X-ray Powder Diffraction in Catalysis

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Introduction: scope of this lecture

This lecture is designed as a practically oriented guide to powder XRD in catalysis, not as an introduction into the theoretical basics of X-ray diffraction.

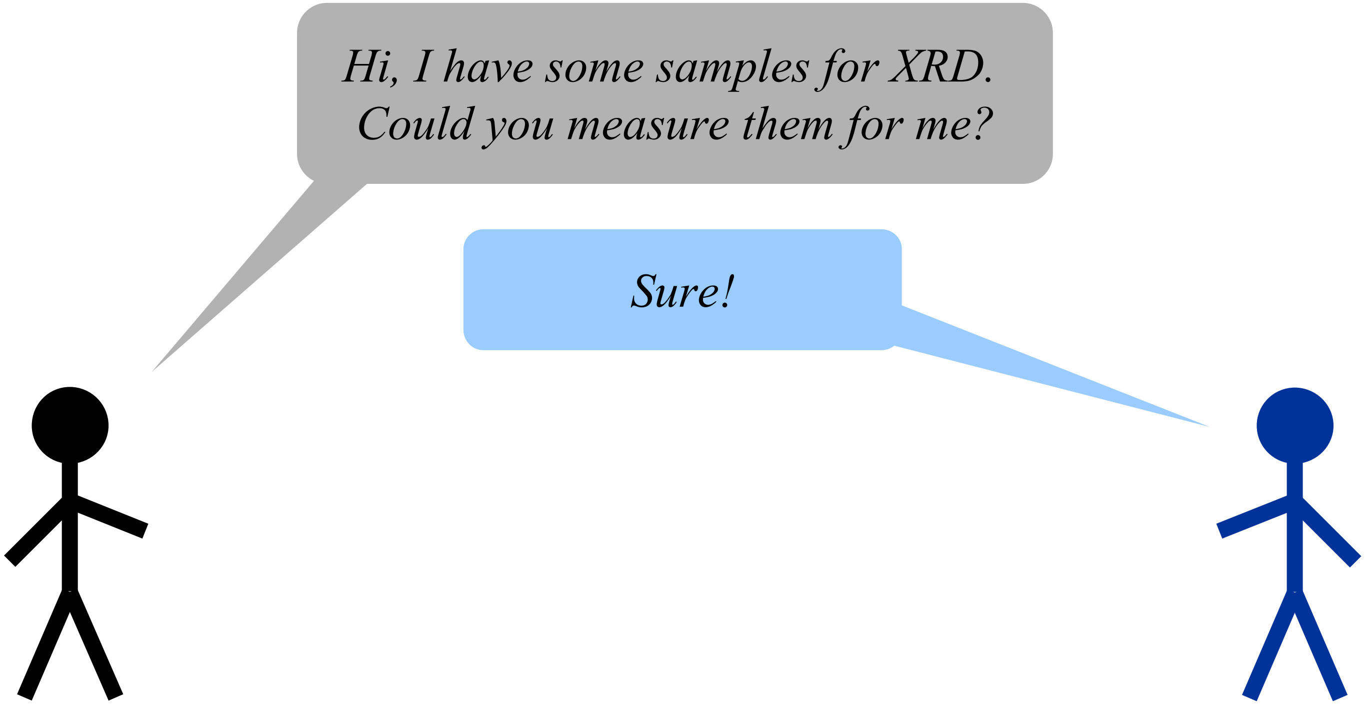
Thus, the following topics are NOT covered here (refer to standard textbooks instead):

- generation of X-rays / working principle of an X-ray tube
- X-ray spectrum:
  continuous spectrum (bremsstrahlung) and line spectrum (characteristic spectrum)
- monochromatization of X-rays
- derivation of the Bragg equation
- lattice planes, Miller indices (*hkl*), d-spacing

Disclaimer:
All references made here to particular hard- or software are based solely on their availability to the author; this does not imply that these are preferable over alternative choices!

Scenario 1

One day, “customer” A (or B, or C) comes to the “XRD service provider”:



Hi, I have some samples for XRD. Could you measure them for me?

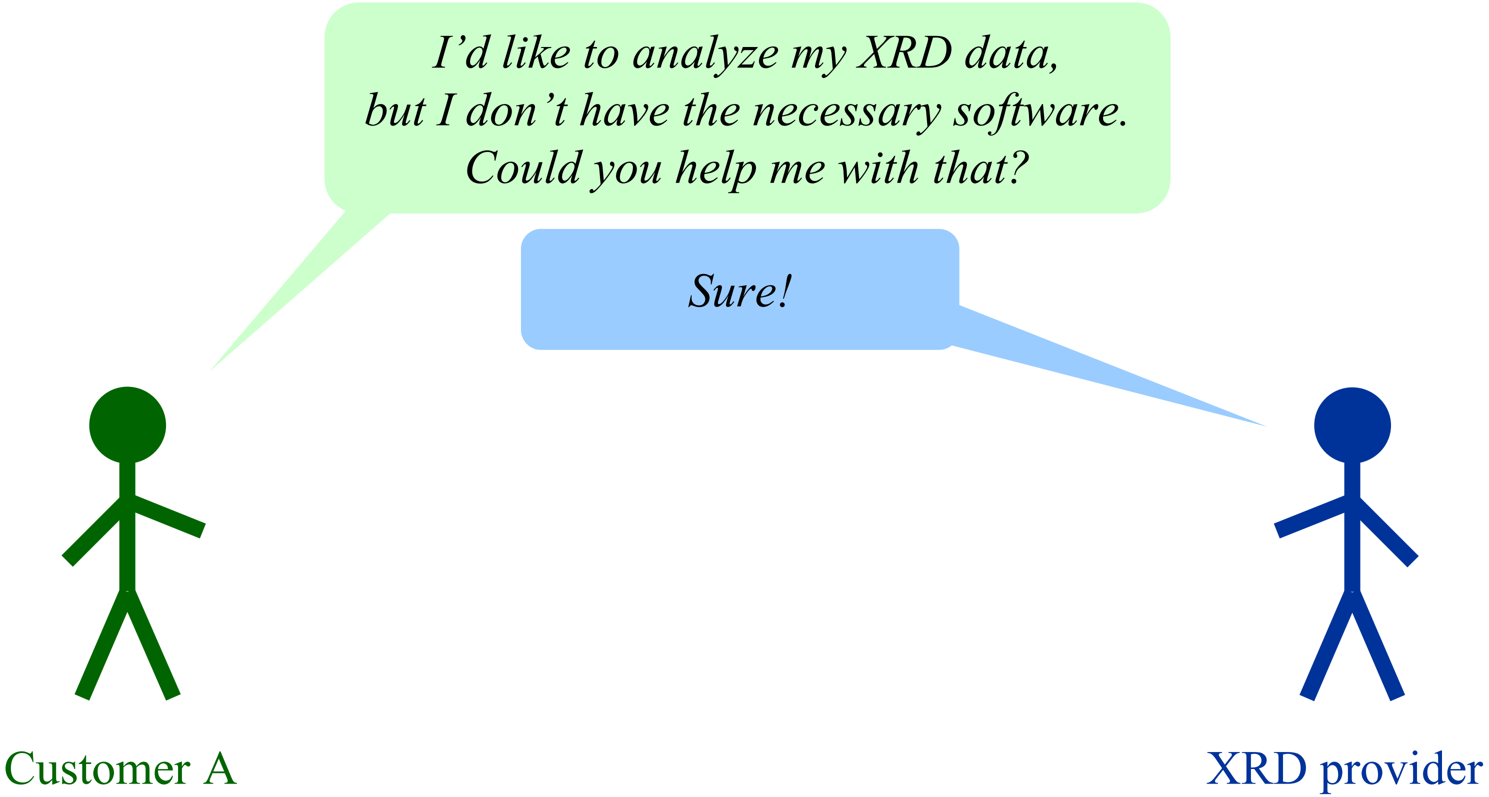
Sure!

Any customer
(could be you)

XRD provider
(could be me)

Scenario 2

Another day (the measurements are finished),
customer A comes again to the XRD service provider:

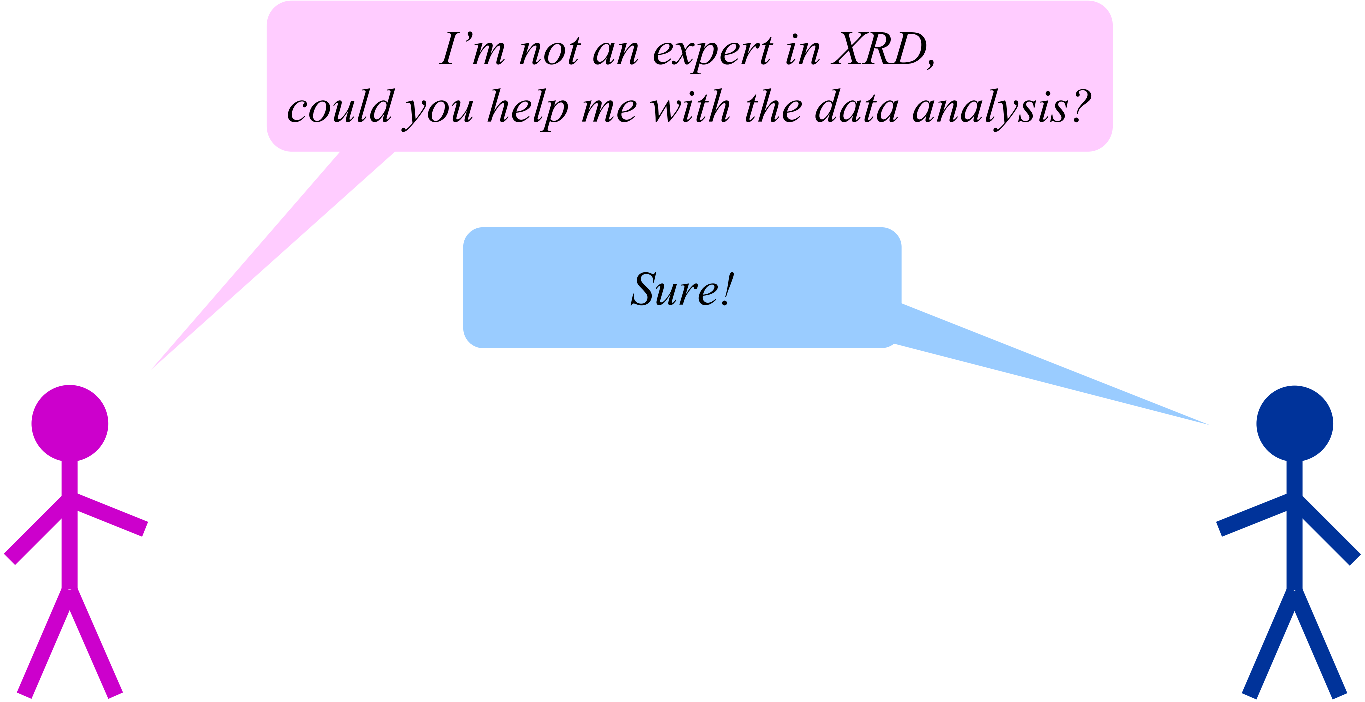


I’d like to analyze my XRD data,
but I don’t have the necessary software.
Could you help me with that?

Sure!

Scenario 3

Yet another day, customer B comes again to the XRD service provider:



I’m not an expert in XRD,
could you help me with the data analysis?

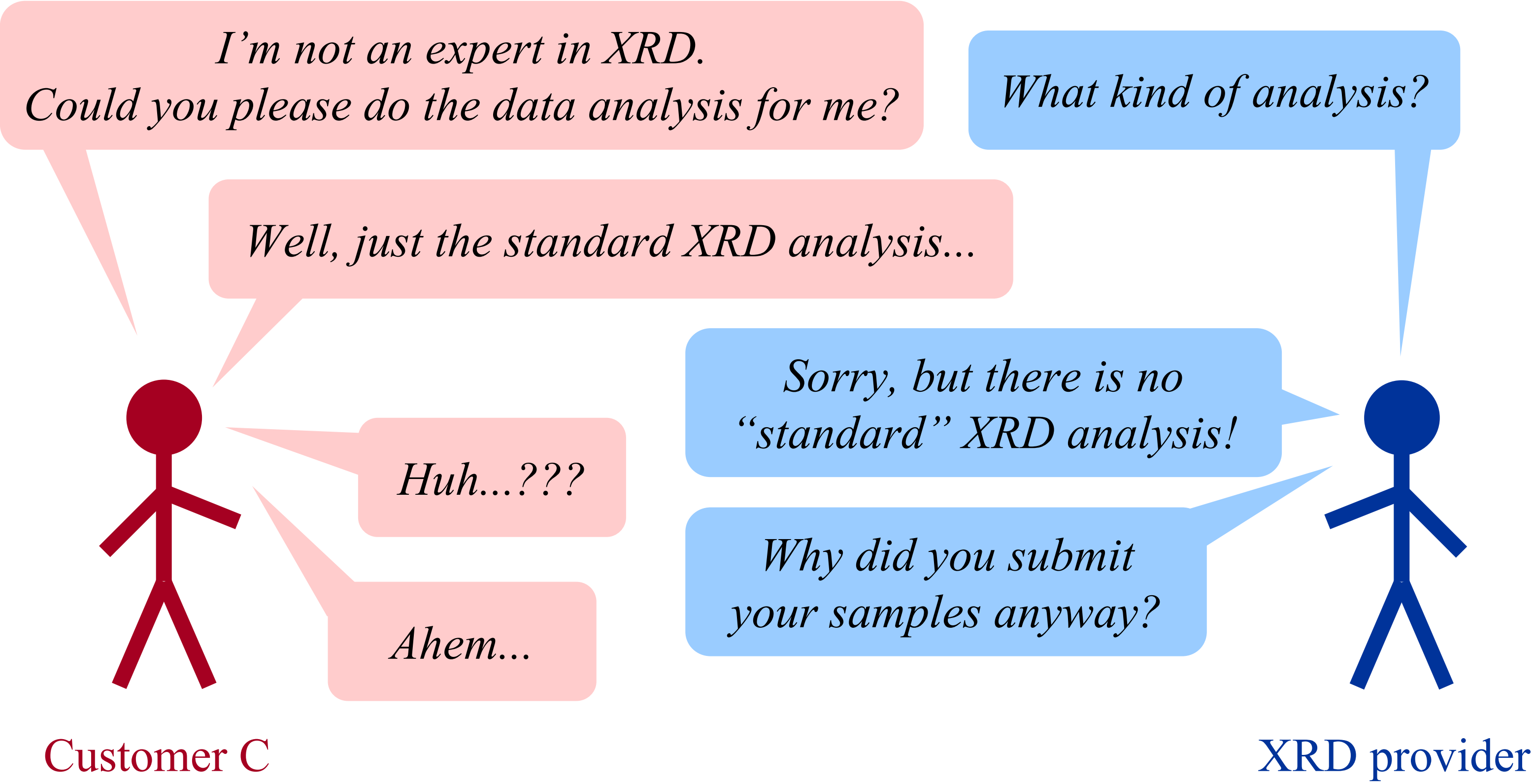
Sure!

Customer B

XRD provider

Scenario 4

Yet another day, customer C comes again to the XRD service provider:



Lessons to be learned:

- There is no such thing as a “standard XRD data analysis”.
- Powder XRD is able to address various questions (with varying amount of effort).
- The data analysis will depend on the kind of scientific question to be answered.
- Ideally, even the measurement conditions should be optimized accordingly (although this is rarely done).
- Communication between “customer” and “service provider” is important!

Goal of this lecture:

After this lecture, you should be able to act like customer A or B (depending on your dedication and skill), and not like customer C!

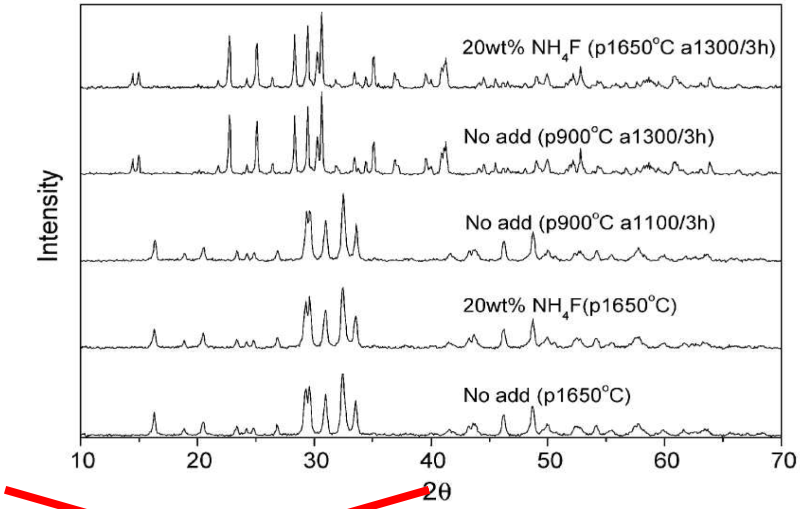
What is diffraction?

- The type of diffraction we will talk about is more properly called ***Bragg diffraction***.
- It occurs when waves of a suitable wavelength interact with periodically ordered matter.
- In the chemical context "periodically ordered matter" usually means crystalline substances, but it may also be ordered arrangements of clusters or pores.

Note: Diffraction is not spectroscopy!

i.e. it is not
- "X-ray spectrum" (that's a different method!),
- "XRD spectrum",
- or "X-ray diffraction spectrum",

but
- ***XRD pattern***,
- ***X-ray diffraction pattern***,
- or ***diffractogram***!



~~Fig. 4. X-ray diffraction spectra of …~~

Diffraction methods

Note: In order to interact with a periodic array of atoms (crystal lattice), the wavelength needs to be roughly in the Ångtröm range (1 Å = 10^{-10} m).

Diffraction methods can be distinguished according to

a) the particles/waves that are diffracted:

- photons (electromagnetic waves): X-rays → X-ray diffraction (XRD)
- electrons: ~10 kV (SEM), ~120 kV (TEM) → electron diffraction
- neutrons: thermal or cold neutrons (slowed down by a moderator when leaving the nuclear reactor) → neutron diffraction

b) the diffracting specimen:

- single crystals → single crystal diffraction
- crystalline powders (and other polycrystalline specimens) → powder diffraction

Characteristics of X-ray diffraction

- X-rays interact with the electron shells of atoms.
- Both the "diffraction power" and the absorption for X-rays increase with the number of electrons (and thus the atomic number), i.e. samples containing heavy elements give higher diffraction intensities, but are also more susceptible to absorption effects.
- Atoms or ions with a very similar number of electrons cannot be distinguished in a crystal structure by XRD.
- XRD is a method to analyze the *average bulk structure* of *long range ordered* materials (*crystalline* substances above a minimum crystallite size).

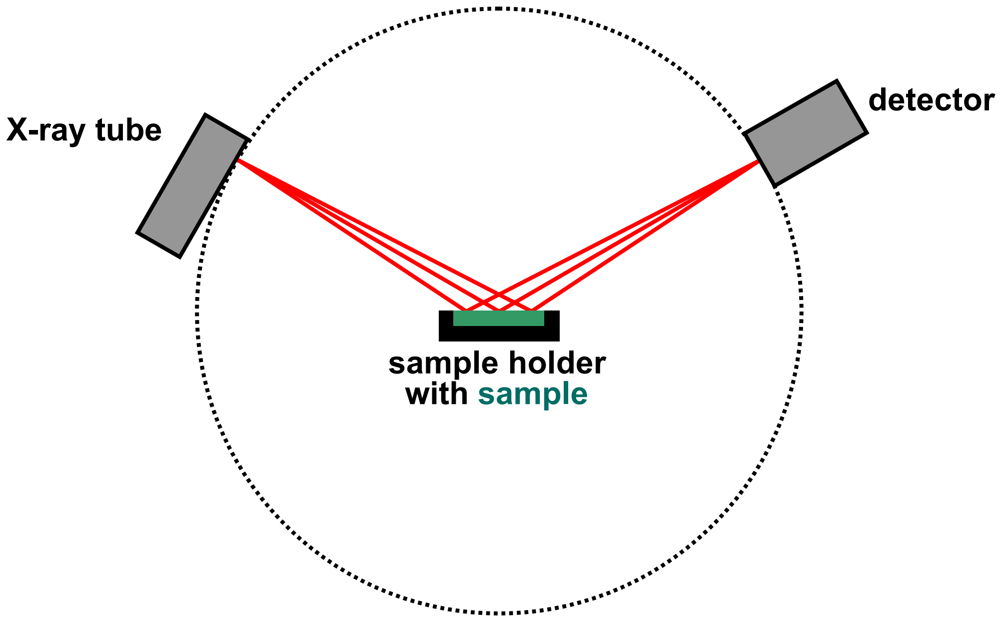
Diffractometer geometries

Classic reflection geometry (Bragg-Brentano geometry)

- divergent primary beam → relatively large sample area illuminated
- illuminated area decreases with increasing diffraction angle (unless variable slits are used)
- sample focuses diffracted beams into the detector slit
- best for strongly absorbing samples
- in addition to powders, solid specimens with a flat surface can be measured (wafers, thin films on a substrate, pellets, ...)
- easily adapted for *in situ* investigations
- secondary monochromatization → usually $K\alpha_{1+2}$ radiation, removal of fluorescence (except anode element)

Diffractometer geometries

Simplified representation of the Bragg-Brentano geometry



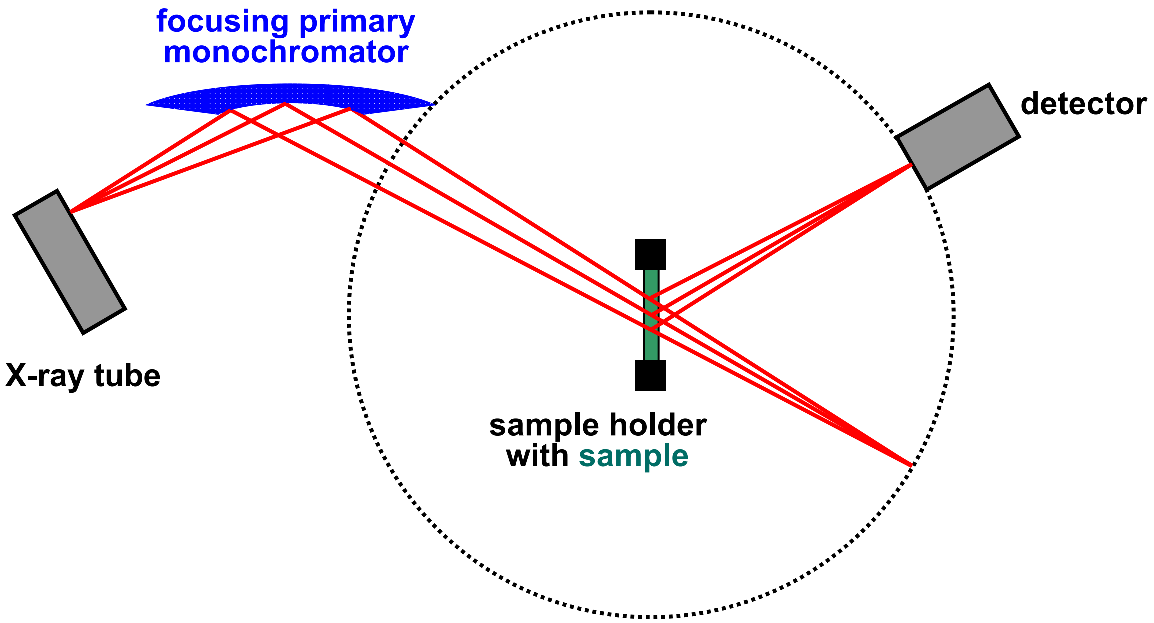
Diffractometer geometries

Classic transmission geometry (Debye-Scherrer geometry)

- bent primary monochromator focuses the primary beam through the sample into the detector slit → relatively small sample area illuminated
- illuminated area increases with increasing diffraction angle
- pure $K\alpha_1$ radiation
- usually no secondary monochromator → fluorescence background from elements left of anode material in the periodic system
- best for samples with low absorption
- capillaries can be used as sample holders (air sensitive samples, suspensions)

Diffractometer geometries

Simplified representation of the Debye-Scherrer geometry



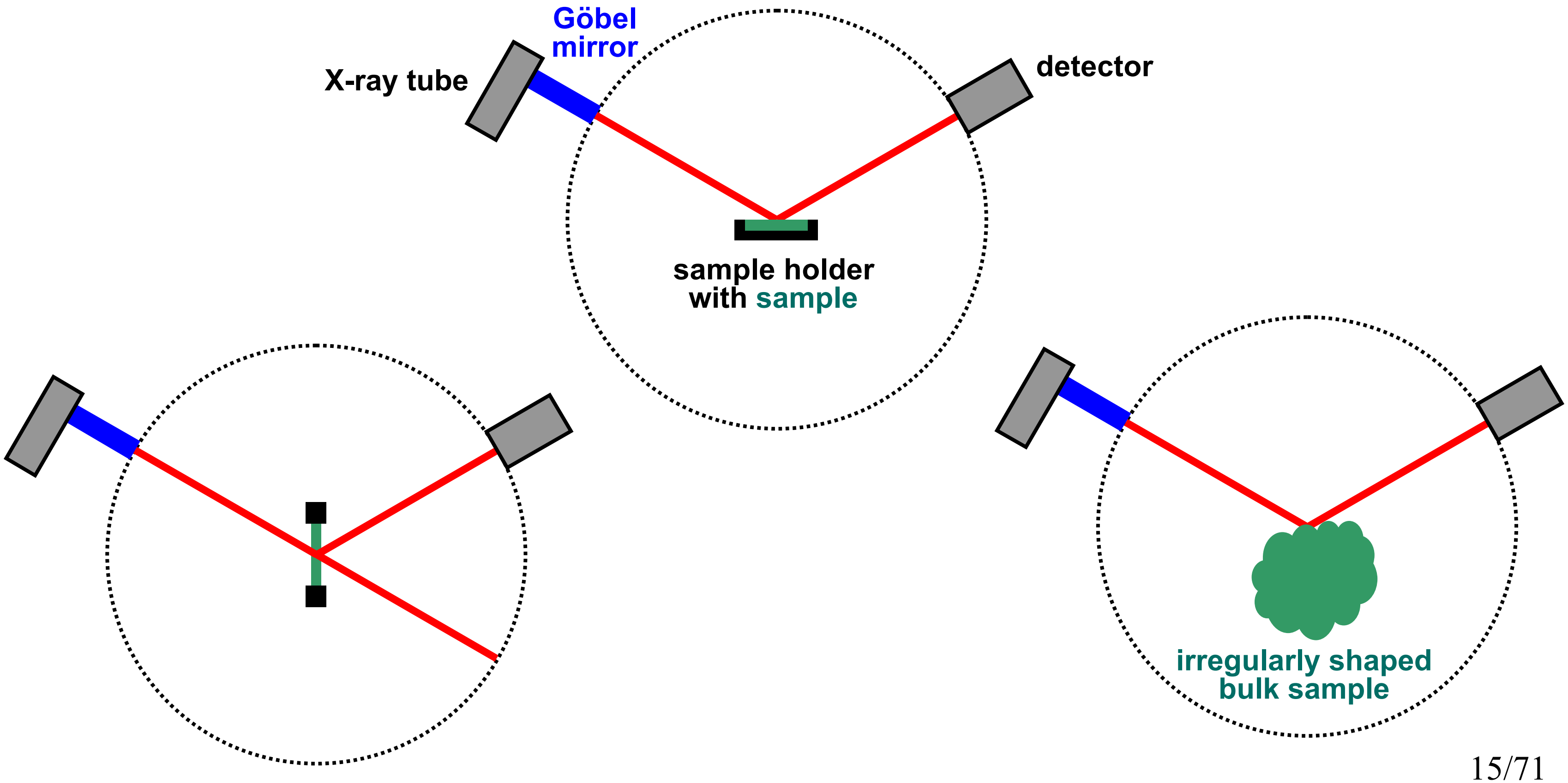
Diffractometer geometries

Parallel beam geometry

- Göbel mirror (parabolically bent multilayer mirror → total reflection of X-rays at take-off angle <1°) focuses divergent primary beam into parallel beam
- small illuminated area with high beam intensity
- can be used for both reflection and transmission measurements
- no displacement (sample positioning) problems → investigation of irregularly shaped samples

Diffractometer geometries

Simplified representation of the parallel beam geometry

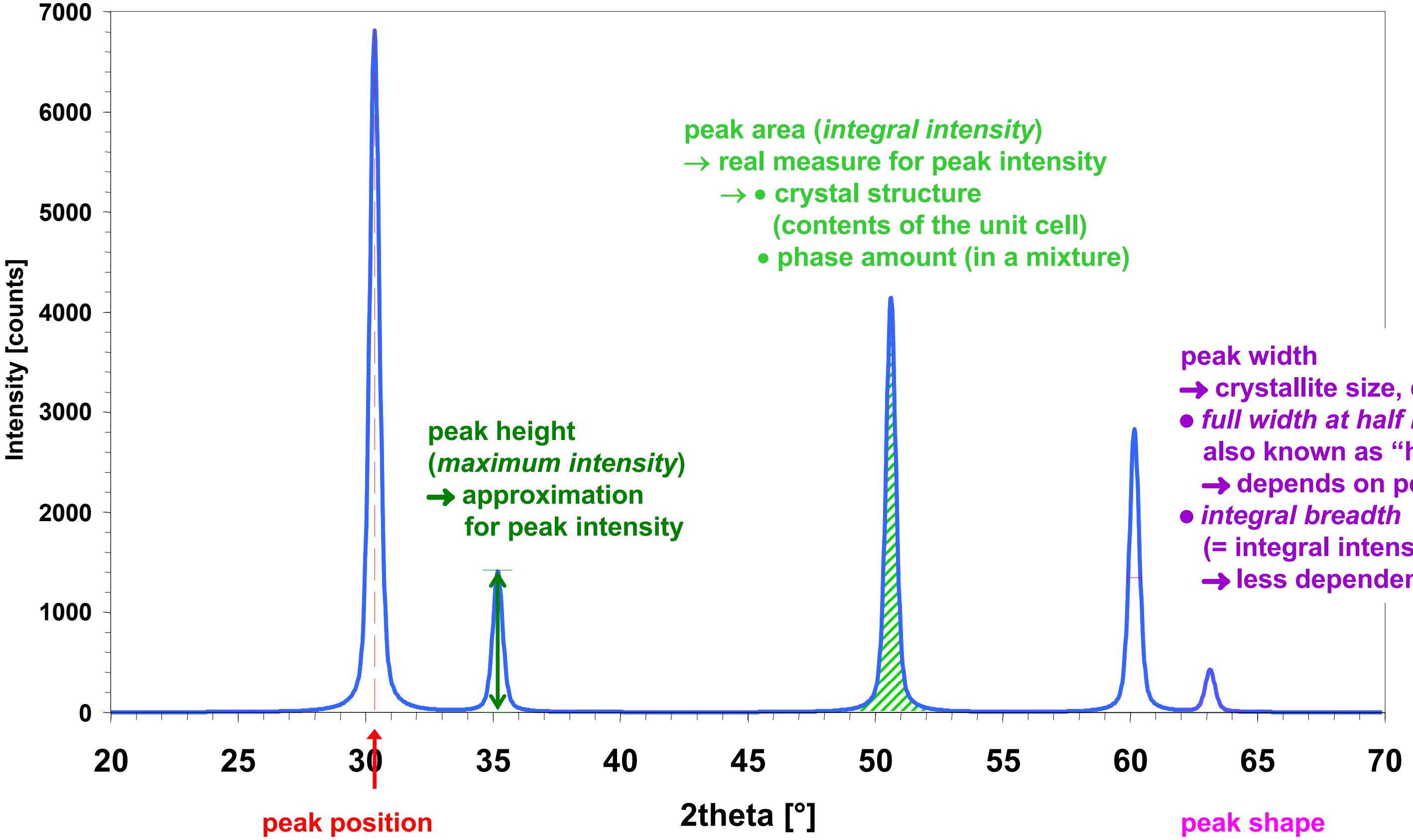


The powder diffraction pattern

- The "signals" in a diffractogram are called (*Bragg* or *diffraction*) *peaks*, *lines*, or *reflections*.
- The intensity of the diffraction signal is usually plotted against the diffraction angle 2θ [°] (2theta [deg.]), but d [Å] or 1/d [$Å^{-1}$] are also used.
- A 2θ plot is pointless if the wavelength used is not stated, because the diffraction angle for a given d-spacing will vary with the wavelength used: $n \lambda = 2\ d \sin(\theta)$ (*Bragg equation*)!

Note: the most common wavelength used in powder XRD is 1.54 Å (Cu Kα).

Information content of an idealized diffraction pattern



peak area (*integral intensity*)
→ real measure for peak intensity
→ • crystal structure
(contents of the unit cell)
• phase amount (in a mixture)

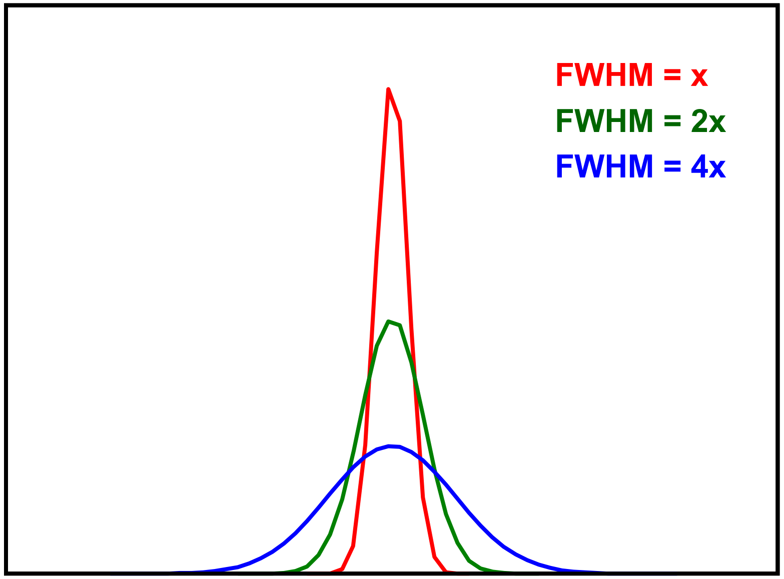
peak height
(*maximum intensity*)
→ approximation
for peak intensity

peak width
→ crystallite size, defects (strain, disorder)
- *full width at half maximum* (FWHM), also known as “half width”
  → depends on peak profile!
- *integral breadth*
  (= integral intensity / maximum intensity)
  → less dependent on peak profile

peak position
→ d-spacing
→ lattice parameters
(metrics of the unit cell)

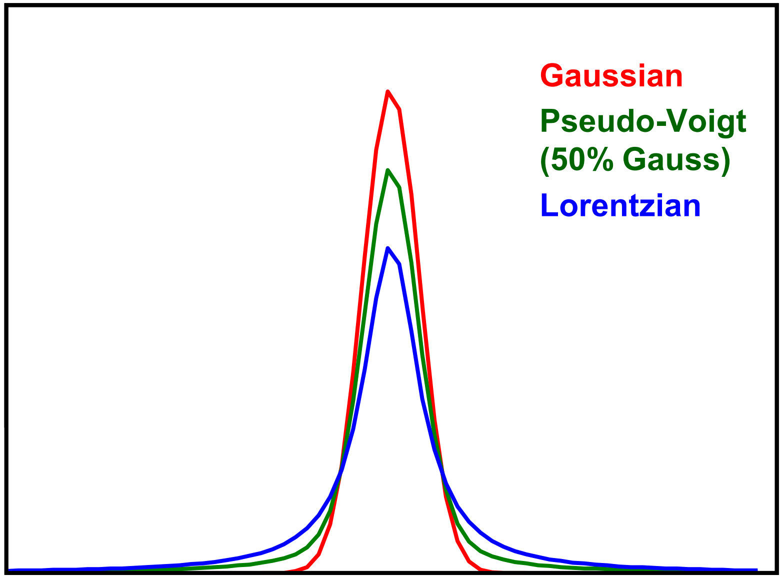
peak shape
(*peak profile*)
→ crystallite size, defects
(strain, disorder)

Idealized diffraction peaks



Change of peak height with FWHM (peak shape and area constant)

→ the stronger the peak broadening, the worse the peak-height approximation for intensity!



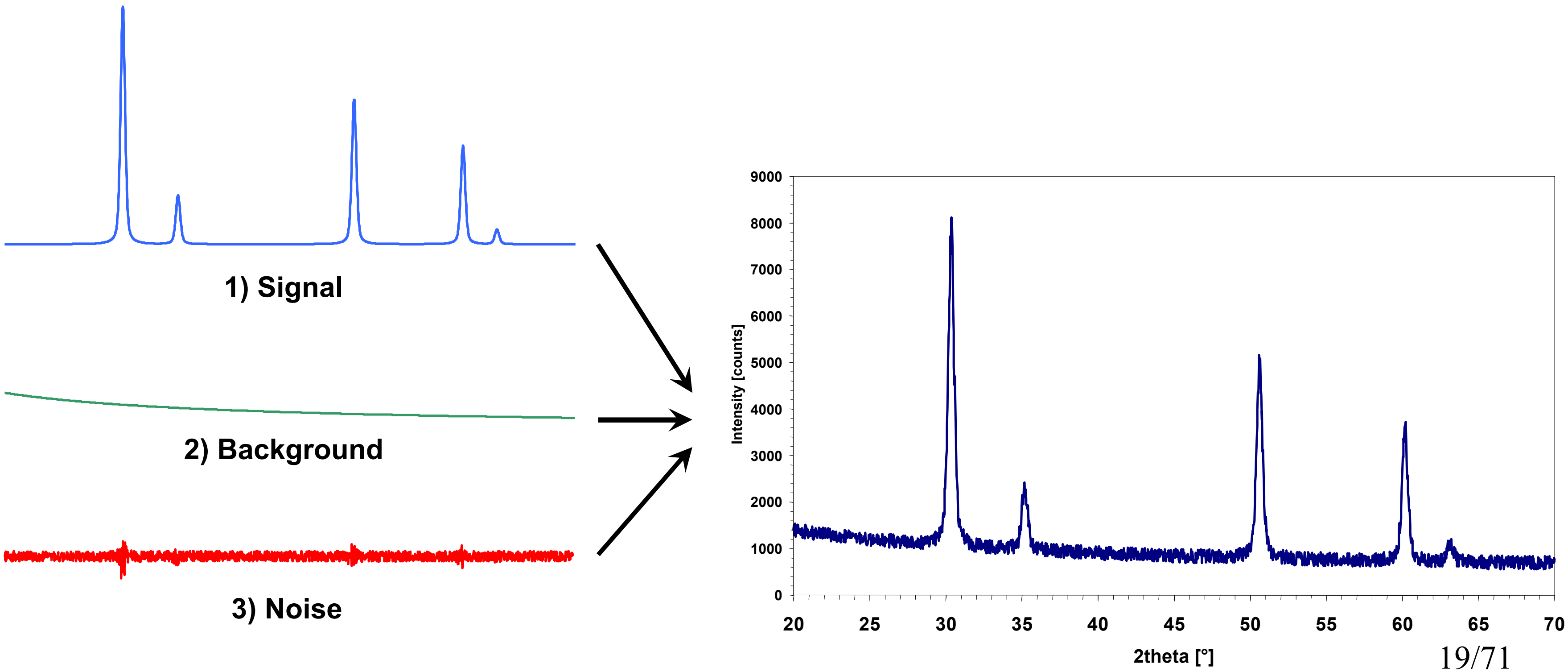
Change of peak height with peak shape (FWHM and area constant)

→ Lorentzian peak profiles extend relatively far from peak center

Components of a real diffraction pattern

What you want:

What you get:



Components of a real diffraction pattern

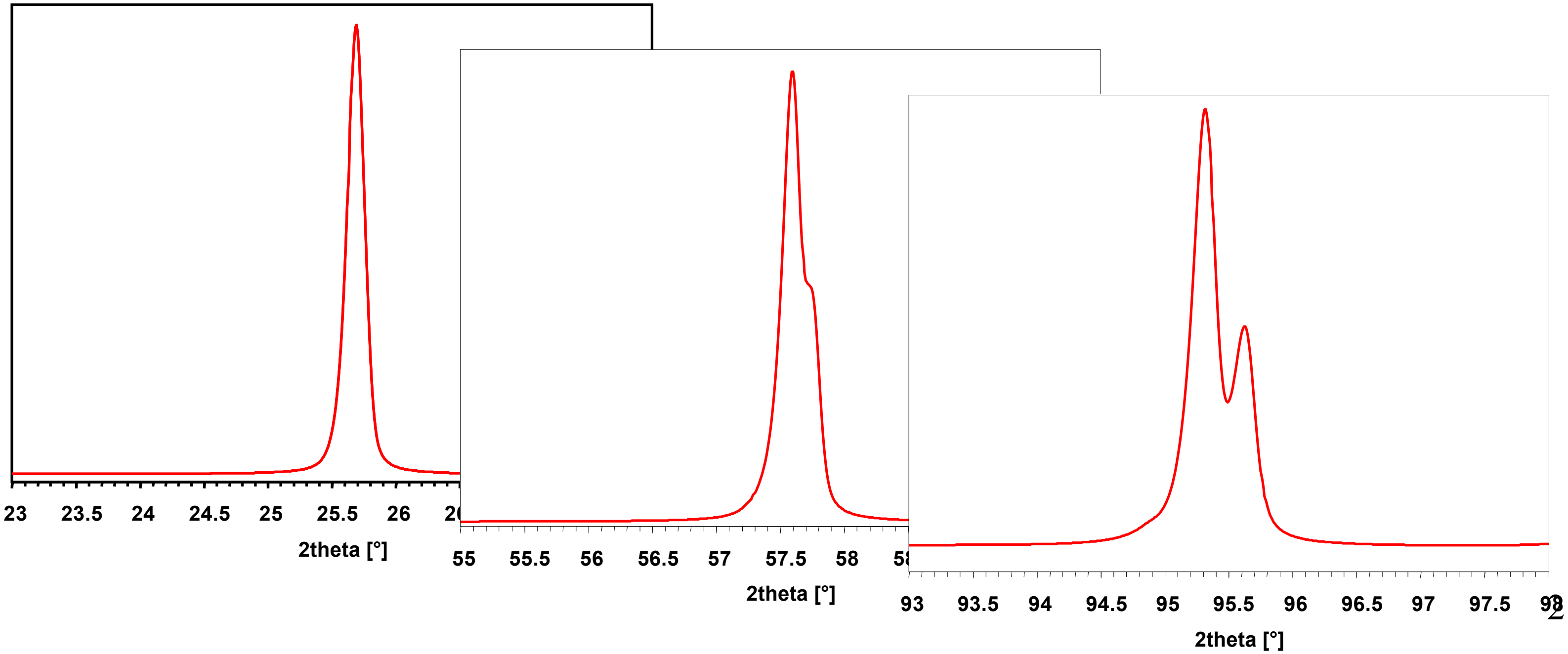
Precise analysis of XRD data requires “separation” of the sample signal from background and noise.

- The signal/noise ratio can be enhanced by measuring more counts, e.g. by
  - ➢ increasing the incoming beam intensity (usually not much room for improvement)
  - ➢ increasing the amount of sample in the beam (illuminated area rather than sample thickness!)
  - ➢ increasing the counting time (but: square-root law!)
- The separation of signal and background is not trivial and thus should be iterative (background refinement instead of background subtraction).
  - ➢ background subtraction only for displaying data, not for analysis (except qualitative analysis)!

Effect of Kα_{1+2} radiation

Secondary monochromators are usually not able to separate Kα_1 and Kα_2 radiation. Thus, each Bragg reflection will occur twice, with slightly different diffraction angles.

- The Kα_2 line lies to the right and has about 1/2 of the intensity of the corresponding Kα_1 line.
- The separation between the two peaks increases with increasing diffraction angle.
- How well the two peaks are resolved also depends on the FWHM of the peaks.



Possibilities of XRD analysis

- Qualitative analysis (identification of crystalline phases)
  needs: peak positions, approximate relative intensities ("fingerprint")
  tools: PDF database (powder diffraction file)

- Quantitative analysis (amount of phases in a crystalline mixture)

  a) crude method: free-hand scaling of PDF patterns to measured data
  needs: I/I_{cor} value for ALL phases involved
  tools: PDF database

  b) sophisticated method: Rietveld quantification
  (fit of calculated intensities to measured data)
  needs: appropriate crystal structure model for ALL phases involved
  tools: crystal structure database (e.g. ICSD, CRYSTMET, CSD, ...)

Possibilities of XRD analysis

- Quantification of crystalline *vs.* amorphous material

  a) using internal standard of known crystallinity (spiking method)
  needs: XRD quantification standard of known crystallinity,
  sophisticated mixing

  b) using external standards
  needs: two reference samples (100% amorphous, 100% crystalline)

  c) using standard free approach
  needs: very precise XRD measurement, reference measurements to correct for air and sample holder contribution, sophisticated software

Possibilities of XRD analysis

- Analysis of phase properties
  - lattice parameters
    needs: peak positions
  - crystallite size, strain
    needs: peak profile shape & width; ***instrument function*** (for correction)
  - crystal structure refinement (Rietveld)
    needs: peak intensities (as accurate as possible!), crystal structure model

- Crystal structure determination (structure solution)
  needs: peak intensities (as accurate as possible!);
  unit cell parameters / indexing of diffraction peaks;
  space group (at least a guess);
  chemical information (e.g. empirical formula)

Peak fitting methods

There are three classes of peak fitting methods:

a) Single peak fitting
- One or more peaks are fitted individually.
- The resulting parameters (e.g. intensity, FWHM, profile shape, peak position) are usually assembled in a peak list.
- The peak list may be the basis for further analysis (pattern matching/identification, refinement of lattice parameters, indexing ...).

b) Whole pattern fitting
- One or more types of parameters are correlated for a set of peaks (which are assumed to belong all to the same phase), some options are:
  - peak shape/width are the same
  - peak shape/width are a smooth function of 2θ
  - peak positions are correlated via the lattice parameters
- Peak intensities are usually free running parameters.

Peak fitting methods

c) Rietveld fitting
  - The peak intensities are not fit parameters but are calculated from the crystal structure of the compound.
  - Optional: The calculated intensities are modified by refinement of a preferred orientation model.
  - Peak shape/width are a smooth function of 2θ.
  - Peak positions are correlated via the lattice parameters.

Phase identification (qualitative analysis)

There are various ways to perform a phase identification. Usually, the diffraction pattern is matched against reference patterns from a database:

- diffraction pattern:
  either the **measured data** (may require background subtraction)
  or a **peak list** (positions and intensities) derived thereof

- peak list generation:
  peak search (position and intensity at maximum height of the peak)
  or **peak fitting** (position and intensity more accurate)

- database:
  commercial (PDF = powder diffraction file, maintained by the ICDD)
  or **user defined** (or combination of both)

- matching process:
  manual or **automatic**

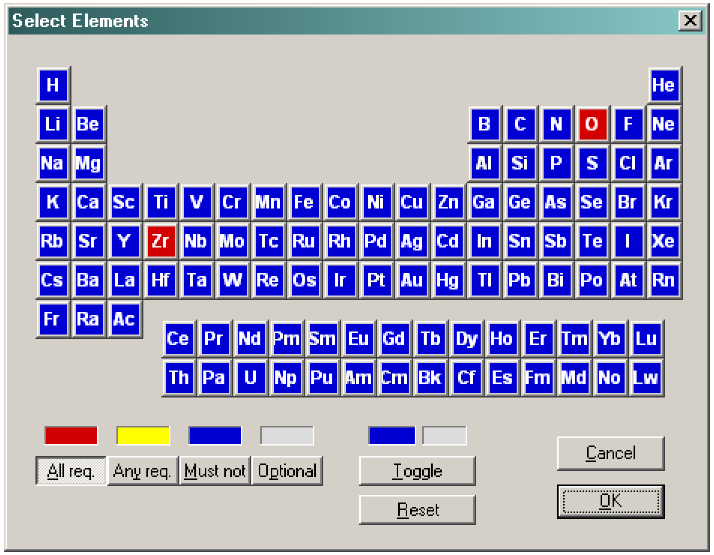
Phase identification process: examples

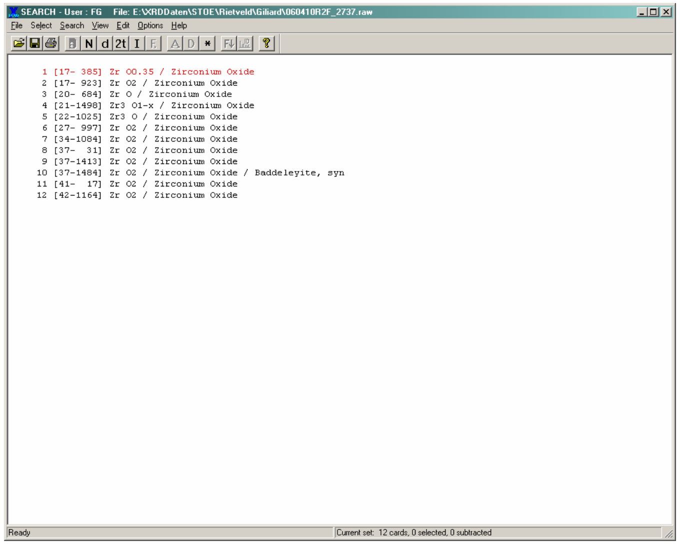
A) Manual matching with the Search/Match option of the WinXPow software (STOE & CIE GmbH)

1. The measured data can be used directly, i.e. the generation of a peak list is not necessary.
2. If the background is high, you may subtract it for convenience (optional).
3. Perform a search in the PDF database, limiting the results via chemical information (elements that must / may / must not be present).
4. Browse through the results and compare the reference patterns (“PDF cards”) with your XRD pattern.
5. Select the reference pattern(s) which match your data.

X-ray Powder Diffraction in Catalysis

Possibilities of XRD analysis: qualitative analysis

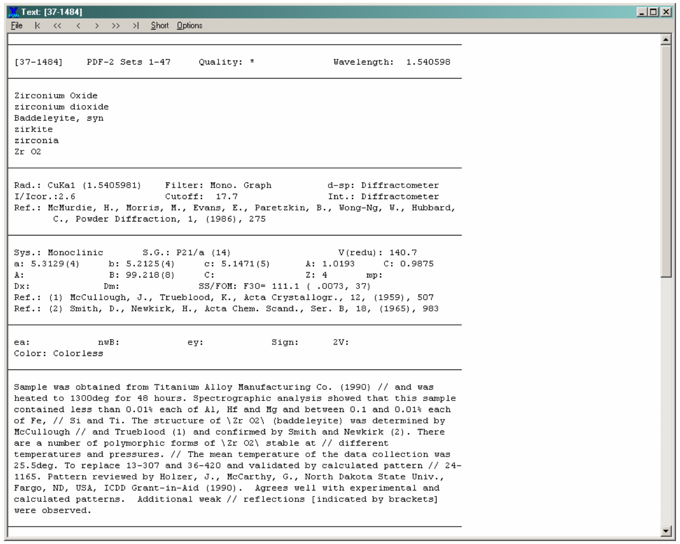




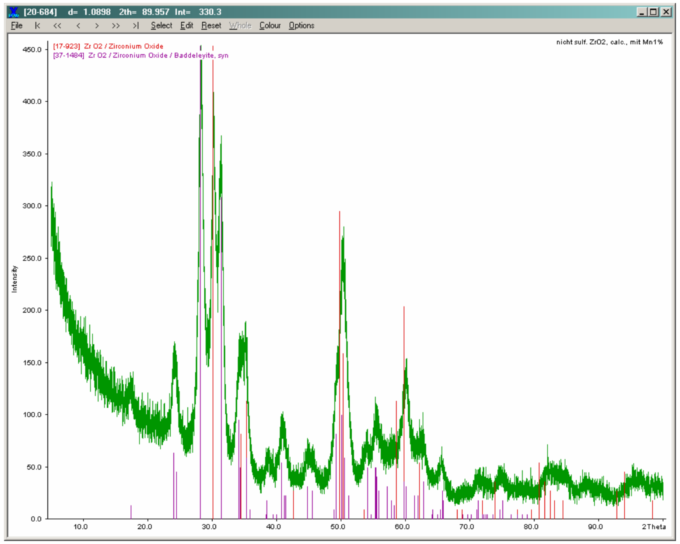
```
 1 [17- 385] Zr O0.35 / Zirconium Oxide
 2 [17- 923] Zr O2 / Zirconium Oxide
 3 [20- 684] Zr O / Zirconium Oxide
 4 [21-1498] Zr3 O1-x / Zirconium Oxide
 5 [22-1025] Zr3 O / Zirconium Oxide
 6 [27- 997] Zr O2 / Zirconium Oxide
 7 [34-1084] Zr O2 / Zirconium Oxide
 8 [37-  31] Zr O2 / Zirconium Oxide
 9 [37-1413] Zr O2 / Zirconium Oxide
10 [37-1484] Zr O2 / Zirconium Oxide / Baddeleyite, syn
11 [41-  17] Zr O2 / Zirconium Oxide
12 [42-1164] Zr O2 / Zirconium Oxide
```

Ready

Current set: 12 cards, 0 selected, 0 subtracted



```
[37-1484]    PDF-2 Sets 1-47     Quality: *           Wavelength:  1.540598

Zirconium Oxide
zirconium dioxide
Baddeleyite, syn
zirkite
zirconia
Zr O2

Rad.: CuKa1 (1.5405981)    Filter: Mono. Graph          d-sp: Diffractometer
I/Icor.:2.6                Cutoff:  17.7                Int.: Diffractometer
Ref.: McMurdie, H., Morris, M., Evans, E., Paretzkin, B., Wong-Ng, W., Hubbard,
      C., Powder Diffraction, 1, (1986), 275

Sys.: Monoclinic       S.G.: P21/a (14)                  V(redu): 140.7
a: 5.3129(4)     b: 5.2125(4)     c: 5.1471(5)      A: 1.0193     C: 0.9875
A:               B: 99.218(8)     C:                Z: 4       mp:
Dx:              Dm:              SS/FOM: F30= 111.1 ( .0073, 37)
Ref.: (1) McCullough, J., Trueblood, K., Acta Crystallogr., 12, (1959), 507
Ref.: (2) Smith, D., Newkirk, H., Acta Chem. Scand., Ser. B, 18, (1965), 983

ea:             nwB:            ey:             Sign:       2V:
Color: Colorless

Sample was obtained from Titanium Alloy Manufacturing Co. (1990) // and was
heated to 1300deg for 48 hours. Spectrographic analysis showed that this sample
contained less than 0.01% each of Al, Hf and Mg and between 0.1 and 0.01% each
of Fe, // Si and Ti. The structure of \Zr O2\ (baddeleyite) was determined by
McCullough // and Trueblood (1) and confirmed by Smith and Newkirk (2). There
are a number of polymorphic forms of \Zr O2\ stable at // different
temperatures and pressures. // The mean temperature of the data collection was
25.5deg. To replace 13-307 and 36-420 and validated by calculated pattern // 24-
1165. Pattern reviewed by Holzer, J., McCarthy, G., North Dakota State Univ.,
Fargo, ND, USA, ICDD Grant-in-Aid (1990).  Agrees well with experimental and
calculated patterns.  Additional weak // reflections [indicated by brackets]
were observed.
```



[20-684] d= 1.0898 2th= 89.957 Int= 330.3

Phase identification process: examples

B) Automatic matching with the Search/Match option of the WinXPow software (STOE & CIE GmbH)

1. Generate a peak list from the measured data by using the Pattern Fitting module:
   a) Perform a peak search (crude) and save the list.
   b) Perform a peak fit (more accurate) and save the list.
2. Perform an automatic search in the PDF database (you may play around with the available search options to optimize the result).
3. Check the results by comparing them with your XRD pattern (best matches are listed first).
4. Decide if one (or several) of the top ranking results match your data.

Phase identification process: examples

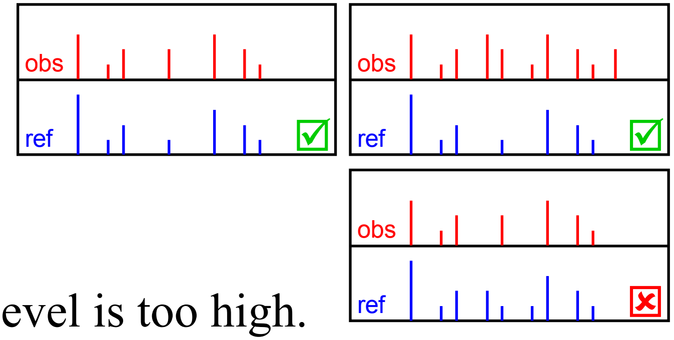
C) Automatic matching with the Search option of the DIFFRAC^{plus} software EVA (Bruker AXS GmbH)

1. Subtract the background from the measured data (mandatory if background is not negligible!).
2. If Kα_2 peaks are present, perform an α_2 stripping.
3. Perform an automatic search in the PDF database (various options for restricting the search are available).
4. Check the results by comparing them with your XRD pattern (best matches are listed first).
5. Decide if one (or several) of the top ranking results match your data.
6. If still some peaks remain unexplained, you may use the “scissors tool” to cut out the already explained peaks and search again...

Phase identification: FAQ

Q: How many peaks must match between a reference PDF pattern and a measured diffractogram?

A: Generally, ALL peaks found in a PDF pattern must also be seen in in the diffractogram, otherwise it is not a valid match.



Possible exceptions:

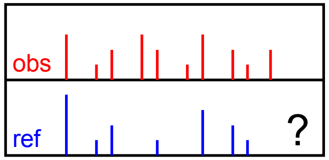
a) Small peaks may be not detectable if the noise level is too high.

b) Missing peaks may be the result of a very strong preferred orientation effect.
→ If this is the case, the relative intensities in general are changed and show a systematic dependence from *hkl*.

c) “Missing” peaks may be the result of anisotropic disorder.
→ If this is the case, the FWHM of the peaks should show a systematic dependence from *hkl* (some reflections become so broad and low that they are not recognized anymore).

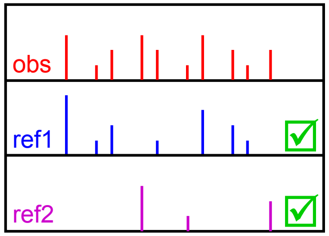
Phase identification: FAQ

Q: All peaks of a PDF pattern are in the measured data, but the measurement contains additional peaks. What does this mean?



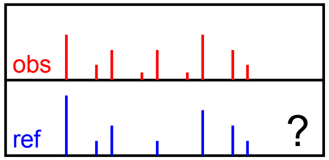
A: The identification is probably correct, but the measured pattern represents a phase mixture.

→ Keep the reference pattern you found, then continue searching for references to explain the additional peaks. Proceed until all peaks are explained.



Phase identification: FAQ

Q: All peaks in my measurement are explained with a PDF reference, except for some very small ones. I tried to identify them as an impurity, but failed. What could this mean?



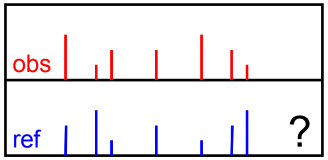
A: Two possible reasons are:

a) The peaks are artifacts resulting from spectral impurities (other wavelengths, e.g. Kβ, W L). Thus, they are weak “duplicates” of very strong peaks.
→ Ask your XRD expert to check this.

b) The peaks are real, but they belong to the reference compound, not an impurity. It may be that your diffraction pattern is “better” in terms of signal/noise ratio than the (possibly old) PDF pattern. After all, the diffractometers have improved with time.
→ Use an *hkl* or Rietveld fit to check if the positions of the additional peaks matches the unit cell parameters of the reference compound.

Phase identification: FAQ

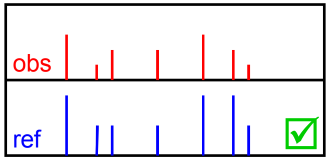
Q: The position of all peaks matches between PDF reference and measurement, but the relative intensities disagree. What does this mean?



A: There are various possible reasons:

a) The identification is correct, but there are preferred orientation effects in the measured data.
→ The deviation of intensities should be systemetic with *hkl*
→ Check with Rietveld fit including a preferred orientation model

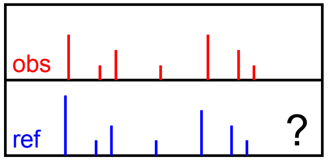
b) The identification is correct, but the PDF intensities have a low level of precision.
→ Check if the PDF intensities have only discrete, round values (e.g. 100%, 80%, 50% etc.). If so, this data originally comes from visual evaluation of a photographic film.



c) The identification is incorrect, the peak positions coincide by chance (not very likely, but possible).

Phase identification: FAQ

Q: The intensity pattern of the PDF reference and the measured peaks look very similar, but the peaks positions deviate. What does this mean?



A: The identification is more or less correct, but the lattice parameters differ slightly. Possible reasons are:

a) Thermal expansion leads to a change in the lattice parameters and thus of the peak positions.
→ The reference pattern may have been measured at a different temperature.
→ Check the details of the PDF entry!

b) The chemical composition is different (doping, solid solution, isostructural compound, variable amount of vacancies, ...).
→ Check if adjustment of the lattice parameters gives a satisfactory match. If so, you have at least identified the structure type.

<u>Example</u>: Instead of AO_2, you may have $A_{1-x}B_xO_2$, BO_2, AO_{2-x}, ...

Phase identification: FAQ

Q: All peaks of my diffraction pattern are explained with the reference PDF card of my target compound. The peak positions and intensities agree very well. Does this mean that my sample is pure?

A: No. Your sample may or may not be pure. There could be impurities which are invisible to XRD, either because the amount is below the detection limit, or because they are “XRD amorphous”.

Phase identification: FAQ

Q: My diffraction pattern shows no peaks. Does this mean that my sample is amorphous?

A: Not necessarily. If you want to be safe, you should say that it is “XRD amorphous”. This means that it may be either truly amorphous, or that the crystallite size is below the detection limit for XRD (roughly 30 Å). In the latter case, a TEM analysis may reveal small crystallites with lattice fringes.

Quantitative Rietveld analysis

Rietveld fitting can be used to quantify crystalline compounds in a mixture.

Preconditions and limitations:

- A crystal structure model is required for each compound to be accounted for.
- The accuracy of the fit will not only depend from the usual factors like data quality (signal/noise ration) and detection limits, but also from the appropriateness of the structure models used.
- The level of accuracy is usually unknown, unless the procedure can be checked with known mixtures.
- “100%” corresponds to the total of all phases accounted for in the fit, which is not necessarily identical to 100% of the sample (neglected: XRD amorphous material, unknown phases, known phases without crystal structure model).
- The results may be re-scaled using a known amount of an internal diffraction standard.

Quantitative Rietveld analysis: theoretical example

Let us assume that a sample has the following composition:	A Rietveld fit using structure models of phases A and B will yield:
40% crystalline phase A	57.1% phase A
(crystal structure known)	
30% crystalline phase B	42.9% phase B
(crystal structure known)	
20% unknown crystalline phase	(plus extra peaks...)
10% XRD amorphous material	

→ You can quantify only what you know and what you can see!

The result is limited to the determination of the ratio between the phases A and B, and the realization that there is at least one unknown crystalline phase.

Quantitative Rietveld analysis: theoretical example

Now we mix the same sample with a diffraction standard (100% crystalline, crystal structure known), e.g. in an amount of 50 wt.% (spiking method).

The sample composition is now:	A Rietveld fit will yield:	Re-scaling the standard to 50% gives:	Re-calculating the result gives:
50% diffraction standard 20% crystalline phase A 15% crystalline phase B 10% unknown crystalline phase 5% XRD amorphous material	58.8% standard 23.5% phase A 17.6% phase B	50.0% standard 20.0% phase A 15.0% phase B *15.0% unknown material*	40.0% phase A 30.0% phase B *30.0% unknown material*

The absolute amounts of the phases A and B are now determined.
However, how much XRD amorphous material is present (if any) must remain unknown, because of the presence of an undescribed crystalline phase!

Using an internal XRD quantification standard: practical aspects

For successful use of an internal quantification standard, the portion of sample exposed to the X-ray beam must be representative for the whole sample.

→ The original sample must be homogeneous (this is true for all quantification!).

→ The original sample must be homogeneously mixed with the standard.

→ Ideally, standard and sample should have the same particle size (differently sized particles tend to unmix easily!).

Lattice parameter determination

The diffraction angle of a peak is related to the d-spacing of the corresponding lattice planes via the Bragg equation. If both d-spacings and Miller indices (*hkl*)* are known for a set of reflections, the lattice parameters (a, b, c; α, β, γ) of the unit cell can be refined.

- The minimum number of independent reflections required is equal to the number of lattice parameters.
- Refinement of angle correction parameters (zero shift and/or displacement) requires a minimum of one additional reflection (per parameter).
- More reflections will yield better results.
- Higher angle reflections have a higher precision than lower angle peaks.

* Note: the Miller indices of individual reflections need not be known explicitly. Knowing the approximate unit cell parameters is usually sufficient to allow an assignment of *hkl* indices to the reflections.

Lattice parameter determination

There are various routes to obtain refined lattice parameters, which can be divided into two groups:

a) The determination of d-spacings (peak list generation) and unit cell refinement are conducted as two consecutive steps.
  - Advantage: Relatively simple procedures/software (only single peak fitting required).
  - Disadvantage: Errors in the first step will irreversibly influence the second step.

b) Peak fitting and cell parameter refinement are performed simultaneously.
  - Advantage: The simultaneous refinement imposes restrictions on the refined parameters, which minimizes errors.
  - Disadvantage: More sophisticated fitting procedure/software is needed (whole pattern fitting or Rietveld fitting required).

Size/strain analysis: peak broadening

A sample consisting of ideal crystallites measured on an ideal diffractometer would yield sharp (zero width) diffraction lines. However, no ideal crystals or diffractometers exist in reality.

→ XRD peak profile shape and width are the result of imperfections in both the experimental setup and the sample.

Observed peak broadening combines the effects of instrumental broadening and sample broadening.

→ In order to investigate sample broadening, the contribution of instrumental broadening (*instrument function*) must be known!

Size/strain analysis: instrument function

The instrumental broadening contribution to a diffraction peak profile is a function of the diffraction angle 2θ (thus the term *instrument function*).

The instrument function of any setup can be determined by measuring an appropriate diffraction standard material.
→ Sample broadening of the standard must be negligible.

For some diffraction geometries (Bragg-Brentano and parallel beam), a good approximation for the instrument function can be calculated from the hardware parameters (goniometer radius, slit width, sample size, ...) if they are known sufficiently well (*fundamental parameters approach*).
→ Standard-free analysis of sample broadening possible!

Size/strain analysis: sample broadening

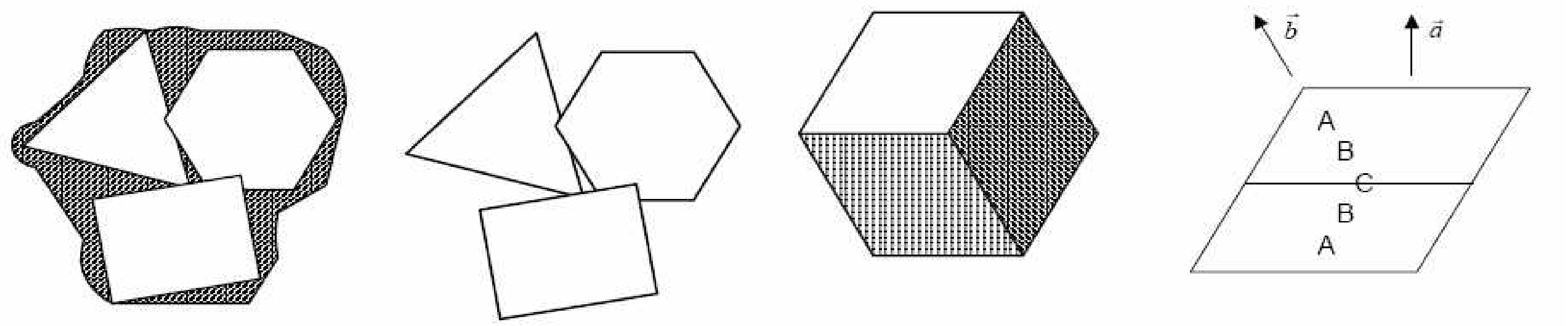
The Bragg diffraction occurs within coherently scattering regions of the crystals. Thus, both the finite size of these coherent regions and disturbances within the regions will lead to a broadening of the diffraction peaks. These two sources of sample broadening are usually termed *size* and *strain* effect, respectively.

Size effect: Bragg diffraction would be perfect only with infinitely large crystals. The termination of the crystal periodicity at the crystallite boundaries is an imperfection leading to peak broadening:
smaller crystallite → smaller number of periods (unit cells) = smaller *column height* → larger imperfection → stronger broadening.
Size broadening usually becomes apparent for crystallites smaller than ca. 1000 Å. Below ca. 30 Å, the peaks become so broad and low that they cannot be distinguished from the background. The material is then “XRD amorphous”.

Strain effect: dislocations, vacancies, interstitials, substitutionals, and similar defects are imperfections which generate a distribution in the d-spacings of lattice planes and thus result in peak broadening.

Size/strain analysis: size effect

First, the term “size” needs to be defined more carefully:



particle or grain size ≥ ***crystal size*** ≥ ***crystallite size*** ≥ ***domain size***

Methods:
light microscopy, SEM, laser size analysis, sieving, ...

Problems:
agglomeration

Methods:
XRD, HRTEM

Problems:
XRD only indirect!

(Figure taken from the TOPAS Users Manual, Bruker AXS)

Size/strain analysis: size effect

Powder XRD is only able to determine the so-called *column height* from the size broadening effect. How this translates into crystallite size depends on many (usually unknown) factors, like crystallite shape, domain structure, nature of the size distribution etc.

→ Work with column heights rather than crystallite sizes!

There are dozens of methods for crystallite size determination by XRD, which will all yield different results. Even when using the same method on the same material, different choice of calibration or pre-assumptions may yield different results.

→ Comparison of results from different groups or people is impossible in most cases.

→ Results should be published with a detailed description of the determination procedure if the absolute crystallite size values are meant to be used for external comparison.

→ Use a constant procedure for a series of samples and rely on the relative trends seen in the results rather than believe in absolute values!

Size/strain analysis: the Scherrer formula

1918 Scherrer proposed the following equation for the dependence of the peak width from the crystallite size:

$$\beta = \lambda / (\varepsilon \cdot \cos\theta)$$

β: FWHM of the peak profile (corrected for instrumental broadening)

ε: “apparent crystallite size”
→ depends on “true crystallite size” and *hkl*
→ no physical interpretation!

A relation between ε and the *volume averaged column height* L_{vol} can be established by introduction of the Scherrer constant k:

$\varepsilon = L_{vol} / k$ — k depends on the crystallite shape and is usually unknown, but is often assumed to be $\cong 0.89$

Thus, we get: $\beta = k \cdot \lambda / (L_{vol} \cdot \cos\theta)$

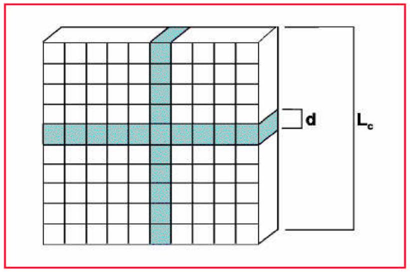
Size/strain analysis: volume averaged column height

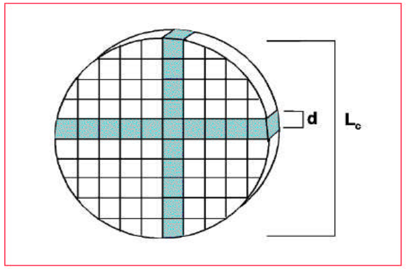
The relationship between individual column heights, the volume averaged column height, and the nominal crystallite dimensions (crystallite size) will depend on the crystallite shape.

Examples:

a) <u>cubic crystallite</u>
L_{vol} = individual column height
= L_c (crystallite edge length)
(for reflections of lattice planes parallel to the cube faces)

b) <u>spherical crystallite</u>
individual column height
≤ L_c (crystallite diameter)
L_{vol} = 3/4 L_c
(for all reflections)





(Figures taken from the TOPAS Users Manual, Bruker AXS)

Size/strain analysis: strain effect

Lattice strain (*microstrain*) is caused by lattice defects like dislocations, vacancies, interstitials, substitutionals, etc. These defects lead to displacements of atoms from their sites in the idealized crystal structure, thus causing a variation in the lattice plane d-spacings.

Strain is usually quantified as $\varepsilon_0 = \Delta d/d$, with d the idealized d-spacing and Δd the most extreme deviation from d.

The peak broadening due to strain is assumed to have the following dependence:

$$\beta = 4 \cdot \varepsilon_0 \cdot \tan\theta$$

Size/strain analysis: peak broadening summary

The observed peak broadening β_{obs} is composed of instrumental and sample broadening, where the latter encompasses size and strain broadening:

$$\beta_{obs} = \beta_{instr} + \beta_{sample} = \beta_{instr} + \beta_{size} + \beta_{strain}$$

The instrumental broadening β_{instr} can be determined experimentally with a diffraction standard or calculated with the *fundamental parameters approach*.

The separation of the size and the strain effect on the sample broadening, however, is more complicated and depends on the method used.

Most methods consider the following angular dependencies:

$$\beta_{size} \propto 1/\cos\theta$$

$$\beta_{strain} \propto \tan\theta$$

Note: depending on the analysis method used, β may either mean the FWHM or the integral breadth of the peak!

Size/strain analysis: methods

The various methods for size/strain analysis can be systematized in the following way:

1) Model independent approaches

- Mainly instrumental broadening correction with Fourier-deconvolution (Stokes method), followed by
- Warren-Averbach method for separation of size and strain effect.
- Yields *area weighted column heights* and *mean-square strain*.

2) Model dependent approaches

- Mainly integral breadth methods.
- Preceding instrumental broadening correction (which depends on the method).
- Profile fitting to model the peak broadening (e.g. Double-Voigt approach).
- Yields *volume weighted column heights* and *maximum strain*.

Size/strain analysis: double-Voigt approach

The Voigt function is a convolution of a Gauss and a Lorentz function. The Double-Voigt approach uses a convolution of two Voigt functions, one with a 1/cosθ (“size”) and one with a tanθ (“strain”) dependence, to model the sample contribution to the peak profiles.

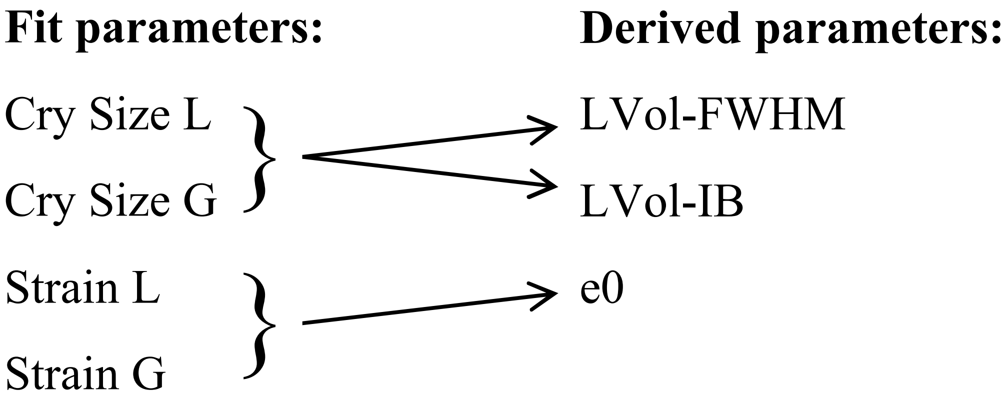
The Double-Voigt approach as implemented in the program TOPAS (Bruker AXS):

- All peak profile contributions (instrumental, size, strain) are convoluted into peak profiles numerically in the fit.
- Instrumental broadening can be accounted for in various ways:
  - Calculated with the *fundamental parameters approach*.
  - Modeled according to theoretical or experimental (reference) data using the “additional convolutions” option.
  - Ignored (makes sense if $\beta_{instr} << \beta_{sample}$).

Size/strain analysis: double-Voigt approach

- Sample broadening can be modeled with a set of four fit parameters:
    - **Cry Size L** (Lorentzian part of the crystallite size contribution)
    - **Cry Size G** (Gaussian part of the crystallite size contribution)
    - **Strain L** (Lorentzian part of the strain contribution)
    - **Strain G** (Gaussian part of the strain contribution)
- From these fit parameters, which have no direct physical meaning, three derived parameters are calculated:
    - **LVol-FWHM** (*volume averaged column height* calculated from the FWHM; uses the Scherrer constant *k*, which needs to be specified (default: 0.89); use not recommended)
    - **LVol-IB** (*volume averaged column height* calculated from the integral breadth; no crystallite shape included ($k = 1$); use recommended)
    - **e0** (FWHM based strain calculation; Δd/d with 50% probability)

Size/strain analysis: double-Voigt approach



Fit parameters:

Cry Size L

Cry Size G

Strain L

Strain G

Derived parameters:

LVol-FWHM

LVol-IB

e0

Double-Voigt approach with TOPAS: practical aspects

Generally, the number of free running parameters in any fit should be kept as low as possible to describe the experimental data. “Over-fitting” will lead to large error bars due to parameter correlations and will probably yield physically unreasonable values as a result.

A good strategy to find a reasonable set of fit parameters is the following:

1. Refine all four profile parameters.
2. If any parameter runs towards the limits (very large Cry Size, very small Strain), or shows a very large error, switch it off and refine again.
3. If necessary, repeat step 2.
4. If all refined parameters show reasonably small errors, keep the result.
   If, however, some errors seem too high, try to deactivate another fit parameter and repeat the fit. Then switch it on again, deactivate another one, and refine again. Do so for all possible combinations of parameters.
5. Compare the alternative results with respect to the fit quality and the parameter errors. Decide which alternative is the best.

Double-Voigt approach with TOPAS: practical aspects

It is important to realize that, just like all other methods for size/strain analysis, the Double-Voigt approach has the following limitations:

- Other sources of sample broadening, e.g. disorder, are not considered. Thus, in the presence of disorder, the size/strain calculation must be wrong!
- The crystallite size distribution is assumed to be homogeneous and relatively narrow. If this is not true, e.g. in the case of a bi-modal distribution, the calculated values will be wrong!
- The Double-Voigt approach works only if the profile shape and width are a smooth function of the diffraction angle. In the case of pronounced anisotropy of size and/or strain, the peak profiles depend more on *hkl* than on 2θ. Thus, the Double-Voigt approach must fail here.

Double-Voigt approach with TOPAS: practical aspects

- Since every diffraction peak has a profile shape and width, any size/strain analysis may be applied to any diffraction data, and will yield numerical values. However, XRD offers no means to check whether any of the pre-assumptions made is valid or not. Consequently, the accuracy of any stand-alone size/strain analysis is generally uncertain, i.e. the calculated values may have a physical meaning or not.
- TEM is one possibility to check the results of an XRD analysis. But we should be aware of the fact that TEM size statistics yield *number weighted* values, as opposed to the *area* or *volume weighted* results from XRD analysis.

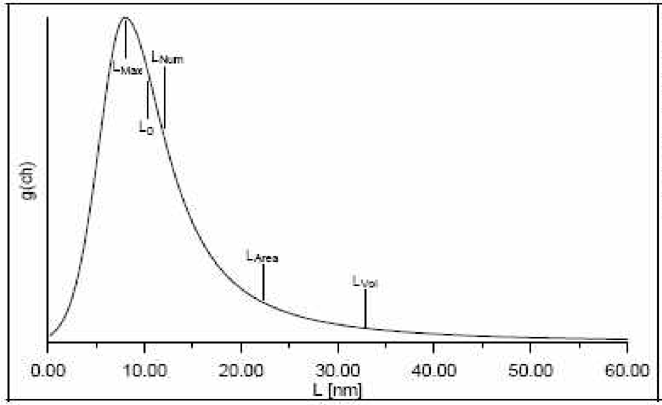


Fig. 3-20: Schematic representation of a column height distribution g(ch) showing the following characteristic points:

L_{Max} : most probable value
L_0 : median
L_{Num} : number weighted mean
L_{Area} : area weighted mean
L_{Vol} : volume weighted mean

(Figure taken from the TOPAS Users Manual, Bruker AXS)

Practical aspects of size/strain analysis: conclusion

- Do not trust the results too much in terms of absolute values.
- Do not seriously compare results from different sources.
- If you have a set of samples to be analyzed and want to compare them with each other, make sure that the same procedure is applied to the whole set.
- Interpret the results in relative terms, i.e. use them to identify trends in the series.
- Don’t be surprised if other analytical methods (e.g. TEM) yield different results.
- Unfortunately, people tend to believe in numbers. Uncertainties which do not appear as “error bars” are easily forgotten. Thus, if you give results from an XRD size/strain analysis to other people (e.g. as a table in your thesis), be aware that they will probably be taken more serious than they should ...

Non ambient XRD (*in situ* XRD): terminology

“Non ambient XRD” simply means XRD under non ambient conditions, e.g.

- elevated or reduced temperature,
- elevated or reduced pressure,
- vacuum,
- defined gas atmosphere.

In catalysis research, the equivalent term “*in situ* XRD” is used more often.

Literally, the Latin *in situ* means “at location”.

However, when some catalysis researchers say “*in situ*”, they often mean specifically “under catalytic reaction conditions”, which is just a special case of “*in situ*”.

Thus, the term “*in operando*” was coined to refer explicitly to investigations under catalytic reaction conditions.

In situ XRD

In situ and *in operando* investigations can yield valuable information on catalytically relevant materials, which would otherwise not be available.

Thus, there is a strong interest in developing *in situ* versions of all characterization techniques used in this field of research.

Among the various *in situ* analytical techniques, X-ray based methods have a comparably long tradition.

This is due to the fact that the matter penetrating properties of X-rays facilitate the construction of environmental cells (sample holders), while other methods may have more problems (e.g. choice of appropriate window materials, absorption of the gas phase).

In situ XRD

In general, *in situ* XRD is a useful analytical tool in solid state chemistry and physics. It may help to access the following information:

- Temperature or pressure induced phase transitions
- Solid/solid reactions
- Solid/gas reactions
- Formation of reaction intermediates
- Time resolved measurements → reaction kinetics

In situ XRD

In the catalysis context, the application of *in situ* XRD may help with:

- Characterization of the active catalyst
- Activation/deactivation behavior of the catalyst

→ Structure/activity correlations

- Characterization of catalyst precursor materials
- Investigation of some catalyst preparation steps (e.g. *in situ* calcination)

→ Preparation/structure correlations (chemical memory)

→ Knowledge based catalyst design!

- Investigation of catalyst material reactivity (oxidation, reduction, decomposition reactions)
  → Clues for understanding activity/mechanisms

<u>Example</u>: If the onset temperatures of reduction and catalytic activity coincide, we may suspect that lattice oxygen is involved in the catalytic reaction mechanism.

In operando XRD

In order to take full advantage of *in situ* investigations on catalysts under operation conditions, the catalytic activity must be monitored simultaneously!

This is the only way to ensure that the catalyst is characterized in a state which is catalytically relevant.

Different *in situ* techniques may require different compromises concerning operation conditions. Thus, monitoring the activity may provide a common scale to correlate the results of several *in situ* methods applied to a system.

On-line monitoring of the gas phase is usually performed by either

- mass spectrometry
  (high time resolution, but often only semi-quantitative),

or

- gas chromatography
  (lower time resolution (minutes scale), but better quantification).

In situ XRD: relevance for catalysis

X-ray diffraction is a method to characterize the *average bulk structure* of *crystalline* material. Thus, it is valid to ask if the results obtained with XRD are relevant for catalysis, because:

- Catalytic reactions usually occur at the *surface* of a heterogeneous catalyst.
- *Active sites* will usually be different from the *average* structure.
- The catalytically active phase may be *XRD amorphous*.

The answer to this is: Depending on the system under investigation, XRD *may potentially* give clues relevant for catalysis, since:

- There is no surface without bulk, and no bulk without surface.
  Modifications of the bulk structure will probably affect the surface structure!
- Careful analysis of XRD data may shed light on specific *defects* (i.e. deviations of the *real structure* from the *ideal structure*, like *disorder* or *strain*) which can be relevant for catalytic activity.

XRD and complementary methods

Like all other analytical methods, XRD has strengths on the one hand, and limitations and weaknesses on the other hand.

It is generally a good idea to combine a number of characterization techniques in order to answer specific scientific questions.

Some techniques are particularly well suited to complement XRD, which are listed comparatively in the following.

XRD and TEM (transmission electron microscopy)

XRD	TEM
averaging over the whole sample	local
limited to larger crystallites (> 30 Å)	limited to smaller crystallites (beam transparency required!)
amorphous material invisible	amorphous material visible
3D distribution of d-spacings (but collapsed into 1D)	2D projection of d-spacings
usually no beam damage	beam damage quite possible

XRD and EXAFS (extended X-ray absorption fine structure)

XRD	EXAFS
analysis of long range order	analysis of short range order
limited to crystalline material	covers both crystalline and amorphous material
not element specific	element specific
distinguishes different crystallographic sites	averages over different sites (for the same element)
averages over different elements on the same crystallographic site	distinguishes different elements on the same crystallographic site
distinguishes different (crystalline) phases	averages over different phases (containing the same element)

XRD and neutron diffraction

XRD	**Neutron diffraction**
interaction with electron shell	interaction with nucleus
atomic order only	atomic and magnetic order
scattering power depends on atomic number	scattering power depends on nucleus structure
cannot distinguish isotopes or neighboring elements in PSE	distinguishes isotopes and neighboring elements in PSE
light elements hard to localize (hydrogen almost invisible)	no problem with light elements (vanadium almost invisible)

Databases

PDF:

- Powder Diffraction File
- contains single-phase X-ray powder diffraction patterns (no crystal structures!)
- maintained by the ICDD (International Centre for Diffraction Data),
  formerly known as JCPDS (Joint Committee on Powder Diffraction Standards)
  (renamed in 1978!)
- link: **http://www.icdd.com/** (info)

Databases

ICSD:

- Inorganic Crystal Structure Database
- contains inorganic crystal structures (inorganic = no C-H bond)
- originally no metal alloys included (→ CRYSTMET), but now successively incorporated
- structures determined with various methods (single crystal or powder diffraction, XRD or neutron diffraction, even some theoretical structures!)
- maintained by the FIZ (Fachinformationszentrum) Karlsruhe
- links: **http://www.fiz-karlsruhe.de/ecid/Internet/en/DB/icsd/index.html** (info), **http://icsd.fkf.mpg.de/index.php** (online access for MPG members)

Databases

CRYSTMET:

- contains crystal structures of metals, including alloys, intermetallics and minerals
- currently maintained by Toth Information Systems (since 1996)
- link: **http://www.tothcanada.com/databases.htm** (info)

Databases

CSD:

- Cambridge Structural Database
- contains organic and organometallic crystal structures (at least one C-H bond), excluding proteins and oligonucleotides
- maintained by the CCDC (Cambridge Crystallographic Data Centre)
- links: **http://www.ccdc.cam.ac.uk/products/csd/** (info)

- hint: due to the special definiton of “organic” (see above), some crystal structures contained in the CSD may be interesting for inorganic chemists, e.g. acetates and formates!

Quality indicators in the PDF database

Each entry (“card”) in the PDF database has a quality indicator assigned.

The meaning of these is the following:

*: high quality experimental pattern
(indexed; observed and calculated peak positions agree very well)

C: pattern calculated from crystal structure data (ICSD number given on the card)

I: indexed (but observed and calculated peak positions do not agree very well)

N: not indexed

Q: questionable

D: deleted (was found to be faulty or was replaced by another pattern; although marked as “deleted”, it is still contained in the database for reference; usually contains a comment explaining the reason for deletion; it will depend from the interface software used to search the database whether deleted cards can be accessed or not)

The new PDF numbering scheme

Since 2003, the entries (“cards”) in the PDF database are numbered according to a new numbering scheme.

Originally the scheme was VVV-PPPP, with VVV being the number of the “set” and PPPP the card number within the set, e.g. 46-1045 for “Silicon Oxide / Quartz, syn” (leading zero in VVV omitted).

The new scheme builds on the old one, expanding the number with two leading digits: SS-VVV-PPPP, e.g. 00-046-1045 for the same entry.

The digits SS have the following meaning:

00 = experimental patterns (historically including also calculated patterns which predate the new numbering scheme!)

01 = calculated pattern from the ICSD

02 = calculated pattern from the CSD (only included in the PDF-4 organics database)

03 = calculated pattern from the NIST (National Institute of Standards and Technology)

Powder diffraction standard materials

The NIST (National Institute of Standards and Technology) offers several “standard reference materials” (SRM) for XRD:

- SRM 640c:
  silicon powder (lattice parameters/peak positions certified; 2θ standard)
- SRM 660a:
  LaB_6 powder (lattice parameters/peak positions certified; very large crystallites, negligible strain; determination of instrument function (peak profile standard), 2θ standard)
- SRM 1976:
  sintered alumina plate (lattice parameters/peak positions certified; relative intensities certified; instrument sensitivity standard, 2θ standard)