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