$$\sigma^2 = \langle d_{hkl}^{-4} \rangle - \langle d_{hkl}^{-2} \rangle^{-2} = \sum_{HKL} S_{HKL} h^H k^K l^L, \qquad (3.2.17)$$

where the sum is over terms with $H + K + L = 4$. This leads to a contribution to the width of a diffraction peak proportional to $\Gamma_{2\theta} = d^2 \sqrt{\sigma^2} \tan\theta$ for angle-dispersive measurements, and $\Gamma_t = td^2\sqrt{\sigma^2}$ for time-of-flight neutron measurements. Strain broadening in real samples frequently leads to peak shapes that are closer to Lorentzian than Gaussian, and the justification of this expression breaks down because the second moment of the distribution of d^{-2} is then not defined. Nevertheless, this method is often successful at modelling the phenomenology of anisotropic peak broadening.

The parameters S_{HKL} arise from the nature of the strain and the values of elastic constants for any particular sample. Typically, they must therefore be regarded as phenomenological, and can be adjusted in fitting a model to observed data. They are constrained by the symmetry of the Laue group of the sample, which leads to restrictions on the S_{HKL} terms for the various Laue classes, listed in Table 3.2.1 (Popa, 1998).

Table 3.2.1
Restrictions and reflections of anisotropic strain parameters for the various Laue classes

$\bar{3}$, $\bar{3}m1$, $\bar{3}1m$: hexagonal indices.

Class	$\langle 1/d^2 \rangle^2$
$\bar{1}$	$S_{400}h^4 + S_{040}k^4 + S_{004}l^4 + S_{220}h^2k^2 + S_{202}h^2l^2 + S_{022}k^2l^2 + S_{310}h^3k + S_{130}hl^3 + S_{301}h^3l + S_{103}hl^3 + S_{031}k^3l + S_{013}kl^3 + S_{211}h^2kl + S_{121}hk^2l + S_{112}hkl^2$
$2/m$ (b-axis unique)	$S_{400}h^4 + S_{040}k^4 + S_{004}l^4 + S_{220}h^2k^2 + S_{202}h^2l^2 + S_{022}k^2l^2 + S_{301}h^3l + S_{103}hl^3 + S_{121}hk^2l$
$2/mmm$	$S_{400}h^4 + S_{040}k^4 + S_{004}l^4 + S_{220}h^2k^2 + S_{202}h^2l^2 + S_{022}k^2l^2$
$4/m$	$S_{400}(h^4 + k^4) + S_{004}l^4 + S_{220}h^2k^2 + S_{202}(h^2 + k^2)l^2 + S_{310}(h^3k - hk^3)$
$4/mmm$	$S_{400}(h^4 + k^4) + S_{004}l^4 + S_{220}h^2k^2 + S_{202}(h^2 + k^2)l^2$
$\bar{3}$	$S_{400}(h^2 + k^2 + hk)^2 + S_{202}(h^2 + k^2 + hk)l^2 + S_{004}l^4 + S_{211}(h^3 - k^3 + 3h^2k)l + S_{121}(-h^3 + k^3 + 3hk^2)l$
$\bar{3}m1$	$S_{400}(h^2 + k^2 + hk)^2 + S_{202}(h^2 + k^2 + hk)l^2 + S_{004}l^4 + S_{301}(2h^3 + 3h^2k - 3hk^2 - 2k^3)l$
$\bar{3}1m$	$S_{400}(h^2 + k^2 + hk)^2 + S_{202}(h^2 + k^2 + hk)l^2 + S_{004}l^4 + S_{211}(h^2k + hk^2)l$
Hexagonal	$S_{400}(h^2 + k^2 + hk)^2 + S_{202}(h^2 + k^2 + hk)l^2 + S_{004}l^4$
Cubic	$S_{400}(h^4 + k^4 + l^4) + S_{220}(h^2k^2 + h^2l^2 + k^2l^2)$

3.2.3.5. *Preferred orientation (texture)*

The discussion of diffraction-peak intensities in Section 3.2.2.2 above presumes that the sample is a random powder, with every orientation equally probable. Real samples frequently exhibit some deviation from that ideal case, perhaps because of the way that grains of platy or acicular (needle-like) habit settle into a sample holder, or because a solid polycrystalline sample crystallized or grew anisotropically, or was formed or worked as a solid. The latter case is generally called texture, and can provide a fruitful basis for understanding the history or mechanical properties of a sample. The topic is further discussed in Chapter 5.3 of this volume. For the present purposes, deviation from a collection of randomly oriented grains will be regarded as an artifact to be minimized and/or modelled.

The distribution of orientations of crystallites in a sample can be studied using pole figures. For a given reflection **G**, the pole figure is defined as the probability density over a spherical surface that **G** falls in a particular direction relative to the sample. For a random powder, all pole figures would be uniform; for a single crystal, each pole figure would be a set of delta functions. Modelling of preferred orientation in the sample is accomplished by multiplying the theoretical intensity by the pole-figure density in the direction of the diffraction vector. Here we discuss two different treatments of preferred orientation.

The symmetrized spherical-harmonic approach follows Järvinen (1993), considering samples that are axially symmetric about some axis **P**. Experimentally, this can be ensured by rotating the sample about **P** during data collection. Take α to be the angle between **P** and the diffraction vector: α is zero for a conventional symmetrical flat plate and 90° for Debye–Scherrer geometry.

For a given reflection hkl, the polar-axis density in the diffraction direction may be expanded in spherical harmonics as

$$A(hkl, \alpha) = \sum_{ij} C_{ij} Y_{ij}(\theta_{hkl}, \varphi_{hkl}) P_i(\cos\alpha),$$

where Y_{ij} and P_i are the usual spherical harmonics and Legendre polynomials, and θ_{hkl} and φ_{hkl} are the spherical coordinates of the hkl reflection relative to some chosen axis of the crystal.

In general, there will be several reflections equivalent to hkl by the Laue symmetry of the crystalline phase, and so symmetry-adapted functions should replace the spherical harmonics in the above equation. Only even orders i are considered, because of the inversion symmetry of diffraction (neglecting imaginary atomic scattering amplitudes). The Laue symmetry of the crystalline phase implies that certain of the harmonics are zero; see the original article by Järvinen (1993) for explicit functional forms of the harmonics and a tabulation of which are allowed for each Laue group.

The second approach considered here is the widely used March (1932)–Dollase (1986) model, which is applicable to the most common powder-diffraction sample geometries of axial symmetry either along the diffraction vector or perpendicular to the diffraction plane, for samples whose preferred orientation arises from the settling of either disc- or rod-shaped crystallites in the sample holder. The cylinder axis **H** governs the preferred orientation. For any Bragg reflection **G**, the pole density in the diffraction direction is hypothesized to be a particular function of the angle α between **H** and **G**, *viz*.

$$A(G) = (R^2 \cos^2\alpha + \sin^2\alpha / R)^{-3/2}.$$

Here R is a parameter describing the degree of preferred orientation; it is less than unity for maximum pole density at $\alpha = 0$, *i.e.*, $\mathbf{H} \parallel \mathbf{G}$, as would be found for disc-like samples preferentially lying in the reflection plane. $R > 1$ corresponds to maximum pole density at $\alpha = 90°$, as might be found for acicular crystallites in either a flat-plate or Debye–Scherrer geometry. The particular functional form has some theoretical justification as a model for grain rotation in settling of a granular sample, as well as being properly normalized, suitable for oblate or prolate grains with a single parameter, and in agreement with pole distributions observed in many samples. To apply this model to powder-diffraction data, one must find the appropriate axis **H**, either through prior knowledge of growth habit or by trial and error.

3.2.3.6. *Extinction*

The analysis of diffracted intensities in this chapter has been premised on the assumption that the diffracted beam produced by each crystallite is much weaker than the incident beam, known

  references