Synchrotron X-ray Powder Diffraction

APPLICATIONS
Synchrotron X-ray Powder Diffraction

INSTRUMENTATION
Light source:
- Bending magnet
- Critical energy: 3.2keV (2.0), 5.5keV (2.4)

X-rays at sample:
- Energy range: 6-21 keV
- Photon flux: \(10^{11}\) photons/sec
- Beam size at sample: 10x1 mm\(^2\) - 0.3x0.3 mm\(^2\)
- Energy resolution: \(\Delta E/E = 2\times10^{-4}\)
Light source:
In vacuum undulator

X-rays at sample:
Energy range : 6-80 keV
Beam size can be focused to 50 um
Diffractometer MCX
X-ray detectors

0D – (spot) detectors: Scintillators

1D – Line detectors: Gas detectors, Strip

2D -- Area detectors: Image plate, CCD, Pixel
Scintillator detector (0D)

Ionizing radiation

Photocathode

Photomultiplier tube

Sodium iodine crystal

Optical window

Anode

Hands-on Software, IAEA - Trieste
Mythen detector (1D)
Mythen detector (1D)

<table>
<thead>
<tr>
<th>Sensor material</th>
<th>Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensor</td>
<td>Reverse biased pn-junction array</td>
</tr>
<tr>
<td>Detection principle</td>
<td>Single photon counting</td>
</tr>
<tr>
<td>Sensor thickness [µm]</td>
<td>320, 450, 1000</td>
</tr>
<tr>
<td>Number of channels/module</td>
<td>1280</td>
</tr>
<tr>
<td>Sensitive area (width x length) [mm²]</td>
<td>64 x 8</td>
</tr>
<tr>
<td>Dimensions of one channel (width x length) [µm²]</td>
<td>50 x 8000</td>
</tr>
<tr>
<td>Read out time [ms]</td>
<td>0.3</td>
</tr>
<tr>
<td>Maximum count rate per channel [X-rays/s]</td>
<td>&gt;1x10⁶</td>
</tr>
<tr>
<td>Energy range [keV]</td>
<td>5 – 40</td>
</tr>
<tr>
<td>Point-spread function</td>
<td>1 channel</td>
</tr>
<tr>
<td>Dynamic range [bit]</td>
<td>4, 8, 16, 24 (1 : 16777216)</td>
</tr>
</tbody>
</table>
Image plate (2D)

Unrecorded Imaging Plate

X-ray Photons

He-Ne Laser Beam Scanning

Exposure

Luminescence (400nm)

Plate is ready for use again

Erasing

Visible Light

BaFBr:Eu²⁺

Support
Pilatus detector (2D)
Pilatus detector (2D)

Sensor Pixel

Readout Pixel

Direct detection of X-rays in semiconductor sensor
→ Point Spread Function 1 pixel

Single Photon Counting ASIC
→ No readout noise or dark current
→ High dynamic range (20 bit)
→ Fast readout
## Pilatus detector (2D)

<p>| | |</p>
<table>
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</tr>
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<tr>
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<td>Reverse biased pn-junction array</td>
</tr>
<tr>
<td><strong>Detection principle</strong></td>
<td>CMOS hybrid-pixel technology - single photon counting</td>
</tr>
<tr>
<td><strong>Sensor thickness [µm]</strong></td>
<td>320</td>
</tr>
<tr>
<td><strong>Number of pixels/module</strong></td>
<td>1475 x 1679 = 2476525 pixels</td>
</tr>
<tr>
<td><strong>Sensitive area (width x length) [mm²]</strong></td>
<td>254 x 289</td>
</tr>
<tr>
<td><strong>Dimensions of one pixel (width x length) [µm²]</strong></td>
<td>172 x 172</td>
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<tr>
<td><strong>Read out time [ms]</strong></td>
<td>3.6 (frame rate 30Hz)</td>
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<tr>
<td><strong>Maximum count rate per channel [X-rays/s]</strong></td>
<td>&gt;1x10⁶</td>
</tr>
<tr>
<td><strong>Energy range [keV]</strong></td>
<td>3 - 30 keV (quantum efficiency: 3 keV 80%; 8 keV 99%; 15 keV 55%)</td>
</tr>
<tr>
<td><strong>Point-spread function</strong></td>
<td>1 pixel</td>
</tr>
</tbody>
</table>
Diffractometer ID22-ESRF
Diffractometer I11 - Diamond

- MACs
- Robotic arm
- Diffractometer
- PSD
- Large sample table
- Carousel (200 samples)
Diffractometer MS
Elettra – Sincrotrone Trieste
Synchrotron X-ray Powder Diffraction APPLICATIONS
MCX @ Elettra

Phase Identification

Structure Determination

Line Profile Analysis

Phase identification

- Cultural heritage: What materials did artists use centuries ago
- Chemistry: How is your reaction proceeding?
- Identification of minerals in geological samples
- Grade control of ores and rocks: for exploration of mineral deposits.
- Detection of polymorphs for the pharmaceutical industry.
- Quality control: determination of the presence of impurities in a pure phase. Detection of phase transitions under non-ambient conditions, such as variable temperature or humidity
- Forensics: phase identification can be a deciding factor in determining the origin of traces found at crime scenes.
- Corrosion in boilers and power plants: the phases found give valuable information about the conditions and reactions leading to problems
- Much more, but there is no more space on this page
Information from powder diffraction

![Graph showing powder diffraction peaks with 2 Theta values and counts.]

- Peaks labeled 110, 111, 200, 210, 211, 220, and 300.
- Counts on the y-axis range from 0 to 5000.
Information from powder diffraction

- The diffraction peak positions give information on the size and shape of the unit cell.

\[ \lambda = 2d \sin \theta \]

- The Intensity of a diffracted beam, \( I_{hkl} \) is related to an imaginary number called the structure factor, \( F_{hkl} \): \( I_{hkl} \propto |F_{hkl}|^2 \)

\[
F(hkl) = \sum_n f_n N_n e^{2\pi i (hx_n + ky_n + lz_n)} e^{-B\sin^2 \theta / \lambda}
\]

- The Intensity of a diffracted beam gives information on the positions of the atoms in the unit cell and hence the ‘atomic structure’ of the material

- The shape of the peak give information about the microstructure of the materials
Phase Analysis
Phase Analysis
Phase Analysis
Phase Analysis
Phase Analysis

![Graph showing phase analysis data]

Hands-on Software, IAEA - Trieste

J.R Plaisier, July 27th 2022
What is a powder?

- Crystalline
- Polycrystalline
- Amorphous
What is a powder?
An airplane is a powder! (more or less)
Objects of interest can be anything!
Data processing

- Background subtraction
- Smoothing
- Peak search
- Result: list of d’s and l’s
Databases

- **PDF-4+** 2022 contains 460,900+ entries. It combines the world’s largest sources of inorganic diffraction data from crystals and powders into a single database. The result is a comprehensive collection of inorganic materials, produced in a standardized format that can be rapidly searched for unknown phase identification. Extensive data mining is facilitated with 134 display fields coupled with 80 searches.

- **COD**: Open-access collection of crystal structures of organic, inorganic, metal-organic compounds and minerals, excluding biopolymers.
Search software

- **QualX2.0** (IC-CNR, Bari)
- **Sieve** (ICDD)
- **HighScore** (Malvern Pananalytical)
- **Match!** (Crystal Impact)
- **DIFFRAC.EVA** (Bruker)
- And others…
Search methods (Sieve)

- **Hanawalt**: Matches the eight most intense (strongest) d spacings of the reference pattern to the experimental data. This is an extension of the historic 1930’s algorithm that uses the 3 strongest lines.

- **Fink**: Matches the 8 longest and strongest lines. Sorts the most intense peaks by largest d-spacing. Originally developed in the 1950’s for identifying organic compounds and zeolites.

- **Long8**: Matches the eight longest d-spacings independent of intensity.

*A deep-learning technique for phase identification in multiphase inorganic compounds using synthetic XRD powder patterns*
Software in action
Software in action
Software in action
Phase identification - example

Basilica dei santi Giovanni e Paolo

XIII-XVI century
End XV large stained glass windows
Glass samples: Grisaille

- Low melting glass ($\text{SiO}_2$, $\text{PbO}$)
- Pigment (metal oxides)
- Paint medium (water, vinegar, oil)
- Firing to fuse the grisaille on the glass
Phase identification - example

SSGP1/2
SSGP2
SSGP3

SSGP1
SSGP2
SSGP3

IAEA - Trieste
Phase identification - example

\[ E = 9.4 \text{ keV} \]
\[ \lambda = 1.319 \text{Å} \]
Phase identification - example

Spinel
CoAl$_2$O$_4$
01-082-2422
Phase identification - example

Spinel
CoAl_2O_4
01-082-2422

Laurionite
PbCl(OH)
04-012-3672
Phase identification - example

- **Spinel**
  - CoAl$_2$O$_4$
  - 01-082-2422

- **Laurionite**
  - PbCl(OH)
  - 04-012-3672

- **Anglesite**
  - PbSO$_4$
  - 04-008-8386
Phase identification - example

**GRISAGLIA**

- CoAl$_2$O$_4$
- PbSO$_4$
- Pb(OH)Cl

**PATINA**

- Amorphous

**Pb$_2$Sb$_2$O$_7$; PbSO$_4$; CaSO$_4$(H$_2$O)$_2$; CaAl$_2$Si$_2$O$_8$$^{\text{GRISAGLIA}}$**

- FeO(OH); FeSO$_4$(OH)(H$_2$O)$_2$
- PbSO$_4$; CaSO$_4$(H$_2$O)$_2$
- Al$_2$Si$_2$O$_5$(OH)$_4$

**CoAl$_2$O$_4$; PbSO$_4$; CaPO$_3$( OH )$_2$H$_2$O $^{\text{GRISAGLIA}}$**

- SiO$_2$; PbS; PbSO$_4$
- CaCO$_3$ (vat)$_2$
- CaPO$_3$( OH )$_2$H$_2$O
Phase identification - example

- $\text{Pb}_2\text{Sb}_2\text{O}_7$ : original pigment

- $\text{SO}_4^{2-}$, $\text{S}^{2-}$, $\text{CO}_3^{2-}$ : alteration product seawater-aerosol, acid rain

- $\text{FeO(OH)}$; $\text{FeSO}_4(\text{OH})(\text{H}_2\text{O})_2$ : alteration product of original pigments

- $\text{CO}_3^{2-}$, $\text{PO}_3^{3-}$: biological origin

- $\text{CoAl}_2\text{O}_4$ : intervention at later date?
Operando battery studies

- Li batteries

Anode    Electolyte    Cathode

Li  Li+  Li+  Li+
Operando battery studies

- Li batteries

Anode  Electrolyte  Cathode

Li → Li⁺  e⁻  Li⁺  Li⁺  Li⁺  Li⁺
Operando battery studies

batteries

Li → Li⁺ → Li⁺ → Li⁺ → Li⁺

Anode  Electrolyte  Cathode

e⁻ →

Hands-on Software, IAEA - Trieste
Extended Limits of Reversible Electrochemical Lithiation of Crystalline V2O5

Lithiation of Crystalline $V_2O_5$/RGO

- Vanadium (V) oxide was suggested as an attractive host for electrochemical lithium yet in 1970s due to ability of multielectron redox in layered $V_2O_5$.

- Insertion of extremely high amounts of lithium (up to 3 moles per mole of oxide) is possible, however, it is believed that insertion/extraction of about 1.8 moles of Li$^+$ can enable sustainable cycling.
Lithiation of Crystalline $V_2O_5$/RGO

$V_2O_5 + xLi^+ + xe^- \rightleftharpoons Li_xV_2O_5 \quad (0 < x < 3)$
Lithiation of Crystalline $V_2O_5$/RGO

\[ \text{Lithiation of Crystalline } V_2O_5 / \text{RGO} \]
Operando battery studies on $V_2O_5/RGO$
Operando battery studies on $V_2O_5$/RGO

The experiment:

- Cathode: Airbrushed slurry of $V_2O_5$ (85%), RGO (10%) and PVDF (5%) on Al
- Anode: Lithium
- Electrolyte: 1 M LiClO$_4$ in PC/DME
- Wavelength 1.033 Angstrom
- 2θ range 8° to 35° with a 0.01° step
- 0.5 s/point acquisition
Operando battery studies on V$_2$O$_5$/RGO
Operando battery studies on $\text{V}_2\text{O}_5$/RGO

![Graphs and charts demonstrating operando battery studies on $\text{V}_2\text{O}_5$/RGO.](image-url)
Beyond the Oxygen Redox Strategy in Designing Cathode Material for Batteries: Dynamics of a Prussian Blue-like Cathode Revealed by Operando X-ray Diffraction and X-ray Absorption Fine Structure and by a Theoretical Approach

Angelo Mullaliu, Giuliana Aquilanti, Lorenzo Stievano, Paolo Conti, Jasper Plaisier, Sylvain Cristol, Marco Giorgetti
Prussian Blue Analogues: CuNP

Copper nitroprusside (CuNP), Cu[Fe(CN)$_5$(NO)]
The experiment:

- Cathode: CuNP (70%), carbon black (10%), vapor-grown carbon fibers-high density (10%) and PTFE (10%)
- Anode: Lithium
- Electrolyte: 1 M LiPF$_6$ in EC/DC
- Wavelength 1 Angstrom
- 2θ range 10° to 30° with a 0.01° step
- 0.5 s/point acquisition
- Discharge to 1.8 V versus Li$^+$/Li and subsequent charge to 3.5 V versus Li$^+$/Li at C/22 current rate
Operando battery studies: CuNP
Operando battery studies: CuNP
**Operando battery studies: CuNP**

![Graph showing changes in lattice parameters with Li content](image)

**a dimension**

- **Lattice parameter / Å** vs. **Li / equivalents**
- Data points showing a decrease in lattice parameter with increasing Li content.

**c dimension**

- **Lattice parameter / Å** vs. **Li / equivalents**
- Data points showing an increase in lattice parameter with increasing Li content.

+ Li
**Operando XRD on batteries**

![XRD diagram with labels for anode, electrolyte, and cathode]

**Titanium-based potassium-ion battery positive electrode with extraordinarily high redox potential**
*Nature Communications* 11, pp. 1484 2020
Information from powder diffraction

• The diffraction peak positions give information on the size and shape of the unit cell.

\[ \lambda = 2d \sin \theta \]

• The Intensity of a diffracted beam, \( I_{hkl} \) is related to an imaginary number called the structure factor, \( F_{hkl} \):

\[ I_{hkl} \propto |F_{hkl}|^2 \]

\[ F(hkl) = \sum_n f_n N_n e^{2\pi i (hx_n + ky_n + lz_n)} e^{-B \sin^2 \theta / \lambda} \]

• The Intensity of a diffracted beam gives information on the positions of the atoms in the unit cell and hence the ‘atomic structure’ of the material

• The shape of the peak give information about the microstructure of the materials
Structure determination in non ambient conditions
Structure determination in non ambient conditions
Furnace Design

In situ reaction furnace for real-time XRD studies
Riello P., Lausi A., MacLeod J., Plaisier J.R., Zerauschek G., Fornasiero P.
2D-3D transition
In Cu–TiS$_2$ system

• Phase transitions between 2D (layered) and 3D (cubic) phases in Cu$_x$TiS$_2$ ($x = 0-0.5$) intercalation compounds have been studied \textit{in situ} by the X-ray diffraction technique in the temperature range 20–1000 °C.

• The discovery of CDW (charge density wave) quantum states and superconductivity in the Cu–TiSe$_2$ system arouses interest to isostructural materials, but known phase transformations to the spinel structure make comparison difficult.

• Samples were prepared by intercalation of Cu at room temperature. All samples had the layered hexagonal structure.

2D-3D transition in Cu–TiS$_2$ system
Shkvarina EG, Titov AA, Doroschek AA, Shkvarin AS, Starichenko DV, Plaisier JR, Gigli L, Titov AN.
\textit{The Journal of Chemical Physics} 147, 044712 (2017)
2D-3D transition
In Cu–TiS$_2$ system
2D-3D transition
In Cu–TiS$_2$ system
2D-3D transition
In Cu–TiS$_2$ system
2D-3D transition
In Cu–TiS$_2$ system

<table>
<thead>
<tr>
<th>T ($^\circ$C)</th>
<th>1T layered phase</th>
<th>Cubic spinel phase</th>
<th>$R^2$ (%)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu$_{0.2}$TiS$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>206</td>
<td>3.4269(1) 5.8106(2) 0.2438(5) 0.198(2) ...</td>
<td>...</td>
<td>5.96</td>
<td>1.880</td>
</tr>
<tr>
<td>320</td>
<td>3.4331(1) 5.8252(2) 0.2452(5) 0.195(2) ...</td>
<td>...</td>
<td>6.44</td>
<td>1.688</td>
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<tr>
<td>451</td>
<td>3.4401(1) 5.8037(2) 0.2593(8) 0.064(2) ...</td>
<td>0.005(3)</td>
<td>9.9816(4) 0.763(8) 0.2502(5)</td>
<td>3.90</td>
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<tr>
<td>483</td>
<td>3.4405(1) 5.7942(3) 0.249(1) 0.059(3) ...</td>
<td>...</td>
<td>9.9631(3) 0.611(5) 0.2526(3)</td>
<td>2.89</td>
</tr>
<tr>
<td>514</td>
<td>3.4421(1) 5.7937(3) 0.253(1) 0.045(3) ...</td>
<td>0.017(4)</td>
<td>9.9592(2) 0.564(4) 0.2530(2)</td>
<td>3.18</td>
</tr>
<tr>
<td>546</td>
<td>3.4441(1) 5.7982(4) 0.260(1) 0.030(4) ...</td>
<td>0.018(5)</td>
<td>9.9604(2) 0.521(3) 0.2529(3)</td>
<td>2.78</td>
</tr>
<tr>
<td>600</td>
<td>3.4482(1) 5.8083(4) 0.243(1) 0.005(3) ...</td>
<td>0.074(6)</td>
<td>9.9642(1) 0.512(3) 0.2536(2)</td>
<td>4.55</td>
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<td>637</td>
<td>3.4498(1) 5.8133(4) 0.249(1) 0.038(3) ...</td>
<td>0.018(5)</td>
<td>9.9660(1) 0.503(3) 0.2532(1)</td>
<td>1.86</td>
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<tr>
<td>735</td>
<td>3.4543(1) 5.8365(4) 0.246(1) 0.057(3) 0.45(3) 0.013(2) ...</td>
<td>0.020(5)</td>
<td>9.9726(1) 0.467(3) 0.2538(2)</td>
<td>2.89</td>
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<td>828</td>
<td>3.4603(1) 5.8677(3) 0.243(1) 0.032(3) 0.454(7) 0.037(2) ...</td>
<td>0.029(4)</td>
<td>9.9846(1) 0.474(3) 0.2536(2)</td>
<td>2.72</td>
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<tr>
<td>874</td>
<td>3.4626(1) 5.8881(2) 0.240(1) 0.040(2) 0.431(6) 0.041(2) ...</td>
<td>0.031(4)</td>
<td>9.9908(1) 0.498(4) 0.2535(2)</td>
<td>2.92</td>
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<tr>
<td>918</td>
<td>3.4654(1) 5.9051(3) 0.239(1) 0.060(2) 0.445(8) 0.032(2) ...</td>
<td>0.001(4)</td>
<td>9.9662(4) 0.533(6) 0.2540(3)</td>
<td>4.12</td>
</tr>
</tbody>
</table>

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<tr>
<td></td>
<td>Cu$_{0.1}$TiS$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>525</td>
<td>3.4422(1) 5.7990(2) 0.2460(6) 0.044(2) 0.35(2) 0.013(2) ...</td>
<td>0.024(3)</td>
<td>9.9701(8) 0.66(2) 0.2547(8)</td>
<td>8.16</td>
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<tr>
<td>647</td>
<td>3.4494(1) 5.8129(2) 0.2448(6) 0.038(2) 0.37(2) 0.015(2) ...</td>
<td>0.023(4)</td>
<td>9.9690(4) 0.50(2) 0.2544(6)</td>
<td>7.05</td>
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<tr>
<td>918</td>
<td>3.4650(1) 5.8691(2) 0.2428(7) 0.055(2) 0.42(2) 0.020(3) ...</td>
<td>0.002(4)</td>
<td>...</td>
<td>...</td>
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<tr>
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<tr>
<td></td>
<td>Cu$_{0.25}$TiS$_2$</td>
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<td></td>
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<tr>
<td>918</td>
<td>3.4664(2) 5.9140(8) 0.236(2) 0.009(6) 0.46(1) 0.052(4) ...</td>
<td>10.0075(1) 0.512(4) 0.2531(2)</td>
<td>6.42</td>
<td>10.81</td>
</tr>
</tbody>
</table>
2D-3D transition
In Cu–TiS$_2$ system
2D-3D transition
In Cu–TiS$_2$ system
2D-3D transition
In Cu–TiS$_2$ system
2D-3D transition
In Cu–TiS$_2$ system

• It has been found that the stability of the layered phase is
determined by the distribution of copper atoms between the
octahedral and tetrahedral crystallographic sites.

• The occupation of octahedral sites dominates at low
temperatures.

• Upon heating, tetrahedral site occupation is limited and the
layered phase becomes unstable and transforms to the spinel.

• Further heating allows the distribution of copper between
octahedral and tetrahedral sites; the layered phase becomes
stable again.
Information from powder diffraction

- The diffraction peak positions give information on the size and shape of the unit cell.
  \[ \lambda = 2d \sin \theta \]

- The Intensity of a diffracted beam, \( I_{hkl} \) is related to an imaginary number called the structure factor, \( F_{hkl} : I_{hkl} \propto |F_{hkl}|^2 \)

\[ F(hkl) = \sum_{n} f_n N_n e^{2\pi i (hx_n + ky_n + lz_n)} e^{-B \sin^2 \theta / \lambda} \]

- The Intensity of a diffracted beam gives information on the positions of the atoms in the unit cell and hence the ‘atomic structure’ of the material

- The shape of the peak give information about the microstructure of the materials
Diffraction for stress analysis

- The stresses in a material are the sum of the contributions from any externally applied load (applied stress) and those arising from the interactions between individual grains or components that are not completely relaxed when no external load is present (residual stresses).

- Stresses lead to deformation, the distances between lattice planes changes in the direction where stress is present.

- Measuring how the peak position (related to the lattice plane distance by braggs law) changes, at different orientations of the sample gives us information on the amount of stress
Diffraction for stress analysis

- Not being aware of residual tensile stresses, that make materials weaker can have disastrous consequences in construction for example:

Residual stress is often a cause of premature failure of critical components, and was one factor in the collapse of the suspension bridge at Silver Bridge in West Virginia in December 1967. The eyebar links were castings which showed high levels of residual stress, which in one eyebar, encouraged crack growth. When the crack reached a critical size, it grew catastrophically, and from that moment, the whole structure started to fail in a chain reaction. Because the structure failed in less than a minute, 46 drivers and passengers in cars on the bridge at the time were killed.
Diffraction for stress analysis

- On the other hand residual stresses may be induced in materials on purpose. Compressive residual stress maybe induced in order to strengthen it and increase its fatigue life.

- A material in tensile stress is closer to the situation of cracking, whereas in compressive stress the material is further away from cracking than the unstressed material and therefore stronger.
It is strain that is actually measured: $\Delta d/d_0$

Residual strain changes interplanar spacings, which shifts the positions of diffraction peaks.

Strain is resolved differently in different physical directions in the sample.

Engineering materials are polycrystalline, so some grains are always oriented to diffract enabling stress tensors to be determined.
Diffraction for stress analysis

- When the d-spacing of a reflection is measured, only grains with the planes oriented in a given direction contribute to diffraction. If we change the orientation of the specimen and remeasure the d-spacing we are looking at a different population of grains and we get a different d-spacing due to different stress levels.
Alloys of aluminium used in the airplane industry were measured to see the effectiveness of laser peening around a hole.
Diffraction for stress analysis
- The same diffraction peak is measured for different orientations of the sample
Diffraction for stress analysis

- The position of the diffraction peak is determined for each orientation (d)
Diffraction for stress analysis

- D is plotted vs. $\sin^2 \psi$ and from the slope the stress can be calculated. In this example the stress is compressive.
**Diffraction for stress analysis**

- The result showed that laser peening after drilling the hole actually weakens the material, whereas first applying laser peening and subsequently drilling the hole results in a stringer material.
Information from powder diffraction

- The diffraction peak positions give information on the size and shape of the unit cell.
  \[ \lambda = 2d \sin \theta \]

- The Intensity of a diffracted beam, \( I_{hkl} \) is related to an imaginary number called the structure factor, \( F_{hkl} \):
  \[ I_{hkl} \propto |F_{hkl}|^2 \]

- The Intensity of a diffracted beam gives information on the positions of the atoms in the unit cell and hence the ‘atomic structure’ of the material

- The shape of the peak give information about the microstructure of the materials

\[ F(hkl) = \sum_{n} f_n N_n e^{2\pi i(hx_n+kyn+lzn)} e^{-B \sin^2 \theta / \lambda} \]
Line profile analysis - example

- Correlation between microstructure and bioequivalence in Anti-HIV Drug Efavirenz, C. Fandaruff et al., *European Journal of Pharmaceutics and Biopharmaceutics* 91, 52-58 (2015)
Polymorphism and particle size distribution can impact the dissolution behaviour and, as a consequence, bioavailability and bioequivalence of poorly soluble drugs, such as Efavirenz (EFV).

The aim of this work was to study microstructure, a solid-state property of current interest in the pharmaceutical area, in order to find an explanation for the dissolution and bioequivalence behaviour.

The microstructure of EFV raw materials was studied by Whole Powder Pattern Modelling (WPPM) of X-ray powder diffraction data.
Line profile analysis - example
Line profile analysis - example
Line profile analysis - example

![Graph showing line profile analysis example]

Frequency

D (nm)

BIOEQUIVALENT

NON-BIOEQUIVALENT

Batch 1, Batch 4
Batch 2, Batch 5
Batch 3, Batch 6
Line profile analysis - example

Crystalline Domain Size Distribution of efavirenz

Dissolution Efficiency (%) vs. Average crystalline domain size <D> (nm)
Thank you!