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Characteristics of materials structure by the X-ray diffraction XIII Rietveld method

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International interdisciplinary PhD Studies in Materials Science with English as the language of instruction

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Principles of the Rietveld method

In the first step we start with an approximate scaling of the intensity of I_{k0} in order to calculate the new intensities in the iteration cycle n + 1, using the formula:

$$I_k^{n+1} = \sum_i I_k^n \Omega_{ik} \frac{y_{io} - y_{ib}(n)}{y_{ic}(n) - y_{ib}(n)}$$

I_k^{n+1}

Where y_{ib} is the background to the i-th measured intensity of y_{io}.

The method proposed by Rietveld [1967] is numerically more stable and effective than Pawley's approach. The method initially developed for powder analysis using monochromatic neutron diffraction was extended to monochromatic X-ray analysis. It should be stressed that many other later algorithms [Taylor 1985, Le Bail 1992, Rodriguez 2003] are based on the Rietveld method. It is currently the most widely used powder diffraction technique for reasons of efficiency where the crystalline structure of the sample is known.

Rietveld's algorithm uses all the information contained in the experimental spectrum.

The following variables shall be used:

- apparatus characteristics (curve of diffractometer resolution, displacement parameters describing goniometer deregulation, experiment geometry, detector characteristics ...)
- structural parameters (parameters of the elementary cell, positions of atoms, thermal vibrations, ...)
- microstructure parameters (mean crystallite sizes and micro-stress, defects ...)
- sample parameters (preferred orientation, residual stress, thickness, transparency, absorption, phase fractions ...)

Modeling parameters

Background

The measurement background at the i-th point can be modelled in two ways, depending on the extent to which a physical explanation of the background signal can be found.

Empirical approach

In an empirical approach, the data provided by the user can be selected and interpolated, and filtered by the program. Interpolation or filtering is carried out using polynomials or analytical functions in the form of a Fourier series of expansions [Richardson 1993].

Physical approach

When determining y_{ib}, phenomenological functions may be used (when the function describing physical reality is known: amorphous dissipation, thermal dissipation ...) [Riello et al. 1995, Riello et al. 1995A].

Preferred orientation of crystals (crystallographic texture)

In the case of a preferential occurrence of certain crystallographic directions in the sample, an appropriate adjustment should be made (due to these preferences). Crystals may be oriented in one or more directions of the sample. Such preferences are particularly strong in materials with easy cleavage or where there has been anisotropic crystalline growth or where the samples have been developed using anisotropic techniques. For example, NaCl crystallises as rectangular crystallites bounded by planes (001) which tend to orientate parallel to the surface of the sample.

·The texture effect and the effect of under-representation (insufficient statistics) of 'illuminated' crystals should not be confused. Both of these effects amplify several peaks. In the latter case, the effect of insufficient statistics is more or less stochastic. In the first one, there is gain for all hkl, 2h2k2l, 3h3k3l ... (if hkl is the preferred texture).

There are two types of ways to include texture in Rietveld's analysis. If the texture is uncomplicated - high symmetry and regular distribution - it can be modelled with the use of classical analytical functions, e.g. Gauss. If the texture is more complex - you can distinguish between several components and an irregular distribution - **then a quantitative analysis of the texture is needed.**

Peak asymmetry

It is often observed that diffraction peaks show some asymmetry, especially in the range of low Bragg angles in Bragg-Brentano configuration. **This effect may be related to the combination of the gap shape of the goniometer and the signal from the sample.** Geometrically, an intersection between the linear detection gap and the Debye-Scherrer cone may cause interference in peak shape. The effect can be corrected by multiplying y_{io} by an appropriate asymmetry factor (of different shapes).

Peak flow

Diffraction diagrams may contain systematic errors from both the diffractometer and the sample (misaligned instrumentation, misalignment of the sample) [Wilson 1963].

All types of errors cause some peak displacement that changes with the Bragg angle. Errors depend on the geometry of the diffractometer and the nature of the aberration. Rietveld's software allows you to eliminate them.

Correction for volume, absorption and thickness of sample

Many programmes include corrections due to sample volume and absorption, but these corrections can be applied to different experimental geometries.

They also depend on the sample geometry, for example signal analysis from thin layers requires particularly careful correction.

Localization correction

Locational corrections - when moving from the angular coordinates of the space in which the intensities were measured (diffractometer) to the space in which the modelling takes place, for example to the space of polar figures.

Correction for roughness

The correction of microabsorption or surface roughness is applied for highly absorbent preparations.
With this type of material, a systematic decrease in intensity at low angles can be observed. Several empirical formulae are given in the literature to describe this phenomenon.

Correction for wavelength

In experiments with monochromatic radiation, the spectral distribution of the incident beam is never completely monochromatic. Spectrum broadening causes peak broadening, which must be taken into account when developing the results. The extension is calibrated using the diffractometer's resolution curve.

Thank you

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