is ρdV.

2.3. - *Thomson coherent diffusion*
2.3.2. – Scattering by an atom: atom scattering factor

For two elemental volumes dV1 and dV2 with electronic density $\rho 1$ and $\rho 2$, the scattered photons will interfere
we have to consider the distance $r = |\mathbf{r}|$ between the two elemental volumes as well as unit vectors $\mathbf{s_0}$ and $\mathbf{s}$ defining the incident and scattered directions.
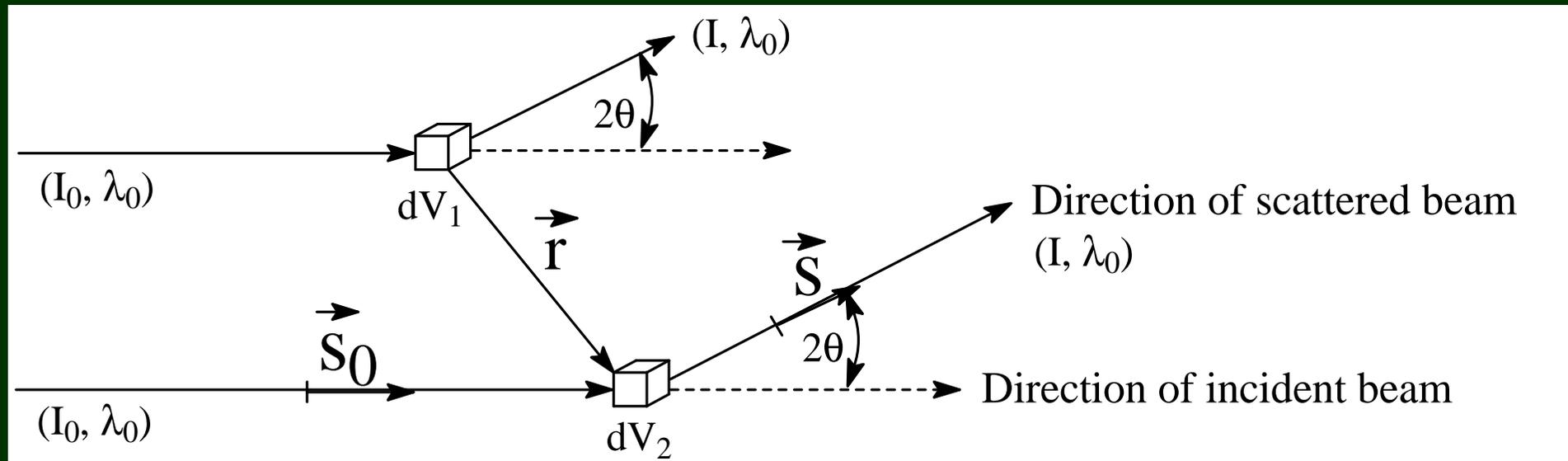
The path difference δ for the secondary photons emitted by dV1 and dV2 is:

$$\delta = (\mathbf{s} \textbf{-} \mathbf{s_0}).\mathbf{r} \qquad \text{with} \ \ |\mathbf{s} \textbf{--s_0}| = 2 \sin\theta$$

Or in term of wave vector: $\qquad \delta/\lambda = (\mathbf{k\textbf{-}k_0}).\mathbf{r} \qquad$ with $|\mathbf{k} \textbf{--k_0}| = 2 (\sin \theta) / \lambda$

The integration is done for the whole volume occupied by the cloud, that is for all $\mathbf{r}$ values.

2.3. - Thomson coherent diffusion
2.3.2. – Scattering by an atom: atom scattering factor

We must know the electron density function ρ for all elemental volumes
➔ use the polar coordinates r, θ and φ, starting from the nucleus (r = 0).
➔ take a spherical symmetry for the electron density: ρ depends only on the distance r from the nucleus.

In this case, the scattered amplitude A and intensity I depend on the scattered angle 2θ and on the wavelength λ through the relation $\sin\theta/\lambda$ (this is due to the interference term) and on the electron density ρ

$$A = A_0.f(\sin\theta/\lambda, \rho)$$

the intensity is the square of amplitude

$$I = I_0.f^2(\sin\theta/\lambda, \rho)$$

Remember, the intensity is a scalar number and the amplitude is a complex number.

Once the electron density function is known, we can obtain the function f for all the atoms that is for all the values of the atomic number Z.

The function f characterizes the scattering power of the atoms and depends on the atomic number Z and the term $\sin\theta/\lambda$.

2.3. - Thomson coherent diffusion
2.3.2. – Scattering by an atom: atom scattering factor

When $\theta = 0$, all the elemental volumes are emitting in phase and the amplitude of the scattered beam for one atom corresponds to the number of electrons in the electron cloud: Z for a neutral atom. This value is on the y-axis.
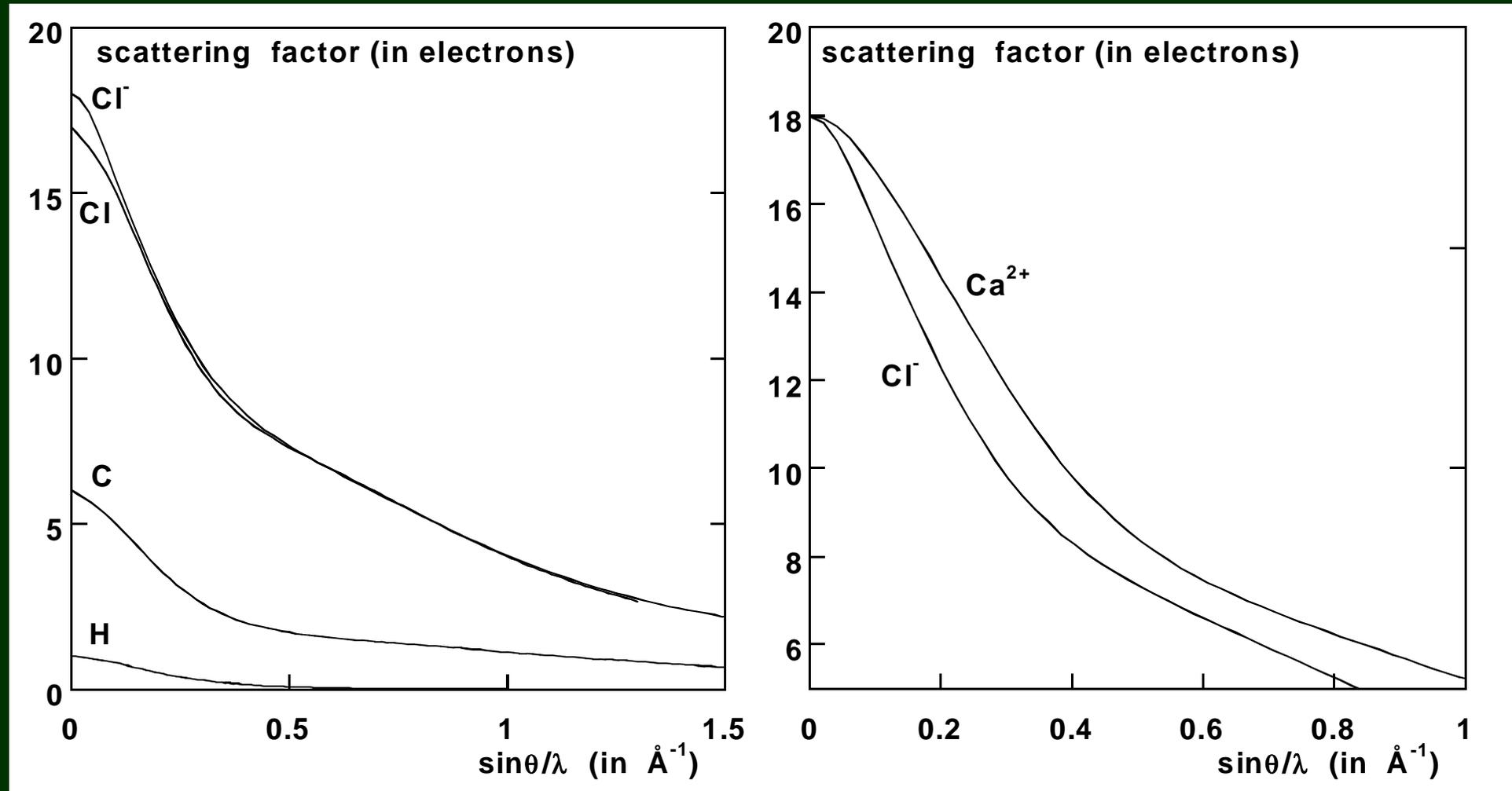
The function f is the atom scattering factor and represents the scattering power of the atom for a X-ray beam

Compare the function f for the elements H, C, Cl and Cl$^-$

When the size of an atom increases, the electron density decreases and the factor f decreases too.

Compare the ions Cl$^-$ and Ca^{2+}

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    3.3. – Bragg's relation

    3.4. - Structure Factor

    3.5. – Systematic absences

    3.6. - Lorentz-polarization Factor Lp

    3.7. - Debye-Waller factor DW
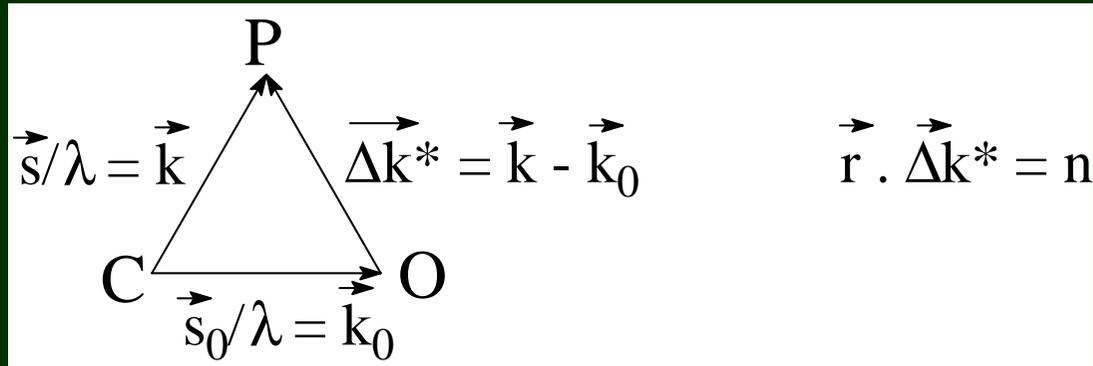
    3.8. - Multiplicity factor M_{hkl}

    3.9. – General relation

    3.10. – Peak width – Scherrer's relation

The next step is to consider the scattering process by a set of atoms in a periodic lattice

We can use the diffraction condition which was demonstrated previously:

$$\vec{s}/\lambda = \vec{k} \qquad \overrightarrow{\Delta k^*} = \vec{k} - \vec{k}_0 \qquad \vec{r} \cdot \overrightarrow{\Delta k^*} = n$$

$$\vec{s}_0/\lambda = \vec{k}_0$$

r is a vector defined in the direct space (crystal space) ➜ **r** = u**a** + v**b** + w**c**
Δ**k*** = **k** - **k**$_0$ is a vector defined in the reciprocal space ➜ Δ**k*** = h**a*** + k**b*** + l**c***
n is a relative integer.

Thus we can present these vectors in a geometrical way

The diffraction condition is: Δ**k*** is a vector of the reciprocal lattice
➜ if the end of vector **k**$_0$ lies at the origin of the reciprocal lattice,
➜ the end of vector **k** must be another point of this reciprocal lattice.

We lie the crystal and the direct lattice at the center C of a sphere of radius $1/\lambda$
We draw the same geometrical construction
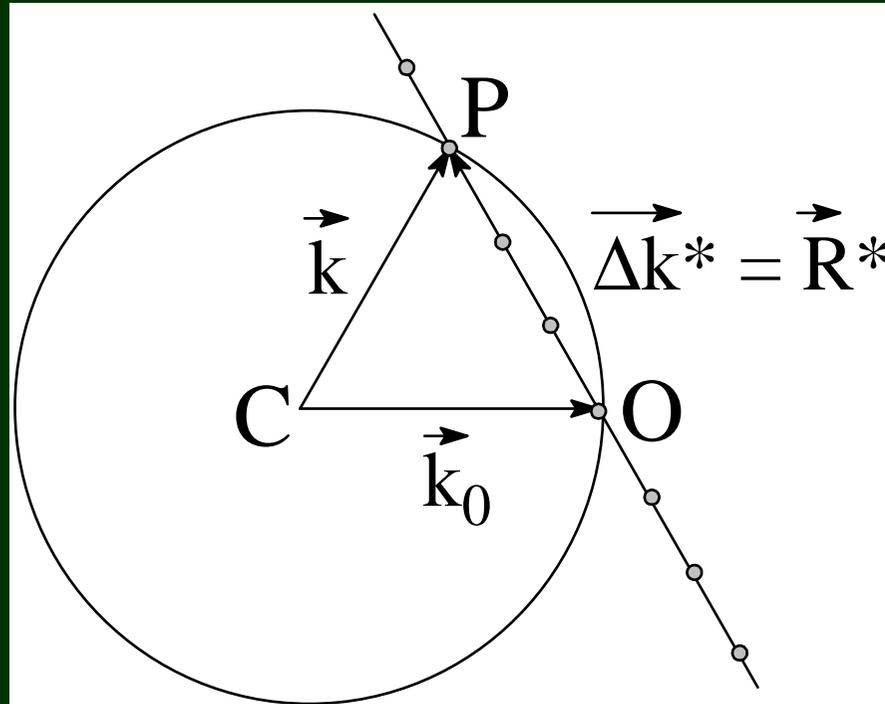
The extremity of vector $\mathbf{k_0}$ lies on the surface of the sphere
The end of vector $\mathbf{k}$ lies at the surface of the sphere too
New formulation of the diffraction condition:
➜ « the end of the reciprocal vector $\mathbf{\Delta k^*}$ must lie onto the sphere »
This sphere is called « Ewald's sphere »

Each time a point of reciprocal lattice lies onto the sphere: diffraction condition is satisfied.
But is it the case?
Generally no, or by chance
How can we brought the reciprocal points onto the surface of the sphere?

First way ➜ move the crystal and you will move the reciprocal lattice
Then points will enter or leave the sphere and therefore cross the surface
➜ the diffraction condition is satisfied and we observe diffracted beams

This is the case for single crystal
diffractometry
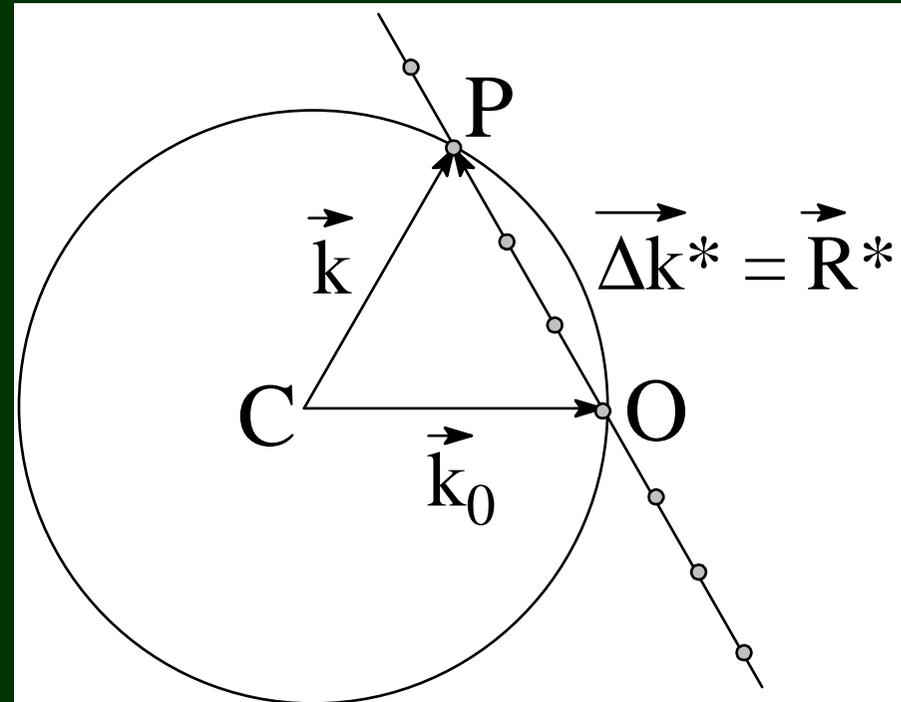
Second way ➜ use a set of numerous very small crystals, with all possible random directions for direct lattice and therefore reciprocal lattice
➜ this increase the chance to have reciprocal points lying on the Ewald's sphere surface

➜ powder diffractometry (XRD)

You have to mill the powder in order to get a grain size about 10 to 5 μm
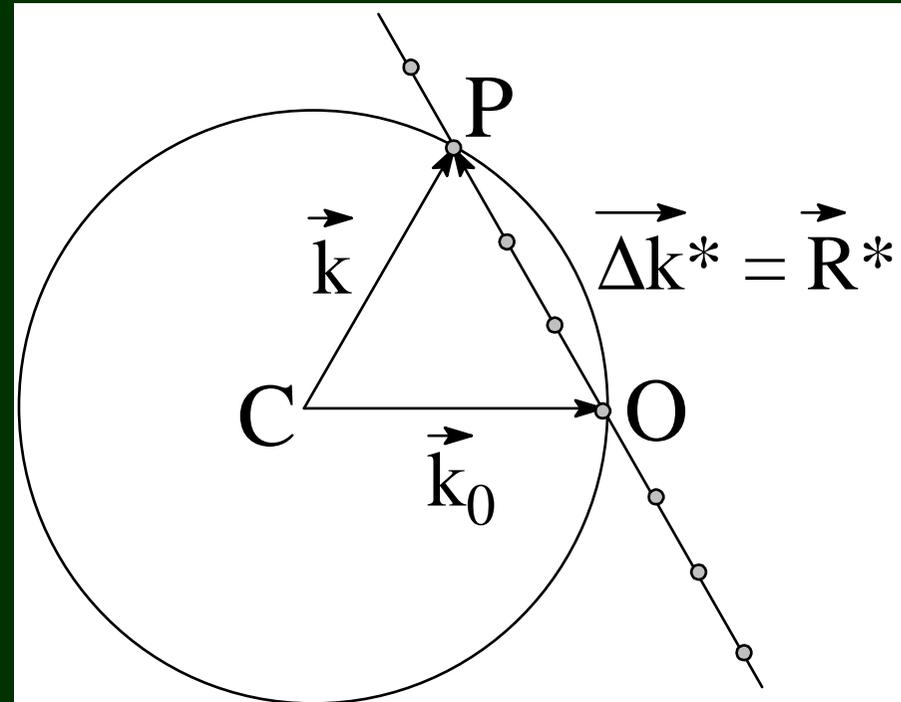
Supplementary condition: **resolution sphere** with a radius of 2/λ
➔ to cross the Ewald's sphere, the reciprocal point must be inside the resolution sphere

P

C 1/λ O 2/λ

Ewald's sphere

Resolution sphere

$$\left|\overrightarrow{\Delta k^*}\right| < 2/\lambda$$

3.3. – Bragg's relation

The reciprocal vector **OP** = **Δk*** defines the line [h k l]
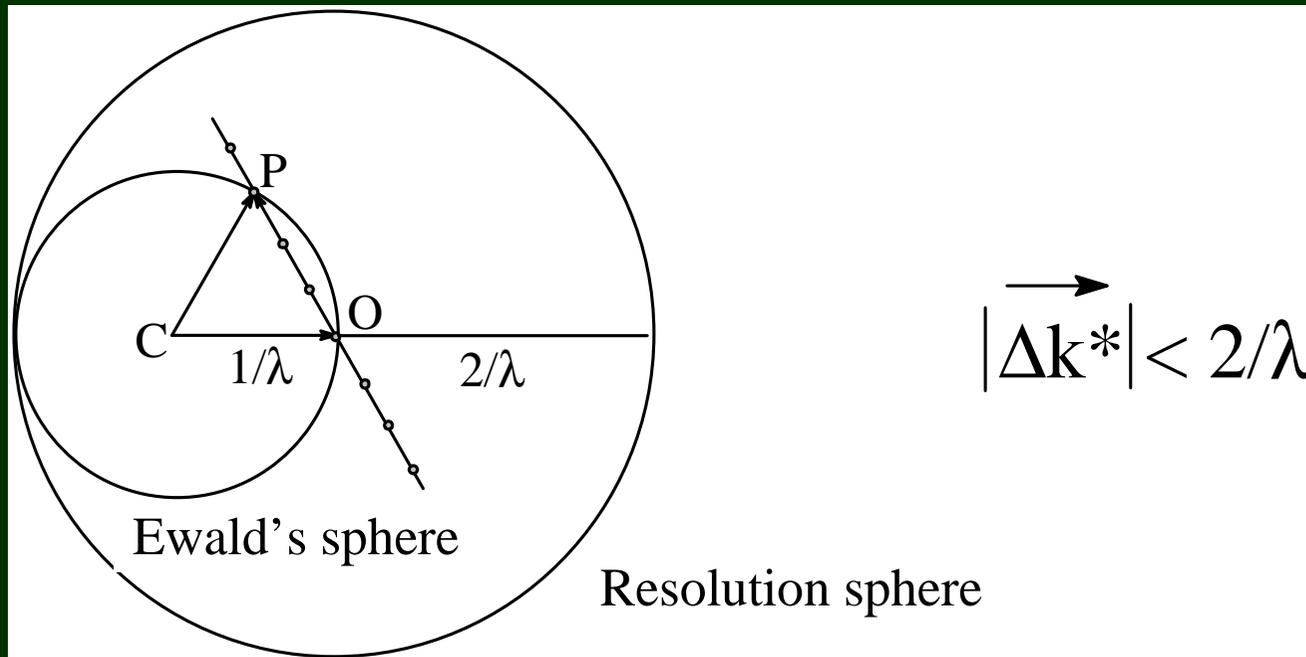
The parameter of this line [h k l] is N_{hkl}^{*}

rayon diffracté
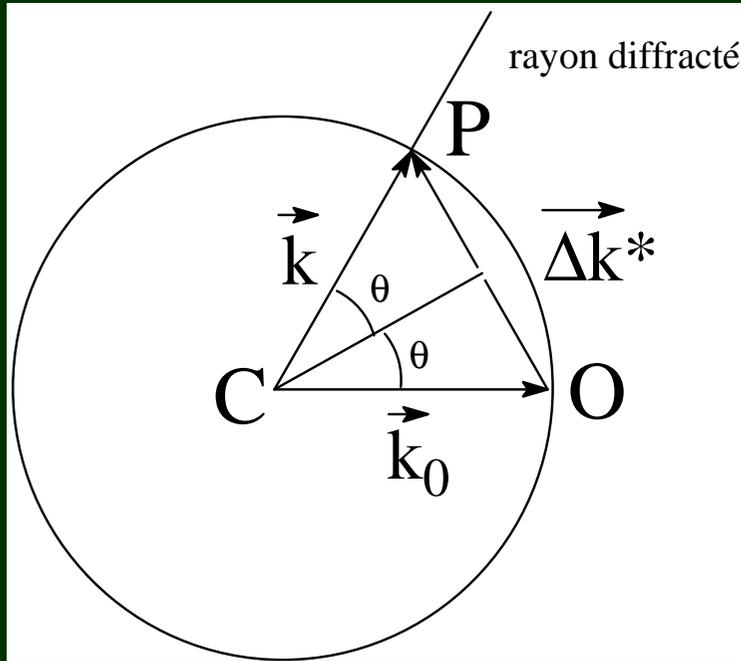
$$\overrightarrow{\Delta k}* = \overrightarrow{OP}* = h\vec{a}* + k\vec{b}* + l\vec{c}*$$

$$N_{hkl}^{*} = 1/d_{hkl} = \left|\overrightarrow{OP}*\right|$$

In the equilateral triangle COP, we have:

$$\sin\theta = \frac{\left|\overrightarrow{\Delta k}\right|/2}{\left|\vec{k}_0\right|} = \frac{N_{hkl}^{*}/2}{1/\lambda}$$

Then we obtain the relation for the diffraction by a family of planes (hkl)

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

3.4. - Structure Factor

$$F_{hkl} = \frac{\text{(amplitude of beam diffracted by atoms in the unit cell)}}{\text{(amplitude of beam scattered by a single electron)}}$$

$$\overrightarrow{OP}_j = x_j \vec{a} + y_j \vec{b} + z_j \vec{c}$$
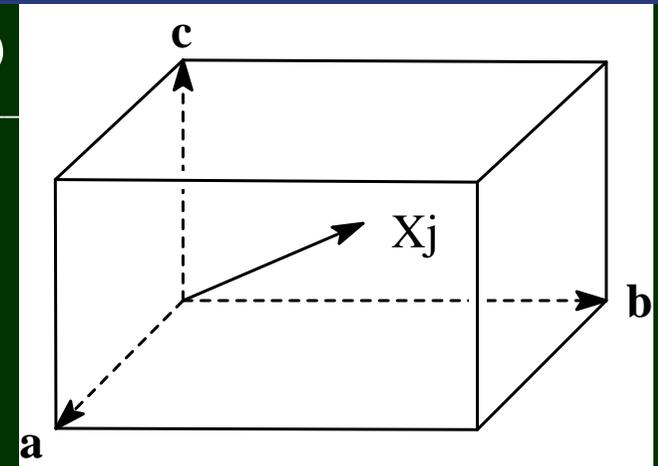
Path difference between the beam from the origin and the beam from atom j, for the direction defined by the reciprocal vector **Δk***

$\delta_j = hx_j + ky_j + lz_j$

Phase difference $\alpha_j = 2\pi\delta_j = 2\pi (hx_j + ky_j + lz_j)$

Structure factor: $F_{hkl} = \sum_{j=1}^{n} f_j \exp [2\pi i (hx_j + ky_j + lz_j)]$

Complex number: $F_{hkl} = TF(\rho(\vec{r})) = \int \rho(\vec{r}) \exp(-2\pi i \overrightarrow{\Delta k} \cdot \vec{r}) \, d\tau$

Intensity: $I_{hkl} = K.F_{hkl}.F_{hkl}^* = K.|F_{hkl}|2$

3.5. – *Systematic absences*

Ex. 1: P lattice → translations **a**, **b** and **c**

there is no additional translation

for an atom at the origin → $F_{hkl} = f_j \exp(2\pi i \cdot 0) = f_j$

Ex. 2: I lattice → translations **a**, **b**, **c** and $(\mathbf{a} + \mathbf{b} + \mathbf{c}) / 2$

Two equivalent atoms are related by the additionnal translation, with coordinates:

0 0 0 and ½ ½ ½

→ $F_{hkl} = [f_j \exp(2\pi i \cdot 0)] + [f_j \exp 2\pi i (h/2 + k/2 + l/2)]$

→ $F_{hkl} = f_j [1 + \cos \pi(h + k + l)]$

h + k + l = 2n → $F_{hkl} = 2 f_j$

h + k + l = 2n + 1 → $F_{hkl} = 0$ → systematic absence

We use the well-known relation $\exp(i\varphi) = \cos(\varphi) + i \sin(\varphi)$ (de Moivre's formula)

3.5. – *Systematic absences*

Ex. 3. F lattice ➔ translations **a**, **b**, **c**, (**a** + **b**)/2, (**b** + **c**)/2 and (**c** + **a**)/2
➔ 4 equivalents atoms at
0 0 0 ; 1/2 1/2 0 ; 1/2 0 1/2 and 0 1/2 1/2.

$F_{hkl} = [f_j \exp(2\pi i . 0)] + [f_j \exp 2\pi i (h + k)/2] + [f_j \exp 2\pi i (k + l)/2] + [f_j \exp 2\pi i (l + h)/2]$

$F_{hkl} = f_j [1 + \cos \pi(h + k) + \cos \pi(k + l) + \cos \pi(l + h)]$

Two possibilities:
      h, k et l   all odd or even   ➔ $F_{hkl} = 4 f_j$
      h, k et l   mixed   ➔ $F_{hkl} = 0$

Exercice: for the cubic system, what are the diffracted beams with an intensity $\neq 0$

$h^2+k^2+l^2$	h k l	P	I	F	(yes or no)
1	100	yes	no	no	
2					

3.6. - *Lorentz-polarization Factor Lp*

Lorentz factor $\qquad$ $L = 1/(\sin^2\theta \cos\theta) = 2/(\sin\theta \sin2\theta)$

Polarization factor $\qquad$ $p = (1 + \cos^2 2\theta)/2$

Lp factor $\qquad$ $Lp(powder) = (1 + \cos^2 2\theta)/(\sin\theta \cdot \sin2\theta)$
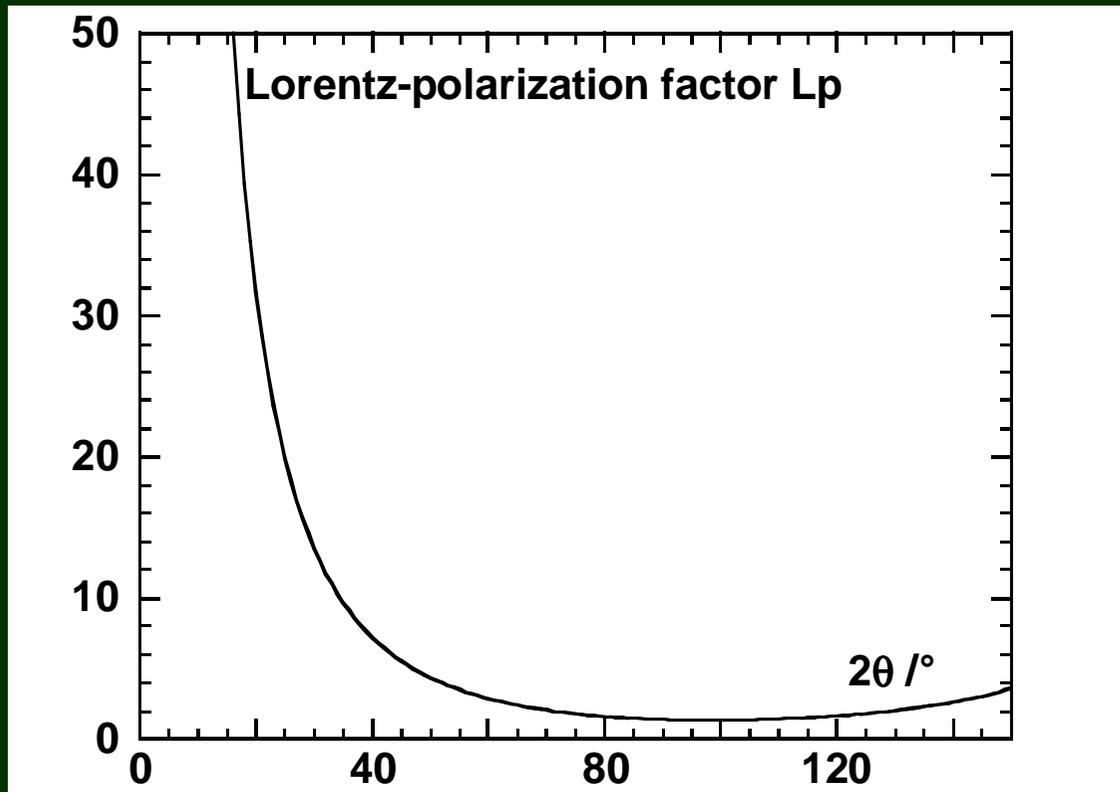
3.7. - Debye-Waller factor DW

Thermal vibrations of the atoms ➜ atomic scattering factors

$$f_j = f_{j0} \cdot \exp(- B_j . \sin^2\theta / \lambda^2)$$

f_{j0} for atom at rest

Average value

$$DW = \exp(- B . \sin^2\theta / \lambda^2) \qquad \text{(isotropic)}$$

$$B = 8\ \pi^2\mu^2$$

μ^2 mean square amplitude of vibration

Cubic system: $d_{hkl} = d_{klh} = d_{lhk} = \ldots$

Ex. what are the plane families with the same d-spacing, starting from (2 2 0)

        (2 2 0), (-2 2 0), (2 -2 0), (-2 -2 0),

        (2 0 2), (-2 0 2), (2 0 -2), (-2 0 -2),

        (0 2 2), (0 -2 2), (0 2 -2), (0 -2 -2)

➔ $M_{hhl} = 12$.

System	hkl	hhl	hh0	0kk	hhh	hk0	h0l	0kl	h00	0k0	00l
cubic	48	24	12	(12)	8	24	(24)	(24)	6	(6)	(6)
tetragonal	16	8	4	(8)	(8)	8	8	(8)	4	(4)	2
hexagonal	24	12	6	(12)	(12)	12	(12)	12	6	(6)	2
orthorhombic	8	(8)	(8)	(8)	(8)	4	(4)	(4)	2	(2)	(2)
monoclinic	4	(4)	(4)	(4)	(4)	(4)	(2)	(4)	2	(2)	(2)
triclinic	2	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)

3.9. – General relation

$$I = I_0 . N . M_{hkl} . |F_{hkl}|^2 \frac{R^2}{d^2} \left(\frac{1+\cos^2 2\theta}{\sin\theta\sin 2\theta} \right) . \exp\left(-B \frac{\sin^2\theta}{\lambda^2} \right)$$

I0 = intensity of the incident X-ray beam
N = cell number
Mhkl = multiplicity factor
R = classical radius of electron
d = distance from sample

$$\left(\frac{1+\cos^2 2\theta}{\sin\theta\sin 2\theta} \right)$$ Lorentz-polarization factor

$$\exp\left(-B \frac{\sin^2\theta}{\lambda^2} \right)$$ Debye-Waller factor

3.10. – Peak width – Scherrer's relation

$$L = 0.94\,\lambda\,/\,B(2\theta)\cos\theta$$

with L = average size of the crystallites (nm)
   $B(2\theta)$ = full width at half maximum (FWHM) (radian)
   θ = Bragg angle
   λ = wavelength (nm)