3.6. WHOLE POWDER PATTERN MODELLING

with the definitions already given in equations (3.6.24) and (3.6.25).

The functional forms of equations (3.6.28) and (3.6.29) clearly suggest that the profile for a log-normal distribution of domains (which is frequently encountered in practice) is not Voigtian: all traditional line-profile analysis methods (based on Voigt or pseudo-Voigt functions) are therefore unable to correctly deal with a log-normally dispersed powder.

By analogy to the monodisperse case, it is possible to relate the parameters of the polydisperse system to the size obtained with traditional methods (Warren–Averbach and Williamson–Hall, respectively). The following holds (Krill & Birringer, 1998; Scardi & Leoni, 2001):

$$\langle L \rangle_S = \frac{1}{K_k} \frac{M_{i,3}}{M_{i,2}}, \quad \langle L \rangle_V = \frac{1}{K_\beta} \frac{M_{i,4}}{M_{i,3}}. \qquad (3.6.30)$$

Here, it is clear that diffraction does not provide the first moment of the distribution directly: ratios between high-order moments are involved.

Using an analytical expression for the description of a size distribution can help in stabilizing the results (as the size distribution curve is forced to be zero at very small and very large size values). Some doubts can, however, arise as to the physical validity of this forcing. An example is the case of a multimodal system. The traditional LPA techniques are unable to directly deal with multimodal size distributions. In cases where the multimodal character is clear and the various distribution are well behaved (*i.e.* when they can be modelled with analytical functions), the pattern can be usually modelled by considering the material as made of different fractions, each of them characterized by a different size distribution.

A possible alternative has been proposed in the literature: replacing the analytical distribution with a histogram. The ability of this model to fit the experimental data has been demonstrated (Leoni & Scardi, 2004; Matěj *et al.*, 2011); a regularization might be necessary to stabilize the shape and/or smoothness of the size distribution. The quality of the measurement and the availability of models describing all contributions to the peak broadening are in most cases the limiting factors for extensive use of the histogram model: correlations of small sizes with the background and with features such as thermal diffuse scattering (Beyerlein *et al.*, 2012) can in fact occur. So far, this is the only available method for exploring cases where the analytical models are unable to correctly describe the observed broadening.

3.6.2.6.5. *Strain broadening (lattice distortions)*

A local variation of the lattice spacing (due, for example, to the presence of a defect) leads to an average phase term that, in general, is a complex quantity:

$$\begin{aligned} \langle \exp[2\pi i \psi_{hkl}(L)] \rangle &= \langle \cos[(2\pi L d^*_{\{hkl\}} \varepsilon_{\{hkl\}}(L)] \rangle \\ &+ i \langle \sin[2\pi L d^*_{\{hkl\}} \varepsilon_{\{hkl\}}(L)] \rangle \\ &= A^D_{\{hkl\}}(L) + i B^D_{\{hkl\}}(L). \end{aligned} \qquad (3.6.31)$$

The strain $\varepsilon_{\{hkl\}}(L)$ represents the relative displacement of atoms at a (coherence) distance L along the scattering vector *hkl*. Knowledge of the actual source of distortion allows the explicit calculation of the various terms (van Berkum, 1994). It is quite customary to assume that the strain is the same for symmetry-equivalent reflections [$\varepsilon_{hkl}(L) = \varepsilon_{\{hkl\}}(L)$]: this is a reasonable

hypothesis for a powder, where we assume that any configuration is equally probable.

Traditional LPA methods such as the Warren–Averbach method (Warren & Averbach, 1950, 1952; Warren, 1990) take a first-order MacLaurin expansion of equation (3.6.31) to extract the microstrain contribution from the measured data:

$$A^D_{\{hkl\}}(L) \cong 1 - 2\pi^2 L^2 d^{*2}_{\{hkl\}} \langle \varepsilon^2_{\{hkl\}}(L) \rangle, \qquad (3.6.32)$$

$$B^D_{\{hkl\}}(L) \cong -\frac{4}{3}\pi^3 L^3 d^{*3}_{\{hkl\}} \langle \varepsilon^3_{\{hkl\}}(L) \rangle. \qquad (3.6.33)$$

The term in equation (3.6.33) would cause peak asymmetry. However, we usually consider only the second-order moment of the strain distribution (*root-mean strain* or *microstrain*) and thus symmetric peaks. Owing to the anisotropy of the elastic properties, the broadening described by equation (3.6.32) is in general anisotropic: an extensive discussion of strain anisotropy and of the order dependence of strain broadening can be found, for example, in Leineweber & Mittemeijer (2010) and Leineweber (2011). It should be stressed that in their original form, traditional line-profile methods are unable to deal with this anisotropy (corrections have been proposed for particular cases, for example, in the so-called modified Williamson–Hall (MWH) and modified Warren–Averbach (MWA) analyses; Ungár & Borbély, 1996).

3.6.2.6.6. *Dislocations*

Dislocations are often the main source of strain broadening. The magnitude of this broadening depends not only on the elastic anisotropy of the material, but also on the relative orientation of the Burgers and diffraction vectors with respect to the dislocation line (Wilkens, 1970*a,b*). This problem was analysed in the 1960s by Krivoglaz and Ryaboshapka (Krivoglaz & Ryaboshapka, 1963; Krivoglaz, 1969) and then subsequently reprised and completed by Wilkens (1970*a,b*). Further elements have been added to put it into the present form (see, for example, Krivoglaz *et al.*, 1983; Groma *et al.*, 1988; Klimanek & Kuzel, 1988; van Berkum, 1994; Kamminga & Delhez, 2000). For the purpose of WPPM, the distortion Fourier coefficients caused by dislocations can be written as

$$A^D_{\{hkl\}}(L) = \exp[-\tfrac{1}{2}\pi b^2 \overline{C}_{\{hkl\}} \rho d^{*2}_{\{hkl\}} L^2 f(L/R'_e)], \qquad (3.6.34)$$

where b is the modulus of the Burgers vector, $\overline{C}_{\{hkl\}}$ is the so-called average contrast factor of the dislocations, ρ is the density of the dislocations and R'_e is an effective outer cutoff radius. Only the low-L trend of equation (3.6.34) is well reproduced by Wilkens' theory: a decaying function $f(L/R'_e)$ has thus been introduced to guarantee a proper convergence to zero of the Fourier coefficients for increasing L. Actually, the function $f^*(\eta)$ is mostly quoted in place of (L/R'_e), where $\eta = (e^{-1/4}/2)L/R'_e$: the multiplicative term can however be dropped, considering that the cutoff radius is an effective value [some discussion of the meaning of the f and f^* functions and of the effective cutoff radius can be found in Scardi & Leoni (2004), Armstrong *et al.* (2006) and Kaganer & Sabelfeld, 2010)].

The most complete definition of $f^*(\eta)$ is from Wilkens (1970*a,b*):