3.2. THE PHYSICS OF DIFFRACTION FROM POWDERS

density. Therefore, the intensity of magnetic neutron diffraction peaks falls off much more rapidly with $(\sin\theta)/\lambda$ than do nuclear neutron diffraction peaks.

3.2.2.3. *Peak shapes*

The shape of a powder-diffraction peak is a convolution of the intrinsic line shape due to the microscopic structure of the sample crystallites (*e.g.* size and strain) and the configuration of the instrument used to record the pattern. A major goal of powder-diffraction analysis is to be able to separate the contributions of instrument and sample, so that information about the micro-structure of the sample can be extracted reliably. On the other hand, in some cases one simply wants to be able to model the combined influence of instrument and sample, to obtain a functional form that permits the most accurate way of apportioning intensities to partially overlapping peaks.

Consider first the sample-dependent factors. The following division into size and strain effects is somewhat artificial, insofar as lattice strains affect the size of the coherently diffracting domain. Nevertheless, it is common to make a distinction between the two, as size broadening produces a peak width proportional to $1/\cos\theta$ in angle-dispersive measurements, whereas the peak width is proportional to $\tan\theta$ for strain broadening.

3.2.2.3.1. *Domain size*

In very general terms, diffraction peaks from an object of linear size L will have a width in Q of the order of $1/L$. As formulated by Scherrer (1918), in an angle-dispersive measurement, the full width at half-maximum (FWHM) in 2θ, measured in radians, is given by

$$\Gamma = \frac{K\lambda}{L\cos\theta}, \tag{3.2.12}$$

where K is called the shape factor and is a number of the order of unity whose precise value depends on the shape of the particles, which are assumed to be of uniform size and shape. The FWHM shape factor for a spherical particle is $K = 0.829$ (Patterson, 1939). Note that if a powder sample is polydisperse (*i.e.*, it contains a distribution of grain sizes), the average grain size is not necessarily given by the Scherrer equation.

Perhaps a more useful measure of the width of a peak is the integral breadth. In an angle-dispersive measurement, the integral breadth of a given peak centred at $2\theta_0$ is defined as

$$\beta = \frac{1}{I(2\theta_0)}\int I(2\theta)\,d2\theta.$$

From a technical point of view, measurement of the integral breadth requires accurate measurement of the intensity in the wings of the diffraction peak, which in turn depends on accurate knowledge of the background intensity.

For any crystallite shape, it can be shown that the integral breadth is related to the volume-average thickness of the crystallite in the direction of the diffraction vector, *viz.*

$$L_V = \frac{\lambda}{\beta\cos\theta} = \frac{1}{V}\int d^3\mathbf{r}\,T(\mathbf{r}, \mathbf{G}),$$

where V is the volume of the crystallite and $T(\mathbf{r}, \mathbf{G})$ is the length of the line inside the crystallite parallel to $\mathbf{G}$ and passing through the point $\mathbf{r}$. For example, if one writes an integral-breadth version of the Scherrer equation,
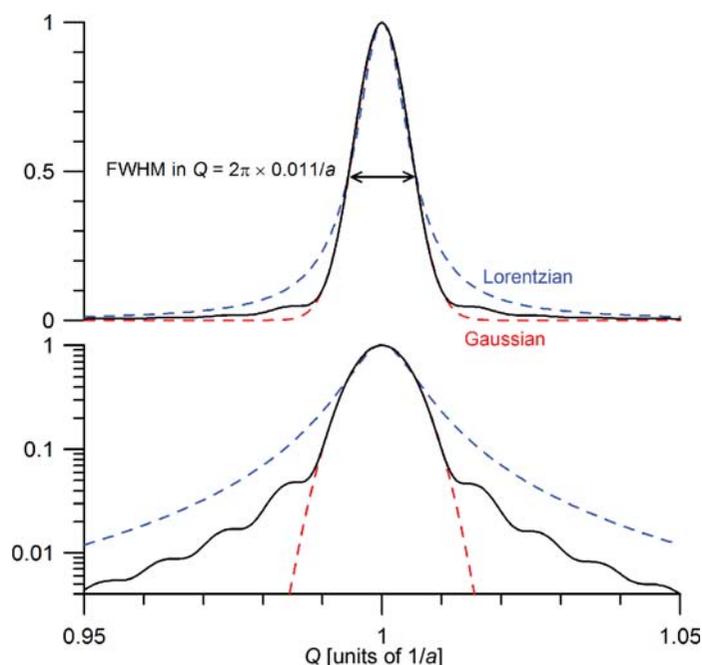

Figure 3.2.1
Computed powder line shape from an ensemble of spherical particles of diameter $100a$, including comparison to Gaussian and Lorentzian line shapes of equal FWHM.

$$\beta = \frac{K_\beta\lambda}{L\cos\theta},$$

the shape factor K_β is unity for $(00l)$ reflections from cube-shaped crystals of size L. $K_\beta = 1.075$ for a sphere of diameter L.

An important feature of the integral breadth is that it has a well defined meaning for a polydisperse sample of crystallites. Assuming that the crystallites all have the same shape,

$$\beta = \frac{K_\beta\lambda\langle L^3\rangle}{\cos\theta\langle L^4\rangle},$$

where $\langle L^3\rangle$ and $\langle L^4\rangle$ are the third and fourth moments of the size distribution (Langford & Wilson, 1978).

In many applications such as Rietveld or profile refinement, it is important to treat the full shape of the diffraction peak instead of merely its width (Loopstra & Rietveld, 1969; Rietveld, 1969). By way of illustration, Fig. 3.2.1 shows one Bragg peak of the computed powder-diffraction pattern from an ensemble of spherical particles of point scatterers in a simple cubic lattice. The lattice parameter is a, and the diameter of the particles is chosen to be $100a$, so that each crystallite consists of approximately 5.2×10^5 'atoms'. (This line shape was calculated using the Debye equation, described in Section 3.2.4.)

Several different analytical functions are frequently used in powder diffraction. In terms of the independent variable x, centred at x_0 with FWHM Γ, the normalized Gaussian function is

$$G(x - x_0) = \pi^{-1/2}\sigma^{-1}\exp-\left(\frac{x - x_0}{\sigma}\right)^2,$$

with $\sigma = \Gamma/2(\ln 2)^{1/2}$. The normalized Lorentzian is

$$L(x - x_0) = \frac{\Gamma/2\pi}{(x - x_0)^2 + (\Gamma/2)^2}.$$

The symmetric Pearson-VII function is a generalization of the Lorentzian, written as

references