2005; Leoni & Scardi, 2004; Leineweber & Mittemeijer, 2004; van Berkum, 1994; Cheary & Coelho, 1992).

The approach is strictly valid when the broadening sources can be considered as diluted and independent (*i.e.* uncorrelated defects). If this does not apply, then cross-terms should be considered and the whole approach revised. In fact, here we assume that the structure factor can be factored and the lattice is fully periodic in three dimensions: under these conditions, structure (peak intensity) and microstructure (peak shape) can be decoupled as the peak positions can be determined in a straightforward way. Extended defects (*e.g.* faults) cause the appearance of diffuse effects and the displacement of the Bragg peaks: in order to calculate the diffraction pattern, the structure and the microstructure must be simultaneously known (see, for example, Drits & Tchoubar, 1990).

3.6.2.6. *Broadening components*

A brief account is given of the main sources of broadening that can be encountered in practice. An accent will be placed on X-rays, but extension to electrons and neutrons is in most cases straightforward. Concerning electron diffraction, precession data can be used in a straightforward way, whereas for traditional data, containing dynamical effects, further calculations, for example of the intensity, are in principle needed.

3.6.2.6.1. *Instrument*

Each of the components of the diffraction instrument (*i.e.* source, optics, specimen stage, measurement geometry and detector) can have a dramatic impact both on the position and the broadening of the peaks. Axial divergence, for instance, introduces both an asymmetric broadening and an apparent shift of the low-angle peaks. When microstructure (*i.e.* specimen-related effects) is the focus of the analysis, the primary recommendation is to try to limit the instrumental influence. Alternatively, it is preferred to have an instrumental profile (no matter how complex) that can be well described and properly simulated: for instance the profile of an instrument with a $K\alpha_1$ primary monochromator (apparently advantageous) might be hard to model if the $K\alpha_2$ removal is not perfect. This becomes more and more important when the instrumental effects are of the same order of magnitude as the specimen-related broadening.

Two possible paths can be followed when dealing with the instrumental contribution: modelling using the fundamental parameters approach (see, for example, Cheary & Coelho, 1992; Kern & Coelho, 1998) or parameterization of the pattern of an ideal specimen. In the fundamental parameters approach, the geometry of the instrument and the effects of each optical component on the peak profile are described mathematically in 2θ. Most of the formulae for the various optical elements can be found, for example, in the work of Wilson (1963), Klug & Alexander (1974) and Cheary & Coelho (1992, 1994, 1998*a*,*b*). The aberration profiles are folded into the (X-ray) source emission profile (Hölzer *et al.*, 1997; Deutsch *et al.*, 2004) to generate a combined instrumental profile.

When no information on the instrument is available, it is possible to predict the instrumental profile just by using the nominal data for the optical components. It is however advised, whenever possible, to tune the instrumental parameters using the pattern of a line-profile standard [*e.g.* NIST LaB_6 SRM 660(x) series; Cline *et al.*, 2010] showing negligible specimen effects. These instrument-only parameters must then be kept fixed for any subsequent microstructure refinement. It is of paramount importance that all instrumental features are well reproduced when dealing with microstructure effects. Provided that this condition is met, we can therefore employ any arbitrary function to describe the instrumental profile. Thus, as an alternative to FPA, we can either 'learn' the instrumental profile from a standard (Bergmann & Kleeberg, 2001) or use a Voigtian to model it. The Voigtian is particularly convenient as it can be defined directly in L space and thus directly enter the Fourier product of equation (3.6.13).

3.6.2.6.2. *Source emission profile*

For X-rays, the source emission profile at an energy E_l can be well described by a Lorentzian of energy width Γ_l (Hölzer *et al.*, 1997; Deutsch *et al.*, 2004),

$$I_l(E) = \frac{2}{\Gamma_l \pi}\left[1 + 4\left(\frac{E - E_l}{\Gamma_l}\right)^2\right]^{-1}. \tag{3.6.14}$$

As $\mathrm{d}E/E = \mathrm{d}\lambda/\lambda = \mathrm{d}s/s$, the function can also be represented as a function of s:

$$I^{\mathrm{IP}}_{hkl,l}(s, d^*_{hkl}) = \frac{2}{\pi}\frac{E_l}{d^*_{hkl}\Gamma_l}\left[1 + 4\left(\frac{s_{hkl}}{d^*_{hkl}\Gamma_l/E_l}\right)^2\right]^{-1}. \tag{3.6.15}$$

For a laboratory tube emitting simultaneously a set of N_λ wavelengths, we have

$$I^{\mathrm{IP}}_{hkl}(s, d^*_{hkl}) = \sum_{l=1}^{N_\lambda} w_l I^{\mathrm{IP}}_{hkl,l}(s, d^*_{hkl}), \tag{3.6.16}$$

where w_l is the relative intensity of the lth wavelength component (referred, for example, to $w_1 = 1$). The corresponding Fourier transform entering (3.6.13) can be written as

$$\begin{aligned} T^{\mathrm{IP}}(L) &= \sum_{l=1}^{N_\lambda} \exp\left[2\pi i d^*_{hkl}\left(1 - \frac{\Gamma_l}{E_l}\right)L\right]\exp\left(-2\pi s_{hkl}\frac{\Gamma_l}{E_l}L\right) \\ &= \sum_{l=1}^{N_\lambda}\left\{\cos\left[2\pi d^*_{hkl}\left(1 - \frac{\Gamma_l}{E_l}\right)L\right] + i\sin\left[2\pi d^*_{hkl}\left(1 - \frac{\Gamma_l}{E_l}\right)L\right]\right\} \\ &\quad \times \exp\left(-2\pi s_{hkl}\frac{\Gamma_l}{E_l}L\right). \end{aligned} \tag{3.6.17}$$

The complex term in (3.6.17) accounts for the shift of each emission component with respect to the reference one. For more flexibility (for example to consider the non-ideal behaviour of the instrument), we can use a pseudo-Voigt (pV) in place of the Lorentzian in equation (3.6.14).

3.6.2.6.3. *Optical elements*

The equation of Caglioti *et al.* (1958), modified by Rietveld (1969) and originally developed for constant-wavelength neutron diffraction, is frequently employed for parameterization of the instrumental profile. The FWHM and the pV mixing parameter η (replacing the Lorentzian and Gaussian widths of the Voigt) are then parameterized according to functions in $\tan(\theta)$ and θ, respectively (Caglioti *et al.*, 1958; Leoni *et al.*, 1998; Scardi & Leoni, 1999),

$$\mathrm{FWHM}^2 = U\tan^2\theta + V\tan\theta + W, \tag{3.6.18}$$

$$\eta = a + b\theta + c\theta^2. \tag{3.6.19}$$

The parameters of the Fourier transform of a Voigt or pseudo-Voigt are then constrained to those of equations (3.6.18) and

(3.6.19). This is particularly convenient, as the Fourier transform of a Voigtian is analytical. In fact, for the pV case we have

$$T_{\rm pV}^{\rm IP}(L) = (1-k)\exp(-\pi^2\sigma^2L^2/\ln 2) + k\exp(-2\pi\sigma L), \tag{3.6.20}$$

where σ = FWHM/2 and where (Langford & Louër, 1982; Scardi & Leoni, 1999)

$$k = \left[1 + (1-\eta)/\left(\eta\sqrt{\pi\ln 2}\right)\right]^{-1}. \tag{3.6.21}$$

Equation (3.6.18) can be found in the literature in a different form and with additional terms accounting, for example, for size effects: besides forcing a symmetry of the profile in 2θ space, these extra terms are a contradiction as they have nothing to do with the instrument itself.

3.6.2.6.4. *Domain size and shape*

In nanostructured materials, the finite size of the scattering domains is usually the dominant source of line-profile broadening. Actually, when dealing with size, we should consider a size and a shape distribution of the domains. In most cases, one or more distributions of similar objects are considered. For an up-to-date description of issues related to size broadening, see Chapter 5.1. The domain shape is not a property of the material and therefore the use of symmetry constraints [*e.g.* spherical harmonics to describe the shape of the scattering object as in the model of Popa (1998) or as a size extension of Stephens' (1999) work] is not justified in the general case (Nye, 1987). Exceptions, however, exist.

The size-broadening contribution in WPPM follows the ideas of Bertaut (1949*a*,*b*, 1950) and of Stokes & Wilson (1942). Bertaut proposed the division of the domains into columns and the analysis of the independent scattering of these columns. The column-length distribution can always be extracted from the data: more complex models involving given shapes or distributions simply modify the way in which the columns are rearranged. Stokes and Wilson introduced the concept of a *ghost* to calculate the Fourier transform for a given shape: the volume common to a domain of shape c and its ghost, *i.e.* a copy of the same domain displaced by a quantity L along the scattering direction hkl, is proportional to the (size) Fourier transform $A^S_{c,hkl}(L, D)$ for the given domain. The calculation has been already carried out analytically for several simple shapes characterized by a single length parameter (Stokes & Wilson, 1942; Lele & Anantharaman, 1966; Wilson, 1969; Langford & Louër, 1982; Vargas *et al.*, 1983; Grebille & Bérar, 1985; Scardi & Leoni, 2001), and can be performed numerically in the general case (Leonardi *et al.*, 2012). It is possible to relate the Fourier coefficients to the size values obtained from traditional methods. In particular, the area-weighted average size $\langle L\rangle_S$ (Warren–Averbach method) and the volume-weighted average size $\langle L\rangle_V$ (Williamson–Hall method) are obtained as

$$\langle L\rangle_S = -\left[dA_c^S(L,D)/dL\big|_{L=0}\right]^{-1} = D/K_k = -D/H_1, \tag{3.6.22}$$

$$\langle L\rangle_V = [\beta(s)]^{-1} = 2\int_0^{D/K} A_c^S(L,D)\,{\rm d}L = D/K_\beta, \tag{3.6.23}$$

where $\beta(s)$ is the integral breadth and K_k and K_β are the initial slope and integral breadth Scherrer constants, respectively (Langford & Wilson, 1978; Scardi & Leoni, 2001).

The average size might have little physical significance in real cases: the size (and shape) distribution can in fact play a key role in determining both the properties and the diffraction line-profile shapes of the powder under analysis. Fortunately, the Fourier coefficients for the polydisperse case can be easily calculated for any given distribution: the log-normal and the gamma distributions are the most common (and the most flexible). The equations and the corresponding moments are

$$g_l(D) = \frac{1}{D\sigma_l\sqrt{2\pi}}\exp\left[-\frac{(\ln D-\mu_l)^2}{2\sigma_l^2}\right],$$
$$M_{l,n} = \exp\left(n\mu_l + \frac{n^2}{2}\sigma_l^2\right), \tag{3.6.24}$$

$$g_g(D) = \frac{\sigma_p}{\mu_g\Gamma(\sigma_g)}\left(\frac{\sigma_g D}{\mu_g}\right)^{\sigma_g-1}\exp\left(-\frac{\sigma_g D}{\mu_g}\right),$$
$$M_{g,n} = \left(\frac{\mu_g}{\sigma_g}\right)^n\frac{\Gamma(n+\sigma_g)}{\Gamma(\sigma_g)}. \tag{3.6.25}$$

The scattered intensity for the given distribution g_i, and the given shape c, is

$$\begin{aligned} I_{c,hkl}(s) &\propto \frac{\int_0^\infty\left[\int_{L=0}^{D/K_{hkl}} A^S_{c,hkl}(L,D)\exp(2\pi iLs)\,{\rm d}L\right]w(D)\,{\rm d}D}{\int_0^\infty w(D)\,{\rm d}D} \\ &\propto \int_{L=0}^\infty\left[\frac{\int_{D=LK_{hkl}}^\infty A^S_{c,hkl}(L,D)w(D)\,{\rm d}D}{\int_0^\infty w(D)\,{\rm d}D}\right]\exp(2\pi iLs)\,{\rm d}L \\ &\propto \int_{L=0}^\infty A^S_{hkl}(L)\exp(2\pi iLs)\,{\rm d}L, \end{aligned} \tag{3.6.26}$$

where $w(D) = g_i(D)V_c(D)$ and where

$$A^S_{hkl}(L) = \frac{\int_{D=LK_{hkl}}^\infty A^S_{c,hkl}(L,D)w(D)\,{\rm d}D}{\int_0^\infty w(D)\,{\rm d}D}. \tag{3.6.27}$$

With a suitable definition of the Fourier coefficients, the polydisperse case therefore becomes analogous to the monodisperse case. Analytic expressions can be obtained in particular cases. For instance, the Fourier coefficients for the log-normal and gamma distributions (Scardi & Leoni, 2001) are

$$A_l^S(L) = \sum_{n=0}^3 {\rm erfc}\left[\frac{\ln(LK_c)-\mu_l-(3-n)\sigma_l^2}{\sigma_l\sqrt{2}}\right]\frac{M_{l,3-n}}{2M_{l,3}}H_n^cL^n \tag{3.6.28}$$

and

$$A_g^S(L) = \sum_{n=0}^3\left(\frac{\sigma_g}{M_{g,1}}\right)^n\frac{\Gamma[\sigma_g+(3-n),K_cL\sigma_g/M_{g,1}]}{\Gamma(\sigma_g+3)}H_n^cL^n, \tag{3.6.29}$$

respectively, where

$$\Gamma(x,a) = \int_a^\infty y^{x-1}\exp(-y)\,{\rm d}y,$$
$$\Gamma(x) = \Gamma(x,0),$$
$${\rm erfc}(x) = 2\pi^{-1/2}\int_x^\infty\exp(-y^2)\,{\rm d}y,$$

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):

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

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:

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

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:

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

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

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

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

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*):

$$f^*(\eta) = -\ln\eta + \frac{7}{4} - \ln 2 + \frac{256}{45\pi\eta} + \frac{2}{\pi}\left(1 - \frac{1}{4\eta^2}\right)\int_0^\eta \frac{\arcsin y}{y}\,\mathrm{d}y - \frac{1}{\pi}\left(\frac{769}{180\eta} + \frac{41}{90}\eta + \frac{\eta^3}{45}\right)(1-\eta^2)^{1/2} - \frac{1}{\pi}\left(\frac{11}{12\eta^2} + \frac{7}{2} + \frac{\eta^2}{3}\right)\arcsin\eta + \frac{\eta^2}{6}, \qquad \eta \le 1, \tag{3.6.35}$$

$$f^*(\eta) = \frac{256}{45\pi\eta} - \left(\frac{11}{24} + \frac{1}{4}\ln 2\eta\right)\frac{1}{\eta^2}, \qquad \eta \ge 1. \tag{3.6.36}$$

For $\eta < 1$, the integral in (3.6.35) can be calculated in terms of special functions as

$$\begin{aligned}\int_0^\eta \frac{\arcsin y}{y}\,\mathrm{d}y &= \frac{i}{12}\left\{\pi^2 - 6\arcsin^2\eta - 12i\ln\left[2\eta\left(\eta - i\sqrt{1-\eta^2}\right)\right]\arcsin\eta - 6\mathrm{Li}_2\left(1 - 2\eta^2 + 2i\eta\sqrt{1-\eta^2}\right)\right\}\\ &= \ln(2\eta)\arcsin\eta + \frac{1}{2}\mathrm{Im}\left[\mathrm{Li}_2\left(1 - 2\eta^2 + 2i\eta\sqrt{1-\eta^2}\right)\right]\\ &= \ln(2\eta)\arcsin\eta + \frac{1}{2}\mathrm{Cl}_2(2\arcsin\eta),\end{aligned} \tag{3.6.37}$$

where $\mathrm{Li}_2(z)$ and $\mathrm{Cl}_2(z)$ are the dilogarithm function (Spence's function) and the Clausen integral, respectively:

$$\mathrm{Li}_2(z) = \sum_{k=1}^{\infty} z^k/k^2, \tag{3.6.38}$$

$$\mathrm{Cl}_2(z) = \sum_{k=1}^{\infty} \sin(kz)/z^2 = -\int_0^x \ln[2\sin(t/2)]\,\mathrm{d}t. \tag{3.6.39}$$

The approximation proposed by van Berkum (1994) for (3.6.35) and (3.6.36),

$$f^*(\eta) = \begin{cases} -\ln\eta + \dfrac{7}{4} - \ln 2 + \dfrac{\eta^2}{6} - \dfrac{32\eta^3}{225\pi}, & \eta \le 1 \\ \dfrac{256}{45\pi\eta} - \left(\dfrac{11}{24} + \dfrac{1}{4}\ln 2\eta\right)\dfrac{1}{\eta^2}, & \eta \ge 1, \end{cases} \tag{3.6.40}$$

should not be employed, as the derivative is discontinuous at $\eta = 1$. A simpler approximation, valid over the whole η range, was provided by Kaganer & Sabelfeld (2010):

$$f^*(\eta) = -\ln\left(\frac{\eta}{\eta_0 + \eta}\right). \tag{3.6.41}$$

With $\eta_0 = 2.2$, the results of equation (3.6.41) are similar to those of (3.6.35) and (3.6.36).

Together with dislocation density and outer cutoff radius, a parameter traditionally quoted for the dislocations ensemble is Wilkens' dislocation arrangement parameter $M = R_e\sqrt{\rho}$ (Wilkens, 1970*a*). By combining the information on dislocation screening and dislocation distance, it gives an idea of the interaction of dislocations (strength of the dipole character; Ungár, 2001). A value close to or below unity indicates highly interacting dislocations (for example, dipole configurations or dislocation walls), whereas a large value is typical of a system with randomly dispersed dislocations (weak dipole character).

The anisotropic broadening caused by the presence of dislocations is mainly taken into account by the contrast (or orientation) factor C_{hkl}. The contrast factor depends on the strain field of the dislocation and therefore on the elastic anisotropy and orientation of the scattering vector with respect to the slip system considered. The average of the contrast factor over all equivalent slip systems, $\overline{C}_{hkl}$, is often used in the analysis of powders. The averaging is usually performed under the assumption that all equivalent slip systems are equally populated. The calculation of the contrast factor can be lengthy: full details can be found in the literature (Wilkens, 1970*a*,*b*, 1987; Krivoglaz *et al.*, 1983; Kamminga & Delhez, 2000; Groma *et al.*, 1988; Klimanek & Kuzel, 1988; Kuzel & Klimanek, 1989) for the cubic and hexagonal cases. For a generalization, the reader is referred to the recent work of Martinez-Garcia *et al.* (2007, 2008, 2009). It is possible to show that the contrast factor of a given material has the same functional form as the fourth-order invariant of the Laue class (Popa, 1998; Leoni *et al.*, 2007):

$$\begin{aligned}d^4_{\{hkl\}}C_{\{hkl\}} &= E_1h^4 + E_2k^4 + E_3l^4 + 2(E_4h^2k^2 + E_5k^2l^2 + E_6h^2l^2)\\ &\quad + 4(E_7h^3k + E_8h^3l + E_9k^3h + E_{10}k^3l + E_{11}l^3h + E_{12}l^3k)\\ &\quad + 4(E_{13}h^2kl + E_{14}k^2hl + E_{15}l^2hk).\end{aligned} \tag{3.6.42}$$

In the general case, 15 coefficients are thus needed to describe the strain anisotropy effects. Symmetry reduces the number of independent coefficients: for instance, two coefficients survive in the cubic case, and the average contrast factor is (Stokes & Wilson, 1944; Popa, 1998; Scardi & Leoni, 1999)

$$\overline{C}_{\{hkl\}} = (A + BH) = A + B\frac{h^2k^2 + h^2l^2 + k^2l^2}{(h^2 + k^2 + l^2)^2}. \tag{3.6.43}$$

The values of A and B can be calculated from the elastic constants and slip system according to the literature (Klimanek & Kuzel, 1988; Kuzel & Klimanek, 1989; Martinez-Garcia *et al.*, 2007, 2008, 2009). Excluding the case of $\overline{C}_{\{h00\}} = 0$, the parameterization $\overline{C}_{\{hkl\}} = \overline{C}_{\{h00\}}(1 + qH)$ proposed by Ungár & Tichy (1999) can also be used. Some calculated values for cubic and hexagonal materials can be found in Ungár *et al.* (1999) and Dragomir & Ungár (2002), respectively.

As the calculation of the contrast factor for a dislocation of general character is not trivial, it is customary to evaluate it for the screw and edge case and to refine an effective dislocation character φ (Ungár *et al.*, 1999),

$$\begin{aligned}\overline{C}_{\{hkl\}} &= [\varphi\overline{C}_{E,\{hkl\}} + (1-\varphi)\overline{C}_{S,\{hkl\}}]\\ &= [\varphi A_E + (1-\varphi)A_S] + [\varphi B_E + (1-\varphi)B_S]H,\end{aligned} \tag{3.6.44}$$

where the geometric term H is the same as in equation (3.6.43). Although not completely correct, the approach proposed in equation (3.6.44) allows the case where a mixture of dislocations of varying character are acting on equivalent slip systems to be dealt with. For a proper refinement, however, the active slip systems as well as the contrast factors of the edge and screw dislocations should be known.

It is worth mentioning that the invariant form proposed by Popa (1998) has been reprised by Stephens (1999) to describe the strain-broadening anisotropy, for example, within the Rietveld method: the formula correctly accounts for the relative broadening (*i.e.* for the anisotropy), but it does not give any information on the actual shape of the profiles. This is the major reason

why the Stephens model can be considered as only phenomenological (it captures the trend but not the details): when the source of microstrain broadening is known, we can obtain the functional form of the profile (as proposed, for example, here for dislocations) and the model can become exact.

3.6.2.6.7. *Twin and deformation faults*

Planar defects, *i.e.* a mismatch in the regular stacking of crystallographic planes, are quite frequent in a vast family of technologically important materials and, in some cases, are responsible for their macroscopic properties. In the general case, the analysis of faulting using a Bragg-type method is troublesome. The local change in the structure causes the appearance of diffuse scattering (*i.e.* extra intensity) between the Bragg spots. This can be handled in the single-crystal case (Welberry, 2004), but can be challenging in a powder, where the reciprocal space is rotationally averaged and the (weak) diffuse scattering is lost in the background. The handling of diffuse phenomena is the main difference between the Rietveld (1969) and the pair distribution function (PDF) (Billinge, 2008) methods.

A simple description of the broadening effects of faulting, useful for WPPM, is available only for a restricted class of systems, namely face-centred cubic (f.c.c.) ($Fm\bar{3}m$), body-centred cubic (b.c.c.) ($Im\bar{3}m$) and hexagonal close packed (h.c.p.) ($P6_3/mmc$) lattices. Monatomic metals with f.c.c. (*e.g.* Cu, Ni and Au), h.c.p. (*e.g.* Ti, Co and Zr) and b.c.c. (*e.g.* W and Mo) structures fall into this list. Faulting in the wurtzite structure ($P6_3mc$) leading to a local transformation into sphalerite ($F\bar{4}3m$) can be handled with rules completely analogous to those for the h.c.p./f.c.c. case. The main types of faults in all of these systems are the so-called deformation and twin faults: looking at the planes on the two sides of the faulting, a deformation fault appears as a shear, whereas twinning causes a mirroring of the atomic positions. The effect of these defects can be modelled using recurrence equations for the stacking. Initially proposed for the h.c.p. case by Wilson (Edwards & Lipson, 1942; Wilson, 1942), this idea was then extended to the f.c.c. case (Paterson, 1952; Gevers, 1954*a*,*b*; Warren, 1959, 1963). More recently, Estevez-Rams *et al.* (2003, 2008) improved the accuracy and extended the validity range by including all terms in the stacking probability formulae, whereas Velterop *et al.* (2000) corrected the formalism to properly take the various *hkl* components of a peak into account.

In an f.c.c. system, reliable information can be obtained up to a few per cent of faults on the {111} plane. The trick is to describe the lattice with hexagonal axes, effectively transforming the problem into that of ⟨001⟩ stacking on the {111} plane. Under these hypotheses, the average phase term due to faulting can be written as

$$\left\langle \exp\left[2\pi i\varphi(L; d^*_{\{hkl\}}, L_0/h_0^2)\right]\right\rangle = A^F_{hkl}(L) + iB^F_{hkl}(L), \qquad (3.6.45)$$

where $L_0 = h + k + l$ and $h_0^2 = h^2 + k^2 + l^2$. The lattice symmetry influences the definitions of these two parameters. Faulting is one of the typical cases where a complex (sine) term is present, as peak shift and asymmetry in the profiles is expected (unless twin faults are absent). Following the treatment of Warren (see, for example, Warren, 1963), a set of recurrence equations can be written for the probability of the occurrence of faulting. The solution of the recurrence equations is used to generate the Fourier coefficients for faulting. In particular, if the probabilities of deformation and twin fault are α and β, respectively, then

$$S^2 = 3 - 12\alpha - 6\beta + 12\alpha^2 - \beta^2 + 24\alpha\beta(1-\alpha),$$
$$Z = \sqrt{(1-\beta^2) + S^2}/2 \qquad (3.6.46)$$

and, introducing the sign function,

$$\sigma_{L_0} = \begin{cases} +1 & \text{for } L_0 = 3N+1 \\ 0 & \text{for } L_0 = 3N \\ -1 & \text{for } L_0 = 3N-1 \end{cases} \qquad N = 0, \pm1, \pm2, \ldots, \qquad (3.6.47)$$

the Fourier coefficients can be obtained as

$$A^F_{hkl}(L) = \exp\left[\tfrac{1}{2}\ln(Z)|Ld^*_{\{hkl\}}\sigma_{L_0}L_0/h_0^2|\right], \qquad (3.6.48)$$

$$B^F_{hkl}(L) = -\sigma_{L_0}\frac{L}{|L|}\frac{L_0}{|L_0|}\frac{\beta}{S}A^F_{hkl}(L). \qquad (3.6.49)$$

Besides being asymmetric, each profile subcomponent can also be shifted with respect to the average Bragg position. For the subcomponent *hkl* the shift is

$$\delta_{hkl} = -\left[\frac{1}{2\pi}\arctan\left(\frac{s}{1-\beta}\right) - \frac{1}{6}\right]d^*_{\{hkl\}}\frac{L_0}{h_0^2}\sigma_{L_0}. \qquad (3.6.50)$$

In a given reflection family {*hkl*}, reflections affected and unaffected by faulting coexist, leading to peculiar shapes of the corresponding peak profiles.

Analogous formulae can be obtained for the b.c.c. and h.c.p. cases. In the former, the selection rule becomes $L_0 = -h - k + 2l$, whereas for the latter $L_0 = l$ and the condition for faulting is based on $h - k = 3N \pm 1$. Implementation requires the application of the proper formula to the particular reflection *hkl* considered in the analysis.

Analysing faults by observing just the peak shift, as in the original treatment of Warren (1959, 1963) or within the Warren–Averbach method (Warren & Averbach, 1950, 1952), would be erroneous, as it does not take the fine details of the broadening into account.

An alternative to the adoption of Warren's formalism was proposed by Balogh *et al.* (2006). Instead of performing the calculation explicitly, the authors parameterized the profiles obtained from the *DIFFaX* software (Treacy *et al.*, 1991) calculated for increasing quantities of faulting. The *DIFFaX* software is based on a recursive description of the stacking: the intensity is calculated along rods in reciprocal space using the tangent cylinder approximation. The parameterization, which is performed in terms of a sum of Lorentzian curves, is then employed for the evaluation of the fault-broadening profile at any angle. The modelling should be performed on a profile that contains a faulting-only contribution: note that for high faulting probabilities, it becomes arbitrary whether to assign the diffuse scattering part to one or another Bragg reflection. This introduces some arbitrariness in the subsequent (directional) convolution of the faulting profile with the other broadening effects. When applicable, however, this parameterization has several advantages: it takes the actual shape of the reciprocal-space rods into account (in an effective way), it does not necessitate any *hkl* selection rule and an analytical treatment can be employed, as the Lorentzian has an analytical transform. With the above caveats, it is in principle not even necessary to decompose the *DIFFaX*-generated profile if a numerical convolution is employed. This would also correspond to an extension of WPPM to the *DIFFaX*+ idea (Leoni, Gualtieri & Roveri, 2004; Leoni, 2008), or *vice versa*, where *DIFFaX*+ uses a corrected and improved version of the recursive approach of *DIFFaX* to

generate the profiles, but allows the refinement of all model parameters. [*DIFFaX+* is available from the author (matteo.leoni@unitn.it) on request.]

3.6.2.6.8. *Antiphase domain boundaries*

In the diffraction pattern of an ordered alloy, a dissimilar broadening can often be observed for structure and superstructure peaks (with the former being present in both the ordered and disordered states). The superstructure peaks, in fact, bear microstructural information on the interface between the ordered regions in the material: broadening occurs when domains meet out of phase, creating an antiphase domain boundary (APB or APDB). A general formula for APDB-related broadening does not exist: for a given ordered structure, the Fourier coefficients correspond to the normalized value of $A_{\mathrm{APDB},hkl}(L) = \overline{F(0)F^*(L)}$, where $F(0)$ is the structure factor of a cell positioned at $L = 0$ and $F^*(L)$ is the complex conjugate of the structure factor of a cell at a distance L along the direction $[hkl]$. Being the result of a combination of probabilities, the peak is always expected to be Lorentzian.

Explicit formulae have been derived for the Cu_3Au ordered alloy ($L1_2$ phase; Wilson, 1943; Wilson & Zsoldos, 1966; Scardi & Leoni, 2005). Several types of boundaries can form, depending on the way that the domains meet: the broadening depends both on the boundary plane and on the local arrangement of Au atoms leading to conservative (no Au atoms in contact) or nonconservative (Au atoms in contact) boundaries. By arranging the indices in such a way that $h \geq k \geq l$ and that l is always the unpaired index, the broadening of the superstructure reflections can be described as (Scardi & Leoni, 2005)

$$A^{\mathrm{APDB}}(L) = \exp[-2L\delta f(h, k, l)]. \tag{3.6.51}$$

In this formula, $\delta = \gamma_{\mathrm{APDB}}/a_0$ is the probability of occurrence of an APDB, a_0 is the unit-cell parameter and $f(h, k, l)$ is a function of hkl defined in Table 3.6.2, obtained from the results of Wilson (1943) and Wilson & Zsoldos (1966).

The average distance between two APDBs is given by $1/\delta$. For a random distribution of faults, the broadening is Lorentzian and $A^{\mathrm{APDB}} = \exp(-4L\delta/3)$.

3.6.2.7. *Assembling the equations into a peak and modelling the data*

As previously mentioned, the broadening contributions briefly illustrated in the previous sections are employed to generate the powder peak profile for reflections from the set of planes $\{hkl\}$ using equations (3.6.11) and (3.6.12) and where

$$\begin{aligned} I_{hkl}(s) &= k(d^*) \int_{-\infty}^{\infty} C(L) \exp(2\pi i L s)\, \mathrm{d}L \\ &= k(s) \int_{-\infty}^{\infty} T_{\mathrm{pV}}^{\mathrm{IP}}(L) A_{hkl}^{S}(L) [A_{hkl}^{D}(L)\cos(2\pi L s) + iB_{hkl}^{D}(L)\sin(2\pi L s)] \\ &\quad \times \ldots \times [A_{hkl}^{F}(L)\cos(2\pi L s) + iB_{hkl}^{F}(L)\sin(2\pi L s)]\, \mathrm{d}L. \end{aligned} \tag{3.6.52}$$

Table 3.6.2
Models for antiphase domain boundaries for the Cu_3Au case
$N = h^2 + k^2 + l^2$.

ID	Model	$f(h, k, l)$
1	Random	2/3
2	{100} planes	$\frac{2}{3}\frac{h+k+l}{\sqrt{N}}$
2.I	{100} planes, no Au–Au contacts	$(k+l)/\sqrt{N}$ if h is the unpaired index $(h+l)/\sqrt{N}$ if k is the unpaired index $(h+k)/\sqrt{N}$ if l is the unpaired index
2.II	{100} planes, only Au–Au contacts	$\frac{2h+k+l}{2\sqrt{N}}$ if h is the unpaired index $\frac{h+2k+l}{2\sqrt{N}}$ if k is the unpaired index $\frac{h+k+2l}{2\sqrt{N}}$ if l is the unpaired index
3	{110} planes	$\frac{2}{3}\frac{4h+2k}{\sqrt{2N}}$
3.I	{110} planes, Au displacement parallel or perpendicular to plane normal	$\frac{4h}{\sqrt{2N}}$ if h is the unpaired index $\frac{2h+2k}{\sqrt{2N}}$ otherwise
3.II	{110} planes, Au displacement at 60° to plane normal	$\frac{2h+2k}{\sqrt{2N}}$ if h is the unpaired index $\frac{3h+k}{\sqrt{2N}}$ otherwise
4	{111} planes	$\frac{8h}{3\sqrt{3N}}$ if $h \geq (k+l)$ $\frac{4(h+k+l)}{3\sqrt{3N}}$ otherwise