

3.6. WHOLE POWDER PATTERN MODELLING

with the definitions of surface-weighted domain size and column-length distribution function' (Balzar & Popović, 1996): integral breadth methods are therefore intrinsically limited for the microstructure analysis of real materials. This is in stark contrast to the fact that equation (3.6.2) is used, for example, by a large number of Rietveld refinement codes to describe the observed trend in line-profile broadening (and to perform a rough microstructure analysis). This situation can be improved a little by properly considering at least the anisotropic broadening component, as performed, for example, in the modified Williamson–Hall method (MWH; Ungár & Borbély, 1996; Ungár, 2001; Scardi *et al.*, 2004). The results are more accurate and related to some physical quantities (a dislocation density and a stacking fault probability), but they are still tightly bound to a Voigtian profile approximation.

An alternative to the integral breadth methods was developed by Warren & Averbach (1950, 1952) almost simultaneously with the idea of Williamson and Hall, but took longer to be fully employed owing to the lack of fast computing tools. It is based on the extensive use of Fourier transforms and represents the starting point of modern line-profile analysis techniques. The whole profile carries information on the microstructure, as each point in reciprocal space is related to the Fourier transform of real space (and thus to the size and shape of the domains and also the deviation from perfect three-dimensional periodicity). Each profile also contributes to a better picture of the microstructure, as it samples along a different direction in space.

For decades, these Fourier methods were only used in a very small number of scientific areas; the availability of fast computers and the fast Fourier transform has contributed greatly to their further diffusion. It is, however, only in recent years that the full power of the Fourier approach has been unveiled, with the development of whole-pattern methods and the extension of most models to a wider range of materials.

3.6.2. Fourier methods

3.6.2.1. Definitions

In the following, the diffraction peaks for a powder will be described in reciprocal space with reference to the Bragg position $d_{\{hkl\}}^*$ expected for the $\{hkl\}$ reflection family in the absence of any type of defect. The coordinate s , where

$$s = d^* - d_{\{hkl\}}^* = \frac{2}{\lambda} (\sin \theta - \sin \theta_{\{hkl\}}), \quad (3.6.3)$$

will be employed. Moving from reciprocal to diffraction space (' 2θ space') involves a trivial but nonlinear change of variables: peaks that are symmetrical in reciprocal space will become asymmetrical in 2θ space and *vice versa*.

3.6.2.2. Peak profile and the convolution theorem

Each peak profile $h(s)$ in a powder diffraction pattern can be described as the convolution of an instrumental profile $g(s)$ with a function $f(s)$ accounting for sample-related effects (microstructure; see, for example, Jones, 1938; Alexander, 1954; Klug & Alexander, 1974; and references therein):

$$h(s) = \int_{-\infty}^{\infty} f(y)g(s-y) dy = f \otimes g(s). \quad (3.6.4)$$

The calculation of the integral in equation (3.6.4) can be simplified through the use of a Fourier transform (FT). In fact,

the convolution theorem states that the FT of a convolution is the product of the Fourier transforms of the functions to be folded:

$$C(L) = \text{FT}[h(s)] = \text{FT}[f(s)] \times \text{FT}[g(s)]. \quad (3.6.5)$$

In this equation, L is the (real) Fourier variable conjugate to s . The properties of the Fourier transform allow equation (3.6.4) to be rewritten as

$$h(s) = \text{FT}^{-1}[C(L)] = \text{FT}^{-1}[\text{FT}[h(s)]] = \text{FT}^{-1}[\text{FT}[f(s)]\text{FT}[g(s)]]. \quad (3.6.6)$$

This equation is the basis of the Warren–Averbach approach and also of all modern LPA methods.

3.6.2.3. The Warren–Averbach method and its variations

The convolution theorem can be employed to disentangle the specimen-related broadening contributions described by $f(s)$. In fact, let us suppose, as in the Williamson–Hall method, that size and microstrain are the only two sources of specimen-related broadening. We call the Fourier transform of the profiles broadened by size and distortion effects only $A_{hkl}^S(L)$ and $A_{hkl}^D(L)$, respectively. As the size and distortion profiles are folded into $f(s)$, the following holds:

$$A(L) = \text{FT}[f(s)] = \text{FT}[h(s)]/\text{FT}[g(s)] = A_{hkl}^S(L)A_{hkl}^D(L). \quad (3.6.7)$$

The separation of the size and distortion terms is straightforward for spherical domains: the size effects for a sphere are independent of the reflection order, whereas those related to distortions (causing the change in the slope of the Williamson–Hall plot) are order-dependent. To describe the distortion term it is convenient to follow the idea of Bertaut (1949*a,b*, 1950), considering the specimen as made of columns of cells along the \mathbf{c} direction. The profile due to distortions is calculated by taking the average phase shift along the column due to the presence of defects. The analytical formula for the distortion term is thus of the type $A_{hkl}^D(L) = \langle \exp(2\pi i L n \varepsilon_L) \rangle$, where $\varepsilon_L = \Delta L/L$ is the average strain along \mathbf{c} calculated for a correlation distance (*i.e.* Fourier length) L .

As a first-order approximation, the distortion terms give no profile asymmetry; $A_{hkl}^D(L)$ is just a cosine Fourier transform. We can thus expand it as (Warren, 1990)

$$A_{hkl}^D(L) = \langle \cos(2\pi L n \varepsilon_L) \rangle = 1 - 2\pi^2 L^2 n^2 \langle \varepsilon_L^2 \rangle. \quad (3.6.8)$$

If we now rewrite equation (3.6.7) on a log scale, taking equation (3.6.8) into account, we obtain

$$\begin{aligned} \ln[A_{hkl}(L)] &= \ln[A_{hkl}^S(L)] + \ln[A_{hkl}^D(L)] \\ &= \ln[A_{hkl}^S(L)] + \ln[1 - 2\pi^2 L^2 n^2 \langle \varepsilon_L^2 \rangle] \\ &= \ln[A_{hkl}^S(L)] - 2\pi^2 L^2 n^2 \langle \varepsilon_L^2 \rangle. \end{aligned} \quad (3.6.9)$$

Equation (3.6.9) represents a line in the variable n^2 : the intercepts at increasing L values provide the logarithm of the Fourier size term, whereas the slopes give the microstrain directly (Warren, 1990). From the size coefficients, we can obtain an average size, again following the idea of Bertaut (1949*a*, 1950), related to the properties of the Fourier transform:

$$\langle D \rangle = \left[\left. \frac{\partial A_{hkl}^S(L)}{\partial L} \right|_{L=0} \right]^{-1}. \quad (3.6.10)$$

This average size is thus related to the initial slope of the Fourier coefficients [assuming that they are well behaved, *i.e.* that the tangent is always below the $A_{hkl}^S(L)$ curve].