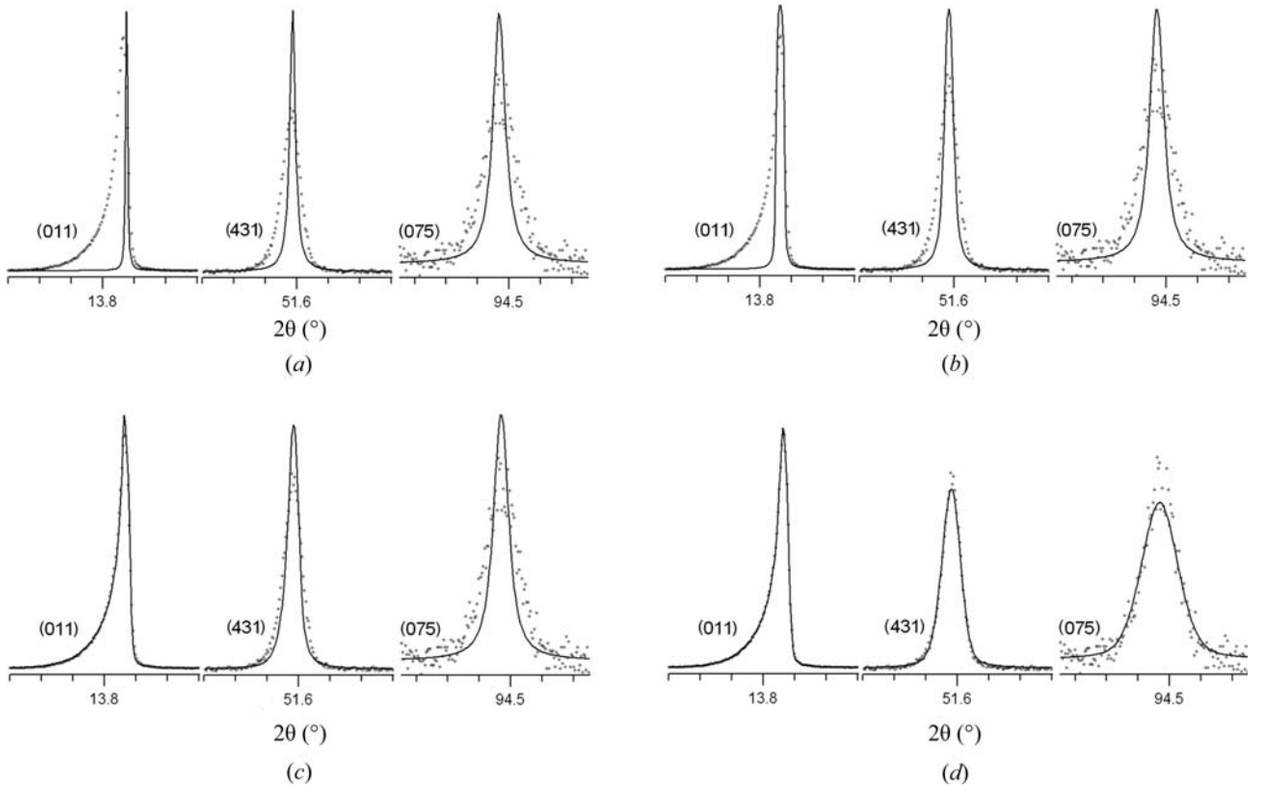

Figure 1.1.19
Peak fits of three selected reflections for an LaB_6 standard measured with Mo $K\alpha_1$ radiation ($\lambda = 0.7093$ Å) from a Ge(220) monochromator in Debye–Scherrer geometry using the fundamental-parameter approach. (*a*) A pure Lorentzian emission profile with a half width of 0.2695 mÅ is applied, refining the peak position and intensity only; (*b*) additionally, a hat shape function of the receiving slit in the equatorial plane with a width of 0.1 mm has been convoluted into the profile; (*c*) additionally, an axial convolution with filament-, sample- and receiving-slit lengths of 8 mm each and a secondary Soller slit with an opening angle of 2.5° has been convoluted into the profile; (*d*) additionally a small contribution of Gaussian broadening coming from the position-sensitive detector is convoluted into the profile. [From Mittemeijer & Welzel (2012). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.]

These functions can be convoluted sequentially as needed, first with the delta-function Bragg peak, and subsequently with the existing profile from the previous convolutions, each time resulting in a new profile that can become quite complex (Fig. 1.1.19). It is often the case that for a particular resolution effect the angular dependence of the profile function is known from the geometry of the measurement, and the convolution function for each peak is determined with only a very small number of parameters.

1.1.4.1. *Sample contributions to the peak profile*

Features of the sample that affect the peak profile include crystallite domain size and shape, dislocations, disclinations, twin and stacking faults, antiphase domains, microstrains, grain surface relaxations, and compositional fluctuations. Here we reproduce some basic results as examples; they also illustrate some fundamental aspects of diffraction from real crystals.

1.1.4.1.1. *Crystallite size*

The starting point for the analysis of finite size effects is the Laue equation, equation (1.1.39), which is reproduced here for a one-dimensional crystal:

$$A(h) = \sum_{j=0}^{n} \exp(2\pi i a j h). \tag{1.1.65}$$

When we were deriving the Bragg equation from the Laue equation we assumed an infinite crystal, and the sum taken to infinity resulted in delta functions at the reciprocal-lattice points. Now we want to consider a finite crystal with n unit cells. There is an analytic form for this sum which, using Euler's identity, is given by

$$\begin{aligned} A(h) &= \frac{\exp\left(2\pi i(n+1)ah\right) - 1}{\exp(2\pi i a h) - 1} \\ &= \frac{\exp\left(i\pi(n+1)ah\right)}{\exp(i\pi a h)} \frac{\exp\left(i\pi(n+1)ah\right) - \exp\left(-i\pi(n+1)ah\right)}{\exp(i\pi a h) - \exp(-i\pi a h)} \\ &= \exp(i\pi n a h) \frac{\sin\left(\pi(n+1)ah\right)}{\sin(\pi a h)}. \end{aligned} \tag{1.1.66}$$

The intensity is obtained by taking the modulus squared of this complex function, resulting in

$$I(h) = \frac{\sin^2\left(\pi(n+1)ah\right)}{\sin^2(\pi a h)}. \tag{1.1.67}$$

This function has sharp maxima when $h = \nu(1/a)$, where ν is an integer. This large central maximum falls off with a width proportional to $1/n^2$ with oscillating tails of intensity where the frequency of the oscillations increases with increasing n. This is illustrated in Fig. 1.1.20 for two different values of n but the same value of a.

In general, the Fourier transforms of periodic patterns become sharper with increasing number of unit cells. The expression $\sin(\pi(n+1)ah)/\sin(\pi a h)$ is also called the geometric factor of the structure amplitude.

This size broadening is often modelled in practice by using an equation due to Scherrer. We now reproduce the simple deri-

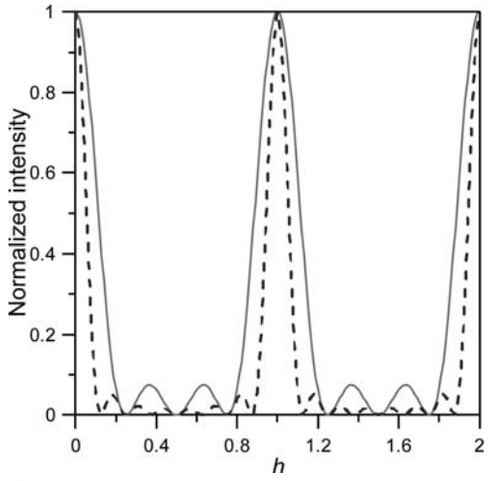

Figure 1.1.20
Normalized intensity from a finite lattice with $n = 3$ (solid curve) and $n = 8$ (dashed line), demonstrating the sharpening of peaks with increasing number of unit cells n. The normalization was done such that the peaks have the same peak maximum rather than the same integrated intensity for a clearer comparison of the relative peak widths.

vation of the Scherrer equation following Klug & Alexander (1974).

Fig. 1.1.21 shows the path-length difference *versus* the depth of the lattice plane. When the angle between the incoming beam and the lattice plane θ is different by an amount ε from the Bragg condition, it is always possible to find a lattice plane inside an infinite crystal where the extra path is $\Delta = \lambda(n + \frac{1}{2})$ for n integer, producing destructive interference. For a thick crystal this is true for arbitrarily small ε, which explains the sharp Bragg reflections. In the case of a crystal with finite dimensions, for small ε the plane for which $\Delta = \lambda(n + \frac{1}{2})$ holds will not be reached, thus leading to an intensity distribution over some small angular range. We can use this idea to estimate the broadening of a Bragg reflection due to size effects.

The thickness of a crystallite in the direction perpendicular to p planes of separation d_{hkl} (Fig. 1.1.21) is

$$L_{hkl} = pd_{hkl}. \tag{1.1.68}$$

The additional beam path between consecutive lattice planes at the angle $\theta + \varepsilon$ is

$$\begin{aligned}\Delta &= 2d\sin(\theta+\varepsilon)\\ &= 2d(\sin\theta\cos\varepsilon + \cos\theta\sin\varepsilon)\\ &= n\lambda\cos\varepsilon + 2d\sin\varepsilon\cos\theta\\ &\simeq n\lambda + 2d\sin\varepsilon\cos\theta.\end{aligned} \tag{1.1.69}$$

The corresponding phase difference is then

$$\delta\varphi = 2\pi\frac{\Delta}{\lambda} = 2\pi n + \frac{4\pi}{\lambda}\varepsilon d\cos\theta = \frac{4\pi\varepsilon d\cos\theta}{\lambda} \tag{1.1.70}$$

and the phase difference between the top and the bottom layer (layer p) is then

$$p\delta\varphi = p\frac{4\pi\varepsilon d\cos\theta}{\lambda} = \frac{4\pi L_{hkl}\varepsilon\cos\theta}{\lambda}. \tag{1.1.71}$$

Rearranging equation (1.1.71) leads to

$$\varepsilon = \frac{\lambda\delta\varphi}{4\pi L_{hkl}\cos\theta}, \tag{1.1.72}$$

which gives an expression for the misalignment angle in terms of the crystallite size L_{hkl} and the phase difference $\delta\varphi$ between the

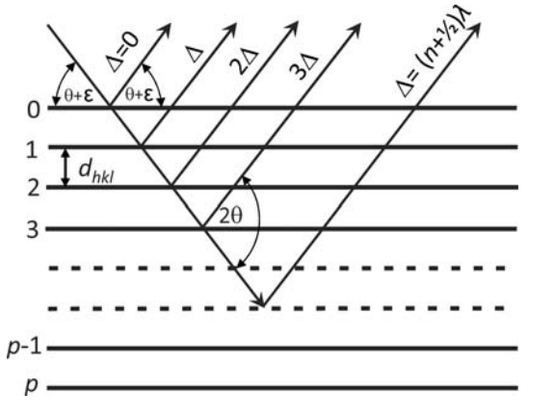

Figure 1.1.21
Path-length difference of the scattered ray *versus* the depth of the lattice plane in the crystal. [Reproduced from Dinnebier & Billinge (2008) with permission from the Royal Society of Chemistry.]

reflections originating from the top plane and the bottom plane. Clearly, the scattered intensity is at a maximum for $\delta\varphi = 0$ ($\varepsilon = 0$). With increasing ε the intensity decreases, giving rise to a peak of finite width. Perfect cancellation of the waves from the top and bottom planes occurs for a phase difference of $\delta\varphi = \pm\pi$, at which point $\varepsilon = \pm\lambda/(4L_{hkl}\cos\theta)$. On a 2θ scale, the measured angular width between these points is

$$\beta_{hkl} = 4\varepsilon = \frac{\lambda}{L_{hkl}\cos\theta}, \tag{1.1.73}$$

giving us some measure of the peak width in radians that results from the finite particle size. A full treatment taking into account the correct form for the intensity distribution gives

$$\beta_{hkl} = \frac{K\lambda}{L_{hkl}\cos\theta}, \tag{1.1.74}$$

with a scale factor of $K = 0.89$ for perfect spheres. In general K depends on the shape of the grains (*e.g.* K is 0.94 for cube-shaped grains), but it is always close to unity. This equation is not valid for crystallites[3] that are too large or too small. In the case of large crystallites the peak width is governed by the coherence of the incident beam and not by particle size. For nanometre-sized crystallites, Bragg's law fails and the Debye equation needs to be used instead. The Debye equation (see Section 1.1.5.3) gives the scattering from an isotropically scattering sample such as a glass, liquid or powder, and does not presume that the sample is periodic.

1.1.4.1.2. *Microstrain*

Several important relationships in crystallography, including the effect of strain and microstrain on Bragg peaks, follow directly from a derivative of the Bragg equation (1.1.3). First we rewrite Bragg's law making the d-spacing the subject of the equation:

$$d = \frac{n\lambda}{2\sin\theta}. \tag{1.1.75}$$

The uncertainty of the measured lattice spacing is given by the total derivative dd,

$$\mathrm{d}d = \frac{\partial d}{\partial\theta}\mathrm{d}\theta + \frac{\partial d}{\partial\lambda}\mathrm{d}\lambda, \tag{1.1.76}$$

[3] Strictly speaking, the term crystallite size here refers to the dimension of a coherently scattering domain. Only in a perfect crystal is this the grain size.