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

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 diffusion
      2.3.1. – Scattering by a single electron
      2.3.2. – Scattering by an atom: atom scattering factor
Outline of the course

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
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 $\rho(r, \theta, \phi)$

For a neutral atom

$$\iiint_{V} \rho(x, y, z) \, dx \, dy \, dz = \iiint_{V} \rho(r, \theta, \phi) \, 4\pi r^2 \sin \theta \, dr \, d\theta \, d\phi = Z$$

The integration is 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 $\rho$ works as a charged point for the primary photon. The charge is $\rho dV$. 
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 ρ1 and ρ2, 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 \( \delta \) for the secondary photons emitted by dV1 and dV2 is:

\[
\delta = (\mathbf{s} - \mathbf{s}_0).\mathbf{r}
\]

with \( |\mathbf{s} - \mathbf{s}_0| = 2 \sin \theta \)

Or in term of wave vector:

\[
\frac{\delta}{\lambda} = (\mathbf{k} - \mathbf{k}_0).\mathbf{r}
\]

with \( |\mathbf{k} - \mathbf{k}_0| = 2 (\sin \theta) / \lambda \)

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 $\rho$ for all elemental volumes

- use the polar coordinates $r$, $\theta$ and $\phi$, starting from the nucleus ($r = 0$).
- take a spherical symmetry for the electron density: $\rho$ depends only on the distance $r$ from the nucleus.

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

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

the intensity is the square of amplitude

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

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.

![Scattering factor plots](image-url)
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
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   3.9. – General relation
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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:

\[ \Delta k^* = k - k_0 \]

\[ \Delta k^* = n \]

\[ r \] is a vector defined in the direct space (crystal space) \( r = ua + vb + wc \)

\[ \Delta k^* = k - k_0 \] is a vector defined in the reciprocal space \( \Delta k^* = ha^* + kb^* + lc^* \)

\[ n \] is a relative integer.

Thus we can present these vectors in a geometrical way.

The diffraction condition is: \( \Delta k^* \) is a vector of the reciprocal lattice

\( \Rightarrow \) if the end of vector \( k_0 \) lies at the origin of the reciprocal lattice,

\( \Rightarrow \) the end of vector \( k \) must be another point of this reciprocal lattice.
3.2. – Ewald’s sphere

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 $k_0$ lies on the surface of the sphere
The end of vector $k$ lies at the surface of the sphere too

New formulation of the diffraction condition:

$\Delta k^* = R^*$

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

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

$\Rightarrow$ to cross the Ewald’s sphere, the reciprocal point must be inside the resolution sphere

$$|\Delta k^*| < \frac{2}{\lambda}$$

Diagram showing Ewald’s sphere and resolution sphere with point $P$ 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 \(N_{hkl}^*\)

\[
\Delta \mathbf{k}^* = \mathbf{OP}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*
\]

In the equilateral triangle COP, we have:

\[
N_{hkl}^* = 1 / d_{hkl} = |\mathbf{OP}^*|
\]

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

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

\[
2d_{hkl} \sin \theta = \lambda
\]
3.4. - Structure Factor

(ampitude of beam diffracted by atoms in the unit cell)

\[ F_{hkl} = \frac{\text{(amplitude of beam scattered by a single electron)}}{\text{Path difference between the beam from the origin and the beam from atom j, for the direction defined by the reciprocal vector } \Delta k^*} \]

\[ \delta_j = hx_j + ky_j + lz_j \]

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:

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

Intensity:

\[ I_{hkl} = K |F_{hkl}|^2 = K |F_{hkl}|^2 \]
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 \((a + b + c) / 2\)

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

\[
\begin{align*}
0 & 0 & 0 \\
0.5 & 0.5 & 0.5 
\end{align*}
\]

➔ \(F_{hkl} = [f_j \exp(2\pi i \cdot 0)] + [f_j \exp2\pi i (h/2 + k/2 + l/2)]\)

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

\[
\begin{align*}
h + k + l &= 2n & \Rightarrow & F_{hkl} = 2f_j \\
h + k + l &= 2n + 1 & \Rightarrow & F_{hkl} = 0 & \Rightarrow \text{systematic absence}
\end{align*}
\]

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.

$F_{hkl} = [f_j \exp(2\pi i \cdot 0)] + [f_j \exp2\pi i (h + k)/2] + [f_j \exp2\pi i (k + l)/2] +[f_j \exp2\pi i (l + h)/2]$

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

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 ≠ 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 $L_p$

Lorentz factor \[ L = \frac{1}{(\sin^2 \theta \cos \theta)} = \frac{2}{(\sin \theta \sin 2\theta)} \]

Polarization factor \[ p = \frac{(1 + \cos^2 2\theta)}{2} \]

$L_p$ factor \[ L_p(\text{powder}) = \frac{(1 + \cos^2 2\theta)}{(\sin \theta \cdot \sin 2\theta)} \]
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

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

\[ B = 8 \pi^2 \mu^2 \]

\( \mu^2 \) mean square amplitude of vibration
3.8. - Multiplicity factor $M_{hkl}$

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

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)

$\Rightarrow M_{hhl} = 12.$

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</table>
3.9. – General relation

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

- \( I_0 \) = intensity of the incident X-ray beam
- \( N \) = cell number
- \( M_{hkl} \) = multiplicity factor
- \( R \) = classical radius of electron
- \( d \) = distance from sample

\[ \frac{1 + \cos^2 2\theta}{\sin \theta \sin 2\theta} \]
Lorentz-polarization factor

\[ \exp \left( -B \frac{\sin^2 \theta}{\lambda^2} \right) \]
Debye-Waller factor
3.10. – Peak width – Scherrer’s relation

\[ L = \frac{0.94 \lambda}{B(2\theta) \cos \theta} \]

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