Diffraction from polycrystalline materials

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PART I
• From single-crystal to powder diffraction
• Intensity scattered from a powder sample

PART II
• Features and aberrations of the powder geometry
• Structure factor and intensity calculations
A vector drawn from the origin of the reciprocal lattice to the point $(hkl)$, where $h$, $k$, $l$ are the Miller indices (integer numbers) is given by:

$$
\mathbf{d}_{hkl}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*
$$

where $a^*$, $b^*$, $c^*$ are the reciprocal space vectors.

The vector modulus is the inverse of the interplanar distance for the planes with indices $(hkl)$:

$$
\mathbf{d}_{hkl}^* = \left| \mathbf{d}_{hkl}^* \right| = \frac{1}{d_{hkl}}
$$
Versors $s_0$ and $s$ identify, respectively the incident and scattered beam:

$$\left| \frac{s - s_0}{\lambda} \right| = \frac{2\sin\theta}{\lambda} = \frac{1}{d} = d^*$$

$d^*$ = scattering vector

The Bragg law in reciprocal lattice is:

$$\left| \frac{s - s_0}{\lambda} \right| = d_{hkl}^* = \frac{1}{d_{hkl}}$$
For a **perfect (infinite) crystal**

The **reciprocal lattice** is made of **(infinitely small)** points representing sets of planes of **Miller indices** $hkl$
For a perfect (infinite) crystal the peak width is determined by the instrumental resolution only:

\[
|s - s_0| = \frac{2 \sin \theta}{\lambda} = \frac{1}{d_{hkl}} = d^*_{hkl}
\]
For a finite crystal \( (L<1\mu m) \) Reciprocal lattice points have finite extension. The shape is related to the crystal shape.
Integral breadth: \( \beta (d^*) = \frac{\text{Peak Area}}{\text{Peak Maximum}} = \frac{1}{L} \) (Scherrer formula)

Effect of instrument, domains with different shape/size
For a given wavelength, the Bragg law sets a limit to the interplanar distances for which diffraction is observed:

\[ \sin \theta = \frac{\lambda}{2d} \leq 1 \]

\[ d^* \leq \frac{2}{\lambda} \]

All points representing planes that can diffract are inside a sphere of finite radius, \(2/\lambda\) (limiting sphere).
Diffraction conditions occur when the tip of the scattering vector $d^*$ falls on a point of the reciprocal space.

The condition is fulfilled by all points on the **Ewald sphere**, a sphere of radius $1/\lambda$, tangent to the origin and to the $2/\lambda$ sphere.

In a powder diffraction measurement, the Ewald sphere can be thought as rotating inside the $2/\lambda$ sphere.
As a consequence, the tip of the scattering vector ‘sweeps’ the surface of a sphere of radius $d^*$

During a powder diffraction measurement, the sphere of radius $d^*$ swells (for increasing $2\theta$) and sweeps the reciprocal space within the limits:

$$0 \leq d^* \leq \frac{2}{\lambda}$$

$$(0 \leq 2\theta \leq 180^\circ)$$
Diffraction takes places whenever the scattering vector crosses a reciprocal space point (hkl):

\[
\frac{s - s_0}{\lambda} = d^*_{hkl}
\]

In a powder diffraction measurement, the sphere of radius \(d^*\) progressively 'swells' (increasing 2\(\theta\)) and sweeps the reciprocal space within the limiting sphere:

All reciprocal space points on the PD sphere are in diffraction condition (\(\rightarrow\) multiplicity).
In a powder (polycrystalline material) measurement, several points can be in diffraction condition \textit{simultaneously}, i.e., for the same \(2\theta\).

This property is expressed by the concept of \textit{multiplicity} of a diffraction peak, i.e., the number of equivalent planes.

In cubic structures:

<table>
<thead>
<tr>
<th>Miller indices</th>
<th>hkl</th>
<th>hhk</th>
<th>0kl</th>
<th>0kk</th>
<th>hhh</th>
<th>001</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{Multiplicity}</td>
<td>48</td>
<td>24</td>
<td>24</td>
<td>12</td>
<td>8</td>
<td>6</td>
</tr>
</tbody>
</table>

\[ s_0/\lambda \]

\[ s/\lambda \]

\[ 2/\lambda \]

\[ d' \]

\[ \text{Ewald sphere} \]
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The concept of 'Powder'

An ideal powder is a polycrystalline sample (a true powder or a bulk specimen) such that for every possible orientation a sufficiently high number of grains (→ grain statistics) has atomic planes in Bragg condition (random orientation).

If preferred orientations (texture) are present, suitable models are necessary to account for the 'non-ideal' conditions.
Integrated intensity
Intrinsic features of the sample, instrument and measurement geometry cause a dispersion of the scattered intensity across a finite angular range (a peak). The range (width) changes with $2\theta$. The diffracted signal is better represented by the area of the diffraction peak (integrated intensity) than by maximum intensity.
The integrated intensity of a powder diffraction peak is given by:

\[ I(2\theta) = k' |F_T|^2 \beta \left( \frac{1 + \cos^2(2\theta)}{\sin(\theta) \sin(2\theta)} \right) \]

- **Structure factor**
- **Lorentz-Polarization factor**
- **Molteplicity**
A diffraction measurement basically consists in a cross section through one or more reciprocal space (RS) points.

The measured intensity depends on:

a) The way RS points are crossed;
b) The sampling in RS (considering measurements are in 2θ space);
c) The fraction of diffracted signal collected by the detector.

\[
L = Na
\]

\[
\sin^2 \left( \frac{\pi Nh}{(\pi h)^2} \right)
\]
Points a), b), c) give the so-called Lorentz factor, which depends on the diffraction geometry. As for the way an hkl point in RS is "crossed" during a measurement, the effect is:

\[ \propto \frac{1}{\sin(2\theta)} \]

The fraction of crystalline domains whose planes are in diffraction condition changes with the \( 2\theta \) angle. This fraction is proportional to the ratio between a stripe of width \( r\Delta\theta \) and the total surface of the sphere.

This feature gives a term \( \propto \cos(\theta) \)
Finally, as shown in the figure below, during a traditional powder diffraction measurement, the X-ray detector spans just a portion (h) of the base circle of the diffraction cone.

This gives a further trigonometric term, proportional to the integrated intensity: \[ \propto \frac{1}{\sin(2\theta)} \]
Putting together the trigonometric terms described so far, we obtain the Lorentz Factor for the powder geometry:

$$LF = \frac{1}{\sin 2\theta} \cdot \cos \theta \cdot \frac{1}{\sin 2\theta} = \frac{\cos \theta}{\sin^2 2\theta}$$
An additional trigonometric term is in the Polarization Factor:

\[ PF = \frac{1 + \cos^2(2\theta)}{2} \]
The Lorentz and Polarization factors can be combined in a single trigonometric term: the Lorentz-Polarization factor:

\[ LF = \frac{\cos \theta}{\sin^2 2\theta} \]

\[ PF = \left[ 1 + \cos^2 (2\theta) \right] / 2 \]

\[ LP = \frac{1 + \cos^2 (2\theta)}{\sin \theta \sin (2\theta)} \]
One of the main advantages of the traditional powder diffraction geometry (Bragg-Brentano) is that it does not require $\theta$-dependent correction terms for the absorption of the X-rays.

Consider a beam with cross section $A_0$ and intensity $I_0$ impinging with an angle $\theta_1$. A small volume $dV$, with thickness $dx$ and surface $A_0 / \sin(\theta_1)$ diffracts at the angle $\theta_2$.

\[
dI = I_0 e^{-\mu x (1/\sin \theta_1 + 1/\sin \theta_2)} dV = \frac{I_0 A_0}{\sin \theta_1} e^{-\mu x (1/\sin \theta_1 + 1/\sin \theta_2)} dx
\]
\[ dI = I_0 e^{-\mu x (1/\sin \theta_1 + 1/\sin \theta_2)} dV = \frac{I_0 A_0}{\sin \theta_1} e^{-\mu x (1/\sin \theta_1 + 1/\sin \theta_2)} dx \]

In the traditional powder geometry: \( \theta_1 = \theta_2 = \theta \)

By integrating on the sample thickness:

\[ I = \frac{I_0 A_0}{\sin \theta} \int_0^\infty e^{-2\mu x/\sin \theta} dx = \frac{I_0 A_0}{2\mu} \]

Independent of \( \theta \)
If terms for absorption ($\mu$), cell volume ($v_a$), goniometer radius ($r$) and wavelength ($\lambda$) are written explicitly, $k' = k\frac{\lambda^3}{\mu rv_a}$

\[
I(2\theta) = k\frac{\lambda^3}{\mu rv_a} |F_T|^2 p \left( \frac{1 + \cos^2(2\theta)}{\sin(\theta)\sin(2\theta)} \right)
\]

- **Structure factor**
- **Lorentz-Polarization factor**
- **Molteplicity**
If the secondary circle of a crystal monochromator (analyzer) is present at $\theta_m$, the polarization factor must be written as:

$$I(2\theta) = k' \left| F_T \right|^2 \frac{\lambda^3 p}{\mu r v_a^2} \left( 1 + \cos^2(2\theta_m) \cos^2(2\theta) \right) \frac{1}{\sin(\theta) \sin(2\theta)}$$
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The instrumental profile results from a convolution of several effects:

\[ g = g_I \otimes g_{II} \otimes g_{III} \otimes g_{IV} \otimes \ldots \]

The main contributions are those due to:

- Emission profile
- Flat sample
- Axial Divergence
- Sample transparency
- Receiving slit

............

**DIFFRACTION PROFILE IN THE POWDER GEOMETRY**

\[ g = g_I \otimes g_{II} \otimes g_{III} \otimes g_{IV} \otimes \ldots \]
Emission profile: the $K\alpha_1/K\alpha_2$ doublet.

Cu $K\alpha$ emission profile as modelled by four Lorentzians.
Line width ($\Gamma$), asymmetry ($\kappa$) and emission energy ($E$) for the $K\alpha$ components of Cu, Cr, Fe, Co. Note that two average $K\alpha$ components are most frequently used instead of the four in the previous figure.

<table>
<thead>
<tr>
<th></th>
<th>$K\alpha_1$</th>
<th></th>
<th>$K\alpha_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E$ (keV)</td>
<td>$\Gamma$ (eV)</td>
<td>$\kappa$</td>
</tr>
<tr>
<td>Cu</td>
<td>8.048</td>
<td>2.56</td>
<td>1.12</td>
</tr>
<tr>
<td>Cr</td>
<td>5.415</td>
<td>2.16</td>
<td>1.38</td>
</tr>
<tr>
<td>Fe</td>
<td>6.404</td>
<td>2.35</td>
<td>1.43</td>
</tr>
<tr>
<td>Co</td>
<td>6.930</td>
<td>2.87</td>
<td>1.32</td>
</tr>
</tbody>
</table>
Cu Kα emission spectrum with two components (a). FWHM of the emission spectrum (Kα₁ component) as a function of the diffraction angle, 2θ) (b).

\[
\lambda = \frac{c}{\nu} = \frac{ch}{E} = \frac{12398}{E}
\]

\[
\left| \frac{d \lambda}{\lambda} \right| = \left| \frac{dE}{E} \right| = \frac{2d \cos \theta \cdot d\theta}{2d \sin \theta} = \frac{d(2\theta)}{2\tan \theta} \implies d(2\theta) = 2\left| \frac{dE}{E} \right| \tan \theta
\]
In addition to peak position, maximum and integrated intensity, a useful quantity is the integral breadth ($\beta$), defined as the ratio between peak area and maximum intensity.

Relation between integral breadth in reciprocal space and $2\theta$ space

$$\beta (2\theta) = \beta (d^*) \cdot \frac{\lambda}{\cos \theta}$$
Nowadays, the most popular data processing programs make use of analytical profile fitting. The basic algorithm (even though not the only one, probably not always the best) adopts a non-linear least squares (NLLS) minimization engine.

The quantity to minimize is:

$$S_y^2 = \sum w_i^2 \left[ y_{i,o} - y_{i,c} \right]^2$$

where $y_{i,o}$ and $y_{i,c}$ are respectively the observed and calculated intensities, whereas the weight is $w_i = 1/\sqrt{y_{i,o}}$.

Calculated (model) intensities, $y_{i,c}$, are typically described by bell-shaped analytical curves, like:

- Gaussian
- Lorentzian
- pseudo-Voigt
- Voigt or Person VII functions.
**ANALYTICAL PROFILE FITTING**

Analitycal profile functions commonly used in peak profile fitting:

\[ x = 2\Theta - 2\Theta_0 \text{ or } d^* - d^*_{hkl} \]

\[
G(x, \beta_G) = I_o \cdot \exp \left( -\frac{\pi x^2}{\beta_G^2} \right) \quad \quad C(x, \beta_C) = \frac{I_o}{1 + \frac{\pi^2 x^2}{\beta_C^2}}
\]

\[
pV(x) = I_o \left[ (1-\eta) \cdot G(x, \beta_G) + \eta \cdot C(x, \beta_C) \right] = \]

\[
= I_o \left[ (1-\eta) \cdot \exp \left( -\frac{\pi x^2}{\beta_G^2} \right) + \eta \cdot \frac{1}{1 + \frac{\pi^2 x^2}{\beta_C^2}} \right]
\]
Useful properties of the \( pV \) function are, e.g., that the IB is simply given by:

\[
\beta_{pV} = (1 - \eta) \beta_G + \eta \beta_C
\]

if \( G \) and \( C \) components of the \( pV \) have the same width (HWHM). It is also possible to use ‘Split \( pV \)’, with right (R) and left (L) HWHMs:

\[
pV(x) = I_o \cdot \left[ (1 - \eta) \cdot \exp\left(-\ln(2) \frac{x^2}{\omega_{L,R}^2}\right) + \eta \cdot \frac{1}{1 + \frac{x^2}{\omega_{L,R}^2}} \right]
\]
Fit quality is typically expressed by suitable statistical quality indices:

\[ S_y^2 = \sum_i w_i^2 \left[ y_{i,o} - y_{i,c} \right]^2 \]

\[ R_{wp} = \left\{ S_y^2 / \sum_i w_i y_{i,o}^2 \right\}^{1/2} \]

\[ R_{exp} = \left[ (N - P) / \sum_i w_i y_{i,o}^2 \right]^{1/2} \]

\[ GoF = R_{wp} / R_{exp} \]

where \( N \) is the number of data points, \( P \) is the number of fit parameters.
The observed profile \( h \) is a convolution of the instrumental profile \( g \) with the ‘true’ diffraction profile due to microstructure and lattice defects of the studied sample \( f \)

\[
h(\eta) = f(\eta - \epsilon) \otimes g(\epsilon)
\]

**f** profile \( \rightarrow \) small crystalline domain size, dislocations, faulting, etc.
In many cases f, g, h profiles can be described by Voigtian functions. When using pseudoVoigt functions (x = 2Θ − 2Θ₀ or d* − d*_{hkl}): 

\[ pV(x) = I_o \left[ (1-\eta) \cdot \exp\left( -\frac{\pi x^2}{\beta^2} \right) + \eta \cdot \frac{1}{1 + \frac{\pi^2 x^2}{\beta^2}} \right] \]

For the g (instrumental) profile, mixing parameter (η) and width (β) can be parameterized as:

\[ FWHM = \left( U \tan^2 \theta + V \tan \theta + W \right)^{1/2} \]

\[ \eta = a + b \cdot \theta + c \theta^2 \]
NIST SRM 1976 alumina
XRD-1 beamline
(LNLS, Campinas, Brazil)
$FWHM = \left( U \tan^2 \theta + V \tan \theta + W \right)^{1/2}$

$\eta = a + b \cdot \theta + c \cdot \theta^2$
If both $f$ and $g$ profile components are assumed to be Voigtian, the $h$ profile is also Voigtian and is given by:

$$\beta_{hC} = \beta_{gC} + \beta_{fC}$$
$$\beta_{hG} = \sqrt{\beta_{gG}^2 + \beta_{fG}^2}$$

If $g$ is known, fitting the experimental $h$ profile allows one to obtain the $f$ profile:

$$\beta_f = (1-\eta) \beta_{fG} + \eta \beta_{fC}$$

The integral breadth of the 'true' profile ($f$) can be used, e.g., with the Scherrer formula:

$$L = \frac{Na}{\beta_f}$$

$$\beta_f \propto \frac{\lambda}{L \cdot \cos \theta}$$
ABERRATIONS OF THE POWDER GEOMETRY

\[ g = g_I \otimes g_{II} \otimes g_{III} \otimes g_{IV} \otimes \ldots \]
Analytical expressions of peak position aberrations.

<table>
<thead>
<tr>
<th>Centroid aberration</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample displacement</td>
<td>$-2d \cos \theta \frac{R}{R}$</td>
</tr>
<tr>
<td>Flat specimen</td>
<td>$-\frac{1}{6} \alpha^2 \cot \theta$</td>
</tr>
<tr>
<td>Sample transparency</td>
<td>$-\frac{\sin(\theta)}{2\mu R}$</td>
</tr>
<tr>
<td>Axial Divergence</td>
<td>$-\frac{1}{6} \delta^2 \cot(\theta)$</td>
</tr>
<tr>
<td>Refraction</td>
<td>$2(1-r)\tan \theta$</td>
</tr>
<tr>
<td>Polarization</td>
<td>$\frac{2W \tan \theta}{d^2}$</td>
</tr>
<tr>
<td>Lorentz Factor and Dispersion</td>
<td>$\frac{3W \tan^3 \theta}{\lambda^2}$</td>
</tr>
</tbody>
</table>

As an estimate of $W$, Wilson suggests to use $1/3$ of the square of the doublet separation.
Shift of sample position with respect to the goniometer axis

Width of the divergence slit
Sample transparency

Axial divergence

ABERRATIONS OF THE POWDER GEOMETRY
ABERRATIONS OF THE POWDER GEOMETRY

(radius 250mm, Soller 2°, D.S. 1/2°, R.S. 0.15mm)

- Graph showing variations in 
  $\Delta(2\theta)$ (degrees) against 2\(\theta\) (degrees)

- Legend:
  - Total
  - Axial divergence
  - S. displacement
  - Polarization
  - S. transparency
  - Refraction
  - Flat sample
  - Lorentz/Dispersion
Errors in peak positions: NIST SRM 1976 alumina. D.S. $\frac{1}{2}^\circ$ or $1^\circ$. Other parameters are the same (radius 250mm, Soller $2^\circ$, R.S. 0.15mm).
Like many natural phenomena related to the generation of random events with a finite time average, X-ray emission follows the POISSON statistics

\[ p(n) = \frac{N^n}{n!} e^{-N} \]

where \( n \) is a positive integer. \( N \) is the mean value:

\[
\bar{n} = \sum_{n=0}^{\infty} np(n) = \sum_{n=0}^{\infty} N \frac{N^{n-1}}{(n-1)!} e^{-N} = Ne^{-N} e^N = N
\]

If \( N \) is the mean value of the counts collected for a certain time, the standard deviation \( \sigma_n \) is obtained from:

\[
\sigma_n^2 = (n - N)^2 = \left( n^2 + N^2 - 2nN \right) = N^2 + N - N^2 = N
\]
The standard deviation is given by

\[ \sigma_n = \sqrt{N} \]

And the relative standard deviation is:

\[ \sigma_{n,rel} = \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}} \]
When a background is present with $N_B$ counts, if $N_T = N_P + N_B$ is the total counts ($N_P$ is the net peak area, with background subtracted), the relative standard deviation (in percentage) is:

$$\sigma_P = \sqrt{\frac{N_T}{N_T - N_B}} \times 100$$

The signal-to-noise ratio, $R$, is defined as:

$$R = \frac{N_T}{N_B}$$

$$\sigma_P = \frac{1}{R - 1} \sqrt{\frac{R(R+1)}{N_T}} \times 100$$
COUNTING STATISTICS

\[
\sigma_p = \frac{1}{R-1} \sqrt{\frac{R(R+1)}{N_p}} \times 100
\]

Relative standard deviation (in %) vs. Total counts

- \(R\): Number of repetitions
- \(N_p\): Total counts

Graph showing the relationship between relative standard deviation and total counts for different values of \(R\).
An implicit assumption of all the above reasoning is that the powder sample is homogeneous, even on a microscopic level. This is just an approximation, because samples are made of finite size grains.

If grains (actually, crystalline domains) are not sufficiently small, the concept of powder tends to lose its meaning, in the sense that it is not true anymore that for any direction there is a sufficiently large number of domains with atomic planes in Bragg conditions.

Depending on the absorption coefficient, the critical threshold for the domain size changes. In particular, the problem of having sufficiently small grains is critical for highly absorbing materials.
The figure below shows the intensity collected for the same reflection of quartz for different specimens of the same powder sample (from 1 to 10), prepared by selecting different granulometric fractions. The smallest deviations are obtained below 5 µm.
The data shown before also reveal a further effect. For the large grains, the decrease in intensity caused by absorption is increased by the fact that the fraction of diffracted intensity is also larger for these grains. Consequently, the signal is lower than that given by the same volume made of smaller (less absorbing) grains.

<table>
<thead>
<tr>
<th>Grain Size</th>
<th>Mean 8512</th>
<th>9207</th>
<th>11267</th>
<th>11293</th>
</tr>
</thead>
<tbody>
<tr>
<td>15-50 µm</td>
<td>8512</td>
<td>9207</td>
<td>11267</td>
<td>11293</td>
</tr>
<tr>
<td>5-15 µm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;5 µm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This effect (extinction), together with microabsorption is one of the factors limiting the reliability of powder diffraction measurements. It is a particularly critical issue in quantitative phase analysis.
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Primitive cell (P) (Z=1) with one atomic species only

\[ F = f e^{2\pi i (h \cdot \mathbf{a} + k \cdot \mathbf{b} + l \cdot \mathbf{c})} = f \]

\[ I \propto |F|^2 = f^2 \]

The structure factor is the same for all (hkl) reflections
Body centred lattice (I) (Z=2) with one atomic species only in (0,0,0) and \((\frac{1}{2},\frac{1}{2},\frac{1}{2})\)

\[
F = fe^{2\pi i (0)} + fe^{2\pi i (h/2+k/2+l/2)} = f \left[ 1 + e^{\pi i (h+k+l)} \right] = \begin{cases} 
0 & h + k + l \text{ odd} \\
2f & h + k + l \text{ even} 
\end{cases}
\]

The intensity is proportional to \(4f^2\) for reflections with even sum of indices, and it is zero for those with odd sum of indices.
Face centred lattice (F) (Z=4) with one atomic species only in (0,0,0), (0,1/2,1/2), (1/2,0,1/2) and (1/2,1/2,0)

\[ F = e^{2\pi i(0)} + e^{2\pi i(0+k/2+l/2)} + e^{2\pi i(h/2+l/2)} + e^{2\pi i(h/2+k/2)} \]

\[ = f \left[ 1 + e^{\pi i(k+l)} + e^{\pi i(h+l)} + e^{\pi i(h+k)} \right] = \begin{cases} 0 & h, k, l \text{ mixed} \\ 4f & h, k, l \text{ unmixed} \end{cases} \]

The intensity is proportional to \(16f^2\) for reflections with mixed indices and it is zero for those with unmixed indices.
The structure factor is independent of shape and size of the unit cell.

Rules shown in the previous examples are then valid for any P, I, or F cells.
EXAMPLE

Calculated integrated intensity for the reflections of Fluorite
Fluorite (CaF$_2$): fcc (Z=4) unit cell.

Cations (Ca$^{+2}$, r=0.99 Å) in the origin and positions equivalent by fcc Translations.

Anions (F$^{-1}$, R=1.33 Å) in ($\frac{1}{4},\frac{1}{4},\frac{1}{4}$), ($\frac{1}{4},\frac{1}{4},\frac{3}{4}$) and positions equivalent by fcc Translations.
Ca\(^{+2}\) (0,0,0) + fcc 
F\(^{-1}\) (¼,¼,¼), (¼,¼,¾) + fcc.

\[
F = 4 \left[ f_{Ca} + f_F e^{\frac{\pi}{2} (h+k+l)} + f_F e^{\frac{\pi}{2} (h+k+3l)} \right] = 4 \left[ f_{Ca} + f_F \left( e^{\frac{\pi}{2} (h+k+l)} + e^{\frac{\pi}{2} (h+k-l)} \right) \right] = \\
= 4 \left[ f_{Ca} + 2 f_F e^{\frac{\pi}{2} (h+k)} \cos \left( \frac{\pi l}{2} \right) \right]
\]

\[
|F|^2 = 16 \left\{ f_{Ca}^2 + 4 f_F^2 \cos^2 \left( \frac{\pi l}{2} \right) + 4 f_{Ca} f_F \left[ e^{\frac{\pi}{2} (h+k)} + e^{\frac{\pi}{2} (h+k)} \right] \cos \left( \frac{\pi l}{2} \right) \right\} = \\
= 16 \left\{ f_{Ca}^2 + 4 f_F^2 \cos^2 \left( \frac{\pi l}{2} \right) + 4 f_{Ca} f_F \cos \left[ \frac{\pi}{2} (h+k) \right] \cos \left( \frac{\pi l}{2} \right) \right\}
\]
The expression simplifies considering that $h, k, l$ are integers:

$$|F|^2 = 16 f_{Ca}^2 + 4 f_F^2 + 4 f_{Ca} f_F \cos \left(\frac{\pi l}{2}\right) + 4 f_{Ca} f_F \cos \left(\frac{\pi}{2} (h + k)\right) \cos \left(\frac{\pi l}{2}\right)$$

The expression simplifies considering that $h, k, l$ are integers:

$$|F|_A^2 = 16 f_{Ca}^2 \quad l \text{ odd}$$

$$|F|_B^2 = 16 \left(f_{Ca} - 2 f_F\right)^2 \quad (h + k) \text{ or } l \text{ odd multiple of } 2$$

$$|F|_C^2 = 16 \left(f_{Ca} + 2 f_F\right)^2 \quad (h + k) \text{ and } l, \text{ both odd or both even multiple of } 2$$

<table>
<thead>
<tr>
<th></th>
<th></th>
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<td>(422)</td>
<td>(333)</td>
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| (222)    | (400)    | (331)    | (420)    | (422)    | (333)    | (511)    | (440)    | (531)    | (600)    |
$|F|^2_A = 16 f_{Ca}^2 \quad l \text{ odd}$

$|F|^2_B = 16 (f_{Ca} - 2 f_F)^2 \quad (h+k) \text{ or } l \text{ odd multiple of } 2$

$|F|^2_C = 16 (f_{Ca} + 2 f_F)^2 \quad (h+k) \text{ and } l, \text{ both odd or both even multiple of } 2$

**Atomic scattering factor (f):**

**Dispersion corrections:**

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<th>F</th>
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<tr>
<td>$\Delta f''$</td>
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$\Rightarrow (f + \Delta f') + i \Delta f''$

**Debye-Waller factors:**

$B(Ca) = 0.47 \, \text{Å}^2$, $B(F) = 0.67 \, \text{Å}^2$
\[ |F|^2_A = 16f_C^2 \] \((l \text{ odd})\)

\[ |F|^2_B = 16(f_C - 2f_F)^2 \] \((h + k) \text{ or } l \text{ odd multiple of } 2\)

\[ |F|^2_C = 16(f_C + 2f_F)^2 \] \((h + k) \text{ and } l, \text{ both odd or both even multiple of } 2\)

\[ |F_T|^2_A = 16f_C^2e^{-2M_C} = 16\left[ (f_{0,C} + \Delta f'_{C})^2 + (\Delta f''_{C})^2 \right]e^{-2M_C} \]

\[ |F_T|^2_B = 16(f_Ce^{-M_C} - 2f_Fe^{-M_F})^2 = \]

\[ = 16\left\{ \left[ (f_{0,C} + \Delta f'_{C})e^{-M_C} - 2(f_{0,F} + \Delta f'_{F})e^{-M_F} \right]^2 + (\Delta f''_{C}e^{-M_C} - 2\Delta f''_{F}e^{-M_F})^2 \right\} \]

\[ |F_T|^2_C = 16(f_Ce^{-M_C} + 2f_Fe^{-M_F})^2 = \]

\[ = 16\left\{ \left[ (f_{0,C} + \Delta f'_{C})e^{-M_C} + 2(f_{0,F} + \Delta f'_{F})e^{-M_F} \right]^2 + (\Delta f''_{C}e^{-M_C} + 2\Delta f''_{F}e^{-M_F})^2 \right\} \]
\[ |F|^2_A = 16f_{Ca}^2 \quad l \text{ odd} \]
\[ |F|^2_B = 16(f_{Ca} - 2f_F)^2 \quad (h+k) \text{ or } l \text{ odd multiple of } 2 \]
\[ |F|^2_C = 16(f_{Ca} + 2f_F)^2 \quad (h+k) \text{ and } l, \text{ both odd or both even multiple of } 2 \]
\[ |F|_A^2 = 16 f_{Ca}^2 \]  
\( l \) odd  
\[ |F|_B^2 = 16 (f_{Ca} - 2f_F)^2 \]  
\((h+k)\) or \(l\) odd multiple of 2  
\[ |F|_C^2 = 16 (f_{Ca} + 2f_F)^2 \]  
\((h+k)\) and \(l\), both odd or both even multiple of 2

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\( a_0 = 5.463\text{Å} \)  
\( \theta_m = 13.28^\circ \)  
\( M = B(\sin\theta/\lambda)^2 \)  
\( \lambda = 1.540598\text{Å} \)
Experimental pattern of fluorite powder

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### Experimental pattern of fluorite powder: profile fitting results

<table>
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<th>I_{max}</th>
<th>Area</th>
<th>Int</th>
<th>HWHM f</th>
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## FLUORITE POWDER PATTERN

Comparison between calculated and measured integrated intensities:

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<th>Experimental Integ. Int.</th>
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Counting statistics:

\[ \sigma_P = \frac{\sqrt{N_T + N_B}}{N_T - N_B} \times 100 \]

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<th>( I_{rel} (%) )</th>
<th>( 2\theta_{\text{start}} ) (gradi)</th>
<th>( 2\theta_{\text{end}} ) (gradi)</th>
<th>( N_B ) (conteggi)</th>
<th>( N_T = N_P + N_B ) (conteggi)</th>
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Comparison between calculated and measured integrated intensities:

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Result using the Rietveld method (TOPAS ©):

\[ B(Ca) = 0.43 \, \text{Å}^2 \]
\[ B(F) = 0.76 \, \text{Å}^2 \]

Literature values:

\[ B(Ca) = 0.47 \, \text{Å}^2 \]
\[ B(F) = 0.67 \, \text{Å}^2 \]
REFERENCES


