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Introduction



Bragg Diffraction

- The most commonly exploited phenomenon in X-ray diffraction techniques is called **Bragg diffraction**.
- Bragg diffraction results from **interference phenomena** between a **periodic lattice** (e.g. of atoms, clusters, pores etc.) with waves of a suitable wavelength (usually monochromatic).
- In the case of X-ray diffraction, the medium which interacts with the photons of the X-rays is the electron density.
- Since diffraction is a geometric phenomenon (measured x-axis = diffraction angle, can be transformed into *d*-space), it is not spectroscopy in the strict sense (x-axis = energy or related property). In contrast to spectra, which are additive (spectrum of mixture = weighted sum of component spectra), diffraction patterns are not strictly additive (though it may often seem so). Hence, a diffraction pattern (diffractogram) should not be called "X-ray spectrum" or "XRD spectrum" (despite the fact that many people in the catalysis community do so...).





Introduction

Bragg's Law

- Bragg's law relates the periodically re-occurring distances of lattice planes (*d*-spacings) to the wavelength λ and the Bragg angle θ (*n* is an integer number): $n \lambda = 2 d \sin \theta$
- In conventional diffraction experiments, a fixed wavelength is used (given property); the *d*-spacings are the unknown property of the sample to be analyzed, while the diffraction angles are the resulting observed property.
- Monochromatization of an X-ray beam using a single crystal monochromator just works the other way around: the given property is the *d*-spacing of the monochromator crystal, and the angle of the crystal to the beam is an adjustable variable by which the wavelength of the diffracted beam can be selected.
- In the special case of energy dispersive diffraction, a polychromatic beam is used. The energy sensitive detector records the diffracted beam spectrum at a fixed diffraction angle. Thus, the diffraction pattern is a spectrum in this special case!



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Simplified Derivation of Bragg's Law

 $n\lambda = 2 d \sin\theta$





Introduction



An Idealized Diffraction Pattern







Introduction

Diffraction Peak Positions

- Both the angle between the incident beam and the lattice planes, and the angle between diffracted beam and the lattice planes, are equal to the Bragg angle θ.
 Thus, the diffraction angle under which a reflection is observed (relative to the projected extension of the incident beam) is two times the Bragg angle, i.e. 2θ.
- For a given crystal structure, there is a (theoretically infinite) number of possible lattice plane sets (*d*-spacings). However, these *d*-spacings are not all independent, but result from a maximum of six lattice parameters (*a*, *b*, *c*; *α*, *β*, *γ*) describing the size and shape of the unit cell (smallest repeating unit of the crystal lattice).
- The number of **independent unit cell parameters** depends on the **crystal symmetry**. For the lowest symmetry (*triclinic*), there are six independent parameters as listed above. For the highest symmetry (*cubic*), there is only a single parameter *a*.
- Summary:

Information about the **unit cell metrics** of a crystalline substance is coded in the observed angular **positions** of the diffraction peaks (for a given wavelength).



Introduction



Diffraction Peak Intensities

- Usually, the unit cell of a crystal structure contains more than a single atom.
- Each **sub-lattice** of the structure, based on different atoms, can be imagined to diffract independently.
- All sub-lattices have the same periodicity, and thus the same *d*-spacings.
- While the incident beam is a coherent wave, the waves of the diffracted (sub-)waves will have **phase shifts** relative to each other, depending on the **positions** of the atoms in the unit cell.
- Different **atom types** have different **scattering power**, hence the diffracted (sub-)waves may also have different **amplitudes**.
- Due to these phase shifts and different amplitudes, various degrees of positive and negative **interference** between the diffracted sub-waves will result in an **intensity modulation** for the resulting total of the diffracted beam.





Introduction



Diffraction Peak Intensities

- In the special case of **centered lattices** (same atom type in the unit cell origin and (face or body) center), some reflections have exactly **zero intensity** (= systematic absence of reflections).
- This can be understood by realizing that both sub-lattices have exactly the same scattering power and a defined geometric relation to each other.

As a consequence, the diffracted sub-waves of some lattice planes have the same amplitude and a phase shift of exactly half a period. Thus, the two sub-waves will cancel out completely.

• Summary:

Information about the **unit cell contents** is coded in the **relative intensities** of the diffraction peaks for a given crystalline phase.





Introduction



Diffraction Peak Profiles

- **Theoretically**, ideal Bragg diffraction should yield **infinitely sharp reflections** (delta functions): a single exact wavelength diffracted at lattice planes with an exactly defined *d*-spacing would fulfill Bragg's law only for an exactly defined angle.
- However, neither the experimental setup nor the investigated sample will ever be ideal. All **imperfections** of the **experiment** and the **sample** will contribute to some softening off Bragg's law, resulting in noticeable **broadening** of the observed peak profiles.
- The sum of all **instrument-related broadening** effects is called **instrumental profile**, while the description of the instrumental profile as a function of the diffraction angle is known as the **instrument function**.
- Since the **sample-related contribution** to the peak profile contains information about the sample imperfections, like **crystallite size**, **microstrain**, **stacking faults** and other defects, a careful **peak profile analysis** should yield information about the nature and amount of such **defects** in the sample.
- However, as the peak profile results from **convolution** of all effects mentioned above, the extraction of a single quantity from the total peak profile is intrinsically difficult.



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Diffraction Peak Profiles

- The sample related contribution to the diffraction peak profiles is often described as a combination of **Gauss** and **Lorentz** (Cauchy) functions.
- A **Voigt** function is a **convolution** of a Gauss and a Lorentz function.

- Gaussian Pseudo-Voigt (50% Gauss) Lorentzian
- A **Pseudo-Voigt** function is a **linear combination** (weighted sum) of a Gauss and a Lorentz function. Pseudo-Voigt functions are **easier to handle** and represent a very **good approximation** to Voigt functions.
- **Simple** Gauss and Lorentz functions may also occur, but can be considered as **boundary cases** of Voigt or Pseudo-Voigt functions.
- Another related function which somewhat came out of fashion is the **Pearson-VII** function.
- Empirically, peaks profiles may also have **super-Lorentzian** line shapes, which can be approximated by superposition of two or more Lorentz functions.
- All of the above functions have some properties in common: they are symmetric, and they do not have a defined cutoff, but drop asymptotically towards zero on both flanks. Thus, a perfectly complete integration would have to be performed over an infinite interval.
- The drop-off behavior of peak-shape functions has implications for practical aspects like **peak overlap**, **correlation** between reflection and **background** shapes, and determination of **peak widths**.



Introduction



Diffraction Peak Profiles

- Generally speaking, two important aspects of the peak profile are the **profile shape** and the **peak width**.
- Depending on the peak shape function used, a parameter describing the **shape** could be e.g. the **mixing parameter** between Gauss and Lorentz contributions to the profile.
- The width of a peak profile can be described by different parameters.
 Most commonly, the full width at half maximum (FWHM) or the integral breadth (IB) are used to express peak width.
- The FWHM is colloquially also known as "half width" and describes the width of a peak at half of its height. The FWHM depends strongly from the Gauss/Lorentz contributions to the peak. It has to be noted that the determination of the FWHM suffers if the baseline of the peak is ambiguous, for example due to peak overlap or problems with background definition. The ambiguity of the baseline translates into the question where exactly half the height is, so that different baseline choices will yield different width parameters for the same peak.
- The integral breadth is defined as the integral (= area) of a peak divided by the peak height.
 Alternatively, you can imagine it as the width of a rectangle which has both the same area and height as the peak.
 This measure is less dependent from the shape of the profile.
 - Although baseline ambiguity also affects both the area determination (integration) and the height of a peak, both errors may partially compensate each other.



Introduction



Information Content of an Idealized Diffraction Pattern



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Size Broadening

The Scherrer Equation

In 1918, Scherrer published an article (in German) in which he related the width of X-ray diffraction peaks to the size of crystalline particles.
 Thus, crystallite size broadening was the first sample-related broadening factor recognized, and still is probably the most dominant factor in peak broadening analysis.

$$h = 2 \sqrt{\frac{\ln 2}{\pi}} \cdot \frac{\lambda}{A} \cdot \frac{1}{\cos \vartheta/2}.$$

- However, it should be noted that the use of symbols and terms in Scherrer's original publication differed from what is current convention. If you look up the Scherrer equation in the literature, you will find as many different ways of symbol use as references.
- Most notably, Scherrer used the term **"particle size"**, while nowadays the use of the term particle size in this context refers to a physical quantity which is usually not accessible by XRD.
- Furthermore, Scherrer used the term " $\vartheta/2$ " to express the angular dependence in his formula, defining ϑ as the **diffraction angle** under which a reflection is observed. Later, it became common practice to express the formula using the **Bragg angle** $\theta = \vartheta/2$.

[P. Scherrer: "Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen", Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-Physikalische Klasse, **2** (1918) 98-100.]



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Size Broadening

The Scherrer Equation

- Scherrer published his equation expressing the **inverse dependence** of the **peak width** from the **crystallite size**. For analytical purposes, the formula has to be rearranged to calculate the size from the peak width.
- The representation given here follows Langford & Wilson, while other authors often use various other symbols, especially for crystallite size and peak width:

$$b = K\varepsilon = \frac{K\lambda}{b\cos\theta}$$

- *p*: 'true' crystallite size
- ε: apparent crystallite size
- K: Scherrer constant (shape factor)
- λ : wavelength
- b: width of the diffraction peak (corrected for instrumental broadening), given in radians
- θ : Bragg angle

[J. I. Langford, A. J. C. Wilson: "Scherrer after Sixty Years: A Survey and Some New Results in the Determination of Crystallite Size", *Journal of Applied Crystallography*, **11** (1978) 102-113.]





Size Broadening

A Simplified View on Size Broadening

- A simple and naive view on size broadening is that Bragg diffraction is based on the periodicity of the crystal lattice. Perfect periodicity would mean infinite crystals. As real crystals are finite, the periodicity stops at a certain point.
 - The smaller the crystal, the smaller the number of periods, and thus the less perfect the Bragg diffraction.
- Another simple view builds on the derivation of the Bragg equation.
 - If the angle does not match the Bragg angle, then for each lattice plane, there will be another lattice plane which gives rise to a diffracted wave with exactly opposite phase.
 - However, this is only true if there is an infinite number of lattice planes.
 - For a finite number, the will be some planes diffracting without a corresponding "partner" to cancel out.
 - The smaller the number of planes, the more serious the partner matching problem becomes.
 - Hence, more planes will give rise to waves which "survive" the destructive interference process occurring in the case of angular mismatch, and thus create more tolerance for the observable diffraction angle (peak broadening).



Size Broadening



What Kind of Size?

• In order to understand the effect of size broadening, we first need to clarify some terms, which, unfortunately, are often used carelessly and imprecisely in the literature.



[Figure taken from the TOPAS 3.0 Users Manual, Bruker AXS]



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Size Broadening

What Kind of Size?

- A particle, or grain, may consist of one or more crystals which are fused together. The size of such a particle is generally not accessible with XRD, but with light microcopy, light scattering techniques, sedimentation etc. For smaller sizes, scanning electron microscopy (SEM) is also an option. The Fusion of several crystals into a particle usually involves large angle boundaries.
- The **crystal** size is also not accessible by XRD, unless the crystal is a single crystal (consisting of only a single domain). Possible size determination methods are generally the same as for particle size determination.
- In the general case, a crystal may consist of several crystallites, which are fused by small angle boundaries (mosaic crystal). This means that, except for a certain mismatch in the orientation, the crystallites show some degree of orientational relation to each other. The mismatch, however, is the reason why crystallites diffract separately in XRD.
 Depending on the boundary conditions (see below), crystallite size can be a quantity accessible with XRD.
- A crystallite may be subdivided into two or more **domains** by two-dimensional defects, like twin boundaries or stacking faults. The nature of such defects causes the domains within a crystallite to have a rather well defined relation to each other concerning their crystal lattice. Whether or not domains within a crystallite diffract coherently with each other depends on the nature of the boundary and its relation to the diffracting crystal planes. Within these limitations, domain size is thus accessible with XRD.
- Crystallite and domain structure, and the defects separating domains within a crystallite, can only be directly investigated with high resolution transmission electron microscopy (HRTEM).



Size Broadening



What Kind of Size?

- Generally speaking, XRD is affected by the size of the coherently diffracting domains.
 Depending on whether domains within a crystallite diffract coherently with each other or not, we thus either detect crystallite or domain sizes.
- Without exact knowledge of the nature of the two-dimensional defects forming the domain boundaries, for example from careful HRTEM investigation, we actually can't know whether we see the size of **domains** or **crystallites**. In fact, different reflections may actually represent different types of sizes.
- With this ambiguity in mind, it is not surprising that the terms "crystallite size" and "domain size" are usually used interchangeably in the literature. The alternative, to stay on the safe side, would be to use the rather cumbersome term "size of the coherently diffracting domain", which is very rarely done.
- An alternative term used in the diffraction community is "**column length**", putting emphasis on the picture of a column of unit cells stacked along the normal of the diffracting lattice planes (diffraction vector).



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Size Broadening

What is Size? – The Shape Factor

- When we talk about size, we tend to think that it is a well defined term. The size of a **sphere**, for example, is best described by its **diameter**.
- The size of a cube is most conveniently given by the length of its edge. However, we could also define it via the length of its diagonal, or by the diameter of a sphere of equal volume...
- Less symmetric shapes need more than one parameter to characterize their dimensions: diameter and height for a cylinder, three edge lengths for a cuboid, three diameters for an ellipsoid...
- The more complex the shape, the more difficult it becomes to define the term "size". From the practical point of view, we need to focus on the question which **physical processes** contribute how to the observable size broadening effect.



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Size Broadening

What is Size? – The Shape Factor

- If we consider a **cube** with unit cell columns stacked **parallel** to its edges, then all columns have the **same length**.
- In the case of a sphere, however, only columns running through the center will be of equal length as the diameter of the sphere.
 Parallel columns left and right will be successively shorter.
- The same argument holds if we consider **other directions** in a **cube**, for example parallel to the diagonals...
- As columns of various lengths are present even in a single crystallite, we need to know the **weighting scheme** according to which they contribute to the average size observable by diffraction peak broadening.
- Standard X-ray diffraction is a **volume effect**. Thus, it is not too surprising that each column of unit cells contributes with the **weight of its volume** to the total effect.
- For simple crystallite shapes, geometric considerations will lead to a defined relation between the (volume weighted) mean column length and the diameter or edge length.

Sphere: $<L>_{Vol} = 3/4 D$





[Figures taken from the TOPAS 3.0 Users Manual, Bruker AXS]



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Size Broadening

What is Size? – The Shape Factor

- A sphere is perfectly isotropic, thus the mean column length is the same for every lattice direction and for every diffraction peak in an XRD pattern.
- In the case of other shapes, even of highly symmetric cubic symmetry, the mean column length will **depend from the direction** within the crystal and thus vary more or less from reflection to reflection.
- All these considerations have lead to the introduction of a **shape factor**, also known as **Scherrer constant**, which is meant to convert an **apparent crystallite size** into a **'true' crystallite size** representing the cubic root of the crystallite volume.
- Langford & Wilson published a thorough discussion of the Scherrer constant in 1978. Apart from the shape of the crystallite and the crystallographic direction, the shape of the diffraction peak profile, the definition of the profile width and the size distribution of the crystallites all influence the Scherrer constant. For example, Langford & Wilson tabulated four different shape factors per lattice plane, corresponding to four different definitions of peak width, for cubic, tetrahedral and octahedral crystallite shapes.
- Due to this complexity, the observation that the Scherrer constant is usually close to unity, and the fact that in most cases the actual crystallite shape is either unknown or ill defined, it has become common practice to use an "overall average" shape factor, which is typically around 0.9.

[J. I. Langford, A. J. C. Wilson: "Scherrer after Sixty Years: A Survey and Some New Results in the Determination of Crystallite Size", *Journal of Applied Crystallography*, **11** (1978) 102-113.]

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Size Broadening

Size Distribution and Mean Values

- In most cases, the crystallites within a sample, even if they should all have the same geometric shape, will not all have the same size.
- Instead, they usually will have a size distribution, which may be
 - narrow or broad,
 - symmetric (i.e. normal distribution) or asymmetric (i.e. lognormal distribution),
 - can be **monomodal** or **polymodal**.
- The presence of a size distribution implies that **integral** methods like XRD will usually give some **mean value** for properties like "size". Thus, we need again to consider which **weighting scheme** applies.
- Most methods of XRD size analysis will give volume weighted average values, but some give area weighted means.





Size Broadening

Different Kinds of Mean Values

- There are many different ways to define mean values for a given distribution function:
- The maximum of the distribution curve represents the most common value.
- The **median** is the value at which the integral of the curve is cut into two halves.
- For the **number weighted mean (arithmetic mean)**, all individual values of the distribution are added, and the sum is divided by the total number of values. Thus, each individual value has the **same weight**.
- In **area and volume weighted means**, each value is given a **different weight** according to the fraction that their area or volume contributes to the total area or volume.



[Figure taken from the TOPAS 3.0 Users Manual, Bruker AXS]





Size Broadening

Different Kinds of Mean Values

- A very simple example:
- Let us assume we have just **two crystallites** over which we average: one has a **diameter of 1**, while the second has **diameter of 2**.
- Consequently, the second crystallite has four times the area or eight times the volume of the first one.
- The arithmetic mean size of the two crystallites will be 1.5, the area weighted mean 1.8, and the volume weighted mean 1.89.





Size Broadening

Different Kinds of Mean Values

- There are many **different methods** proposed to extract crystallite size information from XRD patterns.
- Methods which extract the size broadening by **Fourier-deconvolution** (e.g. the Warren-Averbach method) give **area weighted** mean size values.
- Methods which are based on **peak width** analysis, like the Scherrer method, the Williamson-Hall method or the Double-Voigt approach, yield **volume weighted** mean size values.
- **Direct observation** methods, like measuring and counting crystallites by TEM, give histograms which can be fitted with a distribution function (i.e. normal or lognormal). Usually, this distribution is simply summarized in a **most common** or **arithmetic mean** value.

However, from the fitted **distribution function**, it is also possible to **calculate** area or volume weighted means for better **comparison** with XRD results.





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Size Broadening

Size Broadening – A First Summary

- The physics behind the **crystallite size**-related peak broadening in XRD involves **averaging** on several aspects: Averaging of column lengths **within crystallites** (depending on the **shape**) and averaging **between different crystallites** (depending on the **size distribution**).
- **Different methods** of peak analysis may give **different averages**. This must be taken into account when **comparing** results from different evaluation methods, or comparing with other techniques like TEM.
- **Different people** may get **different results** from the same data set even with the same method, e.g. by using **different shape factors** when using the Scherrer method.
- Size broadening analysis works best in the range of several tens to several hundreds of Å.
- In the **upper size range**, the total peak width becomes dominated by the **instrumental broadening**. Thus, precise extraction of the sample-related broadening is increasingly difficult.
- In the **lower size range**, the contribution of the instrument function is negligible. However, the broadness of the peaks causes strong baseline ambiguity, which in combination with the flat slope of the peak flanks makes the **peak width** determination increasingly **imprecise**.
- Crystallite size broadening is proportional to 1/cosθ.



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Strain Broadening

Strain Broadening

- Lattice strain or microstrain is a local deviation of *d*-spacings from the average value, caused by local defects.
- The origin may be **point defects** like interstitial or missing atoms, or substitution with different atoms.
- Since such defects have a **size differing** from that of the regular atoms in the lattice, the *d*-spacings are **contracted** or **expanded** accordingly around the defect.
- **One-dimensional defects**, like screw dislocations, or **two-dimensional defects** like twin boundaries may also cause microstrain, e.g. if the atoms at the boundary need to be slightly **displaced** in order to match the lattices of both domains.
- Typically, the forces of compression and expansion will be **balanced**, and thus result in diffraction **peak broadening** (variation of *d*-spacings translates into variation of diffraction angle), instead of a peak shift.
- This is in contrast to **macrostrain**, or **stress**, which is **directed** an thus causes **peak shifts**, depending on the relation between the diffraction vector and the strain vector.
- While both size and strain broadening affect the width of diffraction peaks, they show a different angular dependence of the peak width.
- The integral breadth of the strain-related diffraction peak broadening is proportional to tan θ .





Strain Broadening

Comparability of Methods

- Similar to size analysis, different approaches to peak profile analysis will give **different measures for strain**, and thus cannot be compared directly:
- Fourier methods like Warren-Averbach analysis deliver mean-square strain values.
- Integral breadth methods yield a maximum (upper limit) strain value.





Size-Strain Analysis

Size-Strain Analysis – A Brief Overview

A single-peak analysis method proposed by de Keijser, Langford, Mittemeijer and Vogels is based on the assumption that strain broadening is Gaussian while size broadening is Lorentzian, i.e. the shape of a Voigt profile is analyzed in terms of its convoluted Gauss and Lorentz contributions.
 [Th. H. de Keijser, J. I. Langford, E. J. Mittemeijer, A. B. P. Vogels, "Use of the Voigt function in a single-line method for the analysis

of X-ray diffraction line broadening.", J. Appl. Cryst. 15 (1982) 308-314]

- Other methods analyze the full diffraction pattern, trying to extract size and strain information based on the different angular dependence of their respective broadening effects (1/cos θ and tan θ , respectively).
- A relatively simple and thus still widely used method is the Williamson-Hall Plot.
 [G. K. Williamson, W. H. Hall, "X-ray line broadening from filed aluminium and wolfram", Acta Metall. 1 (1953) 22-31]
- A more sophisticated method which can be directly integrated into Rietveld software is the **Double-Voigt Approach**. [D. Balzar, "Voigt-function model in diffraction line-broadening analysis" in: Defect and Microstructure Analysis by Diffraction, edited by R. Snyder, J. Fiala, H. J. Bunge, (1999) 94-126. IUCr/Oxford University Press]





Size-Strain Analysis

Williamson-Hall Analysis

- In 1953, Williamson and Hall proposed a method in which the integral breadth of all diffraction peaks (corrected for instrumental broadening) is plotted in a special way (**Williamson-Hall Plot**).
- Assuming that **both size and strain broadening are Lorentzian**, the integral breadths of both components are **additive**. Thus, the width can be plotted as:

$$\beta^* = (\beta \cos\theta)/\lambda = \frac{1}{D} + 2 e d^*$$

in which β represents the (sample related) integral breadth, λ the wavelength, θ the Bragg angle, *D* the volume weighted mean domain size, *e* a measure for the microstrain distribution and $d^* = 1/d$ the reciprocal lattice spacing. [notation following E. J. Mittemeijer, U. Welzel, *Z. Kristallogr.*, **223** (2008) 552-560.]

- By plotting β* versus d*, fitting the data points with a straight line will yield the crystallite size from the intercept and the microstrain from the slope of the line.
- The **root-mean-square strain** can be calculated according to $<\varepsilon_0^2 > 1/2 = (2/\pi)^{1/2} e$.
- Despite the fact that the derivation of the **Williamson-Hall** method explicitly assumes **purely Lorentzian** broadening, which is often not fulfilled in reality, the method is still widely used.
- A severe **limitation** comes from the fact that the **individual peak widths** have to be accessible, i.e. the method will fail in the case of **extensive peak overlap**.



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Size-Strain Analysis

Williamson-Hall Analysis

- Theoretically, **pure size** broadening will give a **horizontal line** (**no slope**), while **pure strain** broadening will yield a line **through the origin** (**no intercept**)
- In the case of **anisotropic** line broadening, i.e. size and/or strain effects which are a function of the direction in the crystal lattice, the data points of the different reflections will **not fall onto a line**.
- In this case, **families** of higher order reflections representing common directions in the crystal (e.g. 00/ etc.) have to be analyzed separately.
- Unfortunately, families with more then two members and well resolved (non-overlapping) diffraction peaks are rarely available.



FIGURE 3. A plot of β^* ($=\beta \cos \theta/\lambda$) due to simultaneous small particle size and strain broadening against d^* ($=2 \sin \theta/\lambda$). Curve (a) is obtained if the broadening functions are of the Cauchy type whilst curve (b) is that obtained if the functions are Gaussians. The dotted curve (c) represents an intermediate case discussed in the text.





[Figure taken from: G. K. Williamson, W. H. Hall, "X-ray line broadening from filed aluminium and wolfram", *Acta Metall.* **1** (1953) 22-31]

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Size-Strain Analysis

Double-Voigt Approach

- In the **Double-Voigt approach**, both size and strain broadening are modeled by Voigt functions. Thus, there is no general limitation to the components being purely Gaussian or Lorentzian.
- The differentiation of size and strain again relies on their different angular dependence.
- In the framework of convolutional whole powder pattern fitting, in which all contributions (including instrumental functions) are convoluted with each other, this concept **couples** the shapes and widths of **all peaks** belonging to the same phase to each other.
- Thus, **peak overlap** becomes much less of an issue, and a good fit may still resolve size and strain from the pattern.
- If a **good fit** over the whole pattern is **not achieved**, then often the underlying **assumption of isotropy** is **not fulfilled**. In this case, peak widths are additionally a **function** of the **crystal direction**, not only the diffraction angle.





Size-Strain Analysis

Anisotropic Peak Broadening

- As said before, size and strain broadening can be differentiated by their **different dependence from the diffraction angle**.
- However, these properties may additionally vary with the **directions in the crystal**, i.e. the width of the diffraction peaks also becomes a **function of the Miller Indices** *hkl*.
- If this effect becomes noticeable by resulting in **systematic misfits** of the peak widths in whole powder pattern fitting, or by **systematic scattering** in a Williamson-Hall plot, we talk about **anisotropic peak broadening**.
- Concerning size broadening, you can easily imagine crystallites which have the shape of **needles** or **platelets** with a **high aspect ratio**.
- In such a case, it should be clear that the apparent crystallite size may differ by some orders of magnitude in different lattice directions.





Size-Strain Analysis

Anisotropic Peak Broadening

- There are two major problems with modelling/fitting anisotropic peak broadening:
 - finding (and implementing) an appropriate model to describe anisotropy, and
 - keeping the number of refinable parameters low enough.
- In a simple approach, you may restrict your analysis to families of reflections for the principal crystal directions, like h00, 0k0 and 00l.

However, this is then not whole pattern analysis, as you omit the information content of the mixed reflections.

- For true whole pattern fitting, you need a model which includes the treatment of intermediate reflections.
- In the literature, you may find e.g. cylindrical or ellipsoidal models for size anisotropy.
- However, to actually use such a model, you either have to code your own Rietveld program, or need to find available software which supports the respective model.
- Concerning **anisotropic strain broadening**, a **phenomenological model** has been proposed by **Stephens**, which has been implemented in the current version (5.0) of the TOPAS software.

[P. W. Stephens: "Phenomenological model of anisotropic peak broadening in powder diffraction", J. Appl. Cryst. 32 (1999) 281-289.]





Size-Strain Analysis

Anisotropic Peak Broadening

- It should be clear that any anisotropic model will involve a larger number of refinable parameters than a simpler isotropic model.
- Thus, you need to take care that you do not run into problems with "overfitting" your data.
- If the **quality of your diffraction data** (signal/noise ratio, number of reflections, extent of peak overlap, peak/background correlation) does not support the **number of parameters** which you refine in your model, your fit will use its meaning.
- While you may obtain a **good** looking **agreement** between the measured and simulated pattern, this is only a **necessary**, but **not a sufficient** criterion for a **good fit**.
- If the number of refined variables is too high, the parameters start to **correlate** with each other during refinement and thus are correspondingly **ill defined** (too large error bars).
- Consequently, these parameters become simple numbers devoid of a physical meaning!
- It is the responsibility of the scientist to chose a **reasonable** model, with a **low enough** number of parameters to stay robust, and still achieve a **good enough** fit to be trustworthy.
- If you succeed, you may at least hope that your extracted parameters have some physical meaning.





Size-Strain Analysis

Anisotropic Peak Broadening

- The effect of anisotropic peak broadening is not to be confused with preferred orientation effects!
- While both may have their origin in a strongly anisotropic crystallite shape, crystallite size anisotropy will affect the peak width, while preferred orientation will affect the peak intensities (areas).
- However, if anisotropic broadening is subtle enough, our eye may easily **misinterpret** the **width misfit** as an **intensity misfit**, because we can process the deviation in the **peak height** easier than appreciate that the **peak areas** are actually correct.



• **Note:** The preferred orientation fit may or may not bring an improvement. If in doubt, the anisotropic fit should always be performed for comparison.

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Size-Strain Analysis





Isotropic size only (inclusion of isotropic strain does not improve the fit)

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Size-Strain Analysis



Anisotropic Fit



Anisotropic strain model (Stephens model)



Size-Strain Analysis



Anisotropic Fit



Anisotropic size model (modified Stephens model with $1/\cos\theta$ instead of $\tan\theta$ term)

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Stacking Faults

Stacking Faults

- Stacking faults are two-dimensional defects which, depending on their nature and concentration, may affect both the peak profile and the (average) peak position.
- In a stacking fault, the ordered sequence of atoms is disturbed.
- Intrinsic stacking fault: a single layer is removed, the remaining blocks are joined. Alternative view: two blocks are displaced against each other by a single slip between two layers.
- Extrinsic stacking fault: two blocks are separated between two layers and a new layer is inserted. Alternative view: two successive slips.
- Twin boundary: two blocks with inverse stacking sequence are joined at a single layer which is coherent with both blocks.





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Stacking Faults

Effects of Stacking Faults

- High concentrations of stacking faults are usually found in **mechanically treated** close packed metals.
- The effects visible in diffraction patterns may include **asymmetric peak broadening**, as well as **peak shifts** out of the ideal positions.
- The peak asymmetry will **vary between different reflections** and cannot be modeled with conventional whole powder pattern fitting.
- Even in the case of **cubic** symmetry (only one lattice parameter *a*), different peaks may **shift in opposite directions**.
- Stacking and twin faults are typically treated with whole powder pattern modelling methods.



FIG. 4. The influence of deformation faulting on the x-ray powder pattern; the heavy vertical lines represent the sharp components and the shaded areas the diffuse components, while the indices indicate the positions of the reflections from perfect material.

[Figure taken from: M. S. Paterson: "X-Ray Diffraction by Face-Centered Cubic Crystals with Deformation Faults", J. Appl. Phys. 23 (1952) 805-811.]



Stacking Faults



Effects of Stacking Faults



Pd_{0.75}Ag_{0.25} alloy (rolled metal foil)





Cu/MgO (MgO is XRD amorphous)

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WPPM



WPPM vs. WPPF

- Whole Powder Pattern Fitting (WPPF) tries to fit the observed diffraction pattern by using pre-defined peak shape functions as detailed in the introduction.
- These peak shapes can be either **empirical** or based on **physical** considerations.
- Size-strain analysis obviously requires a reasonable choice of physical peak profiles, but not necessarily structural information.
- In contrast, a Rietveld refinement of a crystal structure may work as well, or even better, with empirical profiles.
- Ideally, we would hope to get both **crystal structure** and **microstructure** (size-strain) information from a single fit, but in real systems, we often have to sacrifice one for the sake of the other (i.e. perform two fit approaches on one data set).
- Whole Powder Pattern Modelling (WPPM) takes a different approach. Based on some physically based a priory assumptions, the complete peak profiles are synthesized.
- Due to the **complexity** of this approach, the relevant physical parameters have to be **chosen carefully** and **adjusted manually**, as they cannot be simply refined with a least-squares or similar algorithm.
- In contrast to WPPF, **WPPM** is able to deal with effects like **stacking faults**.
- A problem of WPPM is that the "solution" to modelling a powder pattern is often not unique with respect to the physical parameters isnvolved.



WPPM



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- In contrast to WPPF, WPPM is able to deal with effects like stacking faults.
- A problem of WPPM is that the "**solution**" to modelling a powder pattern is often **not unique** with respect to the physical parameters involved.
- **Outlook:** With ever-increasing computer power, we may see a fusion between WPPF and WPPM in the near future.





Phase Inhomogeneity

Super-Lorentzian Profiles

- Sometimes, peak profiles are "super-Lorentzian", i.e. they have a shape which is even broader at the base and sharper at the tip than a normal Lorentzian profile.
- Thus, such a peak cannot be fitted satisfactorily with a Voigt or Pseudo-Voigt profile.
- Usually, a **superposition** of two (sometimes more) Lorentzian profiles at the **same position** allows a good description of the observed profile shape.
- The occurrence of super-Lorentzian profiles is often an indication for a **heterogeneous** (very broad or multi-modal) **crystallite size distribution**.





Phase Inhomogeneity

Lattice Parameter Variation

- Sometimes, peak profiles take odd, **asymmetric** shapes, have "**feet**" or "**shoulders**", which cannot be described with the usual peak shape functions.
- If instrumental reasons can be excluded, then a possible explanation is that the **lattice parameters** show some (non-symmetric) **distribution**.
- A distribution in lattice parameters should have a reason, the most common case being **chemical variation**, like in **inhomogeneous solid solutions** or a **non-stoichiometric** compound with a certain **phase width**.
- Whether the lattice spacings vary within the crystallites (chemical gradients) or between different crystallites is impossible to resolve by XRD.
- A quick check to see if lattice parameter variation is a reasonable hypothesis is to duplicate the phase in question in the WPPF and have the lattice parameters (and peak shapes) of the two phases refined independently. If the pattern is reasonably well described this way, one may assume that the sample is inhomogeneous with respect to its phase composition.
- However, a successful two-phase fit should not be taken as proof that literally two discrete phases are present. Instead, introducing a second phase may be seen as the first-step approximation to a phase continuum.



Phase Inhomogeneity



Lattice Parameter Variation



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Conclusions

Peak Profile Analysis – What NOT to Do

- Especially in the catalysis community, people often rely on a simple Scherrer analysis of XRD peak broadening, often using single peaks, to extract crystallite size information.
- However, the fact that many people do it does not necessarily mean that it is correct to do so!
- Presence of strain, stacking faults and other defects will also affect the peak broadening, so that they will mess up your results (without you noticing it).
- Use of an **arbitrary shape factor** for lack of better knowledge should be avoided, as introduces further unnecessary ambiguity into your results.
- Single peak analysis, in contrast to multi-peak or whole pattern analysis, will not be able to give you hints concerning the presence of strain. You will also miss any anisotropy effects.
- My favorite quote (by M. Leoni, on the question how to chose a single peak for Scherrer analysis):

 I think you can use the same criterion you use to select numbers to play bingo.
 As (I hope!) you are going to use Scherrer formula on one peak just to get a number (and not to get any physically meaningful information), just select the most isolated, most intense one. At least you play with a better statistics..."
- Overall, I believe that only few of the Scherrer calculations published in the catalysis literature can be taken seriously!



Conclusions



Peak Profile Analysis – What NOT to Do

- A formula like the Scherrer equation will never refuse to do its "job": You feed it with a number, and it will give you another number in return.
- Whether this number bears any physical meaning is a completely different question.
 It is within the responsibility of the scientist who uses the formula to critically assess whether the underlying assumptions are reasonable or not.
- If it is your ambition just to fill some table column in your thesis with some numbers, then go ahead and use the Scherrer formula.
- If you feel like doing science, you should critically check whether there is a more reasonable way to do the job.
- Remember:

People tend to believe in numbers.

If your thesis or paper contains a table with crystallite sizes,

and a whole paragraph explaining under which assumptions these numbers would be valid,

then most readers will still focus on the numbers,

take them more literally then they should,

and skip reading your careful explanation!



Conclusions



Peak Profile Analysis – What to Do?

- Scherrer's publication is now almost 100 years old.
 In the meantime, many more important contributions to peak profile analysis have been made.
- However, there is **no universal agreement** on which method is "best" suited to extract the desired information.
- The reason is that the validity of a peak profile analysis always depends on the question whether the **basic assumptions** involved in the derivation of the method are met by a particular sample system or not.
- So far, there is **no universally applicable method** of peak profile analysis that would work **for all sample systems**!
- Thus, the method of choice always depends on your system, and has to be critically checked (by independent methods) for validity.
- **Electron microscopy** is the **essential** tool for cross-checking XRD based microstructure analysis.
- If you are lucky, you may be able to separate size and strain effects.
- If you should have a system with stacking faults, there is not much that you can do.



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Conclusions

Peak Profile Analysis – What to Do

- A strategy to establish a reasonable size-strain analysis on a new sample system could be as follows:
- You need a sample series in which the parameter(s) to be analyzed vary sufficiently to yield appreciable differences in the XRD results.
- The analysis method you chose should work reasonably well **for all samples** of the series. Otherwise, your model is obviously missing a crucial component.
- Still, try to keep your model as simple as possible to avoid overfitting of your data.
- Use your **scientific knowledge** to critically review the **assumptions** your model is based on. For example, if you investigate a **solid solution** series with ions of different size, it would be quite unreasonable to ignore the possibility of **strain** which can be expected due to the size mismatch.
- When you find a model which performs well and seems to give **reasonable trends**, you need to **validate** your model with an **independent method** (EM).
- It is not necessary to validate all data points. Just chose some extreme and some average examples for a start.
- If both methods agree (not necessarily quantitatively!), you should get something like a correlation/calibration curve.
- If you are now able to **predict** e.g. the EM size of a new sample by analyzing its XRD pattern (or *vice versa*), then you are obviously on the right track!
- Don't be disappointed if you cannot trust **absolute values** for most methods. In most cases, it is sufficient to recover **trends**.





Suggested Reading

Some selected review papers and books:

R. E. Dinnebier, S. J. L. Billinge (Eds.),
 Powder Diffraction: Theory and Practice,
 RSC Publishing (2008),
 https://dx.doi.org/10.1039/9781847558237

 E. J. Mittemeijer, P. Scardi (Eds.),
 Diffraction Analysis of the Microstructure of Materials, Springer Series in Materials Science Volume 68 (2004), https://dx.doi.org/10.1007/978-3-662-06723-9

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The "state of the art" of the diffraction analysis of crystallite size and lattice strain, *Z. Kristallogr.* **223** (2008) 552-560,

https://dx.doi.org/10.1524/zkri.2008.1213

 D. Balzar, N. Audebrand, M. R. Daymond, A. Fitch, A. Hewat, J. I. Langford, A. Le Bail, D. Louër, O. Masson, C. N. McCowan, N. C. Popa, P. W. Stephens, B. H. Toby,
 Size-strain line-broadening analysis of the ceria round-robin sample, J. Appl. Cryst. 37 (2004) 911-924, https://dx.doi.org/10.1107/S0021889804022551

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