Inorganic materials chemistry and functional materials

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Lectures at CUTN spring 2016
X-ray diffraction and structure analysis
X-ray diffraction; methods and analyses

The powder X-ray diffraction pattern

- Diffraction peak
- Intensity (relative)
- Position (2\(\Theta\), d)
- Peak profile (width)

Diagram showing a diffraction pattern with axes labeled as follows:
- Lin (Counts)
- 2-Theta - Scale
- background
- 2-Theta - Scale
Characteristic features of the pattern

**Diffraction peaks**
- Intensities
- Position (2\(\theta\) \(\rightarrow\) d-values; Braggs law)
- Profile (width FWHM; Gaussian & Lorentzian contributions)
- Due to ONE or MORE crystalline phases

**Background**
- Caused by diffuse scattering etc
- Caused by fluorescence
- Caused by sample holder (capillary); sample prep.
- Caused by amorphous impurities
Information to be analyzed/extracted

• Intensities
  – Presence/absence $\rightarrow$ symmetry (space group)
  – Atomic arrangement = crystal structure; coordinates
  – Preferred orientation of crystallites

• Position ($2\Theta \rightarrow d$-values; Braggs law)
  – Unit cell dimensions

• Profile (width FWHM; Gaussian & Lorentzian)
  – Particle size, strain, stacking disorder

• Intensity+position
  – Phase identification; qualitative + quantitative analysis
  – Crystal structure
Information from powder diffraction

• It is a **fingerprint** of a crystalline compound (or mixtures)
  → phase identification
  → can be used for quantitative phase analysis
• It provides information on the unit cell (crystal system; size)
  → useful for evaluation of doping/substitutions/solid solubility
• It provides information of the atomic arrangement
  → can be used to refine atomic coordinates of a partly known crystal structure
  → can be used to solve an unknown crystal structure
It provides information on particle size, strain, disorder,....
Phase ID and quantification from powder

X-ray diffraction; methods and analyses

example

Silicon 5.51 %
KCl 8.75 %
Apatite-(CaOH) 34.31 %
Arcanite 15.06 %
Calcite 31.55 %
Quartz low 0.87 %
Periclase 3.96 %
State of the sample?

- Amorphous
- Crystalline (repeating atomic arrangement in 3D) (inorganic, organic, biomaterials,...)
- Single crystals
- Powder samples (micron sized particles)
- Nanomaterials (particles, colloids,...)
- Thin films (multilayers, heterostructures)
- Multiphased (composites)
- ...........
Monodisperse Pt-Rh nanoparticles

Small Spheres
mol PVP / mol Precursors = 0.28
900 W, 5 min
DMF, PVP 0.8 gr
mean: 3.3 nm
SD: 0.79

Truncated Cubes
mol PVP / mol Precursors = 0.14
900 W, 5 min
DMF, PVP 0.4 gr
mean: 6.4 nm
SD: 1.1

Dr. M. Kalyva, NAFUMA group
Single crystals

Single crystallites = single crystals; but can be extremely small
OK for electron diffraction (very short wave length)

Larger single crystals;
may ”consist of more” → mosaicity
may consist of twinned crystals (rooted in the symmetry)

Suitable size for home laboratory: some 50 micron and upwards
Suitable size at synchrotron: a few microns and upwards
Thin films and multilayers

- Fe₂O₃ ca 20 nm
- NiTiO₃ ca 12 nm
- Fe₂O₃ ca 20 nm
- NiTiO₃ ca 12 nm
- Fe₂O₃ ca 20 nm

Substrate – Si(100)  JB1044

BF image
EFTEM images

Ni
Fe
Ti
$n \lambda = 2d_{hkl} \sin \theta$

Data collection

The sample

Theory and tools

Results

structure, composition, morphology

Crystal structure
Incident X-rays

SPECIMEN

Fluorescent X-rays

Scattered X-rays

Coherent
From bound charges

Incoherent (Compton modified)
From loosely bound charges

Electrons

Compton recoil
Photoelectrons

Transmitted beam

X-rays can in addition be refracted and also reflected
Principle of X-ray tube (home lab)

- Electrons are emitted by heated cathode and accelerated towards anode.
- They hit the anode which leads to
  - Creation of white radiation (Bremsstrahlung).
  - Emission of characteristic radiation (cf anode material)
  - Heat evolution (98-99% of the total energy!).
  - Hence; cooling by water....
X-ray diffraction; methods and analyses

X-ray diffraction; methods and analyses

Depends on machine and optical elements (magnets)

**A broad range of wavelengths/energies available**
Selected by monochromators

Allows experiments with fixed wavelength (typically for diffraction)
Allows spectroscopy over selected energy ranges

Hard X-rays: for diffraction/scattering, spectroscopy, imaging...
Soft X-rays: for spectroscopy,...
X-ray diffraction; methods and analyses

- Spectrum consists of both white (continuous) radiation and characteristic radiation.

- **Target for use:** the strong $K\alpha$.

- In some cases are $K\alpha_1$ and $K\alpha_2$ overlapping (not resolved). A diffraction experiment can then result in only one single peak. Otherwise partly splitted peaks will be observed.

- The weaker $K\alpha_2$-radiation can be removed by means of a primary monochromator

  (a single crystal of e.g. Ge)
Characteristic radiation

An electron is first kicked out from the inner level

This hole is then filled by an outer electron (L, M shell); and light (X-rays) are emitted

\[ L \rightarrow K \quad K\alpha \quad (2p \rightarrow 1s) \]
\[ M \rightarrow K \quad K\beta \quad (3p \rightarrow 1s) \]

The energy difference depends on the element!

→ Wavelength depends on type of filament in the X-ray tube
X-ray radiation: hazards

The effect of ionizing radiation on living tissue is more closely related to the amount of energy deposited \( \rightarrow \) Absorbed dose

Medical purposes
Mammography

<table>
<thead>
<tr>
<th>Anode material</th>
<th>Atomic number</th>
<th>Photon energy [keV]</th>
<th>Wavelength [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( K_{\alpha 1} )</td>
<td>( K_{\beta 1} )</td>
</tr>
<tr>
<td>W</td>
<td>74</td>
<td>59.3</td>
<td>67.2</td>
</tr>
<tr>
<td>Mo</td>
<td>42</td>
<td>17.5</td>
<td>19.6</td>
</tr>
<tr>
<td>Cu</td>
<td>29</td>
<td>8.05</td>
<td>8.91</td>
</tr>
<tr>
<td>Ag</td>
<td>47</td>
<td>22.2</td>
<td>24.9</td>
</tr>
<tr>
<td>Ga</td>
<td>31</td>
<td>9.25</td>
<td>10.26</td>
</tr>
<tr>
<td>In</td>
<td>49</td>
<td>24.2</td>
<td>27.3</td>
</tr>
</tbody>
</table>

UiO lab: No warning sign for ionizing radiation = safe lab
Bragg’s law

\[ BD = d \sin \theta \quad DC = d \sin \theta \Rightarrow BDC = 2d \sin \theta = n\lambda \]

\[ n\lambda = 2d_{hkl} \sin \theta \]
If Bragg’s eq. is NOT satisfied then NO diffraction can occur
If Bragg’s eq. is satisfied then diffraction MAY occur

Diffraction = Reinforced Coherent Scattering

Reflection versus Scattering

<table>
<thead>
<tr>
<th>Reflection</th>
<th>Diffraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Occurs from surface</td>
<td>Occurs throughout the bulk</td>
</tr>
<tr>
<td>Takes place at any angle</td>
<td>Takes place only at Bragg angles</td>
</tr>
<tr>
<td>~100 % of the intensity may be reflected</td>
<td>Small fraction of intensity is diffracted</td>
</tr>
</tbody>
</table>

X-rays can be reflected at very small angles of incidence; → X-ray reflectometry
X-ray diffraction; methods and analyses

Peak Positions: Miller Indices (hkl)

Intensity

2 Theta (Degrees)

(111) / d = 3.26Å
(200) / d = 2.82Å
(220) / d = 1.99Å
(311) / d = 1.70Å
(400) / d = 1.41Å
→ Gives rise to height error (shift in observed Bragg positions) And may after analyses yield incorrect unit cell dimensions → Hence; height correction must (always) be carried out → Helpful; use of internal standard for calibration
X-ray diffraction; methods and analyses

- Structure factor (F) → Scattering from atoms in the unit cell; coordinates
- Occupation number → Site occupancy for atoms in the unit cell
- Displacement factor → Dynamics of atoms; static displacements
- (hkl) multiplicity → Number of equivalent scattering planes
- Polarization factor → Effect of wave polarization; instrument dependent
  \[ I_P = (1 + \cos^2(2\theta)) \]
- Lorentz factor → Combination of three geometric factors
  \[ \text{Lorentz factor} = \left(\frac{1}{\sin 2\theta}\right)(\cos \theta)\left(\frac{1}{\sin 2\theta}\right) \]
- Absorption factor → Specimen absorption; element dependent
Absorption

- Intensity loss due to sample absorbing the x-ray beam
- Wavelength dependent
- Sample and geometry dependent
- For flat plate absorption is a linear function
- For cylindrical sample/Debye-Scherrer transmission geometry there is angular dependence

- For transmission geometry: the absorption should be calculated prior to data collection, and if needed, the sample should be diluted
Attenuation (loosing intensity) through collisions with atoms

\[ dI = -\mu I \cdot dt \]
\[ I = I_0 \cdot e^{-\mu t} \]

- \( \mu \) linear absorption coefficient [cm\(^{-1}\)]
- dt thickness

Mass absorption coefficient \( \mu_m \)

\[ \mu = \mu_m \rho \]

\[ \mu = \rho \sum P_i(\mu_{mi}) \]

\( \rho = \text{density} \)

If the absorbing sample consists of more elements:

\( P = \text{weight fraction of the relevant element} \)
Radiation with low energy (high $\lambda$) is heavily absorbed

$\Rightarrow$ *Soft radiation (low energy) will not penetrate absorbing samples*

Radiation with higher energy is absorbed less

$\Rightarrow$ *Hard radiation is then useful*

**Home lab:** Energy defined by the type of X-ray tube

**Synchrotron:** all wavelengths available
Linear absorption coefficient $\mu$

- $\mu$ depends on wavelength and sample
- $\mu$ increases with increasing $\lambda$ (i.e. lower energy)
- $\mu$ is discontinuous (due to absorption edges)
- Absorption is at maximum at a slightly lower $\lambda$ (higher E) than the absorption edge
- For medium heavy elements, the K-absorption edge is in the range of commonly used $\lambda$ for X-ray diffraction experiments
- For heavy atoms, K-electrons are hardly excited and hence $\Rightarrow$ L-edge is more important with respect to absorption of home-lab X-rays
Compute X-ray Absorption

Select X-ray Wavelength or Energy: (click for details)
Wavelength (Å) ▼ 0.41

Chemical Formula: (click for details)
Enter using element chemical symbol and formula unit occupancy, e.g. YBa2Cu3O6.5 (proper capitalization is required)

Sample Radius: (click for details)
0.40 capillary radius in mm

Sample Density or Packing Fraction (click for details)
Enter measured sample density or estimated packing fraction (often ~0.6)
Packed Fraction (0.0 - 1.0) ▼ 0.5

Compute  Clear Form

About: This routine estimates capillary sample absorption for transmission geometry (Debye-Scherrer) powder X-ray diffraction measurements. (click here for more information)

Web utility created by Robert B. Von Dreele, Matthew R. Suchomel and Brian H. Toby, based on the python software package Absorb (download here).

» Return to 11-BM X-ray absorption webpage

New feature: define your own custom absorb.php bookmark with default wavelength settings (or sample radius etc).
Example: try the URL http://11bm.xray.aps.anl.gov/absorb/absorb.php?spectrum=1.54&radius=0.5&density=1.0

Last Modified: Feb 2013
Argonne web-page; help to calculate absorption and dilution of sample with an inert

How to reduce absorption (in transmission geometry):

Sample dilution by mixing in:
Silica (will enhance amorphous background)
MgO; a few additional peaks; well-defined, easy to analyse
KCl: a few additional peaks + increased absorption

Just use a smaller capillary; ...
Uneven particle distribution
Poor capillary filling
Fluorescence

Fluorescence by Co compared to Ni when using CuKa1 radiation
Fluorescence reduces the signal-to-noise ratio
Can be filtered electronically in many cases
Alternatively: use a different energy for the X-ray radiation
Fluorescence

Emission of characteristic fluorescent x-rays

Emitted in all directions

Incoming X-rays

Emission of characteristic fluorescent x-rays

Emitted in all directions

Electron kicked out from inner shell

Vacuum level

Energy levels

$E_{L_3}$  $E_{L_2}$  $E_{L_1}$  $E_K$

$L_3$  $L_2$  $L_1$  $K$
Fluorescence occurs when electrons are excited to high energy states by incoming X-rays.

As the electrons return to their normal energy levels, energy is given out as fluorescence.

Lower energy than the incident X-rays.

Co Kα transition (6.9 KeV) is just below Cu Kα (8 KeV).

- Easily excited by Cu radiation.

Fe Kα (6.4 KeV) is also excited by Cu radiation.
Fluorescence

- Atoms in an excited state generated by absorption of X-rays, may emit characteristic radiation by outer electrons falling into vacant inner orbitals.
- Fluorescence has always lower energy (longer wavelength) than the exciting (incoming) X-ray radiation.
- Atoms are excited more strongly by radiation with wavelength close to the absorption edge.
- Fluorescence radiation is the basis for X-ray fluorescence spectrometry (XRF).

NB! For X-ray diffraction fluorescence is a nuisance and experimental conditions should be selected so as to minimize its impact.
Systematic absences (systematic extinctions) arise when symmetry elements containing translational components are present:
- Lattice centering
- Screw axes
- Glide planes

Specific rules can be identified and applied – for determining likely space group, based on the observed diffraction pattern.
Peak Intensities

- Many variables, some instrumental, some **sample dependent**
  - Instrument geometry and optics (transmission, reflection)
  - Radiation choice (\(\lambda\) in the Bragg equation)
  - Lorentz polarisation

- **Sample (crystal structure & symmetry)**
  - Atom type and position in the structure (scattering and structure factors)
  - Occupation number - Site multiplicity (from space group)
  - Thermal displacement parameters
  - Absorption
  - Fluorescence (background; signal-to-noise)

- Sample preparation
  - Poor preparation gives poor data!
  - Preferred orientation
  - Particle size (nanopowders)
Ray $R_3$ reflects from atoms in positions within the unit cell. Ray $R_1$ hits the corner atom $A$ of the unit cell.

In 3D one obtains $\phi = 2\pi(hx' + ky' + hz')$
The sum of all waves scattered by all atoms in the unit cells has a resultant
amplitude which depends on the scattering plane \((hkl)\).

The resultant unit cell scattering factor is termed the **Structure Factor** \((F)\).

When summarizing the scattering amplitudes for all atoms, these must be
weighed by the respective atomic scattering factors \((f)\), which strongly depends
on \(nb\) of electrons in the X-ray scattering case.

\[
F_{n}^{hkl} = \sum_{j=1}^{n} f_{j} e^{i\varphi_{j}} = \sum_{j=1}^{n} f_{j} e^{i[2\pi(hx'+ky'+hz')]}
\]

\[
F = \text{Structure Factor} = \frac{\text{Amplitude of wave scattered by all atoms in unit cell}}{\text{Amplitude of wave scattered by an electron}}
\]

**Diffraction intensity** \(I \propto F^2\)

**Note:**
The structure factor depends on atomic coordinates \((x,y,z)\), type of atoms (atomic
scattering factor), site occupancy, BUT independent of *shape* and *size* of unit cell \((a,b,c)\)
Using the **structure factor** to evaluate **systematic extinctions** for a body centered orthorhombic (I) structure

$$F = f_j e^{i\varphi_j} = f_j e^{i[2\pi(\mathbf{x}_j' + \mathbf{y}_j' + \mathbf{z}_j')]}$$

Bravais lattice \((0,0,0) + (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\); (plus any motif \((x_i, y_i, z_i)\))

$$F_{n}^{hkl} = \sum_{j=1}^{n} f_j e^{i\varphi_j} = \sum_{j=1}^{n} f_j e^{i[2\pi(h x_j'+k y_j'+h z_j')]}$$

Now summarizing over (just) the two atoms at \((0,0,0)\) and \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\):

$$F = f e^{i[2\pi(h\cdot0 + k\cdot0 + h\cdot0)]} + f e^{i[2\pi(h\cdot\frac{1}{2} + k\cdot\frac{1}{2} + h\cdot\frac{1}{2})]}$$

$$= f e^{0} + f e^{i[2\pi \frac{h+k+l}{2}]} = f[1 + e^{i\pi(h+k+l)}]$$

**Note:**

\(e^{n\pi}\)

- = -1 for \(n\) odd
- = +1 for \(n\) even

For \((h+k+l)\) odd, \(F = 0\) and \(I = F^2 = 0\); *e.g.* \((100), (001), (111); (210), (032), (133) will be systematically absent (extinctions)

Whereas, for \((h+k+l)\) even, \(F = 2f\) and \(I = F^2 = 4f^2\), and Bragg reflections like \((110), (200), (211); (220), (022), (310)\) are allowed (have non-zero intensities)
X-ray diffraction; methods and analyses

**Body-centered cubic (bcc)**

Simple cubic lattice with vectors $a_x$, $a_y$, $a_z$. Basis (atoms) at $r_0 = 0$ and $r_1 = (1/2)(a_x, a_y, a_z)$. In such a monatomic crystal, all the form factors $f$ are identical.

The diffracted intensity for a scattering vector $\mathbf{K} = h\hat{x} + k\hat{y} + l\hat{z} = (2\pi/a)(h\hat{x} + k\hat{y} + l\hat{z})$ with respect to the crystal plane $(hkl)$ is

$$F_{\mathbf{K}} = f \left[ e^{-i\mathbf{K}\cdot\mathbf{r}_0} + e^{-i\mathbf{K}\cdot(a/2)(\hat{x}+\hat{y}+\hat{z})} \right]$$

$$= f \left[ 1 + e^{-i\mathbf{K}\cdot(a/2)(\hat{x}+\hat{y}+\hat{z})} \right]$$

$$= f \left[ 1 + e^{-i\pi(h+k+l)} \right]$$

$$= f \left[ 1 + (-1)^{h+k+l} \right]$$

$$F_{hkl} = \begin{cases} 2f, & h + k + l \text{ even} \\ 0, & h + k + l \text{ odd} \end{cases}$$

A requirement for a reflection to appear in the diffraction pattern of a body-centered crystal, is that the sum of the Miller indices $(hkl)$ must be even. If the sum is an odd number, the intensity is zero due to destructive interference.

**Systematic extinction**

This rule applies to all I-centered structures!

Hence, the first diffraction peak to be observed in a powder diffraction pattern will be (110) followed by (200) and (211).
For two-fold screw axes, rules for systematic absences are

For this symmetry operator certain intensities will cancel (become zero).

Consider the structure factor

\[ F = f \cos 2\pi (hx + ky + lz) + f \cos 2\pi (-hx - ky + l [(1/2) + z]) \]

Taking into account \( \cos a + \cos b = 2 \cos (a+b)/2 \cos (a-b)/2 \), we obtain

\[ F = 2f \cos \pi (2lz + l/2) \cos \pi (2hx + 2ky - l/2) \]

This vanishes \( (F=0) \) for \( hkl \) reflections with \( h=0, \ k=0 \) and \( l=2n+1 \).

This defines the systematic absences owing to the given screw axis. We may observe intensity for reflections of type \( 00l \) with \( l=2n \), but not for \( l=2n+1 \).

<table>
<thead>
<tr>
<th>2(_1)[100]</th>
<th>h00</th>
<th>h = 2n</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(_1)[010]</td>
<td>0k0</td>
<td>k = 2n</td>
</tr>
<tr>
<td>2(_1)[001]</td>
<td>00l</td>
<td>l = 2n</td>
</tr>
</tbody>
</table>
# Extinction Rules; lattices

<table>
<thead>
<tr>
<th>Bravais lattice</th>
<th>Reflections that <em>may be</em> present (allowed)</th>
<th>Systematic absences</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primitive (P)</td>
<td>all</td>
<td>None</td>
</tr>
<tr>
<td>Body centred (I)</td>
<td>(h + k + l) even</td>
<td>(h + k + l) odd</td>
</tr>
<tr>
<td>Face centred (F)</td>
<td>h, k, l all even /all odd</td>
<td>h, k, l mixed odd/even</td>
</tr>
<tr>
<td>Side centred (A,B,C)</td>
<td>h + k even</td>
<td>h + k odd</td>
</tr>
<tr>
<td></td>
<td>C centred</td>
<td>C centred</td>
</tr>
</tbody>
</table>

**Additional Extinction Rules;**

Translations: screw axis / glide planes
Peak Intensities

- Many variables, some instrumental, some **sample dependent**
  - Instrument geometry and optics (transmission, reflection)
  - Radiation choice ($\lambda$ in the Bragg equation)
  - Lorentz polarisation

- **Sample** (**crystal structure & symmetry**)
  - Atom type and position in the structure (scattering and structure factors)
  - Occupation number - Site multiplicity (from space group)
  - Thermal displacement parameters
  - Absorption
  - Fluorescence (background; signal-to-noise)

- Sample preparation
  - Poor preparation gives poor data!
  - Preferred orientation
  - Particle size (nanopowders)
Atomic Scattering Factors (form factors, $f$)

- Each atom has a characteristic scattering curve for the radiation used, therefore the scattering strength is usually plotted against $\sin \theta / \lambda$
- The scattering factor decreases with $\theta$
- Scattering increases with atomic number because X-rays are scattered by electrons
- Highly relevant for magnetic scattering when neutrons are used (the magnetic reflections will hence have higher intensities at low angles.)
Thermal Displacement Parameters

- "temperature factors" and "Debye-Waller factors"
- Describe (ideally) the thermal \textit{dynamics} of the atoms
- Difficult to determine due to correlation with background (especially at high diffraction angles), site occupancy, absorption
- Also \textit{static} disorder/displacement may show up as an enhanced displacement parameter
Before experiment: what does my sample contain?

- Just light elements?
- A lot of heavy elements?
- Certain transition elements that may give a lot of fluorescence scattering if Cu-X-rays are used?
- Regular particles, or platelets or needles
- (impurities; amorphous stuff,....)

- Necessary for optimizing the experiment
- Transmission (light elements) vs reflection (heavy)
- Choice of radiation (wavelength)
- Means to reduce preferred orientation
Sample Preparation

- Essential for reliable PXRD data!
- Bad sample preparation can lead to:
  - Incorrect peak positions
  - Bad peak shapes
  - Incorrect intensities
- 5 minutes of sample preparation can save hours of work identifying and fitting phases from bad data!
Sample Preparation

- Sample holder must be full, with powder homogeneously packed
- Top of sample must be flat and level with sample holder

"Powder Valley"
- Wrong peak positions
- Wrong peak intensities
- Broad/double peaks

"Powder Mountain"
- Wrong peak positions
- Wrong peak intensities
- Wrong peak shapes

Correct preparation
Correct peak positions
Correct peak intensities
Sharp peaks
Sample preparation

X-ray diffraction; methods and analyses

Correct

Powder valley

Powder mountain
Preferred orientation issues becomes important when crystallization gives: **needles or platelike crystallites**

When preparing a sample for powder X-ray diffraction, it then becomes difficult to distribute the sample in such a way that all crystal planes are randomly distributed in space.

→ the diffraction pattern is hence reflecting the orientation of the crystallites; results in preferred orientation effects

→ gives systematic enhancement/weakening of certain \( I(hkl) \)

→ May sometimes be helpful to grind the material along with an inert standard.

One may also observe other effects; e.g.
- width of diffraction peaks may vary
Peak Intensity: Preferred Orientation

- Random distribution of crystallites is assumed for powder diffraction
- But real crystallites can have shapes which do not lend themselves to this!
- E.g. mica flakes; tend to lie flat on plate sample holders
Peak Intensity: Preferred Orientation

- Preferred orientation can lead to changes in peak intensity as certain orientations are under represented in the sample.
- Strong P.O. effects can in the extreme case lead to peaks being completely absent from the diffractogram.
- Can be avoided by correct sample preparation:
  - Capillaries
  - Roughened sample holders
- Can also be modelled in profile fits.
Extracting data from the pattern

• Peak positions: unit cell parameters, Miller indices, d-spacings of layers, fingerprint for phases, indexing, spacegroup determination

• Intensities: Atom types present in phases, site occupancies, thermal parameters, instrumental factors(!)

• Peak broadening: Instrumental factors, Crystallite size and strain, shape, structural defects
“Fingerprint” phase identification

- Bragg’s law shows us that the diffraction pattern is very characteristic of the crystal lattice for a given phase
- We can use the diffraction pattern for phase identification
  - Visual (if you know the pattern of your phase)
  - Databases (COD, PDF2, ICDD FindIt)
- When we know the phase we can study it further…
Quantitative Analysis

- If the sample contains more than one phase then the pattern corresponds to the weight percentage of each phase
- Can fit using intensities of single characteristic peaks
- Now easy to determine from full profile using software (TOPAS is excellent for this)
- Common application of XRD in industry
- Be aware that preferred orientation (see later) can cause problems
Indexing and unit cell refinement

- Assignment of Miller indices to a pattern according to a specific unit cell
- Can be done by hand for high symmetry examples
- Use of software is more common (TREOR, TOPAS, DICVOL etc)
- If we know the cell (from indexing or phase identification) we can refine the lattice parameters against the data
Unit cell dimension refinement

- Changes in the unit cell parameters can be used to study phase modifications, e.g.:
  - Substitution of atoms in a phase - the substituent usually has a different atomic radius and different bond lengths to the original atom
  - Unit cell parameters change with substitution
  - Can also be used to look at vacancies, interstitials, etc

- Least squares refinement methods are used. This can be done with simple scripts and spreadsheets or complex software packages like GSAS, FULLPROF and TOPAS

- Care must be taken to assure calibration! Adding of internal standards (silicon, LaB$_6$; high quality standard from NIST); proper zero point and displacement corrections (sample height for reflection geometry)
Peak Shape: Size and Strain

- Peak shapes are made up of two basic contributions:
  - Instrumental (radiation, optics and geometry)
    - Includes the bulk of asymmetric broadening
    - Can be fitted with fundamental parameters of analytical peak shapes
  - Sample (crystallite size and strain, defects, shape)
- Analysis can be complex
Nanomaterials

X-ray diffraction; methods and analyses

Step size gives 4 data points above FWHM
→ Should be minimum 5!

Normal, sharp diffraction peak

Broad peak; high noise

FWHM 0.075°
Peak Shape: Crystallite Size

- Scherrer equation describes the relationship between peak broadening and crystallite size

\[ D_{hkl} = \frac{K\lambda}{\beta \cos \theta_{hkl}} \]

- K: Constant (0.89)
- \( \lambda \): Wavelength (Å)
- \( \beta \): Broadening (rad)
- \( \theta \): Diffraction angle (rad)

Beware! The Scherrer equation is not a panacea (solves it all…):
- Weight averaged size of the crystallites may not represent the real distribution of sizes (Fourier transform methods can help)
- Assumes spherical crystallites- real crystals have many shapes (this can be fitted with more complex methods)
- Strain can also cause similar broadening effects (this can in some cases be deconvoluted)
- Strongly dependent on the quality of peak fit
Peak Shape: Strain

- Strain (simplified)
  \[ \varepsilon_{\text{str}} = \frac{\beta}{4 \tan \theta} \]

- Slightly different broadening effect to crystallite size

Fig. 9-2. Effect of lattice strain on Debye-line width and position.
Space Group Determination

- Crystal symmetry is described by space groups
- Space groups describes the essential symmetry in terms of
  - Bravais lattice centering
  - Mirror planes, inversion centres and rotation axes from molecular symmetry (crystallographic point groups)
  - Translational symmetry (periodic lattices only): Screw axes and glide planes

- Centring and translational symmetry elements lead to further interference phenomena in the diffraction pattern: Systematic absences

- Systematic absences are used to determine the space group based on the diffraction pattern
  - Difficult, limited number of observations in powder data (single crystal is much easier)
  - Usually done with software
Systematic absences
(systematic extinctions) – space groups

EXAMPLE:
The following extinction rule is likely based on careful analysis of a diffraction pattern of an orthorhombic sample (powder XRD data):

- hkl: none
- 0kl: k+l=2n
- hk0: h=2n
- h00: h=2n
- h00: h=2n
- 0k0: k=2n
- 00l: l=2n

Which space groups could be possible?
“Our” likely extinctions:

hkl: none
0kl: k+l=2n
hk0: h=2n
h00: h=2n
0k0: k=2n
00l: l=2n

Using the International Tables of Crystallography to find the likely space group options

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$\text{Mn}_{0.63}\text{Cr}_{0.37}\text{As}$ 10 K
Synchrotron radiation
Swiss Norwegian Beam Line
Grenoble 2001
Step 1: Indexing of diffraction pattern (TREOR, ITO, DICVOL, SIRPOW..)
→ Obtain suggestions for possible unit cell
→ Evaluate thoroughly; figure of merit (size of cell relative to nb. peaks)

Step 2: Profile fitting (Le Bail fitting) (various Rietveld type codes)
→ Are all peaks fitted?
→ Evaluation of possible systematic extinctions
→ Evaluation of likely space groups

Step 3: Sample composition – chemical formula
→ Databasis: any isostructural compound already described (known structure)

Step 4: Rietveld type analysis: refining the crystal structure based on a model
Refinements according to the method described by H. Rietveld

Instrumental/sample dependent parameters
- Absorption
- Zero point or height error
- Peak width
- Background

Crystallographic parameters
- Unit cell dimensions
- Atomic coordinates
- Occupation numbers
- Displacement parameters

Step 1: Determine background – introduce corrections/models
Step 2: Optimize unit cell dimensions and zero point / height error
Step 3: Manually adjust peak width parameters to provide at least fair fit to the observed intensity profiles
Step 4: Refine atomic coordinates; heavy atoms first
Step 5: Refine peak width parameters
Step 6: Refine thermal displacement parameters (and occupation nb)
The FullProf Suite (for Windows and Linux) is formed by a set of crystallographic programs (FullProf, WinPLOTR, EdPCr, GFourier, etc...) mainly developed for Rietveld analysis (structure profile refinement, constant wavelength, time of flight, nuclear and magnetic scattering) or X-ray powder diffraction data collected at constant or variable step in scattering angle 2theta.

The programs can be run either in stand alone form (from a console window or clicking directly in a shortcut) or from the interfaces WinPLOTR and/or EdPCr.

Programs within the FullProf Suite are distributed in the hope that they will be useful, but WITHOUT ANY WARRANTY of being free of internal errors. In no event will the authors (or their employers) be liable to you for damages, including any general, special, incidental or consequential damages arising out of the use or inability to use the programs (including but not limited to loss of data being rendered inaccurate or losses sustained by you or third parties or a failure of the program to operate with any other programs). The authors are not responsible for erroneous results obtained with the programs.

Welcome to the GSAS homepage here on CCP14

To install GSAS follow the links below which will take you to Brian Toby’s Trac website and to APS where the software can be downloaded with accompanying instructions.

The reference to use for GSAS in any resulting publications is:
Contact: Bob von Dreele - vondreele@lanl.gov

The reference to use for EXPGUI in any resulting publications is:
Contact: Brian Toby - brian.toby@anl.gov
Mn$_{0.63}$Cr$_{0.37}$As
at 10, 150, 200, 295 K
Synchrotron radiation
Swiss Norwegian Beam Line
Grenoble 2001
X-ray diffraction; methods and analyses

295 K: Paramagnetic

226 K:
2. Order para – antiferromagnetic transition (incommensurate $H_c$ spiral)

Around 160 K
1. Order magnetostructural phase transition (at LT: incommensurate $H_a$ spiral)

Large jumps in the unit cell dimensions \( \Delta V \neq 0 \)
Practical exercise

Rietveld analysis of powder synchrotron data, for
(a) Orthorhombic MnP-type Mn$_{0.63}$Cr$_{0.37}$As solid solution (*Pnma*)
(b) LaCoO$_3$ rhombohedral perovskite in hexagonal setting (*R-3cH*)

Data files and input parameters:

**Mn$_{0.63}$Cr$_{0.37}$As at 230 K**: a/b/c approx: 5.645/3.561/6.239 Å
Atomic coordinates as given for MnP-type in the compendium
Raw data (format 10 in Fullprof): 230K.epf

**LaCoO$_3$ at 115 K**: a and c approximately 5.430 and 13.035 Å
La: 0,0,1/4
Co: 0,0,0
O: 0.554 0 ¼
Raw data (format 10 in Fullprof): LaCoO3_115K_nofield_1.dat