X School on Synchrotron Radiation: Fundamentals, Methods and Applications
Duino Castle / Trieste, Italy / 7-18 September 2009

Powder Diffraction & Synchrotron Radiation

P. Scardi
Department of Materials Engineering and Industrial Technologies
University of Trento

University of Trento
International Doctoral School in Materials Science & Engineering

About 15 new positions per year

Information and applications:
http://portale.unitn.it/drmse/
next deadline: September 14th

Paolo.Scardi@unitn.it
PRESENTATION OUTLINE

PART I

• Some advantages and peculiarities of synchrotron radiation X-ray powder diffraction (SR-XRPD)
• Main applications of XRPD and RS-XRPD

PART II

• Diffraction from nanocrystalline and highly deformed materials

DIFFRACTION: SINGLE CRYSTAL AND POWDER

single crystal

powder (bulk polycrystalline)
DIFFRACTION: SINGLE CRYSTAL AND POWDER

DEBYE-SCHERRER GEOMETRY
SRXRD POWDER GEOMETRY: A TYPICAL EXAMPLE

ID31 Goniometer and nine-crystal analyzer

Parallel beam geometry at ID31 (ESRF)
capillary holder / high temperature blower

X-ray detector

SRXRD POWDER GEOMETRY: A TYPICAL EXAMPLE

Parallel beam geometry of MCX (Elettra)
SRXRD POWDER GEOMETRY: A TYPICAL EXAMPLE

Parallel beam geometry of MCX (Elettra)

BEAMTIME APPLICATIONS:
DEADLINE IS SEPTEMBER 15th
TYPICAL LAB GEOMETRY: BRAGG-BRENTANO (POWDER)

BULK or POWDER

LAB vs SR XRD

(why) do we need synchrotron radiation?

... don’t use a cannon to kill a fly!

quoted by G. Artioli

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SOME ADVANTAGES OF SRXRD

1) High brilliance, much better counting statistics / shorter data collection time (⇒ fast kinetics, in situ studies)

CuKα λ = 0.15406 nm

ESRF ID31 λ = 0.0632 nm

iron powder (ball milled)

SOME ADVANTAGES OF SRXRD

2) With proper selection of optics, very narrow instrumental profile: increased resolution and accuracy in the measurement of peak position, intensity and profile width/shape.

Lab instrument: FWHM ≈ 0.05-0.1°

ID31 @ESRF: FWHM ≈ 0.003-0.004°
3) Extending the accessible region of reciprocal space well beyond what traditional lab instruments can make.

CuKα, $\lambda = 0.15406$ nm

ESRF ID31, $\lambda = 0.0632$ nm

Some advantages of SRXRD

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4) Tuning the energy according to adsorption edges. Resonant scattering, control of fluorescence emission and depth of analysis.

\[ I = I_0 e^{-\left(\frac{\mu}{\rho}\right)^n} \]

X-RAY POWDER DIFFRACTION

**most frequent applications**

- Crystal structure determination (Powder diffraction structure solution and refinement)
- Phase Identification - pure crystalline phases or mixtures (Search-Match procedures)
- Quantitative Phase Analysis (QPA)
- Amorphous phase analysis (radial distribution function)
- Crystalline domain size/shape and lattice defect analysis (Line Profile Analysis - LPA)
- Determination of preferred orientations (Texture Analysis)
- Determination of residual stress field (Residual Stress Analysis)
Structure solution of heptamethylene-1,7-bis(diphenylphosphane oxide)

Structural formula:
\[ \text{Ph}_2 \text{P(O)(CH}_2)_7 \text{P(O)Ph}_2 \]


Structure solution/refinement of a complex triclinic organic compound \((C_{24}H_{16}O_7)\)


• Narrow peak profiles
• Large number of measurable peaks
• Accurate peak position/intensity
• X-ray energy tuning to adsorption edges
Site occupancy in battery electrode material LaNi$_{3.55}$Mn$_{0.4}$Al$_{0.3}$Co$_{0.75}$


- Narrow peak profiles
- Large number of measurable peaks
- Accurate peak position/intensity
- X-ray energy tuning to adsorption edges
### Site occupancy in battery electrode material LaNi$_{3.55}$Mn$_{0.4}$Al$_{0.3}$Co$_{0.75}$


<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B (\text{Å}^2)</th>
<th>Occupancy (\text{atomic} %)</th>
</tr>
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<tbody>
<tr>
<td>La</td>
<td>1(a)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.06 (2)</td>
<td>1</td>
</tr>
<tr>
<td>Ni</td>
<td>2(c)</td>
<td>1/3</td>
<td>2/3</td>
<td>0</td>
<td>2.38 (2)</td>
<td>1.66 (2)</td>
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<tr>
<td>Mn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.07 (1)</td>
<td>0.032 (4)</td>
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<tr>
<td>Al</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.24 (1)</td>
<td>1.89 (3)</td>
</tr>
<tr>
<td>Ni</td>
<td>3(g)</td>
<td>1/2</td>
<td>0</td>
<td>1/2</td>
<td>1.97 (2)</td>
<td>0.33 (1)</td>
</tr>
<tr>
<td>Mn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.267 (6)</td>
<td>0.51 (1)</td>
</tr>
<tr>
<td>Co</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

![Diagram of the crystal structure of LaNi$_{3.55}$Mn$_{0.4}$Al$_{0.3}$Co$_{0.75}$](image)

- Narrow peak profiles
- Large number of measurable peaks
- Accurate peak position/intensity
- X-ray energy tuning to adsorption edges

---

### STRUCTURE SOLUTION & REFINEMENT: SRXRD


![Diagram of the molecule arrangement of the bromo-thallium(I)oxide structure](image)

- Narrow peak profiles
- Large number of measurable peaks
- Accurate peak position/intensity
- X-ray energy tuning to adsorption edges
- Anisotropic thermal expansion

![Graphs showing temperature dependence of X-ray diffraction peaks](image)
Each crystalline phase has its own pattern that can be used as a ‘fingerprint’. ‘Fingerprints’ of unknown substances can be compared with those of known crystalline phases of a database → Search-Match procedures

ICDD databases
(International Centre for Diffraction Data - www.icdd.com)
Automatic search-match procedures based on peak position / intensity

**PHASE IDENTIFICATION**

Intensity of i-th data-point in the pattern

\[ y_{ci} = \sum_j S_j \sum_k I_{k,j} \cdot \phi_{k,j} \cdot P_{k,j} + y_{bi} \]

Scale factor of j-th phase

Integrated Intensity of k-th peak of j-th phase

Profile function

Preferred Orientation

Background term

**THE RIETVELD METHOD**

From the lecture of G. Zanotti
**THE RIETVELD METHOD**

Intensity of i-th data-point in the pattern

\[ y_{ci} = \sum_j S_j \sum_k I_{k,j} \cdot \phi_{k,j} \cdot P_{k,j} + y_{bi} \]

- Scale factor of j-th phase
- Integrated Intensity k-th peak of j-th phase \( \propto |F|^2 \)
- Profile function
- Preferred Orientation
- Background term

In a polyphasic mixture: weight fraction \( x_j \) of the phase j

\[ x_j = \frac{S_j \rho_j y_j}{\sum_i S_i \rho_i y_i} \]

\( \rightarrow \) normalization condition (\( \sum \) phase fraction = 1)

---

**RIETVELD-BASED QPA**

Example: mixture of mineral phases in a ligand

- Lime CaCO3 26.28%
- Dolomite CaMg(CO3)2 9.49%
- Quartz 2.39%
- Gypsum 0.69%
- Bauxinite 30.67%
- Anhydrite 22.34%
- Belite C2S 8.13%
STRUCTURE SOLUTION IN MULTIPHASE SAMPLES

Structural and electronic properties of noncubic fullerides $A'_40C_{60}$ ($A'$=Ba,Sr)


- Narrow peak profiles
- Large number of measurable peaks
- Accurate peak position/intensity
- X-ray energy tuning to adsorption edges

Table 1: Lattice parameters for orthorhombic Ba$C_{60}$ obtained from Rietveld refinement of the powder X-ray powder diffraction data for a single crystal sample. The lattice parameters are: $a = 0.506$, $b = 0.490$, and $c = 0.496$ nm. The crystal structure is monoclinic, space group $P2_12_12_1$. The neutron data are from Reference [1].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.506</td>
</tr>
<tr>
<td>b</td>
<td>0.490</td>
</tr>
<tr>
<td>c</td>
<td>0.496</td>
</tr>
</tbody>
</table>

Note: The accuracy of the lattice parameters is reported in Reference [1].

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ESRF BM161 $\lambda = 0.084884$ nm

Diffrazione da Materiali Policristallini
AMORPHOUS PHASE ANALYSIS

Crystalline structure \[ \downarrow \]
long-range order

Amorphous phase \[ \downarrow \]
short-range order

Crystalline SiO$_2$

Amorphous SiO$_2$

Amorphous specimen of volume $V$ ($N$ atoms with scattering factor $f$):

$$I(s) \equiv Nf^2 \left( 1 + \frac{1}{2\pi s} \int_0^s 4\pi r \left[ \rho(r) - \rho_0 \right] \sin(2\pi sr) \, dr \right)$$

By Fourier inversion:

$$4\pi r \rho(r) \approx 4\pi r \rho_0 + 8\pi \int_0^s \frac{I(s)}{Nf^2} - 1 \sin(2\pi sr) \, ds$$

AMORPHOUS PHASE ANALYSIS

Diffrazione da Materiali Policristallini
Structure of nanocrystalline materials using atomic Pair Distribution Function (PDF) analysis: study of LiMoS$_2$.

**LINE PROFILE ANALYSIS: SRXRD**

Xerogel obtained by vacuum-drying: broad diffraction lines of nanocrystalline fcc phase

ESRF ID31 - glass capillary, $\lambda=0.06325$ nm

Intensity (counts)

$0.8$ hour

75 peaks

$\langle D\rangle=2.25(10)$ nm

$P.\ Scardi\ &\ Leoni,\ ECS\ Transactions,\ 3(9)\ (2006)\ 125.$

**QUESTIONS??**
Scattering from a small crystal of Cu (fcc)

$$I_c \propto \sum_m A_m \sum_n A_n^* = \sum_m f_m e^{2\pi i (\mathbf{d}^* \cdot \mathbf{r}_m)} \sum_n f_n e^{-2\pi i (\mathbf{d}^* \cdot \mathbf{r}_n)}$$

One scattering centre (electron, atom, unit cell)

$$I \propto |A|^2 = AA^*$$

Scattering from a unit cell of Cu (fcc)

$$I_{uc} \propto \sum_m f_m e^{2\pi i (\mathbf{d}^* \cdot \mathbf{r}_m)} \sum_n f_n e^{-2\pi i (\mathbf{d}^* \cdot \mathbf{r}_n)}$$
SCATTERING FROM NANOCRYSTALS
Scattering from two atoms in a Cu (fcc) unit cell

\[ I_{\text{uc}} \propto \sum_m f_m e^{2\pi i (d^* \cdot s)} \sum_n f_n e^{-2\pi i (d^* \cdot t)} = \sum_m \sum_n f_m f_n e^{2\pi i (d^* \cdot s)} \]

SCATTERING FROM NANOCRYSTALS
Scattering from two atoms in a Cu (fcc) unit cell

\[ d^* = \frac{s - s_0}{\lambda} = \frac{2 \sin \theta}{\lambda} \]

\[ I_{\text{uc}} \propto \sum_m f_m e^{2\pi i (d^* \cdot s)} \sum_n f_n e^{-2\pi i (d^* \cdot t)} = \sum_m \sum_n f_m f_n e^{2\pi i (d^* \cdot s)} \]
Two possible approaches

1. Reciprocal space approach  
   (Laue – Wilson)

2. Direct space (or Real space) approach  
   (Debye)

SCATTERING FROM A POWDER

Two possible approaches

1. Factorize the contribution from a unit cell ($|F|^2 - F$, structure factor)

\[ d^* = \frac{s - s_0}{\lambda} = ha^* + kb^* + lc^* \]

\[ s_n = u_n a + v_n b + w_n c \]

\[ I_s = \sum_m f_m e^{2\pi i (d^* \cdot s)} \sum_n f_n e^{-2\pi i (d^* \cdot s_n)} = \left| \sum_{n=1}^{N} f_n e^{2\pi i (u_n a + v_n b + w_n c)} \right|^2 = |F|^2 \]
SCATTERING FROM A POWDER

Two possible approaches - \#1 reciprocal space

1. Factorize the contribution from a unit cell ($|F|^2 - F$, structure factor)

$$I_{\text{uc}} \propto |F|^2 = \sum_{n=1}^{N} f_n e^{2\pi i (u_n h + v_n k + w_n l)}$$

Then build the diffraction signal for a small crystal (unit cell volume, $V_{\text{uc}}$)

(Interference function) \(\rightarrow\) see ZANOTTI's lecture

$$I_{\text{uc}} \propto \frac{|F|^2}{V_{\text{uc}}} \sin^2 (\pi Nh) \sin^2 (\pi Nk) \sin^2 (\pi Nl)$$

$$\frac{1}{V_{\text{uc}}} = \frac{1}{a^2 b^2 c^2}$$

$$I_{\text{uc}} \propto \frac{|F|^2}{V_{\text{uc}}} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} \frac{\sin^2 (\pi Nh) \sin^2 (\pi Nk) \sin^2 (\pi Nl)}{\pi^2 (h-h')^2 \pi^2 (k-k')^2 \pi^2 (l-l')^2}$$
SCATTERING FROM A POWDER

Two possible approaches - #1 reciprocal space

1. Factorize the contribution from a unit cell (|F|^2 - F, structure factor)

Then build the diffraction signal for a small crystal (unit cell volume, Vuc)

(Interference function)

\[ I_{nc} \propto \frac{|F|^2}{V_{uc}^2} \sum_{h-k-l} \sum_{h-k-l} \sin^2(\pi Nh) \sin^2(\pi Nk) \sin^2(\pi Nl) \]

\[ \frac{4}{\pi^2} \frac{1}{(h-k-l)^2} \]

Example: (100) point

\[ I_{100} \propto \frac{\sin^2(\pi Nh)}{\pi^2(h-1)^2} \]

NANOCRYSTAL \rightarrow POWDER

Two possible approaches - #1 reciprocal space

Diffrazione da Materiali Policristallini
Two possible approaches - #1 reciprocal space

Example: (001) peak, powder made of cubic crystallites, cube edge L

\[
I \propto |F|^2 \int \frac{\sin^2(\pi Nh) \sin^2(\pi Nk) \sin^2(\pi Nl)}{(\pi h)^2 (\pi k)^2 (\pi l)^2} dh \cdot dk \rightarrow |F|^2 \frac{\sin^2(\pi Nl)}{\pi l} \int_{0}^{\infty} \frac{\sin^2(\pi Nl)}{(\pi l)^2} dl = \frac{1}{N}
\]

\[
L = Na
\]

NANOCRYSTAL → POWDER

Two possible approaches - #1 reciprocal space

Prof. Paolo Scardi, Università di Trento
SCATTERING FROM A POWDER

Two possible approaches - #1 reciprocal space

1. Factorize the contribution from a unit cell ($|F|^2 - F$, structure factor)

   Then build the diffraction signal for a small crystal,
   \[
   \sin^2(\pi N_h) \sin^2(\pi N_k) \sin^2(\pi N_l) \\
   \sin^2(\pi h) \sin^2(\pi k) \sin^2(\pi l)
   \]
   and integrate over the powder diffraction sphere for calculating the signal from all domains in the powder.

   \[
   I_{PD} \propto |F|^2 \Phi \left( d^*, D \right)
   \]

SCATTERING FROM NANOCRYSTALS

Two possible approaches - #2 real space

2. Average over all possible orientations of $r_{mn}$ in space

   \[
   I_{nc} \propto \sum_m f_m e^{2\pi i (d^* \cdot \ell_m)} \sum_n f_n e^{-2\pi i (d^* \cdot \ell_n)} \]
   \[
   = \sum_m \sum_n f_m f_n e^{2\pi i (d^* \cdot \ell_{mn})}
   \]

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### Scattering from Nanocrystals

Two possible approaches - #2 real space

1. Average over all possible orientations of $r_{mn}$ in space

\[
\frac{d^*}{d} = \frac{s-s_0}{\lambda} = \frac{2\sin \theta}{\lambda}
\]

\[
d^* \cdot r_{mn} = d^* r_{mn} \cos \phi
\]

\[
I_{sc} \propto \sum_m f_me^{2\pi i(d^* \cdot r_{mn})} \sum_n f_ne^{-2\pi i(d^* \cdot r_{nn})} = \sum_m \sum_n f_m f_n e^{2\pi i(d^* \cdot r_{mn})}
\]

### Scattering from a Powder

Two possible approaches - #2 real space

2. Average over all possible $\cos \phi$ values: $r_{mn}$ is allowed to take all possible orientations in space

\[
d^* \cdot r_{mn} = d r_{mn} \cos \phi
\]

\[
I_p \propto \sum_m \sum_n f_m f_n \left( e^{2\pi i(d^* \cdot r_{mn})} \right) \sum_m \sum_n f_m f_n \frac{\sin(2\pi d^* r_{mn})}{2\pi d^* r_{mn}}
\]
Debye formula for one (fcc) unit cell

\[ I_D = \sum_m \sum_n f_m f_n \frac{\sin 2\pi d^2 r_{mn}}{2\pi d^2 r_{mn}^2} \]

where

- \( r_{mn} = 0 \)
- \( a/\sqrt{2} \)
- \( a \)
- \( a\sqrt{3}/2 \)
- \( a\sqrt{2} \)
- \( a\sqrt{3} \)

\[ I_D = 14 + \frac{72 \sin (ka/\sqrt{2})}{ka/\sqrt{2}} + \frac{30 \sin ka}{ka} + \frac{48 \sin (ka\sqrt{3}/2)}{ka\sqrt{3}/2} + \frac{24 \sin (ka\sqrt{5})}{ka\sqrt{5}} + \frac{8 \sin (ka\sqrt{3})}{ka\sqrt{3}} \]

Scattering from (random oriented) Cu unit cells. Mo K\(\alpha\) (0.07093 nm)

SCATTERING FROM A NANOCRYSTAL POWDER

Cu bars: multiplicity
SCATTERING FROM A NANOCRYSTAL POWDER

Scattering from (random oriented) Cu unit cells. Mo Kα (0.07093 nm)

\[ I_D \cdot LP \cdot e^{-k^2_{\text{eff}}} \]

Cu bars: ICSD #46699

SCATTERING FROM A NANOCRYSTAL POWDER

Scattering from bcc-Fe cubic crystals. Cu Kα (0.15406 nm)
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SCATTERING FROM A NANOCRYSTAL POWDER

Scattering from bcc-Fe cubic crystals. Cu Kα (0.15406 nm)

15x15x15
7471 atoms

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SCATTERING FROM A NANOCRYSTAL POWDER

Scattering from bcc-Fe cubic crystals. Cu Kα (0.15406 nm)

$\text{I(0)} = 55.815.841 = 7471^2$

Twinned spherical domains (fcc, 28897 Au atoms, nominal size 9.8 nm)
The Debye formula approach can be extended to a distribution of nanocrystals, also including a radial, homogeneous strain.

C - cuboctahedron
I - icosahedron
D - decahedron

\[ \text{Graphene (sp}^2\text{ carbon single-layer)} \]

L. Gelisio, Univ. of Trento

\[ \text{Figure 9} \]
- (a) profile best fit and the cumulative domain size distribution (see inset): observed (crosses) and calculated (solid line): intensity, difference plot (below); (b) corresponding size and size-related strain distributions for each structure type.

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SCATTERING FROM A NANOCRYSTAL POWDER

Carbon nanotubes

cluster of nanocrystalline grains: 7.6 million atoms
atomistic simulations - molecular dynamics

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QUESTIONS ??

SCATTERING FROM A POWDER

Two possible approaches

1. Reciprocal space approach
   (Laue – Wilson)

2. Direct space (or Real space) approach
   (Debye)
CRYSTAL, NANOCRYSTAL AND POWDER: SIZE EFFECT

LARGE crystal

NANO crystal

NANO crystal POWDER

NANOCRYSTAL → POWDER

Ewald sphere

Powder Diffraction sphere

\[
\frac{s_0}{\lambda} \quad \frac{s}{\lambda} \quad d \quad 2\theta
\]
Powder made of simple-shape crystallites
(one param., convex solids: sphere, cube, tetrahedron, octahedron,...)

\[ \beta (d^*) = \frac{K \beta}{D} \]

Scherrer formula (1918)

\(K\beta\), Scherrer constant, changes with crystallite shapes and (hkl)
**DIFFRACTION FROM A POLYCRYSTALLINE MATERIAL**

Powder made of simple-shape crystallites
(one param., convex solids: sphere, cube, tetrahedron, octahedron,...)

\[ \beta (d^*) = \frac{K \beta}{D} \]

**Scherrer formula (1918)**

\( K \beta \), Scherrer constant, changes with crystallite shapes and \((hkl)\).

For a sphere:

\[ K \beta = \frac{4}{3} \]

---

**TRADITIONAL LPA: INTEGRAL BREADTH METHODS**

Profile information can be represented by the **Integral Breadth** \( \beta \),
(peak area / peak maximum). Assuming domain size effects only:

\[ \beta (2\theta) = \frac{K \beta}{D \cos \theta} \]

**Scherrer formula**

\[ \beta (d^*) = \frac{K \beta}{D} \]
CAVEAT #1 – what is the true result of the Scherrer formula?

For a DISTRIBUTION of crystallites

\[ g(D) \]

The integral breadth still provides a valid mean size value, but:

\[ \beta (d^*) = \frac{K\beta}{<D>^\nu} = K\beta \frac{M_3}{M_4} \]

where \( M_3, M_4 \) are 3\textsuperscript{rd} and 4\textsuperscript{th} moments of \( g(D) \)

\[ M_i \rightarrow \text{mean} \]
\[ M_i^2 - M_i^2 \rightarrow \text{variance} \]

\[ (M_i = \int D^i g(D)dD) \]

MICROSTRAIN EFFECT IN POWDER DIFFRACTION

CAVEAT #2 – what is the effect of lattice distortions?

Quite complex: unit cells at distance \( L = n \alpha \) can be displaced and rotated.

Neglecting rotation and considering an average strain \[ \varepsilon = dL/L \]

\[ I_c \propto \left| F \right|^2 \times \frac{2\pi Id^\varepsilon(L)}{dL} \]
Considering both domain size and lattice distortion (microstrain) effects

(as a first order approximation):

$$\beta (2\theta) \approx \frac{K_{\beta} \lambda}{<\mathbf{D}>_v \cos \theta} + 2\left(\frac{\epsilon^2}{\lambda^2}\right)^{1/2} \tan \theta$$

[\beta (d^*) = \beta (2\theta) \cdot \cos \theta / \lambda]

\[d^* \quad \text{(nm}^{-1} \text{)} \quad \beta (d^*) \quad \text{(nm}^{-1} \text{)}\]

Williamson-Hall (WH) plot

in a $\beta(d^*)$ vs. $d^*$ plot, intercept and slope of linear regression are related, respectively, to $<\mathbf{D}>_v$ and $\epsilon$
Peak profiles invariably overlap in powder patterns. This can make it difficult to extract profile information directly from observed data.

... a step forward
WHOLE POWDER PATTERN MODELLING

WPPM is based on a direct modelling of the experimental pattern, based on physical models of the microstructure and lattice defects:

\[ \text{Diffraction Pattern} \rightarrow \text{WPPM} \rightarrow \text{Physical Model} \rightarrow \text{Microstructural Parameters} \]


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WHOLE POWDER PATTERN MODELLING

WPPM is based on a direct modelling of the experimental pattern, based on physical models of the microstructure and lattice defects:

- Diffraction Pattern
- Physical Model
- Microstructural Parameters

How does it work??

DIFFRACTION LINE PROFILE: CONVOLUTION OF EFFECTS

So far we consider that different effects affecting the line profile simply 'add', i.e., the peak width is the sum of different components.

According to the Williamson-Hall formula,

\[ \beta(d^*) = \frac{K \cdot \beta}{\langle D \rangle} + 2e \cdot d^* \]

'size' 'strain'

Actually, this is not the general case ...
A diffraction peak is a convolution of profile components produced by different sources: instrumental profile (IP), domain size (S), microstrain (D), faulting (F), anti-phase domain boundaries (APB), stoichiometry fluctuations (C), grain surface relaxation (GSR), etc.

\[ I(s) = I^{IP}(s) \otimes I^{S}(s) \otimes I^{D}(s) \otimes I^{E}(s) \otimes I^{APB}(s) \otimes I^{C}(s) \otimes I^{GRS}(s) \ldots \]

\[ h = g \otimes f \]

What is the difference between convolution and sum of effects??

Example: let’s just consider instrument (IP) and domain size (S):

\[ I(s) = I^{IP}(s) \otimes I^{S}(s) \]

\[ I(s) = \int I^{IP}(t)I^{S}(s-t)\, dt \]

g profile, slit (box) function; f profile, bell-shape function (e.g. gaussian)
A diffraction peak is a convolution of profile components produced by different sources: instrumental profile (IP), domain size (S), microstrain (D), faulting (F), anti-phase domain boundaries (APB), stoichiometry fluctuations (C), grain surface relaxation (GSR), etc.

\[ h = g \otimes f \]

The Fourier Transform of \( I(s) \) is the product of the FTs of the single profile components.
The diffraction profile results from a convolution of effects:

\[ I(s) = I^{PP}(s) \otimes I^{S}(s) \otimes I^{OP}(s) \otimes I^{C}(s) \otimes I^{APB}(s) \otimes I^{GRS}(s) \ldots \]

The Fourier Transform of \( I(s) \) is the product of the FTs of the single profile components.

\[ I(s) = \prod_{i} A_{i} = T_{PP}^{i} \cdot A_{hkl}^{S} \cdot A_{hkl}^{P} \cdot (A_{hkl}^{F} + iB_{hkl}^{F}) \cdot A_{hkl}^{APB} \cdots \]

**A\textsubscript{L}(L) Expressions (Analytical or Numerical Form)**

**Domain size effect: \( \mu, \sigma \)**

\[ A^\sigma(L) = \sum_{p} H^\sigma_{p} \cdot E_{\text{FC}} \left( \frac{\ln(L - K^{p} - \mu - (3 - n)\sigma)}{\sigma \sqrt{2}} \right) \frac{M_{\mu,\sigma}}{2M_{\mu,\sigma}} \]

**Dislocation (strain) effect: \( \rho, \text{Re}(\mathcal{C}_{\text{mm}}) \)**

\[ A_{\text{mm}}^{\rho}(L) = \exp \left( -\frac{1}{2} \rho |h| \sum_{p} \text{Re}(\mathcal{C}_{\text{mm}}) p \cdot d_{\text{mm}}^{p} \cdot E_{\text{FC}}(L/R_{L}) \right) \]

**Faulting: \( \alpha \) (def.), \( \beta \) (twin)**

\[ A_{\alpha,\beta}^{\rho}(L) = (1 - 3\alpha - 2\beta + 3\alpha^2) \frac{L}{d_{\alpha,\beta}} \frac{d_{\alpha,\beta}}{L} \]

\[ B_{\alpha,\beta}^{\rho}(L) = -\sigma_{s} \frac{L}{d_{\alpha,\beta}} \frac{d_{\alpha,\beta}}{L} \beta \left( 3 - 6\beta - 12\alpha - \beta^2 + 12\alpha^2 \right)^{1/2} \]

**Anti-Phase Domains: \( y \)**

\[ A_{\text{APB}}^{y}(L) = \exp \left( -\gamma |h| |k| \frac{L}{d_{\text{APB}}} \frac{d_{\text{APB}}}{L} \right) \]

\[ d_{\text{APB}} = \frac{h^2 + k^2 + l^2}{1/2} \]

\[ \gamma = \gamma_{o} \]

\[ \gamma_{o} = \frac{1}{2} \ln \left( \frac{L}{d_{\text{APB}}} \frac{d_{\text{APB}}}{L} \right) \]

\[ \gamma_{0} = \frac{1}{2} \ln \left( \frac{L}{d_{\text{APB}}} \frac{d_{\text{APB}}}{L} \right) \]

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WPPM APPLICATIONS
TWO EXAMPLES

Whole Powder Pattern Modelling

Xerogel obtained by vacuum-drying: broad diffraction lines of nanocrystalline fcc phase

ESRF ID31 - glass capillary, λ=0.6325 nm

P. Scardi, M. Leoni, ECS Transactions, 3 (2006) 125
WPPM APPLICATIONS: NANOCRYSTALLINE CERIA

Xerogel obtained by vacuum-drying: broad diffraction lines of nanocrystalline fcc phase

ESRF ID31 - glass capillary, $\lambda = 0.6325$ nm

NANOCRYSTALLINE Fe-1.5%Mo POWDER
Planetary ball milling - production of nanocrystalline Fe-1.5%Mo
Ball milled Fe1.5Mo (Fritsch P4) - data collected at ESRF - ID31 \( \lambda = 0.0632 \) nm

NANOCRYSTALLINE Fe-1.5%Mo POWDER

NANOCRYSTALLINE Fe-1.5%Mo POWDER

Ball milled Fe1.5Mo (Fritsch P4) - data collected at ESRF - ID31 $\lambda=0.0632$ nm

In addition to mean values, WPPM provides the size distribution.
Diffrazione da Materiali Policristallini

Prof. Paolo Scardi, Università di Trento

Diffraction Analysis of Materials Microstructure
E.J. Mittemeijer & P. Scardi, editors.

Powder Diffraction: Theory and Practice
R.E. Dinnebier & S.J.L. Billinge, editors.