

DICP Course 2 - Dalian, 2012

POWDER X-RAY DIFFRACTION

Part II – X-Ray DIFFRACTION

Supported by the Chinese Academy of Sciences

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中国科学院
CHINESE ACADEMY OF SCIENCES



Outline of the course

I – CRISTALLOGRAPHY

II – X-RAY DIFFRACTION

→ 1. – INTRODUCTION

2. – INTERACTION BETWEEN X-RAYS AND MATTER

3. - DIFFRACTION BY A PERIODIC LATTICE

III – POWDER DIFFRACTOMETRY

1. INTRODUCTION

Objective of physical crystallography

→ interaction between crystals and radiations

Type of radiation?

- photons
- electrons
- neutrons

Radiation wavelength → same order of magnitude than interatomic distances ~ 0.1 nm

Two main processes:

- primary scattering process: general phenomenon for solid, liquid and gas
- secondary diffraction process: only for crystal, long distance order (> 1 nm)

Course will be limited to photons (X-rays radiation)

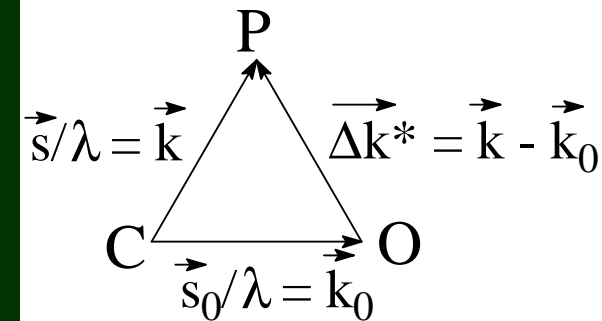
crystalline state = infinite lattice \otimes basis (asymmetric unit content)

\otimes = convolution product

Diffusion in the direction defined by vector $\Delta\mathbf{k}^*$

$$A(\Delta\vec{\mathbf{k}}^*) = \int \rho(\vec{\mathbf{r}}) \exp(2\pi i(\Delta\vec{\mathbf{k}}^* \cdot \vec{\mathbf{r}})) d\mathbf{v}$$

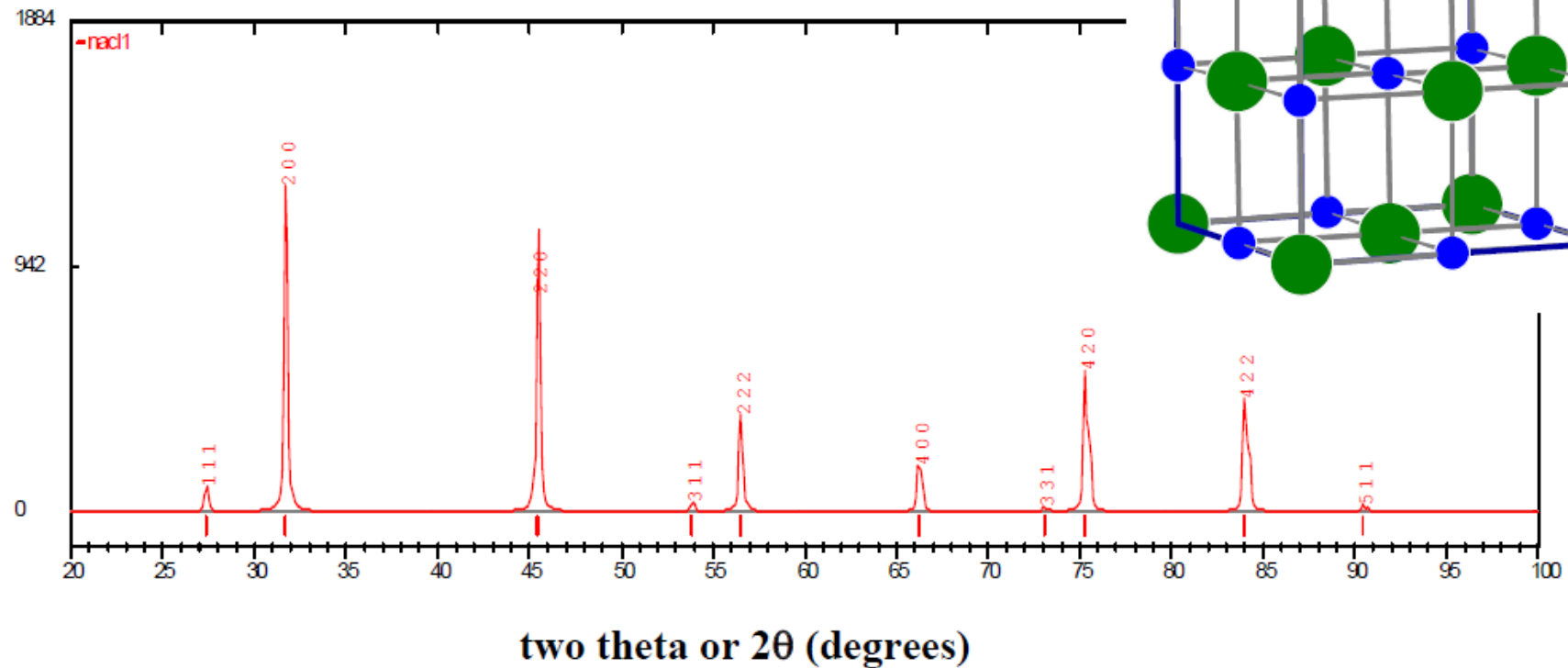
$A(\Delta\mathbf{k}^*)$ = amplitude of the scattered wave



1. INTRODUCTION

One example: NaCl

NaCl powder X-ray diffraction pattern



Position of the diffraction peaks \rightarrow Bragg's law

Intensity \rightarrow structure factor

Profile \rightarrow crystallite size, strain, stress

Outline of the course

1. – INTRODUCTION

2. – INTERACTION BETWEEN X-RAYS AND MATTER

2.1. - *Fundamental processes*

2.1.1. – Photoelectric effect

2.1.2. – Compton scattering

2.1.3. – Fluorescence

2.1.4. – Thomson scattering

2.2. - *Absorption of X-rays*

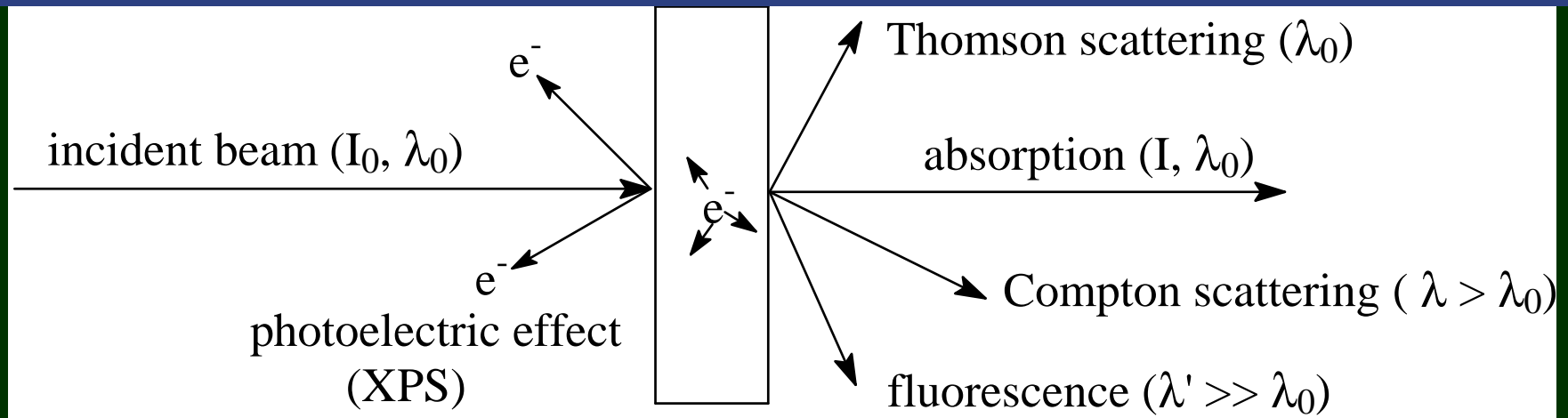
2.3. - *Thomson coherent scattering*

2.3.1. – Scattering by a single electron

2.3.2. – Scattering by an atom: atom scattering factor

2. - INTERACTION BETWEEN X-RAYS AND MATTER

2.1 – Four fundamental processes



– Photoelectric effect: core or valence electrons ejected from their levels \rightarrow low mean free path in matter (few nm); high mean free path in gas under very low pressure (high vacuum) \rightarrow XPS (X-ray Photoelectron Spectroscopy)

– Compton scattering: inelastic collision between photon and electron, loss of X-ray energy

– Fluorescence: linked to photoelectric effect, emission of secondary photons

– Thomson scattering: coherent scattering in all direction \rightarrow diffraction

Absorption spectroscopy \rightarrow EXAFS (Extended X-rays Absorption Fine Structure)

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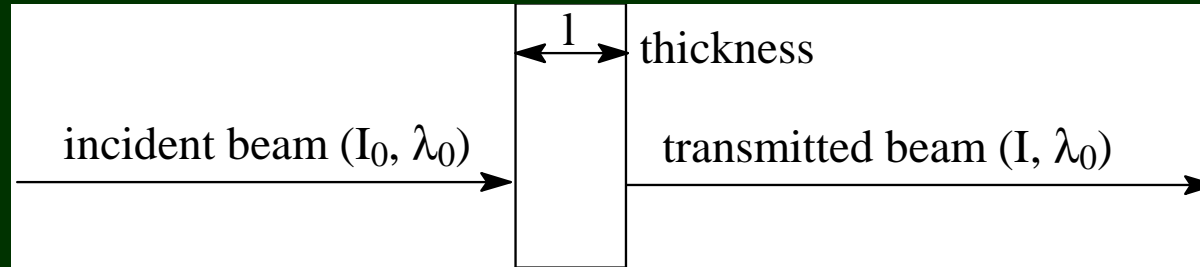
2.2. - *Absorption of X-rays*

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2.2 – Absorption of X-rays



Beer's law: $I = I_0 \exp -\mu l$

l = thickness (in cm)

μ = linear absorption coefficient (in cm^{-1})

depends on:

- wavelength λ_0
- composition and density of the sample: $\mu = (\mu/\rho) \cdot \rho$
- μ/ρ = mass absorption coefficient (in $\text{cm}^2 \text{g}^{-1}$) ρ = density (in g cm^{-3})

Remarks:

- for a powder, ρ is the apparent density to be determined from mass and volume
- for an element i , $(\mu/\rho)_i \rightarrow$ independant of physical state, depends only on wavelength λ_0
- for a sample with mass fraction g_i (elemental composition)

$$(\mu/\rho) = \sum g_i \cdot (\mu/\rho)_i$$

For elemental mass absorption coefficient $(\mu/\rho)_i \rightarrow$ see tables

2.2 – Absorption of X-rays

Ex. 1: determination of the mass absorption coefficient for CuO for $\lambda(\text{Mo K}_\alpha)$?

$$(\mu/\rho)_{\text{Cu}} = 50.9 \text{ cm}^2 \text{ g}^{-1} \quad (\mu/\rho)_i = 1.31 \text{ cm}^2 \text{ g}^{-1}$$

mass fraction of Cu and O?

$$g_{\text{Cu}} = 63.54 / (63.54 + 16.00) = 0.7988$$

$$g_{\text{O}} = 16.00 / (63.54 + 16.00) = 0.2012$$

$$(\mu/\rho) = (50.9 \times 0.7988) + (1.31 \times 0.2012) = \mathbf{40.92 \text{ cm}^2 \text{ g}^{-1}}$$

Ex. 2: determination of the I/I_0 ratio for a Pb leaf with a thickness 1 mm, $\lambda(\text{Mo K}_\alpha)$

For lead $\rightarrow (\mu/\rho)_{\text{Pb}} = 120 \text{ cm}^2 \text{ g}^{-1} \quad \rho = 11.35 \text{ g cm}^{-3}$

$$\mu = (\mu/\rho) \cdot \rho = 120 \times 11.35 = 1362 \text{ cm}^{-1}$$

$$\mu \cdot l = 1362 \times 0.01 = 13.62 \text{ (dimensionless)}$$

$$I/I_0 = \exp(-13.6) = 1.24 \times 10^{-6}$$

Ex. 3: Calculate the I/I_0 ratio for a beryllium window, $\lambda(\text{Cu K}_\alpha)$

For Be $\rightarrow (\mu/\rho)_{\text{Be}} = 1.50 \text{ cm}^2 \text{ g}^{-1} \quad \rho = 1.85 \text{ g cm}^{-3}$

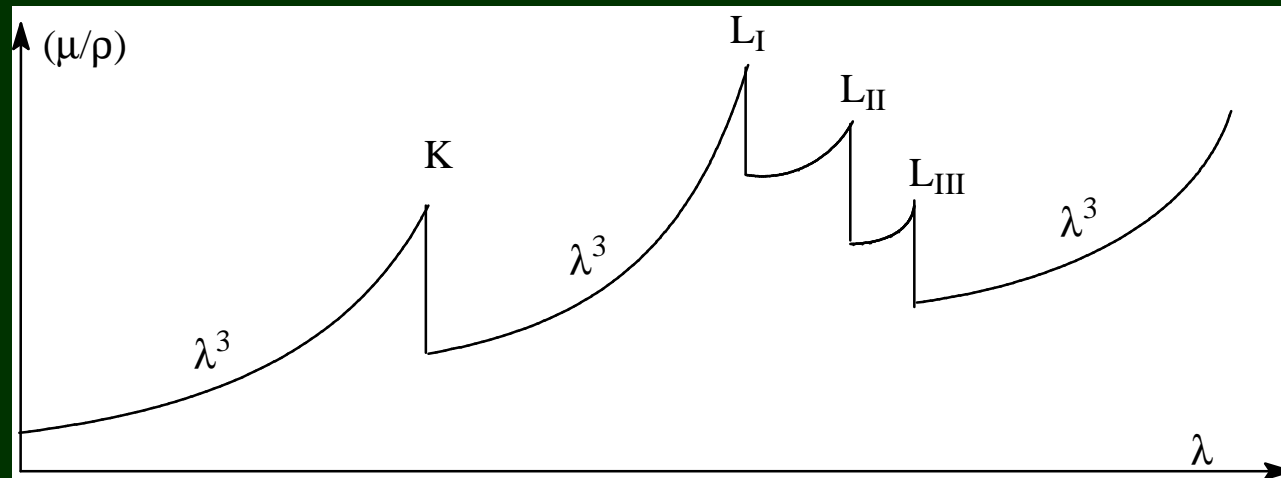
$$\mu = (\mu/\rho) \rho = 1.50 \times 1.85 = 2.775 \text{ cm}^{-1}$$

$$\mu \cdot l = 2.775 \times 0.1 = 0.2775$$

$$I/I_0 = \exp(-0.2775) = 0.758$$

2.2 – Absorption of X-rays

Variation of the mass absorption coefficient $(\mu/\rho)_i$ with the wavelength λ



→ absorption edges due to photoelectric effect

wavelength λ decreases → photon energy increases

when $h\nu = E_B$ (E_B = binding energy of electron in atom)

→ the corresponding electron is ejected

→ sharp increase of the mass absorption coefficient $(\mu/\rho)_i$

→ "absorption edge"

electron from K shell → K-edge

electron from L shell → L-edge

3 possible energy levels due to spin-orbit coupling

electron ejected from subshell 2s → $^2S_{1/2}$ absorption edge L_I

electron ejected from subshell 2p → $^2P_{1/2}$ $^2P_{3/2}$ absorption edges L_{II} and L_{III}

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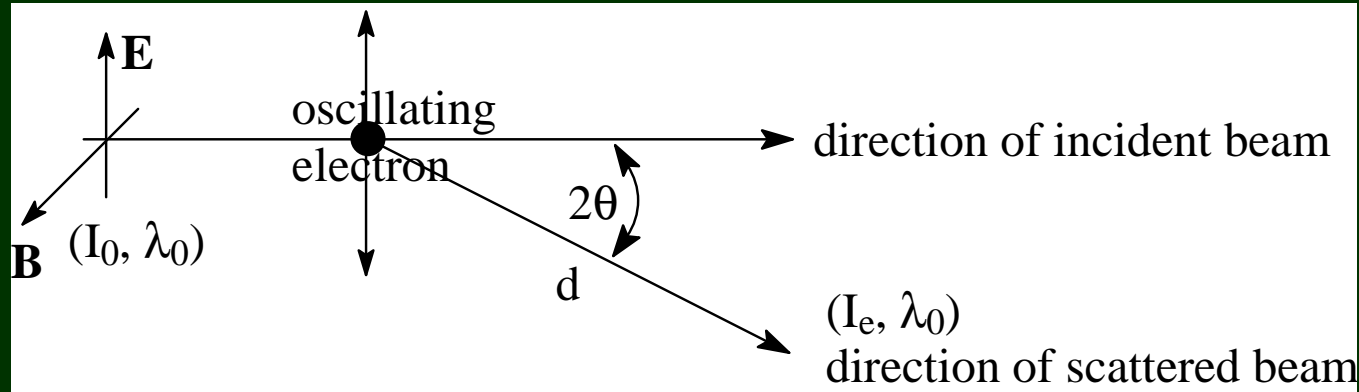
2.3.1. – Scattering by a single electron

2.3.2. – Scattering by an atom: atom scattering factor

2.3 – Thomson coherent scattering

2.3.1. – Scattering by a single electron

No modification of wavelength (elastic scattering) $\lambda_0 = c/\nu_0$



Electron \rightarrow point charge without volume

incident (primary) photons \rightarrow electron oscillates \rightarrow secondary photons in all directions

Assumption: planar waves

Intensity of the scattered beam : $I_e = I_0 f(2\theta, d)$

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

Polarization factor

$$R = \left(\frac{1}{4\pi\epsilon_0} \right) \left(\frac{e^2}{mc^2} \right)$$

R: classical radius of electron = 2.818×10^{-13} cm

e = charge of electron

m = mass of electron

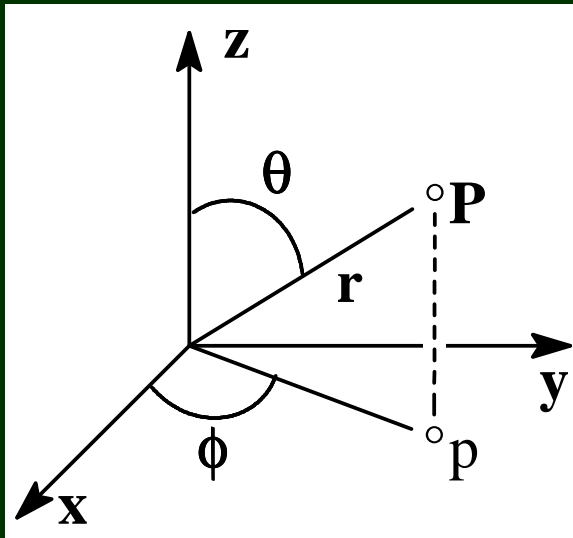
c = speed of light in vacuum

2.3 – Thomson coherent scattering

2.3.2. – Scattering by an atom: atom scattering factor

Neutral atom (atomic number Z):

- positive point charge Z^+ (nucleus) surrounded by an electronic cloud.
- the electronic cloud extends from the nucleus up to several Å
- local electron density $\rho(x,y,z)$
- cartesian coordinates \rightarrow polar coordinates $\rightarrow \rho(r, \theta, \varphi)$



For a neutral atom

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

integration performed 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 .

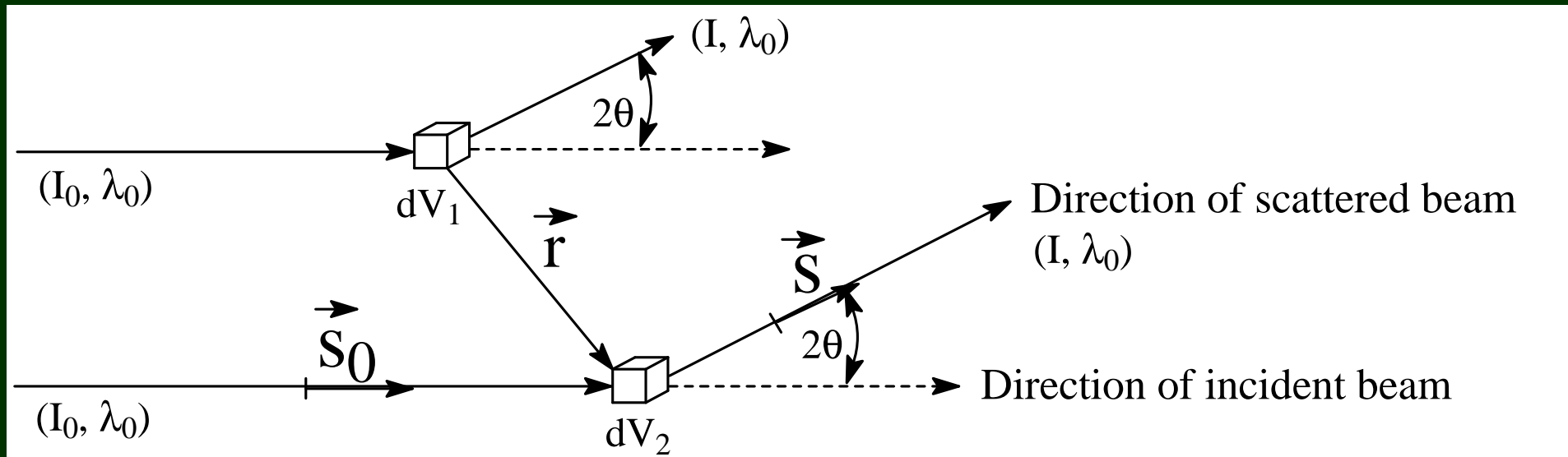
2.3 – Thomson coherent scattering

2.3.2. – Scattering by an atom: atom scattering factor

For two elemental volumes dV_1 and dV_2 with electronic density ρ_1 and ρ_2 , the scattered photons will interfere

Consider:

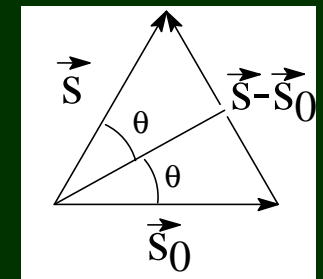
- the distance $r = |\mathbf{r}|$ between the two elemental volumes
- the unit vectors \mathbf{s}_0 and \mathbf{s} defining incident and scattered directions.



The path difference δ for the secondary photons emitted by dV_1 and dV_2 is:

$$\delta = (\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{r} \quad \text{with } |\mathbf{s} - \mathbf{s}_0| = 2 \sin \theta$$

$$\text{Or in term of wave vectors: } \delta/\lambda = (\mathbf{k} - \mathbf{k}_0) \cdot \mathbf{r} \quad \text{with } |\mathbf{k} - \mathbf{k}_0| = 2 \sin \theta / \lambda$$



Integration done over the whole volume occupied by the cloud \rightarrow for all \mathbf{r} values.

2.3 – Thomson coherent scattering

2.3.2. – Scattering by an atom: atom scattering factor

- use polar coordinates r , θ and φ , starting from the nucleus ($r = 0$).
- use spherical symmetry for electron density: ρ depends only on distance r from nucleus.

Scattered amplitude A depends on $\sin\theta/\lambda$ (interference term) and ρ (electron density)

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

The scattered intensity is the square of amplitude

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

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

From electron density function → function f for all atoms defined by atomic number Z

Function f : atom scattering factor → characterizes the scattering power of the atoms

Function $f =$ scattering power of atom / scattering power of electron

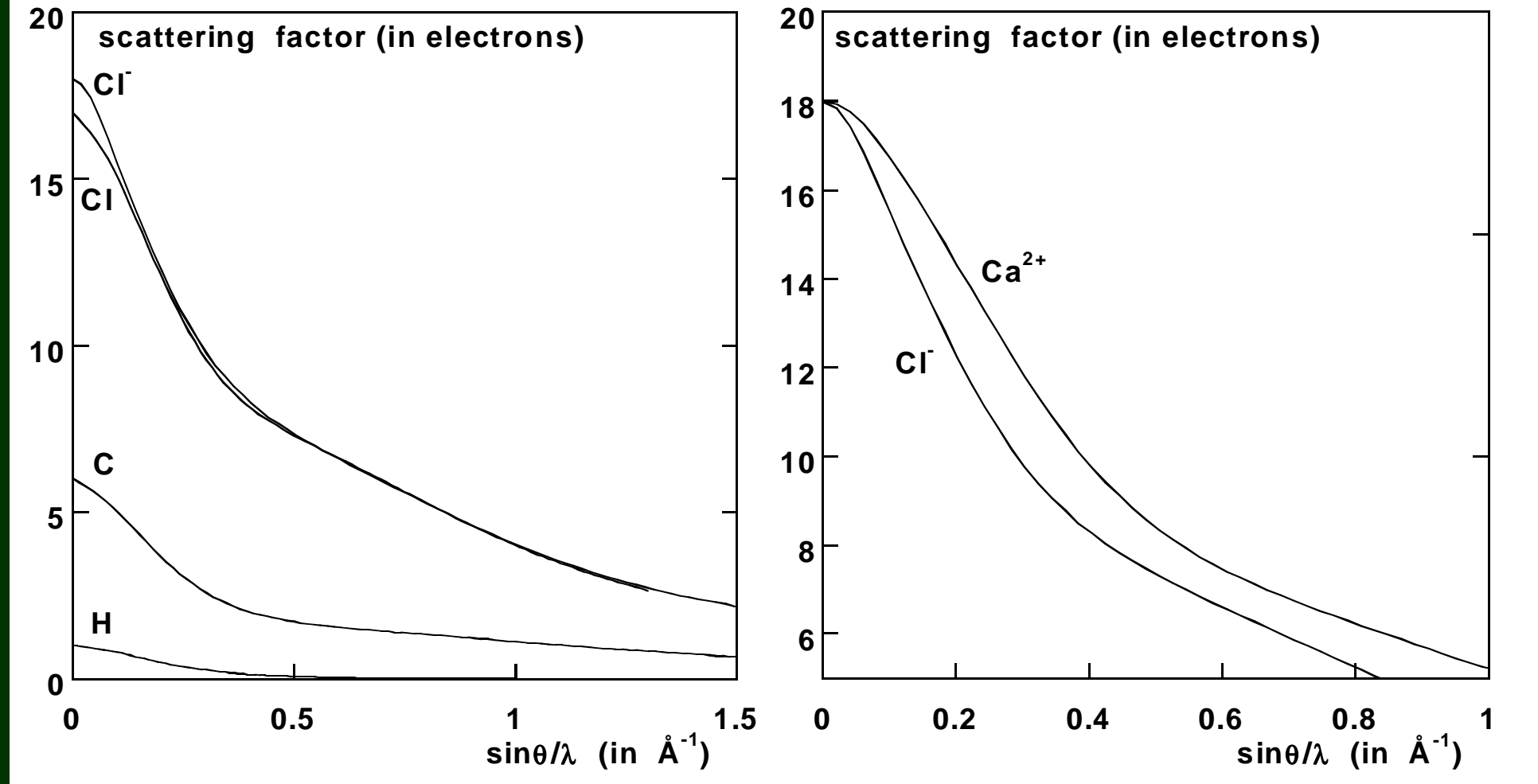
→ depends on atomic number Z and term $\sin\theta/\lambda$ → plot $y = f$ versus $\sin\theta/\lambda$

When $\theta = 0$ → all elemental volumes emit in phase

$f =$ number of electrons in electronic cloud → for a neutral atom $= Z$

2.3 – Thomson coherent scattering

2.3.2. – Scattering by an atom: atom scattering factor



- 1) Compare the function f for the elements H, C, Cl and Cl^-
Same element \rightarrow size increases \rightarrow electron density decreases \rightarrow factor f decreases too.
- 2) Compare the ions Cl^- and Ca^{2+}

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1. – INTRODUCTION

2. – INTERACTION BETWEEN X-RAYS AND MATTER

 **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 L_p

3.7. - Debye-Waller factor DW

3.8. - Multiplicity factor M_{hkl}

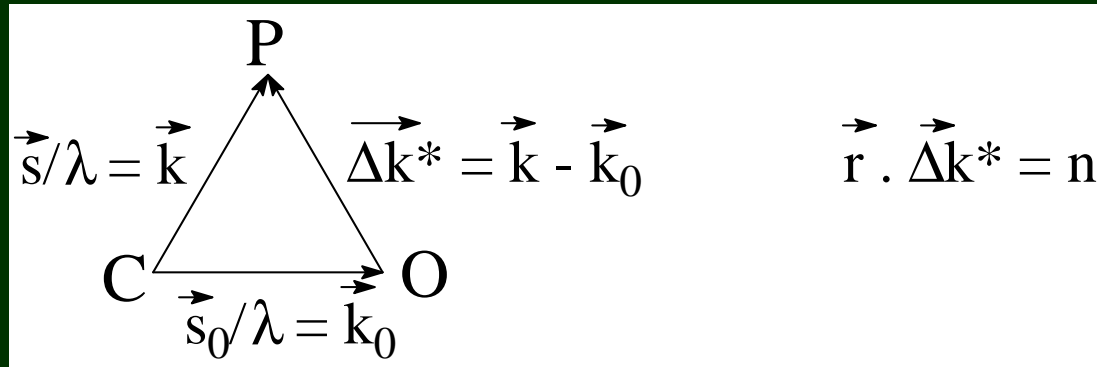
3.9. – General relation

3.10. – Peak width – Scherrer's relation

3.1. - Diffraction condition

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:



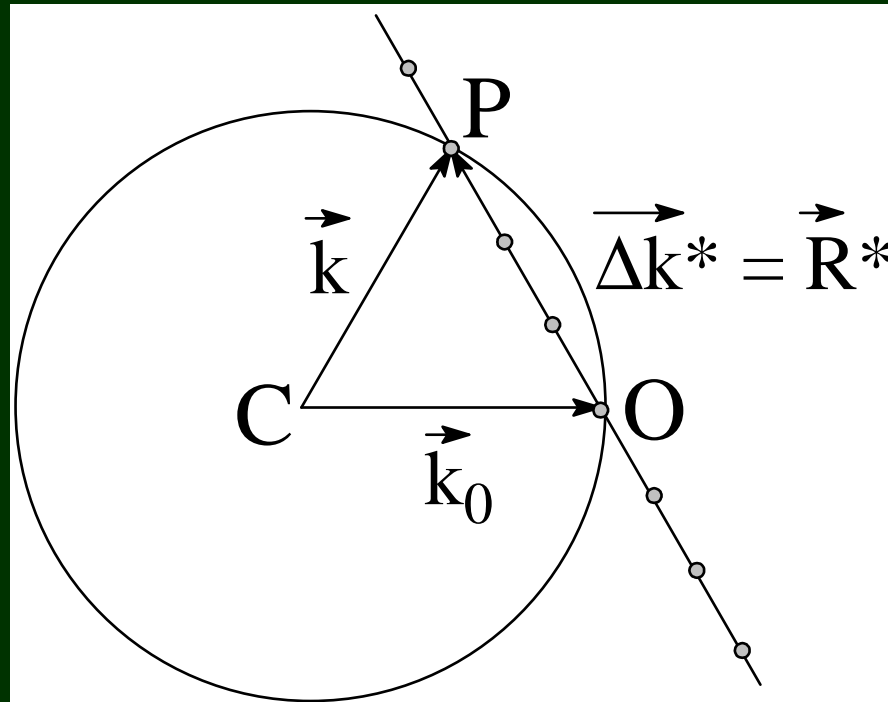
\vec{r} is a vector defined in the direct space (crystal space) $\rightarrow \vec{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$
 $\Delta\mathbf{k}^* = \mathbf{k} - \mathbf{k}_0$ is a vector defined in the reciprocal space $\rightarrow \Delta\mathbf{k}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$
 n is a relative integer.

Thus we can present these vectors in a geometrical way

The diffraction condition is: $\Delta\mathbf{k}^*$ is a vector of the reciprocal lattice
 \rightarrow if the end of vector \mathbf{k}_0 lies at the origin of the reciprocal lattice,
 \rightarrow the end of vector \mathbf{k} must be another point of this reciprocal lattice.

3.2. – Ewald's sphere

We place 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 \vec{k}_0 lies on the surface of the sphere

The end of vector \vec{k} lies at the surface of the sphere too

New formulation of the diffraction condition:

→ « the end of the reciprocal vector $\vec{\Delta k}^*$ must lie onto the sphere »

This sphere is called « Ewald's sphere »

3.2. – 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

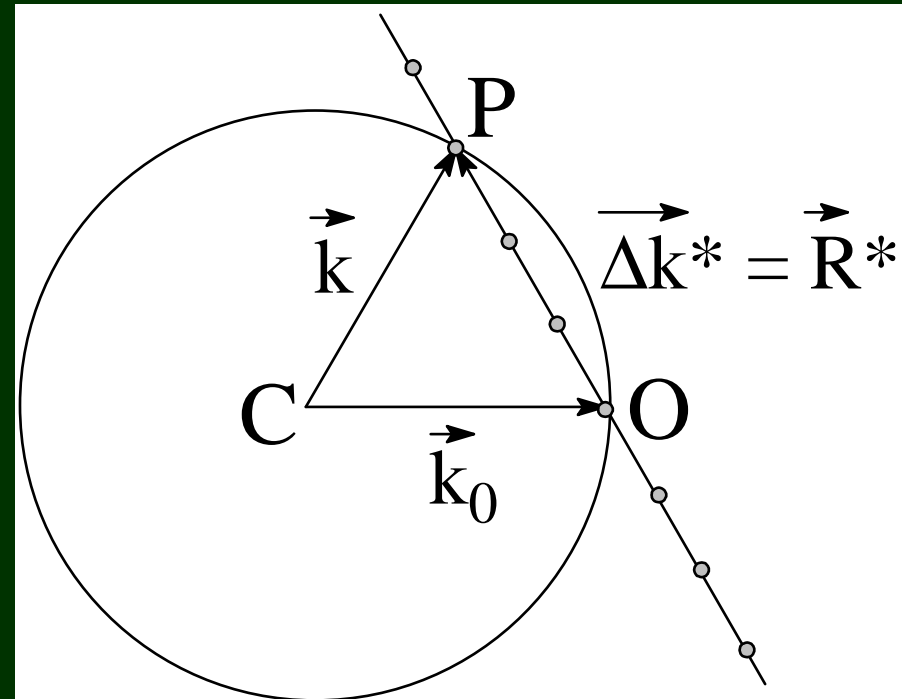
How can we brought the reciprocal points onto the surface of the sphere?

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



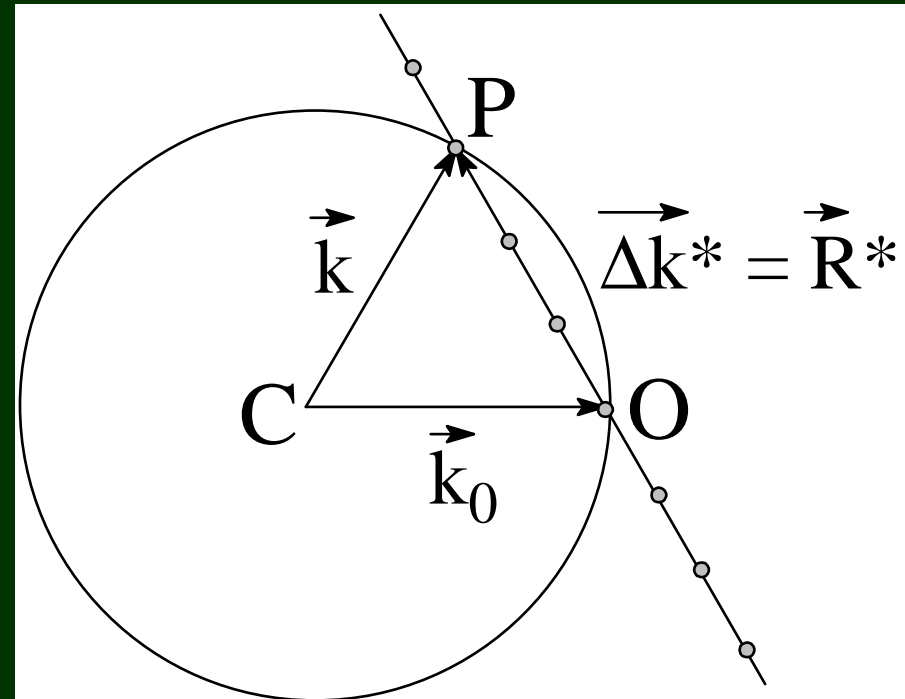
3.2. – Ewald's sphere

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

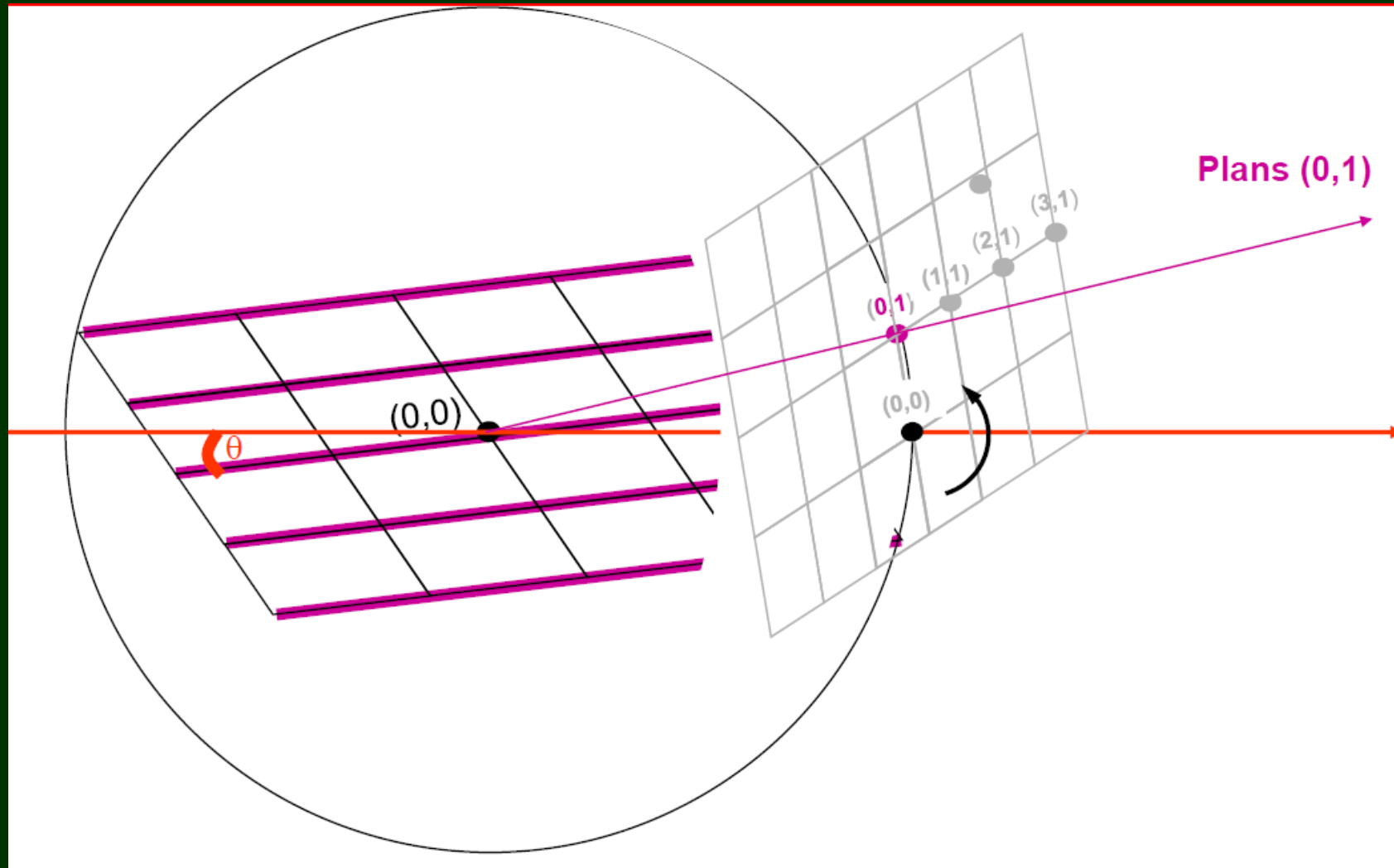
→ powder diffractometry (XRD)

You have to mill the powder in order to get a grain size about 10 to 5 μm



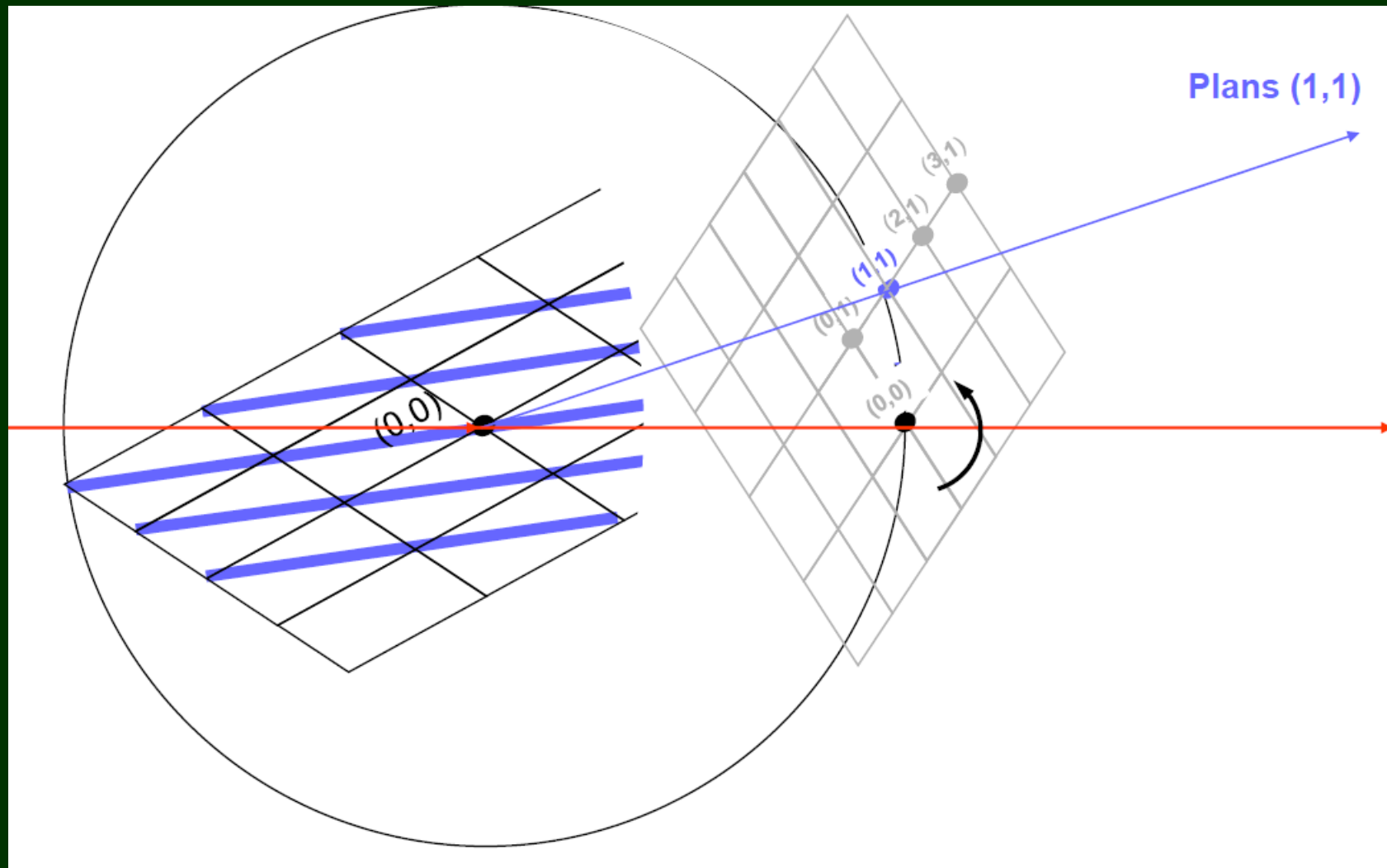
3.2. – Ewald's sphere

Example



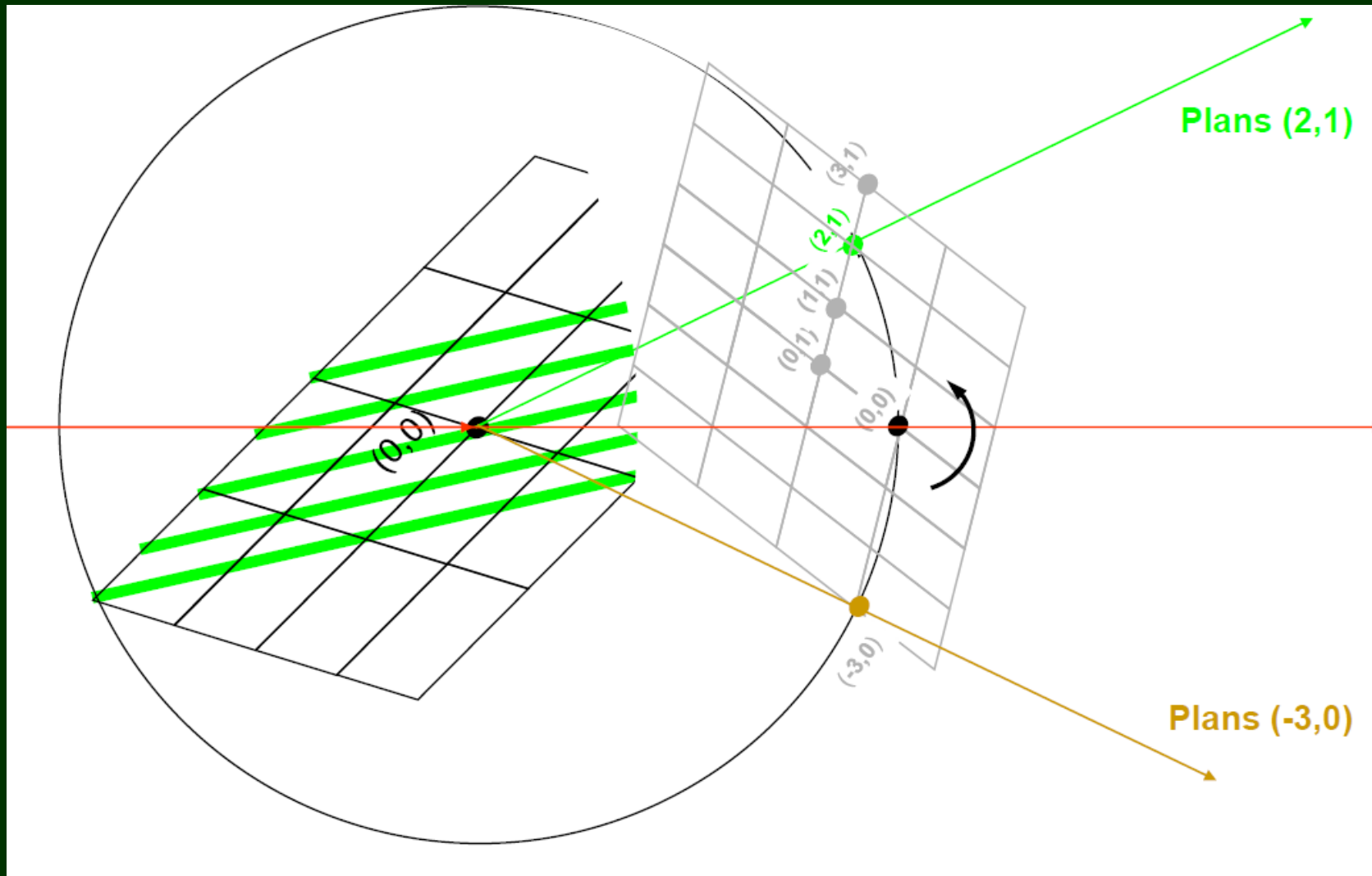
3.2. – Ewald's sphere

Example



3.2. – Ewald's sphere

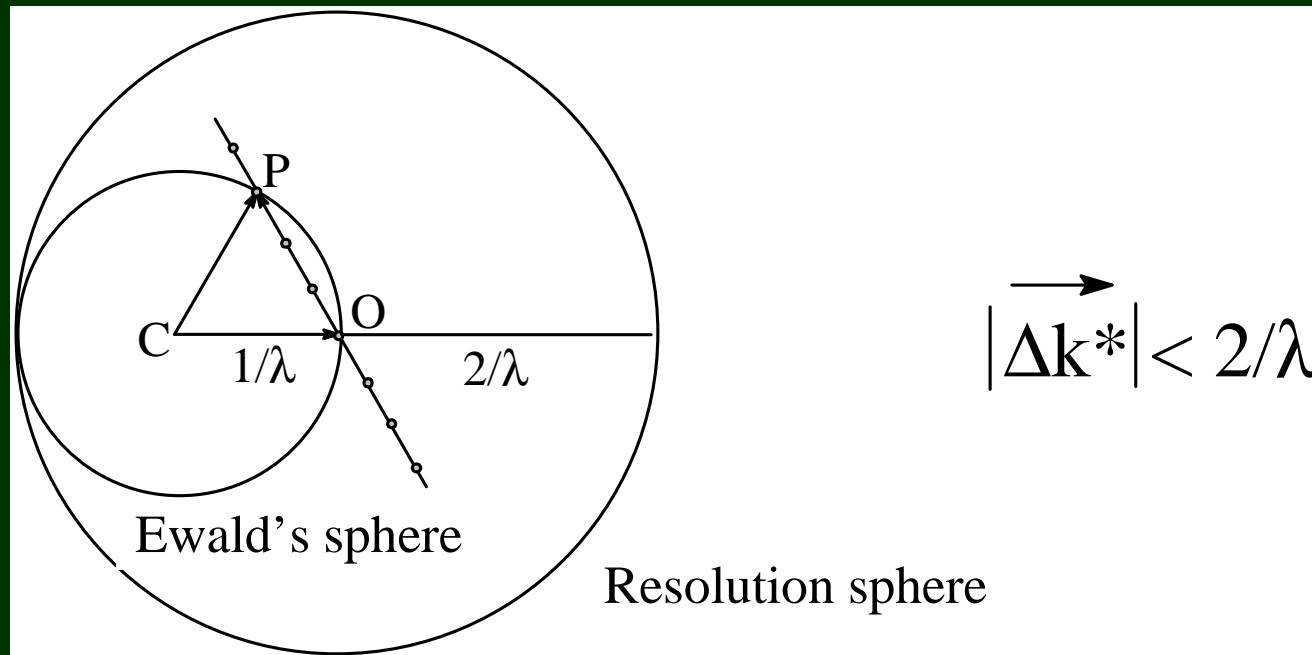
Example



3.2. – Ewald's sphere

Supplementary condition: **resolution sphere** with a radius of $2/\lambda$

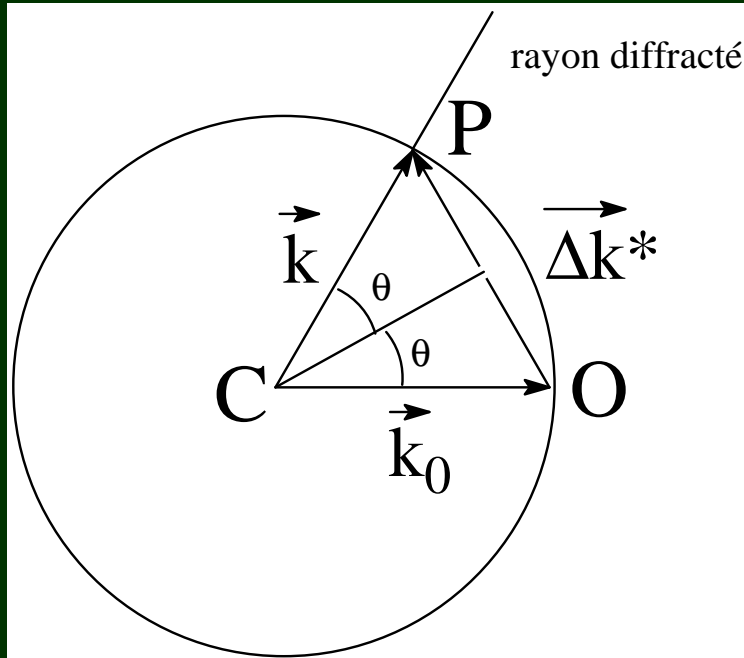
→ to cross the Ewald's sphere, the reciprocal point must be inside the resolution sphere



3.3. – Bragg's relation

The reciprocal vector $\mathbf{OP} = \Delta\mathbf{k}^*$ defines the line $[h\ k\ l]$

The parameter of this line $[h\ k\ l]$ is N_{hkl}^*



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

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

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

In the equilateral triangle COP, we have:

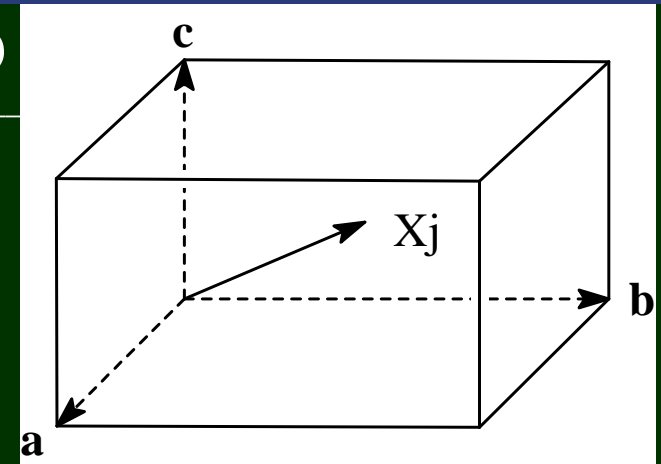
Then we obtain the relation for the diffraction by a family of planes (hkl)

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

3.4. - Structure Factor

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

$$\vec{OP}_j = x_j \vec{a} + y_j \vec{b} + z_j \vec{c}$$



Path difference between the beam from the origin and the beam from atom j, for the direction defined by the reciprocal vector $\Delta \mathbf{k}^*$

$$\delta_j = hx_j + ky_j + lz_j$$

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

$$\text{Structure factor: } F_{hkl} = \sum_j f_j \exp(i\alpha_j) = \sum_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)]$$

$$F_{hkl} \text{ is a complex number: } F_{hkl} = a + ib \quad F_{hkl}^* = a - ib$$

$$\text{Intensity: } I_{hkl} = K \cdot F_{hkl} \cdot F_{hkl}^* = K \cdot |F_{hkl}|^2$$

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

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 additional translation, with coordinates:

$$0 \ 0 \ 0 \quad \text{and} \quad \frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}$$

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

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

$$h + k + l = 2n \quad \rightarrow \quad F_{hkl} = 2 f_j$$

$$h + k + l = 2n + 1 \quad \rightarrow \quad F_{hkl} = 0 \quad \rightarrow \quad \text{systematic absence}$$

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**, $(\mathbf{a} + \mathbf{b})/2$, $(\mathbf{b} + \mathbf{c})/2$ and $(\mathbf{c} + \mathbf{a})/2$

→ 4 equivalent atoms at

$0\ 0\ 0$; $1/2\ 1/2\ 0$; $1/2\ 0\ 1/2$ and $0\ 1/2\ 1/2$.

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

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

Two possibilities:

h, k, l all odd or even → $F_{hkl} = 4 f_j$

h, k, l mixed → $F_{hkl} = 0$

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

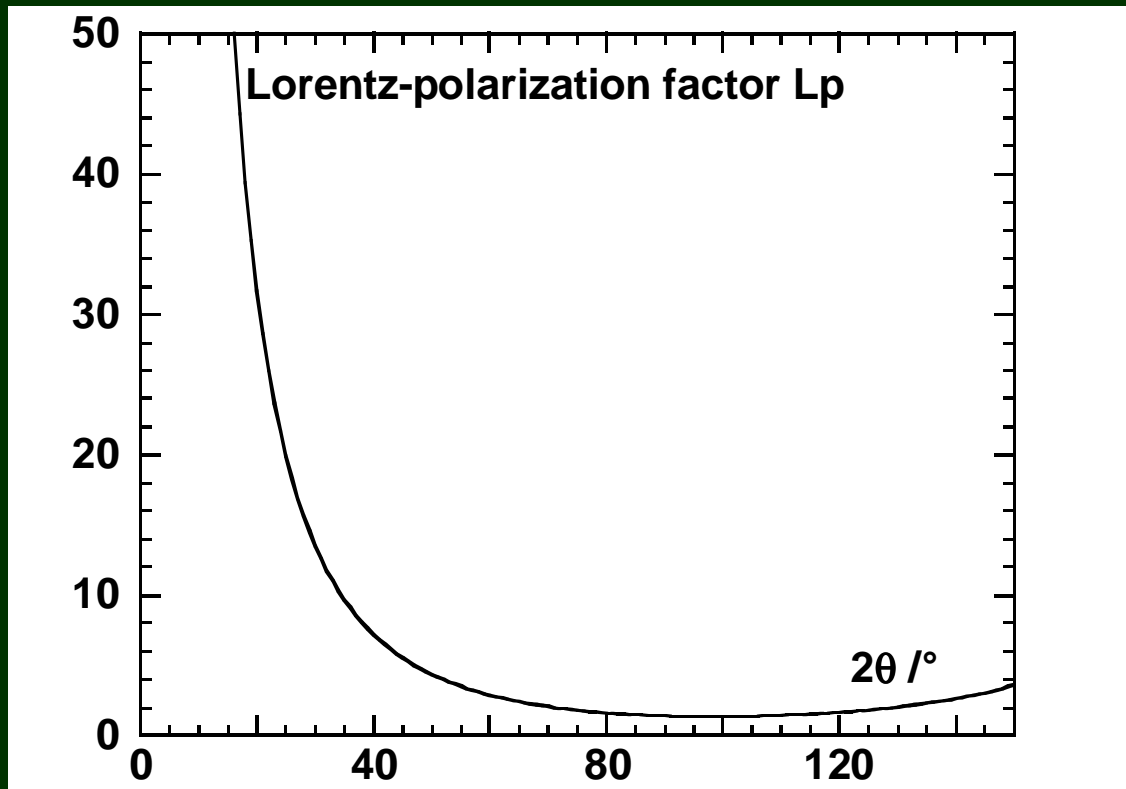
$h^2+k^2+l^2$	$h\ k\ l$	P	I	F	(yes or no)
1	100	yes	no	no	
2	110	yes	yes	no	
3	111	yes	no	yes	

3.6. - Lorentz-polarization Factor Lp

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

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

Lp factor $L_p(\text{powder}) = (1 + \cos^2 2\theta) / (\sin\theta \cdot \sin 2\theta)$



3.7. - Debye-Waller factor DW

Thermal vibrations of the atoms → atomic scattering factors

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

f_{j0} for atom at rest

Average value

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

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

μ^2 mean square amplitude of vibration

3.9. – General relation

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

I_0 = intensity of the incident X-ray beam

N = cell number

M_{hkl} = multiplicity factor

R = classical radius of electron

d = distance from sample

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

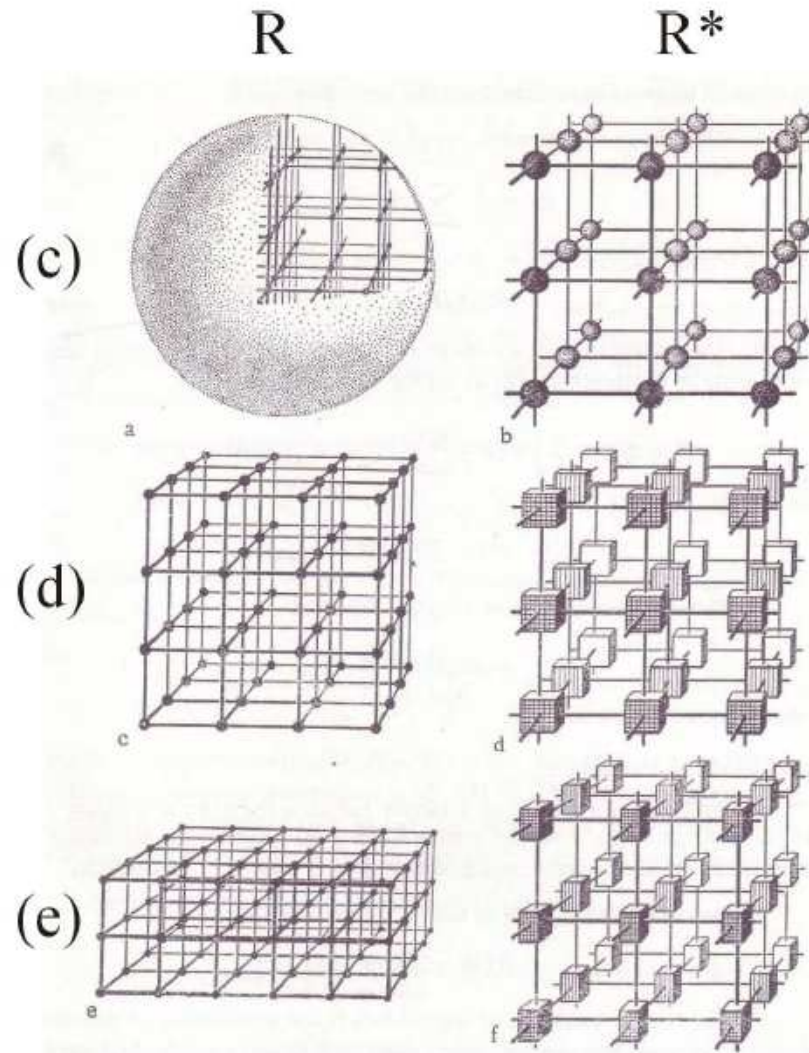
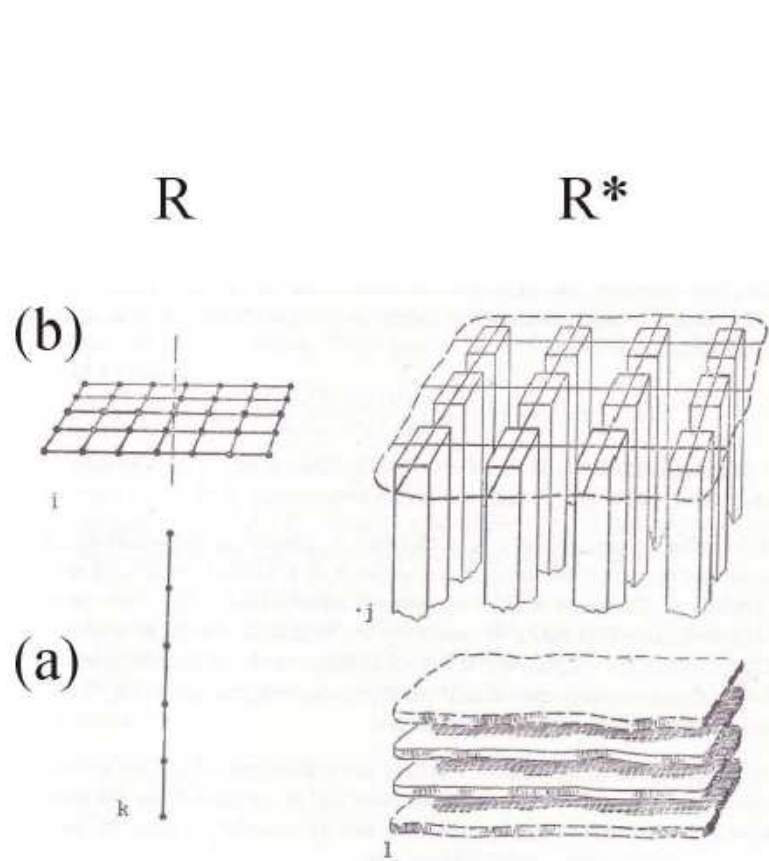
Lorentz-polarization factor

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

Debye-Waller factor

3.10. – Peak width – Scherrer's relation

A crystal has a limited size \rightarrow the points of the reciprocal space have volume



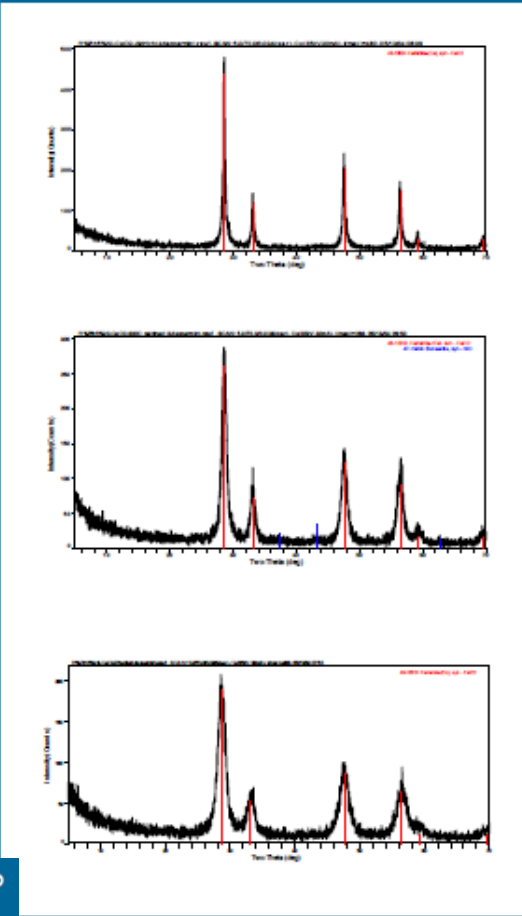
3.10. – Peak width – Scherrer's relation

A crystal has a limited size → the points of the reciprocal space have volume
→ the width of the diffraction peaks increases and the intensity decreases

Crystallite Size Measurement

Rh-Ni CeO₂ powders

Decreasing
crystallite
size



$$\tau = \frac{K \lambda}{\beta \cos \theta}$$

τ = particle size

K = shape factor

(typically 0.85-0.9)

λ = wavelength (Angstroms)

β = corrected FWHM (radians)

θ = $\frac{1}{2} 2\theta$ (peak position)

Good for particle sizes

< 500Å and no strain.

If strain, other Methods:

Warren / Averbach

Williamson-Hall plot

3.10. – Peak width – Scherrer's relation

→ determination of mean crystallite size → $L = 0.94 \lambda / \beta \cos\theta$

L = mean size of the crystallites (nm) λ = wavelength (nm)

θ = Bragg angle

$\beta(2\theta)$ = corrected Full Width at Half Maximum (FWHM) (radian)

