Powder Diffraction

Powder diffraction is used in many contexts, and especially in industrial applications such as quality control.

-- qualitative phase analysis

-- quantitative phase analysis, or composition

-- lattice parameters

-- identification of polymorphs

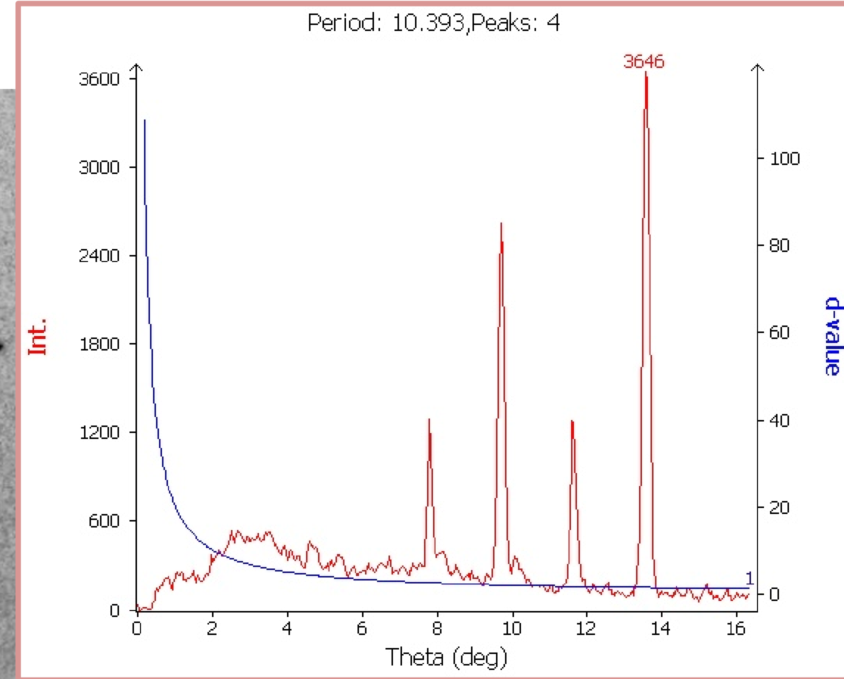
-- refinement of structural parameters, for a variation on a known structure

-- *ab initio* determination of structure, with refinement

-- physical properties, stress, texture, lattice defects, domain size

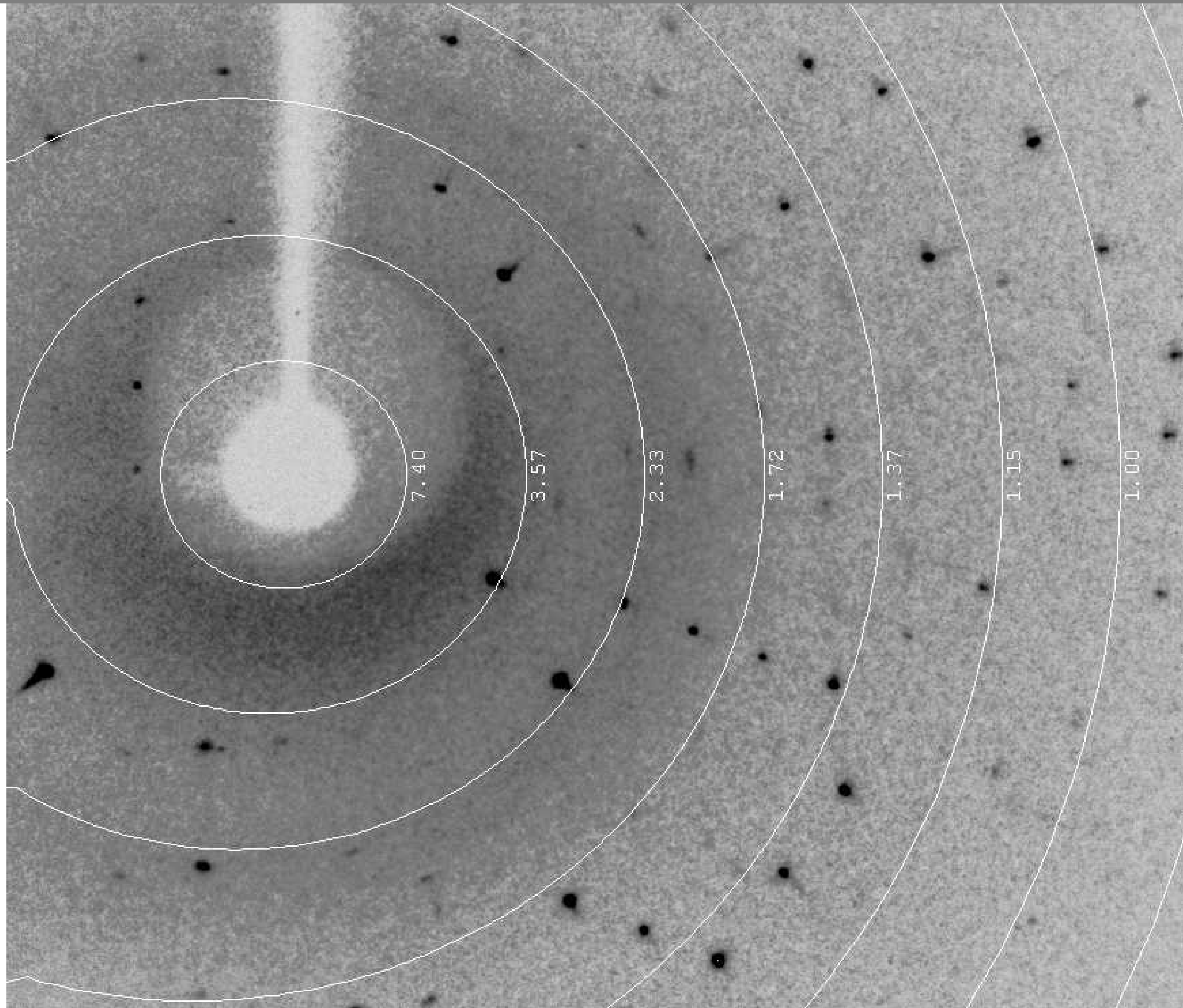
Powder Diffraction

Characteristics of powder diffraction patterns

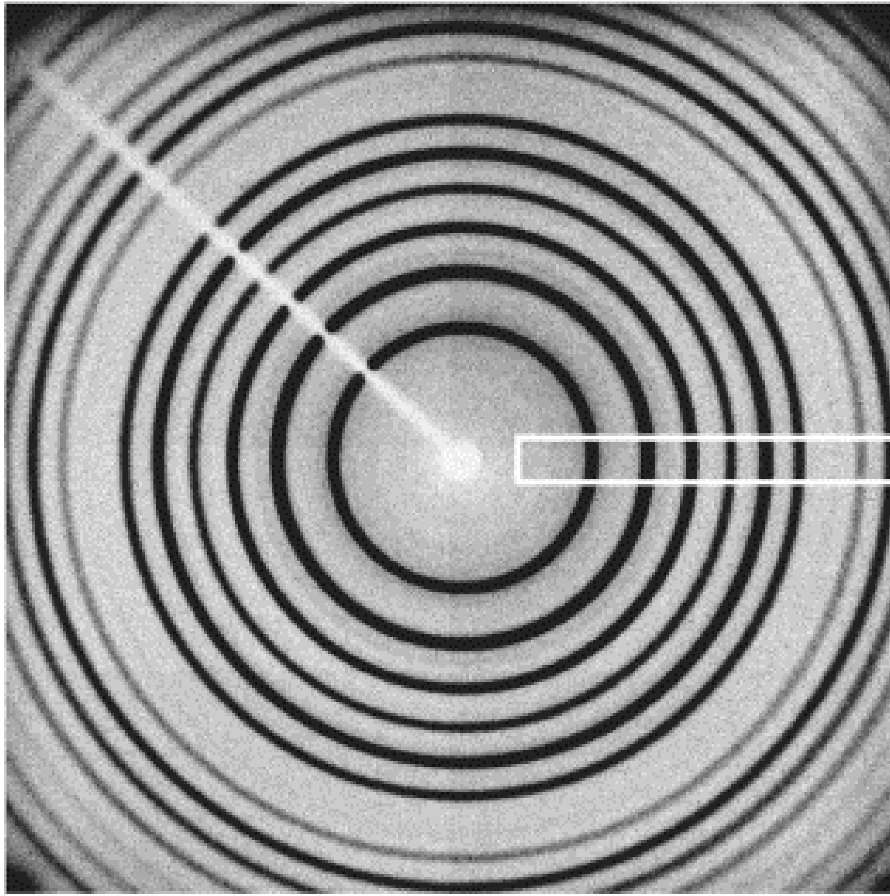


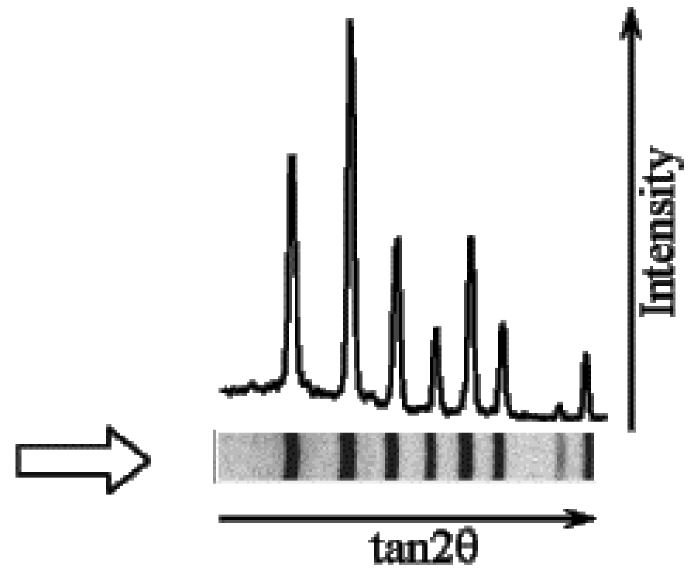
Powder Diffraction

Rings of equal resolution

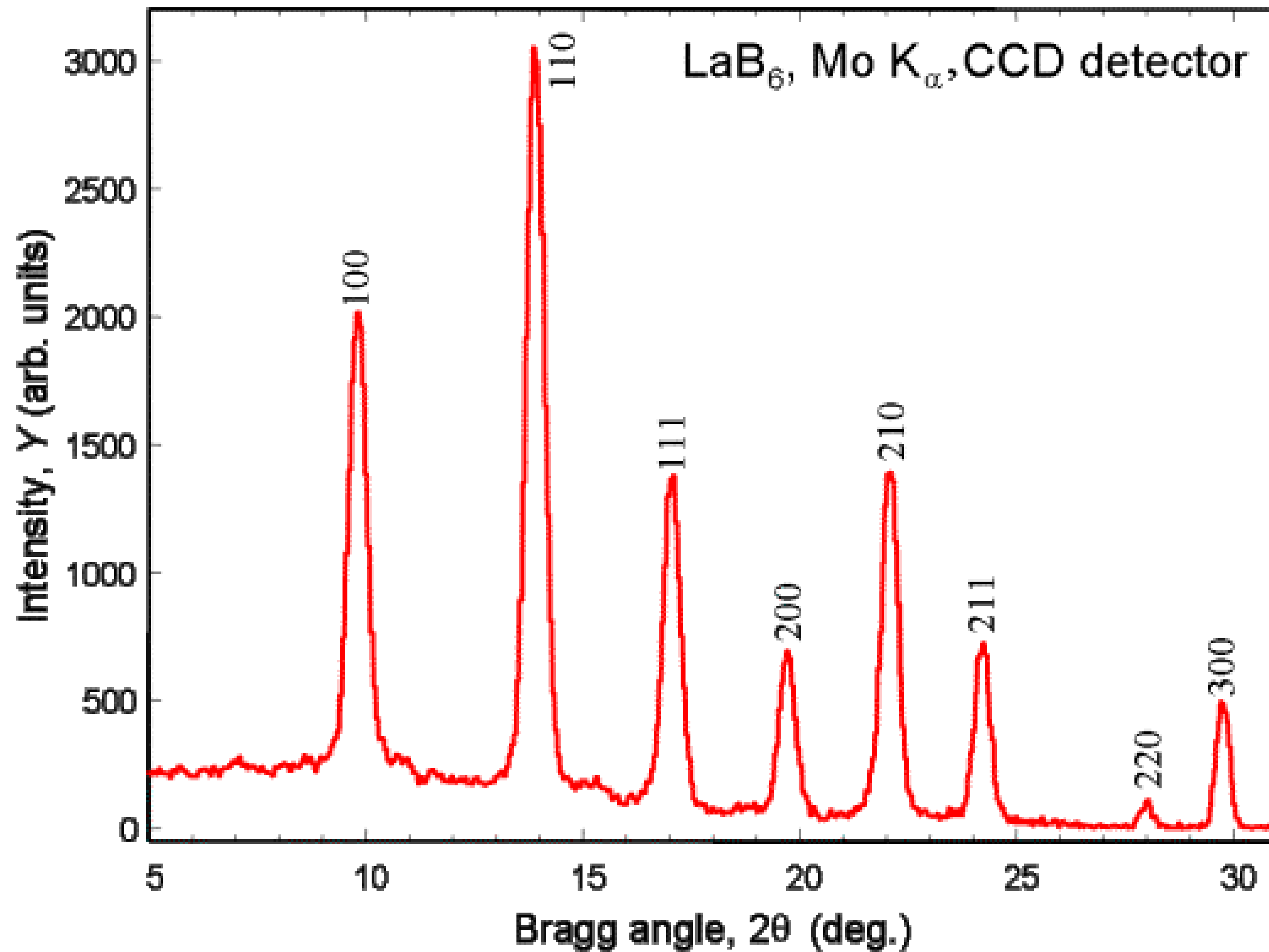


Powder Diffraction Patterns



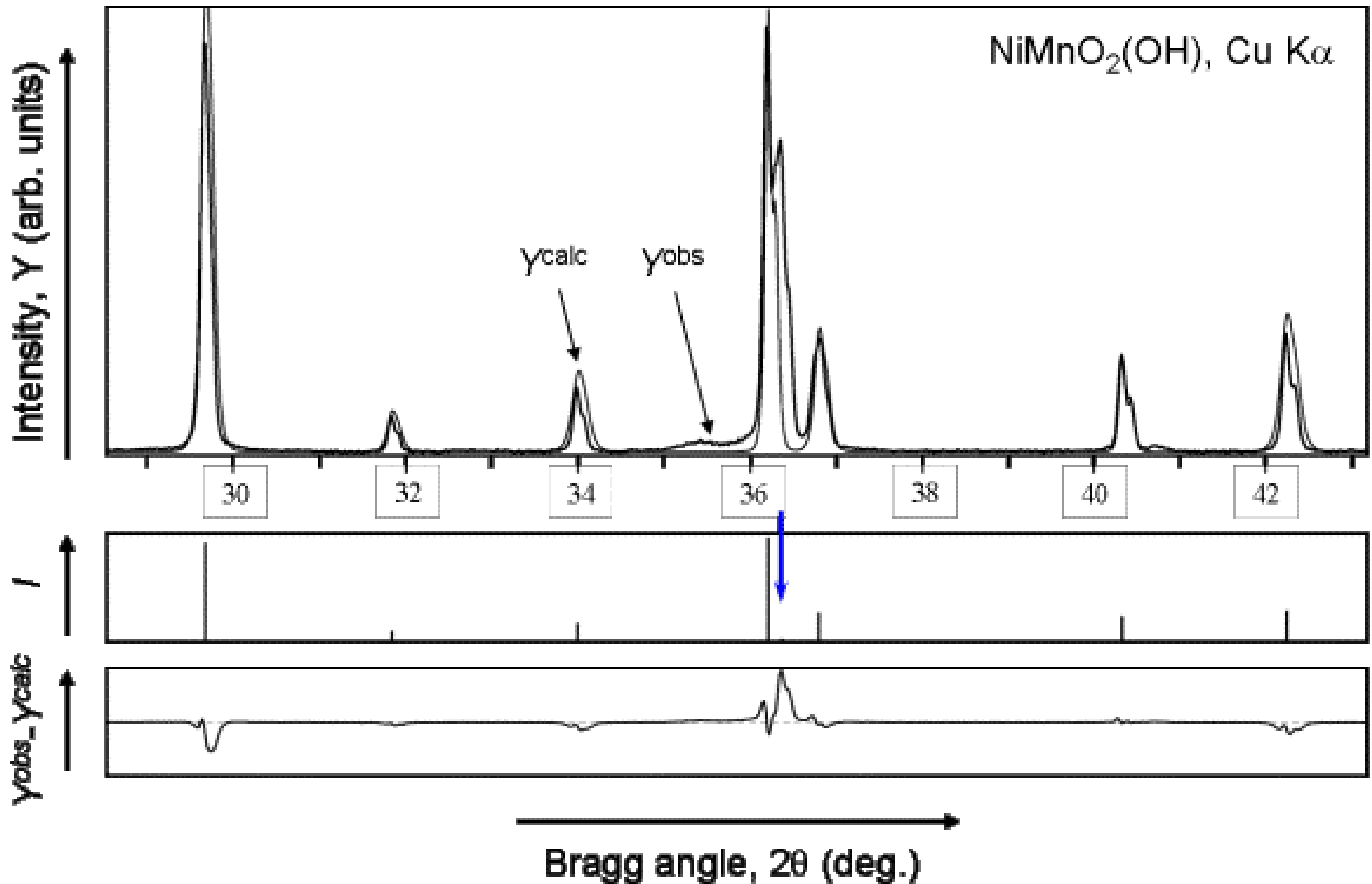


Powder Diffraction Patterns



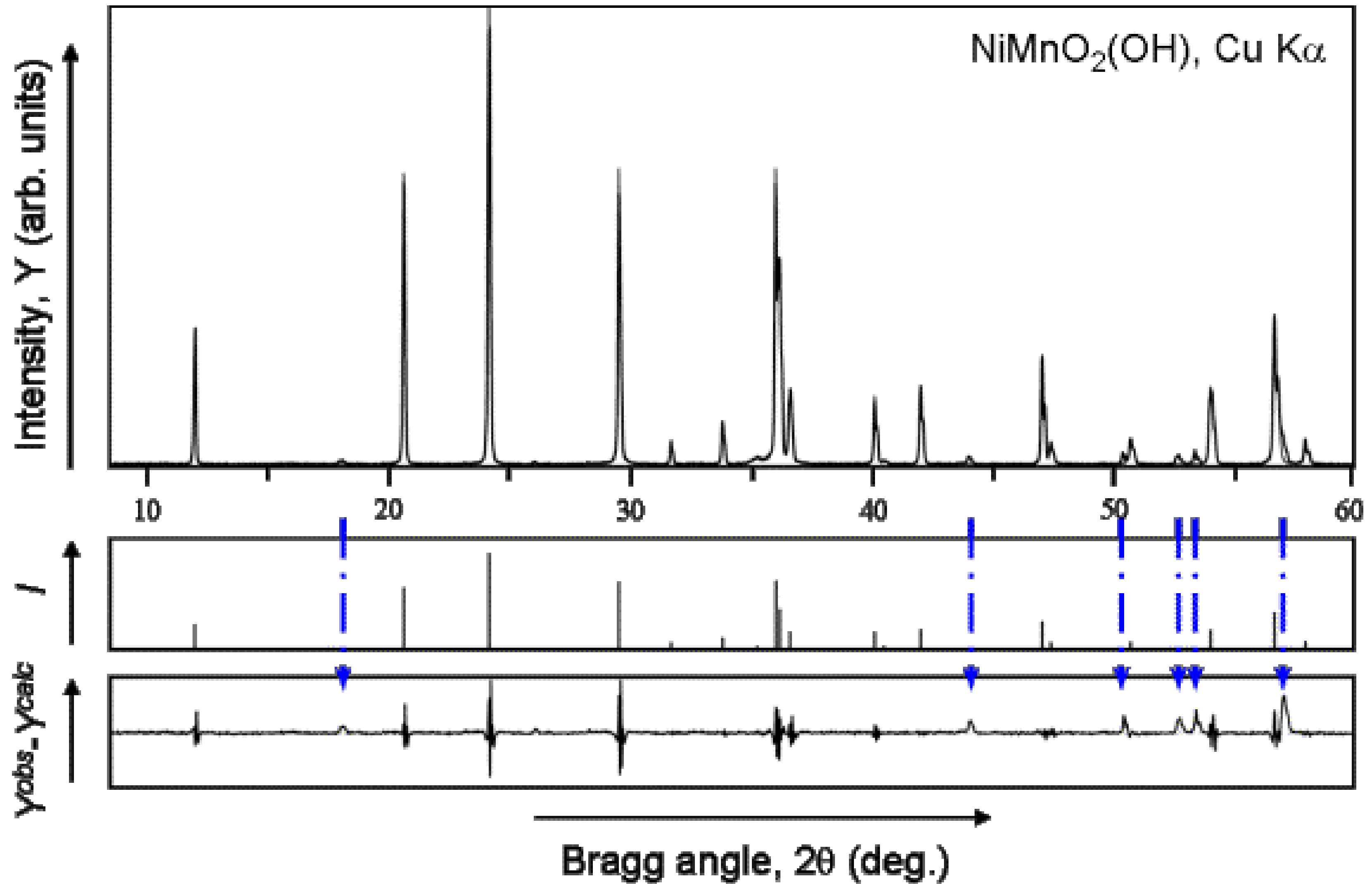
V. K. Pecharsky & P. Y. Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials, Springer, 2005.

Powder Diffraction Patterns



V. K. Pecharsky & P. Y. Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials, Springer, 2005. Fig. 4.9.

Powder Diffraction Patterns



V. K. Pecharsky & P. Y. Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials, Springer, 2005. Fig. 4.14. Flechas azules señalan picos que todavía no están incluidos en el ajuste.

Peak Shapes in Powder Diffraction

For any application for which a high degree of accuracy is needed, such as profile fitting or Rietveld refinement, it is essential to model the peak shapes in the diffraction pattern. Peak overlap and other factors that depend on the instrument, on the radiation and on the sample itself, combine to make peak-shape modeling a non-trivial process.

The description of the peak shapes can be:

- purely empirical, fitting the profile with parametric functions.
- based on fundamental parameters, with realistic models for instrumental factors, or for the effects of characteristics of the sample, or for wavelength dispersion, all of which contribute to the peak shapes.
- semi-empirical, with a realistic model for the sample contribution and with empirical models for instrumental and wavelength dispersion effects.

Peak Shapes in Powder Diffraction

Gaussian: $$y(x) = G(x) = \frac{C_G^{1/2}}{\sqrt{\pi}H}\exp(-C_G x^2)$$

Lorentzian: $$y(x) = L(x) = \frac{C_L^{1/2}}{\pi H'}(1 + C_L x^2)^{-1}$$

x is the coordinate $(2\theta_i - 2\theta_k)/H_k$, in which $2\theta_i$ is the Bragg angle (2θ) for point i and $2\theta_k$ is the Bragg angle for the peak $hk\ell$. H_k is the FWHM (full width at half maximum) and C_G and C_L are normalization factors such that:

$$\int_{-\infty}^{\infty} L(x)\,dx = 1 \qquad \int_{-\infty}^{\infty} G(x)\,dx = 1$$

Peak Shapes in Powder Diffraction

Pseudo-Voigt, combination of Gaussian and Lorentzian:

$$PV(x) = \eta \frac{C_G^{1/2}}{\sqrt{\pi} H} \exp(-C_G x^2) + (1-\eta) \frac{C_L^{1/2}}{\pi H} (1 + C_L x^2)^{-1}$$

η: mixing parameter

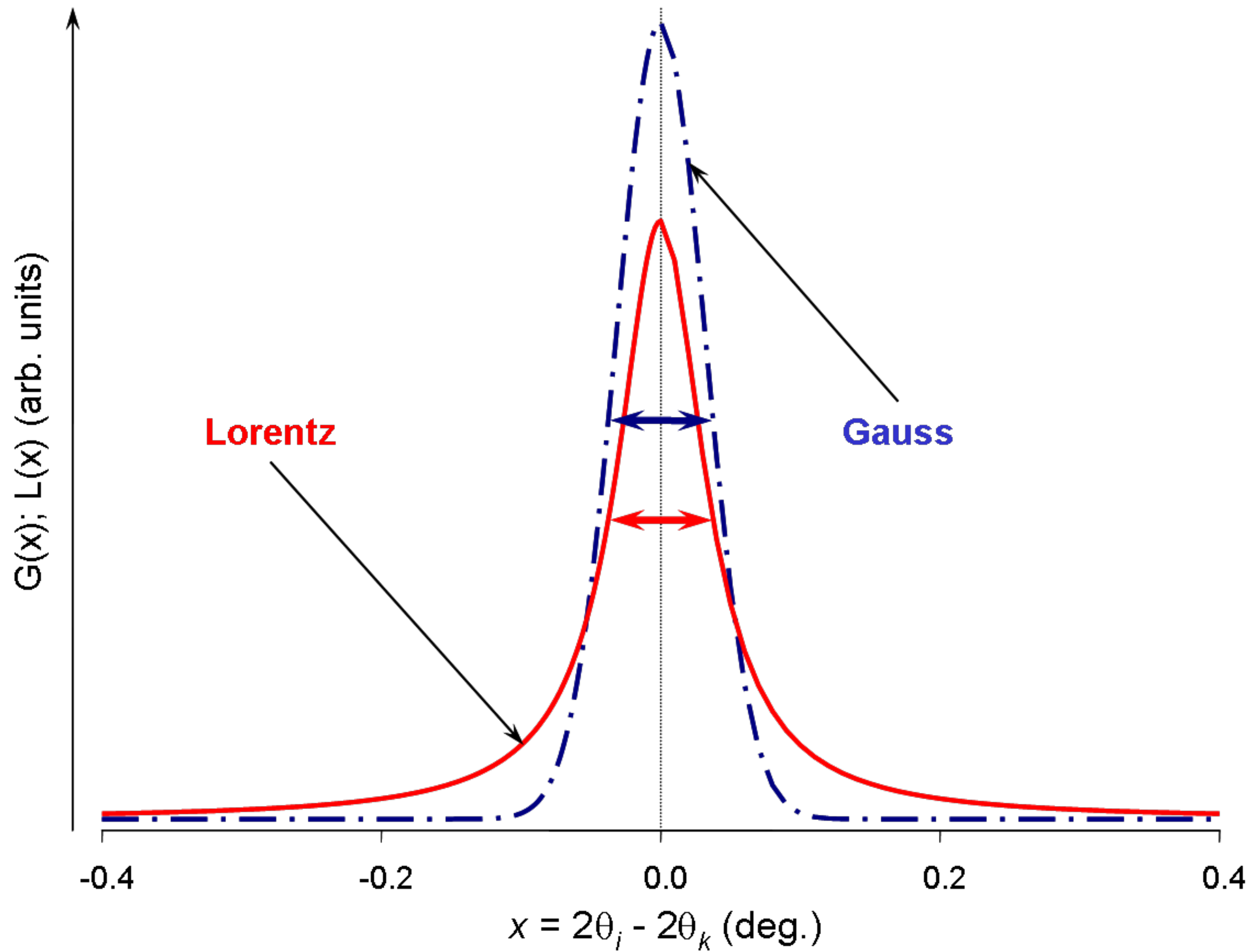
Pearson - VII:

$$y(x) = PVII(x) = \frac{\Gamma(\beta)}{\Gamma(\beta - 1/2)} \frac{C_P^{1/2}}{\sqrt{\pi} H} (1 + C_P x^2)^{-\beta}$$

Γ: gamma function. C_P: normalization factor such that:

$$\int_{-\infty}^{\infty} PVII(x)\, dx = 1$$

Peak Shapes in Powder Diffraction



Pecharsky & Zavalij, Figure 2.42.

Peak Shapes - Asymmetry

The peaks in a powder diffraction pattern are not normally symmetrical about their midline. Because of various experimental effects, such as axial dispersion, it is commonly observed that a peak is wider on its low-angle side, especially for low-2θ peaks.

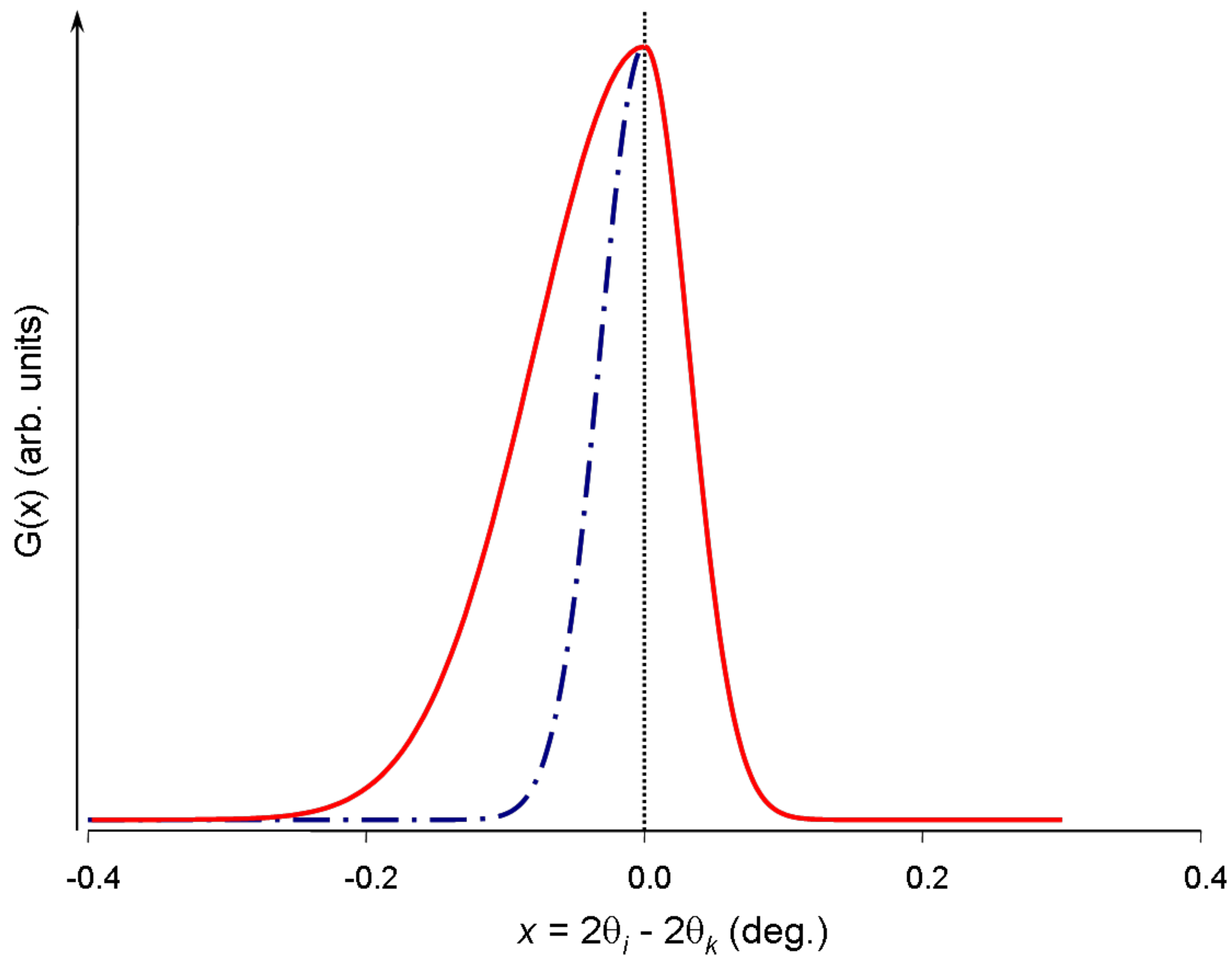
With Soller slits the effects of axial divergence can be minimized, but it is not possible to eliminate the asymmetry completely. Thus, it is necessary to have peak-asymmetry models for use in modeling the diffraction pattern.

Some simple models use an asymmetry parameter α in the mathematical descriptions of peak asymmetry.

Another approach to the question of peak asymmetry consists of the use of split functions for the peak shapes, so that there are two sets of shape parameters, one for the low-angle side and the other for the high-angle side.

Thus, we have the "split pseudo-Voigt" y "split Pearson-VII“ models.

Peak Shapes - Asymmetry



Pecharsky & Zavalij, Figure 2.45.

Multiplicity

Reciprocal lattice points that are equivalent under the Laue symmetry of the crystal give rise to diffracted peaks that have the same scattering angle 2θ. In the powder diffraction pattern these are overlapped, giving a diffracted intensity that is augmented according to the corresponding symmetry multiplicity.

There are a great number of symmetry relationships of this type, so the appropriate multiplicity factor has to be included when modeling the powder pattern.

For a centrosymmetric crystal, the multiplicity of a general reflection is equal to the multiplicity of the Laue group. For example, for an orthorhombic crystal a general reflection $hk\ell$ mas multiplicity 8 (Laue group *mmm*).

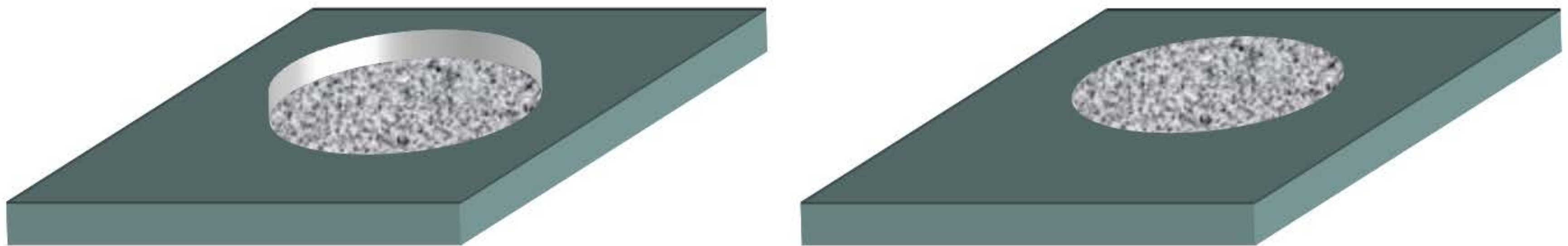
Multiplicity

Special reflections – whose reciprocal lattice points lie on point symmetry elements – have reduced multiplicity. For example, in the orthorhombic Laue group *mmm* (multiplicidad 8), a reflection of the type *h00* (*mm2* symmetry in the Laue group) has a multiplicity of 2 and a reflection in the net *hk0* (symmetry *m*) has a multiplicity of 4.

If the point group of the crystal is not centric, for accurate applications we use the point group of the crystal (not the Laue group) to calculate the multiplicity, because of resonant scattering (anomalous dispersion) and the resulting deviations from Friedel's Law.

Preferred Orientation

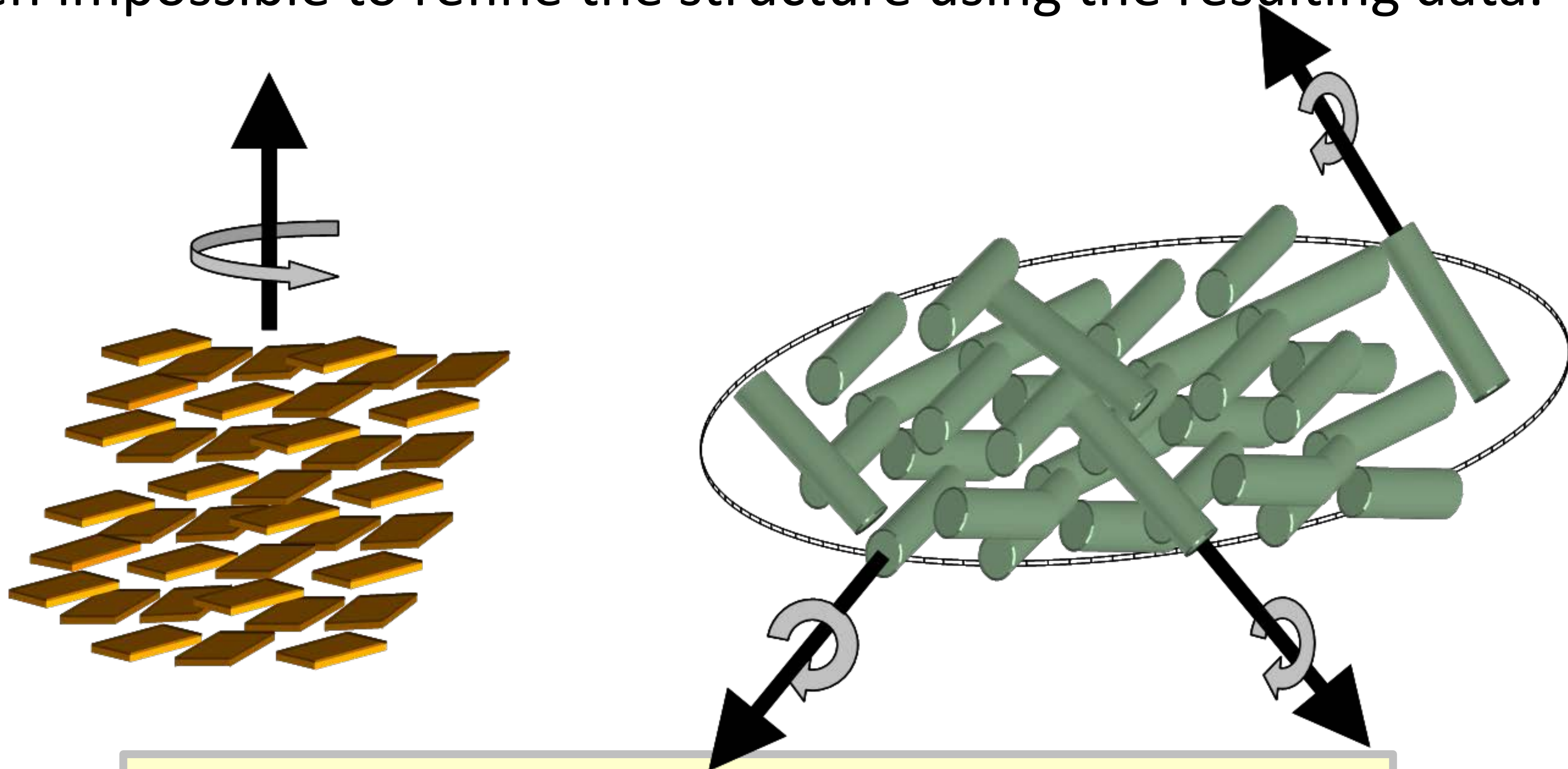
Ideally, a powder sample will have a ‘large’ number of particles, all spherical, with random orientations.
En reality, the crystallites can have different shapes, which include plates or needles, that can align themselves preferentially in the bulk sample.
Moreover, the user can provoke the phenomenon of preferred orientation, for example by pressing the sample into the sample holder.



Pecharsky & Zavalij, Figure 3.21, p. 292.

Preferred Orientation

Preferred orientation, with its corresponding variation from the model of the powder as a large number of microcrystallites with completely random orientations, gives rise to systematic variations in the intensities of the diffraction peaks. This renders it difficult or even impossible to refine the structure using the resulting data.



Pecharsky & Zavalij, Figure 3.20, p. 291.

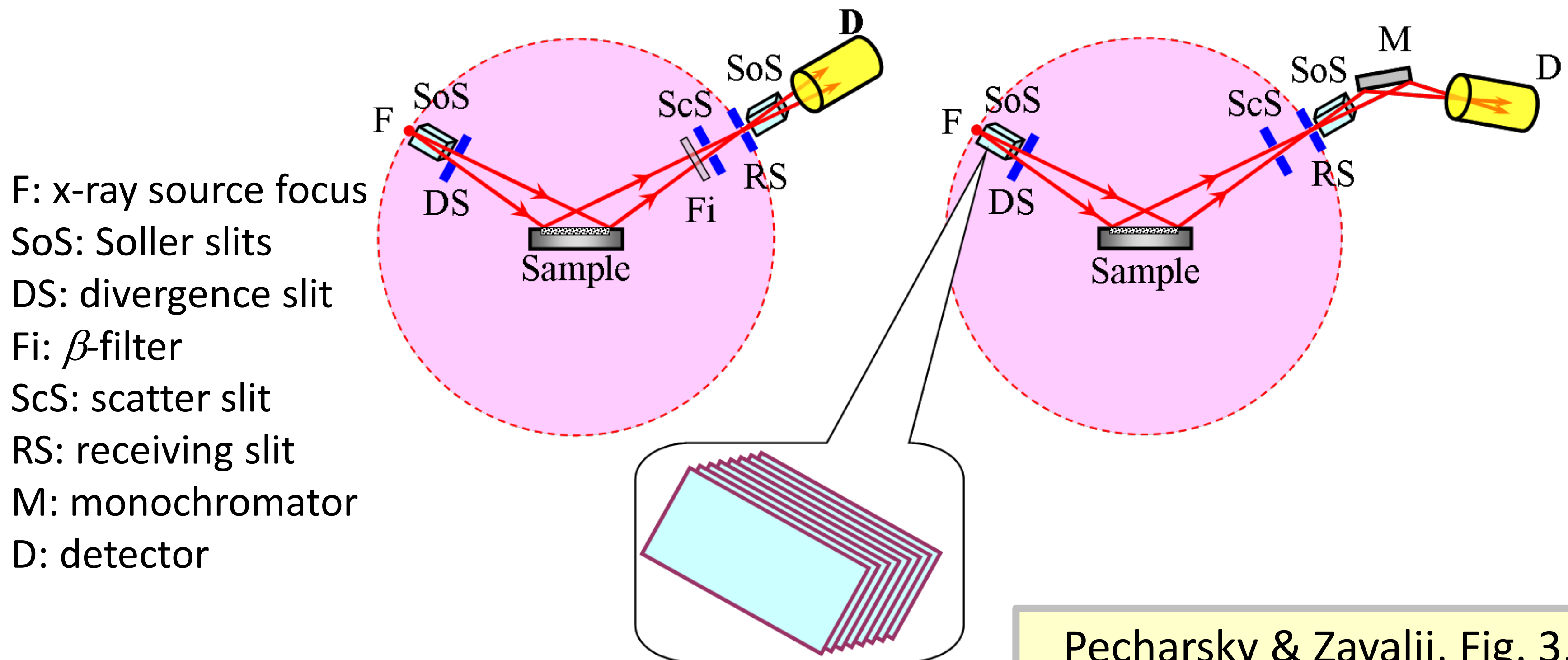
Preferred Orientation

When refining a structural model using powder diffraction data, it is possible to refine a model of the preferred orientation. Several models exist.
If the particular preferred-orientation problem fits one of the theoretical models, it is possible to arrive at a correct refinement.

Pecharsky, V. K., Akselrud, L. G. & Zavalij, P. Y. (1987).Sov. Phys. Crystallogr. 32, 514.
Dollase, W. A. (1986). J. Appl. Cryst. 19, 267-272. doi:10.1107/S0021889886089458

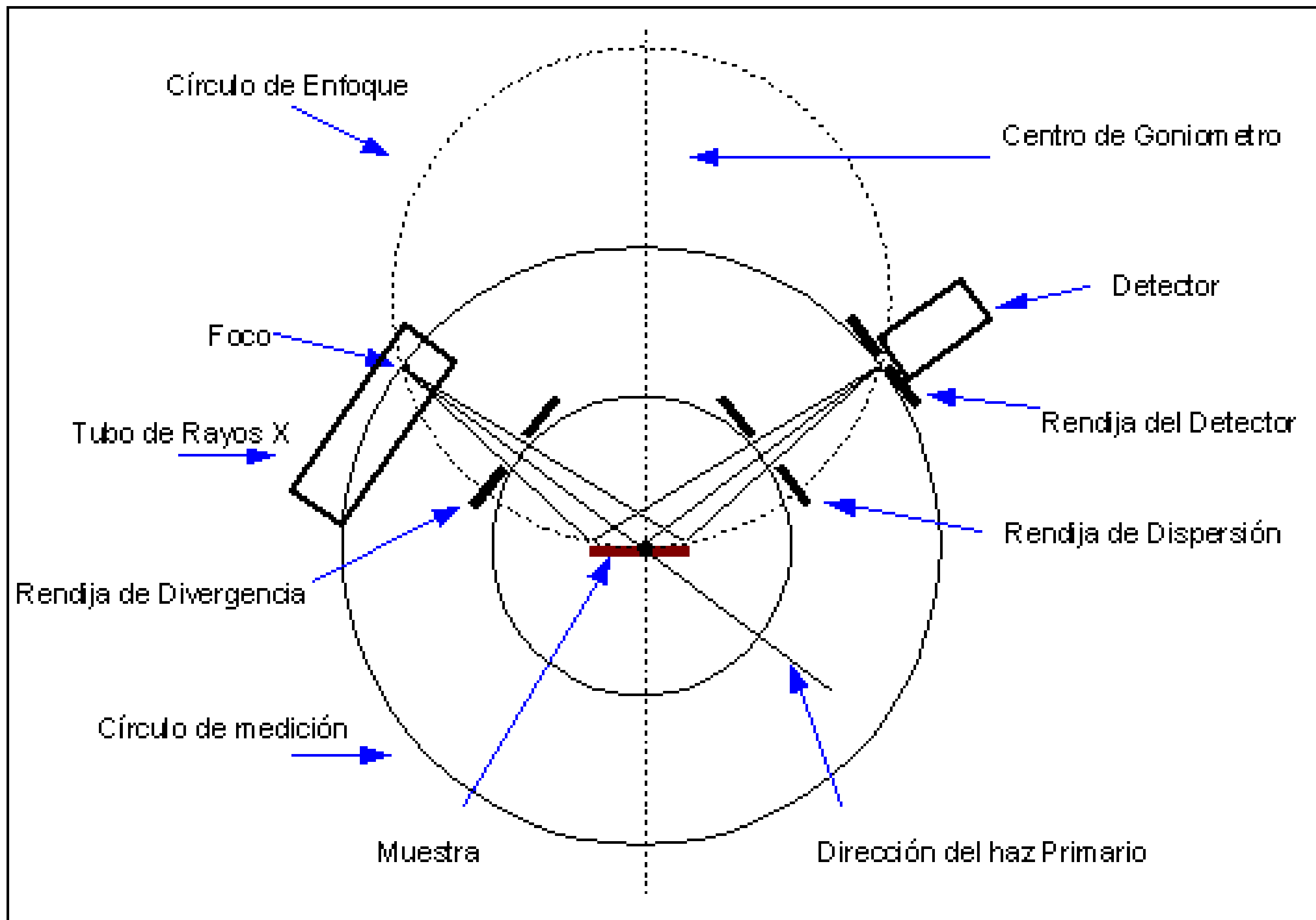
Bragg-Brentano Geometry

The most commonly used diffractometer configuration is that with Bragg-Brentano geometry, and specifically that with focusing Bragg-Brentano geometry. There exist many variations of the technique, but the basic principles are the same in all cases.



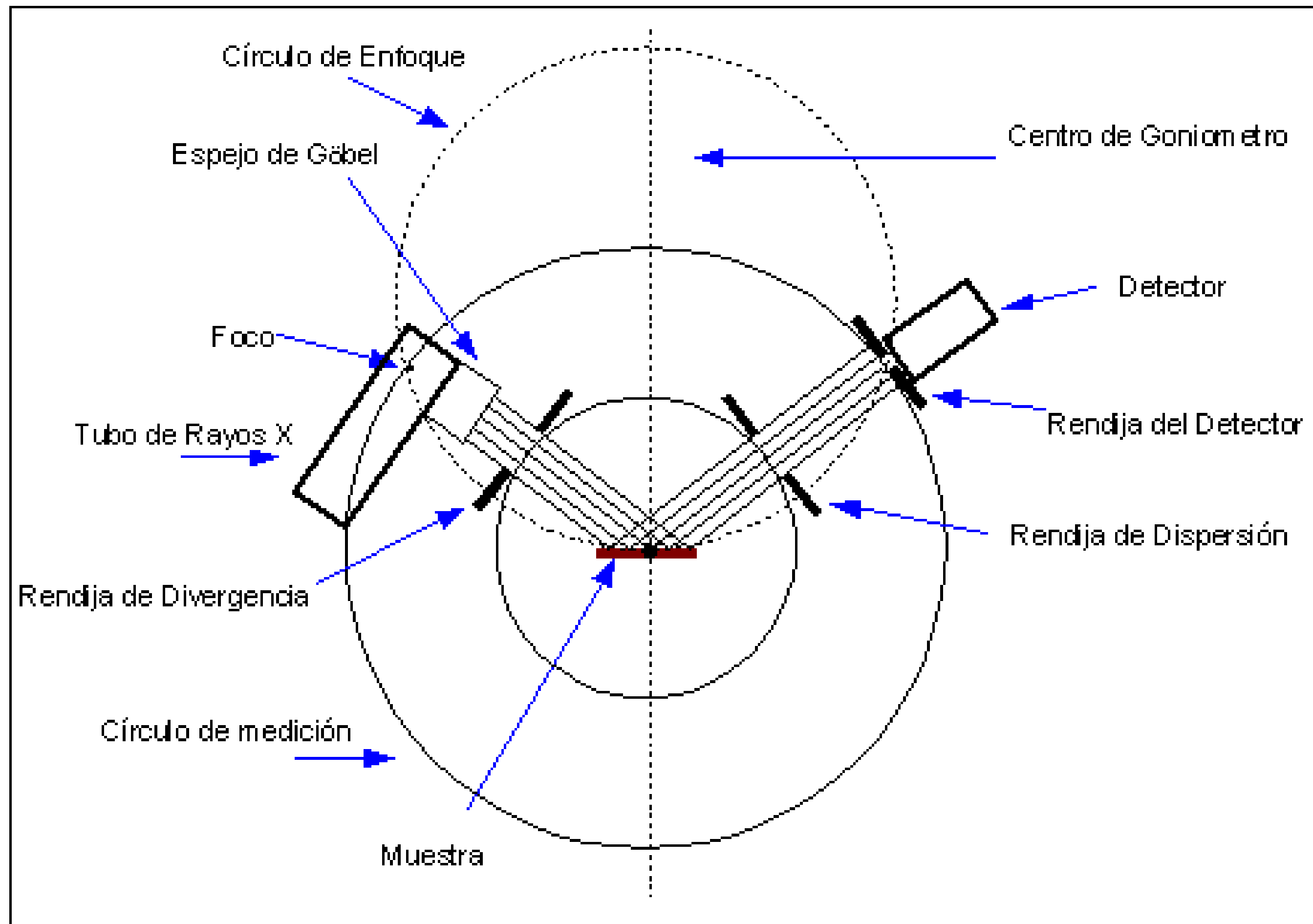
Pecharsky & Zavalij, Fig. 3.6.

Bragg-Brentano Geometry



http://servicios.fis.puc.cl/rayosx/teoria.html

Parallel Beams



If the sample is irregular, it can be studied using a parallel beam.
http://servicios.fis.puc.cl/rayosx/index.html

Powder Diffraction Data Processing

The manner in which powder diffraction data are processed depends on the objective of the analysis, which could be, for example, the identification of the phase(s) present, or the determination of the unit-cell dimensions, or a complete structure analysis.

It is normally necessary to derive the so-called reduced data, which consist of a list of data in terms of the reciprocal lattice – for each point we will have *hkℓ,* the scattering angle 2θ (or $d_{hk\ell}$ or $d^*_{hk\ell}$) and its intensity (or the square root of the intensity, which is the structure factor modulus $|F_{hk\ell}|$).

There are various ways to process the data so as to eliminate instrumental effects and other possible errors.

Background Correction

The background noise in a powder diffraction pattern has its origins in instrumental factors (incomplete monochromatization, scattering from the sample holder, detector electronics) and in scattering processes (inelastic scattering, air scattering, fluorescence).
For some purposes, such as the elimination of the scattering of $K\alpha_2$ radiation, it is necessary to eliminate the background noise.
For other purposes, such as the refinement of structural parameters, the background is not eliminated; rather, it is modeled as part of the refinement.

Background Correction

The elimination of the background noise consists of subtracting the background intensity from the total intensity at each point in the diffraction pattern.

The intensity of the noise is calculated by interpolating between selected points, which are chosen either automatically by a program or manually by the user.

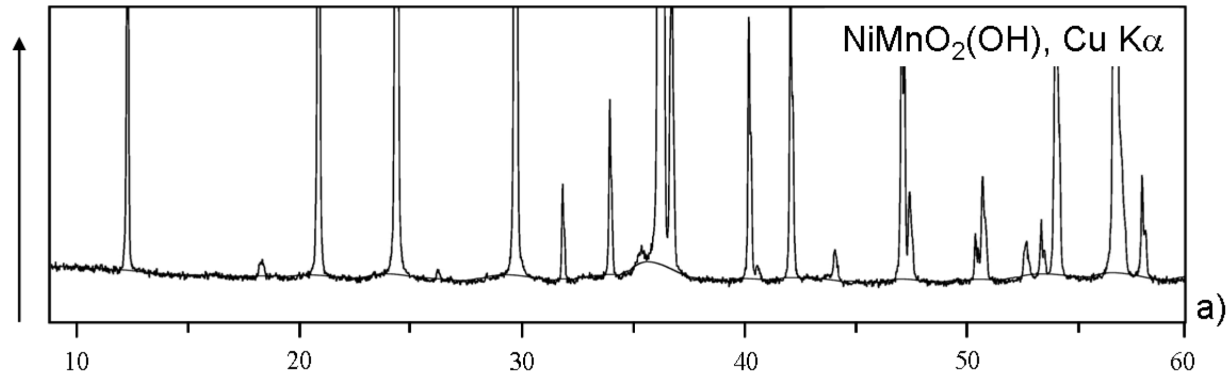
The interpolation is normally done using polynomial or Fourier expansions.

The polynomial can be, for example, a simple expansion in powers of 2θ, or it can be a Chebyshev or Fourier polynomial.

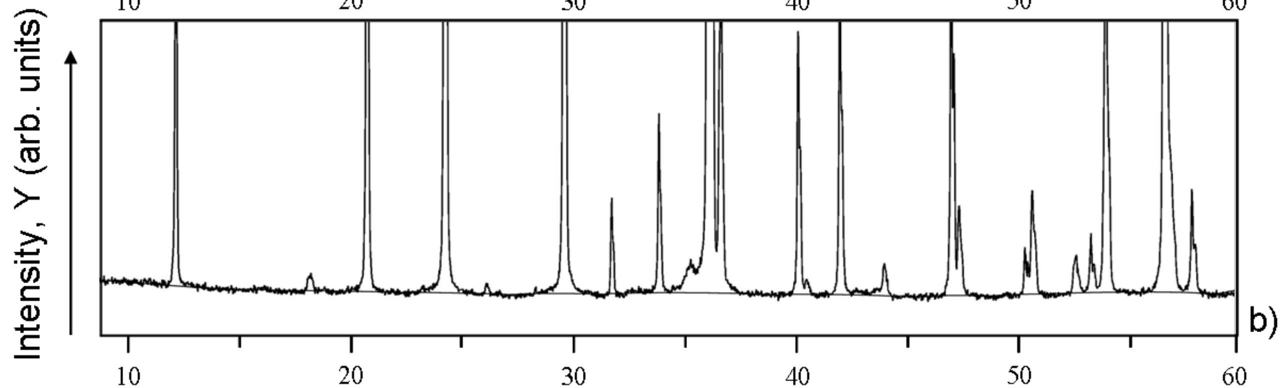
Pecharsky & Zavalij, p. 351.

Background Correction

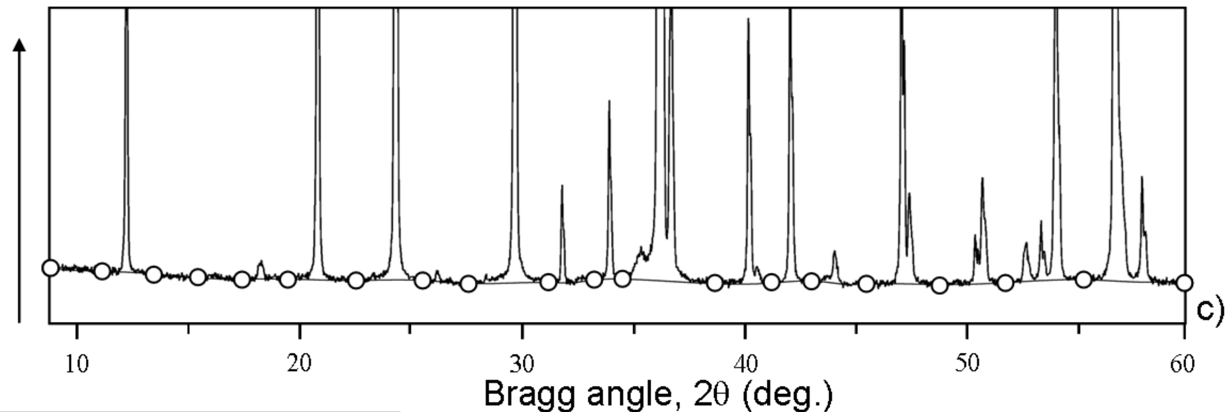
Automatic, non-ideal result.



Automatic, a better result but still not ideal at the bases of the strong peaks.



Manual, the user has selected the points indicated by circles; this is the best of the three results in this case.



Pecharsky & Zavalij, Figure 4.4.

Smoothing

Diffraction pattern smoothing eliminates the statistical noise that has its origins in the random errors in intensity measurements. Although the resulting powder pattern has a better appearance, smoothing is not able to improve the quality of the data.
Smoothing can help to improve the results of $K\alpha_2$ elimination, or in peak searching.
Smoothing is not performed on data that will be used in accurate calculations in which background noise is modeled, for example in structure refinement (Rietveld) or in profile fitting.

Smoothing

Smoothing is done by calculating the weighted mean of a data point and a certain range of adjacent points. For example, a five-point smoothing could have w_o = 1 (for the point being smoothed), w_1 = 0.5 for its immediate neighbors and w_2 = 0.25 for its second neighbors.

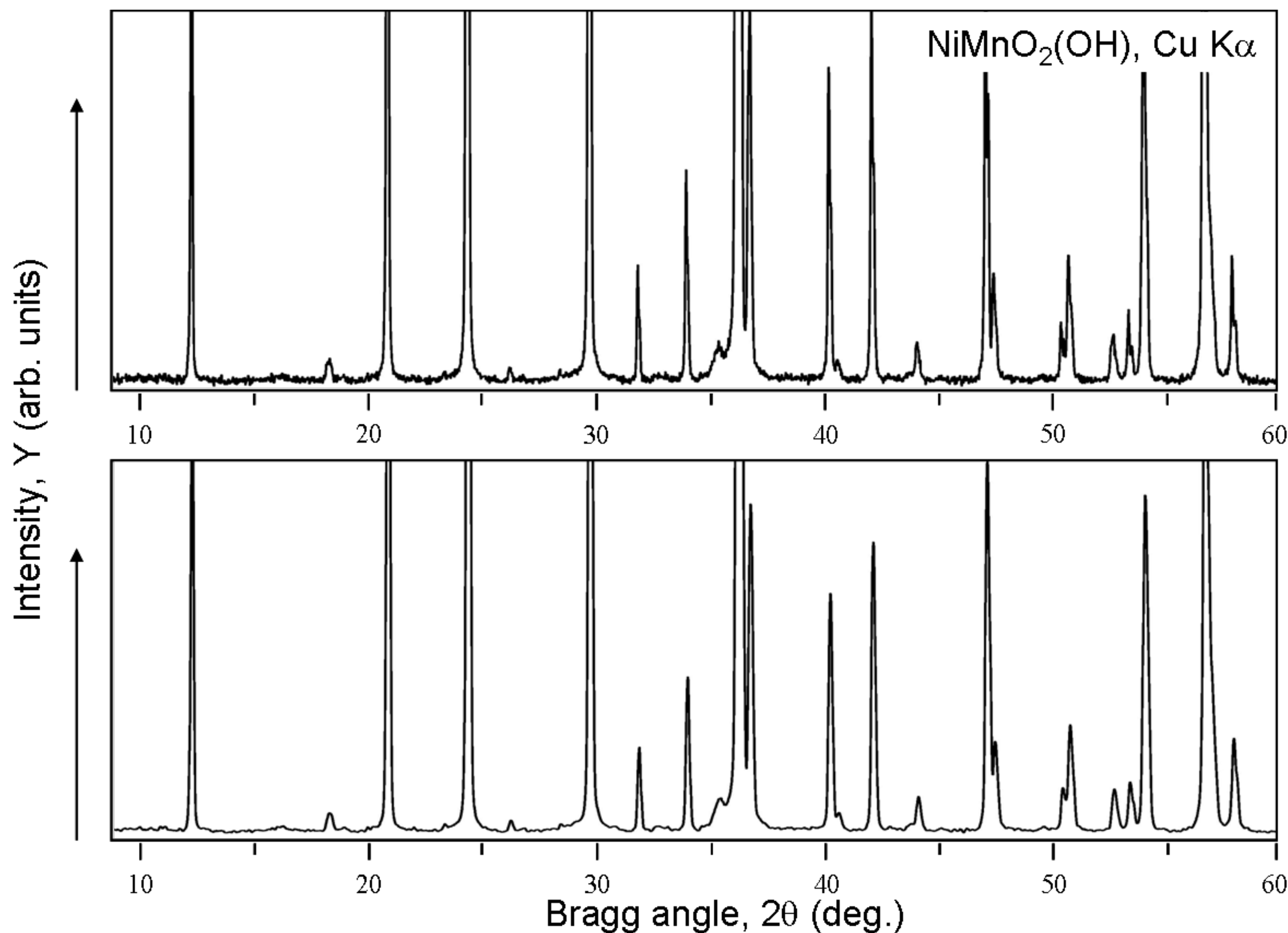
$$Y_o^{smoothed} = \frac{w_2 Y_{-2} + w_1 Y_{-1} + w_o Y_o + w_1 Y_1 + w_2 Y_2}{2w_2 + 2w_1 + w_o}$$

Other methods of data smoothing also exist.

Smoothing

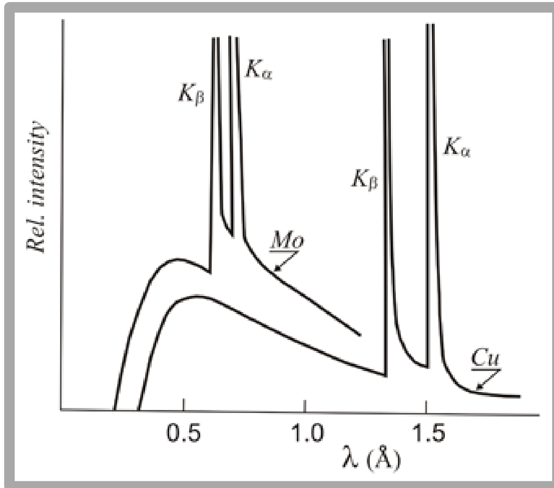
Data with background removed, not smoothed.

Data with background removed, after smoothing.



Pecharsky & Zavalij, Figure 4.5.

$K\alpha_2$ Contribution

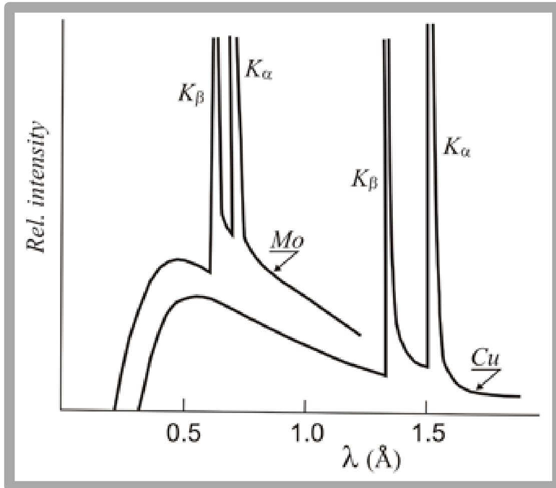


The characteristic radiation from normal in-house x-ray sources, for example that from Cu or Mo, consists of two $K\alpha$ radiations with similar wavelengths. These are not normally separated by monochromation.

$$CuK\alpha_1: \lambda = 1.540562\ (2)\ \text{Å}$$
$$CuK\alpha_2: \lambda = 1.544390\ (2)\ \text{Å}$$

At low values of 2θ in the diffraction pattern, the peaks arising from $K\alpha_1$ and $K\alpha_2$ are almost overlapped. At high 2θ angles, the two peaks are sufficiently separated so as to allow 2θ to be identified correctly for both. However, at intermediate values of 2θ, they are neither fully overlapped nor well separated, which in a peak search would give an erroneous value of 2θ. The solution to this problem is to suppress the $K\alpha_2$ contribution in the peak search.

$K\alpha_2$ contribution



$CuK\alpha_1$: λ = 1.540562 (2) Å

$CuK\alpha_2$: λ = 1.544390 (2) Å

$$\frac{sin\theta_1}{\lambda_{K\alpha_1}} = \frac{sin\theta_2}{\lambda_{K\alpha_2}}$$

$$I_{K\alpha_1} : I_{K\alpha_2} = 2 : 1$$

With defined relationships between the positions of peaks arising from the $K\alpha_1$ and $K\alpha_2$ radiations, and with a concrete relationship between the intensities of the two radiations, the contribution from $K\alpha_2$ can be calculated on the basis of the intensity derived from $K\alpha_1$.

The $K\alpha_2$ contribution is subtracted.

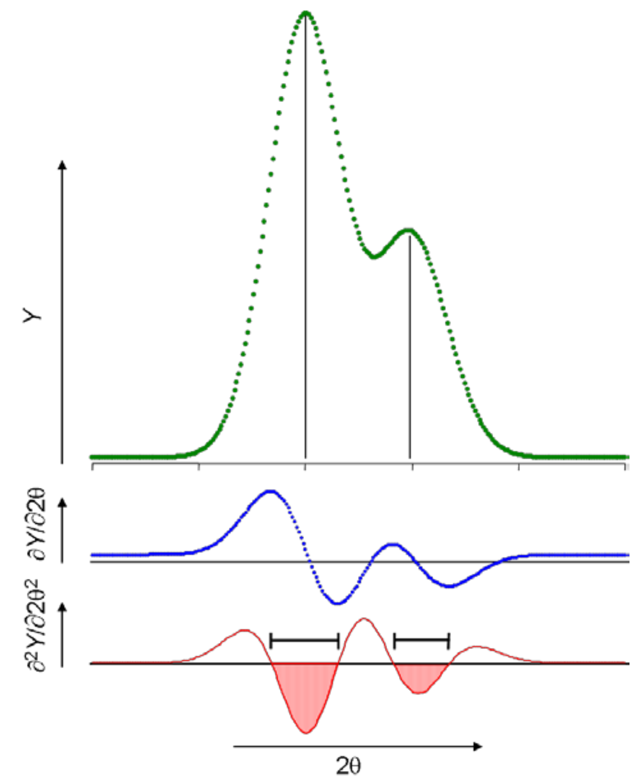
This process is employed in preparing powder diffraction data for a subsequent peak search.

The $K\alpha_2$ contribution is not removed from data to be used in structure refinement.

Peak Search and Profile Fitting

The goal of peak searching is a list of peaks in the diffraction pattern, with each peak characterized by its scattering angle, 2θ, and if possible by an estimate or more accurate calculation of its intensity.

The peak search can be done manually, but in practice a computer program does it. In either case, the maximum can be the point of maximum diffracted intensity, or the midpoint of the FWHM (full width at half maximum). Computer algorithms employ the derivatives of I vs. 2θ to locate the inflection points more accurately. For this method the background and $K\alpha_2$ are removed, and if necessary the data are smoothed.



Pecharsky & Zavalij, Figure 4.7.

Peak Search and Profile Fitting

To estimate the intensity of each peak, an idealized peak shape is used; this can be a Pearson-VII or pseudo-Voight function. Depending on the algorithm used, it may or may not be necessary to subtract the background noise. It is not usually necessary to remove $K\alpha_2$ scattering or to smooth the pattern.

The result of the peak search is a list of reflections in which each peak is characterized by its 2θ and intensity. The user can intervene at this point, with the aid of an interactive graphical interface, to remove false peaks and/or to add peaks that were missed.

Peak Search and Profile Fitting

In principle, profile fitting is the most accurate method of deriving the positions, shapes and intensities of the peaks in a powder diffraction pattern.

It is based on a non-linear least-squares fit of the peak profiles in the diffractogram.

The parameters used in the fit are:

- The positions (2θ) of the peaks.
- The peak-shape parameters, which can be the FWHM (full width at half maximum, H), the asymmetry (α), the exponent (β) for Pearson-VII or the mixing parameter (η) for pseudo-Voigt.
- The integrated intensity (I) for each peak.

Peak Search and Profile Fitting

In profile fitting, the user can fit the entire powder pattern at once, or can select different parts to fit independently. The starting parameters can be selected by the user, or the process can be run automatically.
The result of profile fitting is a list of peaks, each characterized by its values of 2θ, *Y(max),* FWHM(°) and intensity (area).
In principle the peaks derived from profile fitting do not suffer bias.
Peak fitting can be done with or without various types of restraints, for example the use of a common asymmetry parameter for all of the peaks. The need to remove the effects of $K\alpha_2$ – or not -depend on the program.

Indexing

The term “indexing” is used for the process of identifying a correct unit cell, which is accompanied by the assignment of indices $hk\ell$ to all of the peaks in the powder pattern. In powder diffraction, indexing is analogous to the similar process in single-crystal diffraction; but in powder diffraction it is complicated by the fact that the powder pattern is a one-dimensional projection of the three-dimensional reciprocal lattice. Indexing begins with a set of values of 2θ, which can also be represented by $|d^*_{hk\ell}|$ or $d_{hk\ell}$ (which is $1/|d^*_{hk\ell}|$). The description of each reciprocal lattice point in terms of the reciprocal basis vectors is $\overrightarrow{d^*_{hk\ell}} = h\overrightarrow{a^*} + k\overrightarrow{b^*} + \ell\overrightarrow{c^*}$.

Indexing

The degree of difficulty in indexing a powder diffraction pattern depends on two principal factors:

- Prior knowledge of the unit cell parameters – if the unit cell parameters are known, it is easier to assign indices $hk\ell$ to the peaks.
- Symmetry – the presence of crystallographic symmetry and the corresponding relationships between cell parameters, limits the number of distinct values of 2θ that the reflections can have. For example, in the cubic system we have this relationship:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + \ell^2}{a^2}$$

  and thus the possible values of $d_{hk\ell}$ and their corresponding 2θ values depend on just one lattice parameter instead of six, as would be the case for a triclinic crystal.

As always, the quality of the data has to be sufficient to permit the analysis. It is important to avoid systematic errors and it is important that the sample be pure.

Indexing – figures of merit

$$F_N = \frac{N}{N_{pos}} \times \frac{1}{|\overline{\Delta 2\theta}|} = \frac{N^2}{N_{pos} \sum_{i=1}^{N} |2\theta_i^{obs} - 2\theta_i^{calc}|}$$

N_{pos} is the number of Bragg reflections possible up to the Nth observed peak. F_N is normally presented in this way:

$$F_N = (number)\left(|\overline{\Delta 2\theta}|, N_{pos}\right)$$

For reliable indexing, $F_N \geq 10$, $|\overline{\Delta 2\theta}| < 0.02°$ y N_{pos} equal to, or slightly larger than, N.

$$M_{20} = \frac{1}{N_{pos}} \times \frac{Q_{20}}{2|\overline{\Delta Q}|} = \frac{10 Q_{20}}{N_{pos} \sum_{i=1}^{20} |Q_i^{obs} - Q_i^{calc}|}$$

$$Q = {d^*}^2 = 1/d^2$$

It is difficult to define a threshold for M_{20}, but the bigger M_{20} is, the more reliable is the indexing, as is true for F_N.

Deriving structure factors from powder diffraction data

For structure solution or refinement, it is necessary to use the structure factor moduli. These quantities, or alternatively the intensities $I_{hk\ell}$ associated with the reciprocal lattice points $hk\ell$, are derived by "full pattern decomposition," also called "full pattern deconvolution." The diffraction pattern is used without removing the background, which is modeled in the process, and without removing $K\alpha_2$, which is also part of the model. The calculation is based on an expression for the intensity measured at each point in the pattern. Here i is a point and k indexes the reflections that overlap at point i:

$$Y_i = b_i + \sum_{k=1}^{m} I_k[y_k(x_k) + 0.5y_k(x_k + \Delta x_k)]$$

Deconvolution of the peaks

$$Y_i = b_i + \sum_{k=1}^{m} I_k[y_k(x_k) + 0.5y_k(x_k + \Delta x_k)]$$

In peak deconvolution (or “full pattern decomposition,” the background noise, peak shapes and lattice parameters are modeled.

In the method proposed by Pawley, the intensities I_k are variables to be derived from the calculation.

In cases without too much peak overlap and without an excessive number of peaks (less than about 1000), Pawley decomposition works well. In more complex cases, the calculation can become unstable.

G. S. Pawley (1981). *J. Appl. Cryst.* 14, 357-361.

Deconvolution of the peaks

$$Y_i = b_i + \sum_{k=1}^{m} I_k[y_k(x_k) + 0.5y_k(x_k + \Delta x_k)]$$

The Le Bail method begins with an iqual division of intensity among all of the reflections *k* that overlap at a point *i*. The intensity I_k of a reflection is not a refined parameter, but rather is derived between refinement cycles.
In the Le Bail decomposition, the variables are the background, the peak shapes, and the lattice parameters. Thus, the number of parameters is independent of the number of reflections that contribute to the diffraction pattern.

A. Le Bail, H. Duroy & J. L. Fourquet (1988). *Mat. Res. Bull.* 23, 447-452.

Identification and analysis of crystalline phases

In a powder diffraction pattern, the peak positions, characterized by their scattering angles 2θ, depend on the size and shape of the unit cell of the sample (or of the unit cells if the sample contains more than one phase). The intensities depend on the distribution of atoms in the unit cell (or unit cells) and of the symmetry of the phase or phases.

The distribution of intensities and positions in a diffraction pattern is a unique "fingerprint" of the substance that produces the pattern. There may exist coincidental correspondences, but in general the diffraction pattern is a unique characteristic of the sample. Moreover, in terms of information technology, it is easy to maintain a data base of powder patterns; thus data bases are commonly used in the identification of crystalline phases.

Data bases

There exist a number of crystallographic data bases, the majority of them specialized.
For powder diffraction, the most complete group of data bases is that of the ICDD ("International Centre for Diffraction Data"), a non-profit scientific organization. Its data bases contain both the diffraction patterns and the structural data, when the latter are available. ICDD has a general data base and specialized data bases (for example a database of organic compounds).
http://www.icdd.com
A list of crystallographic data bases can be found here:
http://www.iucr.org/resources/data

Qualitative and quantitative analysis

Qualitative analysis:

It is possible to perform an analysis manually, if the subset of the data base to be considered is relatively small.

In other cases, an automated analysis performed by a computer is rapid and effective.

The user normally specifies (explicitly or by default):

- The number of peaks that have to correspond in 2θ.
- The number of the strongest reflections in the data base to be used in the comparisons.
- Tolerance – the maximum discrepancy permitted between a 2θ value (or $d_{hk\ell}$ or d^* or equivalent) from the data base and that from the experimental powder pattern.

Qualitative and quantitative analysis

Qualitative analysis:

At the end of an analysis it is usual to perform a visual comparison between the experimental powder pattern and that from the data base which has been chosen as having the best correspondence with experiment. It is important to check the following:

- That all strong peaks from the data base pattern are observed in the experimental pattern (unless a strong case can be made for a preferred orientation effect).
- The relative intensities in the model pattern (from the data base) correspond to those in the experimental pattern, at least in general terms.

Qualitative and quantitative analysis

Qualitative analysis:
If an automatic analysis produces a large number of hits (correspondences), it is possible to limit the results by imposing criteria related to the chemical composition of the sample.

See Pecharsky & Zavalij, Section 4.4.2, for some examples of qualitative analysis.

Qualitative and quantitative analysis

Quantitative analysis:

A number of methods exist for performing quantitative analyses based on powder diffraction data.

Two of the most practical and reliable techniques are:

1) The internal standard method. This method uses the relationship:

$$\frac{I_{a,hk\ell}}{I_{b,(hk\ell)'}} = K\frac{X_a}{Y_b}$$

Various quantities Y_b of a standard phase *b* are added to the sample, and a reference reflection *(hkℓ)'* from the standard is measured, along with a reflection *(hkℓ)* of the test substance, *a*. The slope of a plot of this equation is *K*. X_a, the unknown fraction of *a* in the sample, is derived from this equation.

Qualitative and quantitative analysis

Quantitative analysis:

2) Refinement using the Rietveld method. Rietveld refinement requires a correct structural model, consisting of atomic positions and symmetry. High quality data are also needed.

Rietveld refinement for a multiphase sample produces scale factors for all phases, which are proportional to the number of unit cells present for each phase. This information is easily converted into mass or molar fractions.

There are other methods of quantitative analysis, see Pecharsky & Zavalij, Section 4.4.3.

Rietveld Method

The Rietveld method is a method of refining structural and instrumental parameters using powder diffraction data. In the Rietveld method, each measured data point in a powder pattern is a datum in the fit. It is thus different from methods in which the integrated intensity associated with a reciprocal lattice point is the datum.
In a Rietveld refinement, all of the structural and instrumental parameters enter into the model, which is fitted to all of the points in the measured powder pattern.

H. M. Rietveld (1967). *Acta Cryst.* 22, 151-152. *Line profiles of neutron powder-diffraction peaks for structure refinement.*
H. M. Rietveld (1969). *J. Appl. Cryst.* 2, 65-71. *A profile refinement method for nuclear and magnetic structures.*

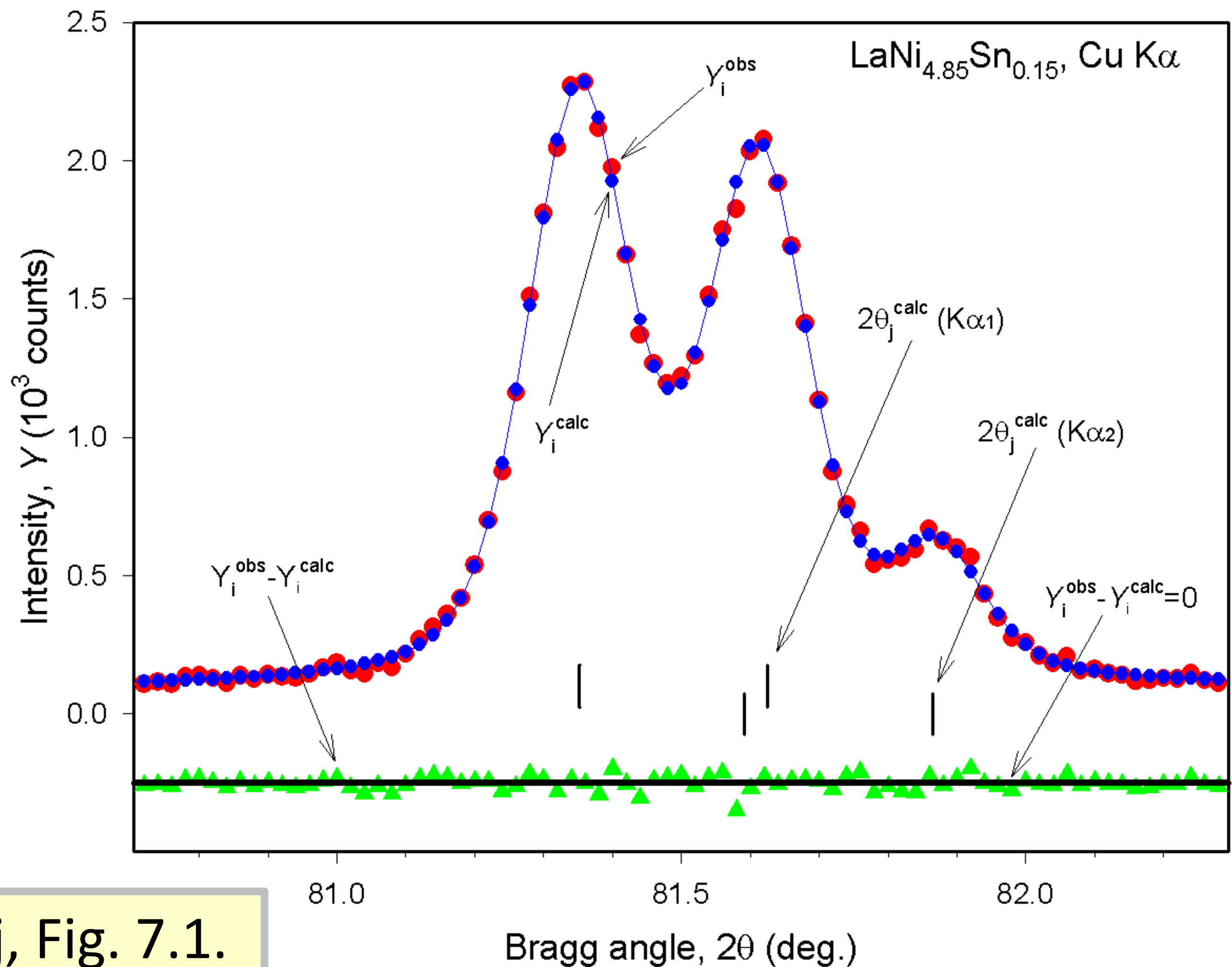
Rietveld Method

The Rietveld method is also called full profile refinement or full pattern refinement.
The background, peak shapes and other relevant items are treated as parameterized elements of the model. The structure factors and corresponding intensities are calculated on the basis of the structure, in the same way as in single-crystal diffraction. In this the Rietveld method is different from the Pawley full-pattern decomposition method, in which the intensity of a reflection is a parameter in the refinement, and from the Le Bail method, in which the intensities are derived between cycles.
Rietveld refinement requires data of sufficient quality.

Rietveld Method

The intensity at each point in the pattern is modeled considering all of the reciprocal lattice points *hkℓ* that contribute intensity to the data point.

It is important to use an adequate peak shape model.



Pecharsky & Zavalij, Fig. 7.1.

Basics

For a powder pattern with *n* measured points, each with intensity Y^{obs} we want to reproduce the data with Y^{calc}, that is, with model data:

$$Y_1^{calc} = kY_1^{obs}$$

$$Y_2^{calc} = kY_2^{obs}$$

…

$$Y_n^{calc} = kY_n^{obs}$$

We have to minimize:

$$\Phi = \sum_{i=1}^{n} w_i \left(Y_i^{obs} - Y_i^{calc}\right)^2$$

Basics

In order to minimize:

$$\Phi = \sum_{i=1}^{n} w_i \left(Y_i^{obs} - Y_i^{calc}\right)^2$$

we expand Y_i^{calc} in terms of all of the reflections *hkℓ* that contribute intensity to the point *i*:

$$\Phi = \sum_{i=1}^{n} w_i \left(Y_i^{obs} - \left[b_i + K \sum_{j=1}^{m} I_j y_j(x_j) \right] \right)^2$$

This equation is valid if there is just one wavelength (*i.e.,* without $K\alpha_2$).

b_i is the background at point *i*; K is the scale factor for the phase; m is the number of Bragg reflections that contribute intensity to point *i*; I_j is the integrated intensity of Bragg reflection *j*; $y_j(x_j)$ is the peak shape function; $x_j = 2\theta_j^{calc} - 2\theta_i$.

Basics

If $K\alpha_2$ radiation is present:

$$\Phi = \sum_{i=1}^{n} w_i \left(Y_i^{obs} - \left[b_i + K \sum_{j=1}^{m} I_j \left\{ y_j(x_j) + 0.5 y_j(x_j + \Delta x_j) \right\} \right] \right)^2$$

The factor of 0.5 is the relative intensity of $K\alpha_2$, and Δx_j is the difference between the positions of $K\alpha_1$ y $K\alpha_2$.

The importance of minimizing the experimental background is evident from these equations. The background, b_i, provides no structural information; and if it is large, the minimization of the function Φ will depend too much on the background model. It could turn out to be impossible to model the structure.

Basics

For the case of multiple phases and just one wavelength, we minimize:

$$\Phi = \sum_{i=1}^{n} w_i \left(Y_i^{obs} - \left[b_i + \sum_{\ell=1}^{p} K_\ell \sum_{j=1}^{m} I_{\ell,j} y_{\ell,j}\left(x_{\ell,j}\right) \right] \right)^2$$

For multiple phases and with $K\alpha_2$ present, we minimize:

$$\Phi = \sum_{i=1}^{n} w_i \left(Y_i^{obs} - \left[b_i + \sum_{\ell=1}^{p} K_\ell \sum_{j=1}^{m} I_{\ell,j} \left\{ y_{\ell,j}\left(x_{\ell,j}\right) + 0.5 y_{\ell,j}\left(x_{\ell,j} + \Delta x_{\ell,j}\right) \right\} \right] \right)^2$$

In these expressions, there are p phases; ℓ indexes the phase.

Assuming that the data have only statistical errors:

$$w_i = \left[Y_i^{obs}\right]^{-1} \quad \left[o\ w_i = 1/\sigma^2\left(Y_i^{obs}\right)\right]$$

usually calculated without removing the background

Classes of parameters

Unlike the case of structure analysis using single crystal diffraction data, in Rietveld refinement we are using the raw experimental data, not reduced data; and we model all of the relevant experimental and structural parameters that contribute intensity to the data points in the powder pattern.

N.b., the order in which the various parameters enter into the refinement is important. This was described by Young, and is also discussed in the book by Pecharsky and Zavalij.

R. A. Young, *Introduction to the Rietveld Method,* en R. A. Young, Ed., *The Rietveld Method,* Oxford University Press, 1993.
Pecharsky y Zavalij, Table 7.1.

Classes of parameters

- Background, as per any of various models.
- Sample displacement, zero-point correction of the instrument.
- Peak-shape parameters, according to one of the various models available. The specific parameters depend on the model used. They can include FWHM (full width at half maximum), and an asymmetry parameter.
- Lattice parameters, that is, the unit cell dimensions for each phase.
- If needed: Preferred orientation, absorption, extinction, sample porosity.
- Scale factors for the phases present.
- Fractional crystallographic coordinates for the atoms in the structure, one set of coordinates for each phase being refined.
- Site occupation parameters in the structure, in the case of partial atomic occupancy.
- Atomic displacement parameters for the atoms in the structure.

Not all of the parameters enter as variables in all refinements. Some parameters or others may be refined, depending on circumstances. The user’s judgement on this will depend on the quality of the data and the purpose of the analysis.

Figures of merit and quality of the refinement

These figures of merit serve to assess the quality of a Rietveld refinement. They are also useful (all except R_B) to assess the quality of Pawley or Le Bail full pattern decomposition. The main figures of merit are:

Profile residual, R_p;

Weighted profile residual, R_{wp};

Expected profile residual, R_{exp};

Goodness of fit, χ^2;

Bragg residual, R_B;

Definitions: n = number of measured points in the powder pattern; m = number of independent Bragg reflections; p = number of independent parameters in the refinement; Y_i^{obs}, Y_i^{calc} = observed and calculated intensities for point i in the diffraction pattern; I_j^{obs}, I_j^{calc} = *obs* and *calc* intensities for a Bragg reflection, w = weighting factor for point i in the refinement.

continued

Figures of merit and quality of the refinement

For R_p, R_{wp} y R_B, smaller residuals signify better fits, *i.e.*, better agreement between observed and model data.

Profile residual, R_p:

$$R_p = \frac{\sum_{i=1}^{n} \left| Y_i^{obs} - Y_i^{calc} \right|}{\sum_{i=1}^{n} Y_i^{obs}} \times 100\%$$

Weighted profile residual, R_{wp}:

$$R_{wp} = \left[\frac{\sum_{i=1}^{n} w_i \left(Y_i^{obs} - Y_i^{calc} \right)^2}{\sum_{i=1}^{n} w_i \left(Y_i^{obs} \right)^2} \right]^{1/2} \times 100\%$$

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Figures of merit and quality of the refinement

Expected profile residual, R_{exp}; a small value in principle signifies that the data are of good quality:

$$R_{exp} = \left[\frac{n-p}{\sum_{i=1}^{n} w_i \left(Y_i^{obs}\right)^2}\right]^{1/2} \times 100\%$$

Goodness of fit, χ^2:

$$\chi^2 = \left[\frac{R_{wp}}{R_{exp}}\right]^2 = \frac{\sum_{i=1}^{n} w_i \left(Y_i^{obs} - Y_i^{calc}\right)^2}{n-p}$$

The ideal value of χ^2 is 1.0, but in practice this value is not usually observed.

continued

Figures of merit and quality of the refinement

Bragg residual, R_B:

$$R_B = \frac{\sum_{j=1}^{m} \left| I_j^{obs} - I_j^{calc} \right|}{\sum_{j=1}^{m} I_j^{obs}} \times 100\%$$

There are also other indicators of the quality of a refinement. For example, the Durbin-Watson statistic can reveal sequential correlations (that is, correlations between successive points in the powder pattern) in the results of a refinement. More information:

M. Sakata y M. J. Cooper (1979). *J. Appl. Cryst.* 12, 554-563.

R. J. Hill y H. D. Flack (1987). *J. Appl. Cryst.* 20, 356-361.