tillator detector behind a receiving slit that defines the angular resolution of the measurement, at each position the detector samples a point on the two-dimensional diffraction pattern shown in Fig. 1.1.13. As the detector is moved to higher 2θ angles the locus of the points that are sampled is a horizontal or vertical (depending on whether the detector is moving in the horizontal or the vertical plane) line across the two-dimensional image. The intensity that is detected is low except where the detector crosses the circles of high intensity. This type of measurement is preferred for obtaining the highest resolution, especially if a highly perfect analyser crystal is used instead of a slit for defining the angle of the scattered beam. However, if the full rings, or fractions of them, are detected with two-dimensional detectors, the counting statistics can be improved enormously by integrating azimuthally around the rings at constant $|\mathbf{h}|$. This mode is becoming very popular for time-resolved, *in situ* and parametric studies where rapid throughput is more important than high resolution. It is also useful for samples that are weakly scattering and for nanometre-sized crystals or defective crystals, which may not show sharper peaks even when measured at higher resolution.

If the powder is non-ideal, the intensity distribution around the ring is no longer uniform, as illustrated in the right part of Fig.

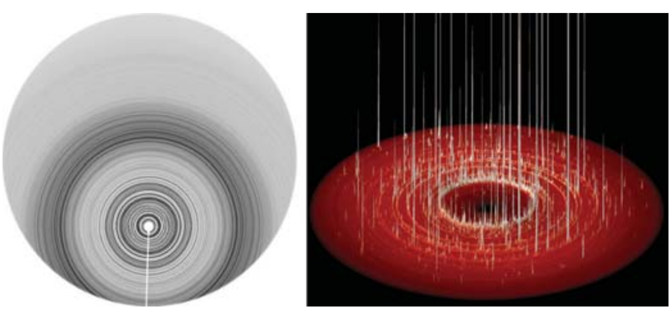

Figure 1.1.13
Left: Debye–Scherrer rings from an ideal fine-grained powder sample of a protein (courtesy Bob Von Dreele). Right: perspective view of Debye–Scherrer rings from a grainy powder sample of $BiBO_3$ at high pressure in a diamond anvil cell.

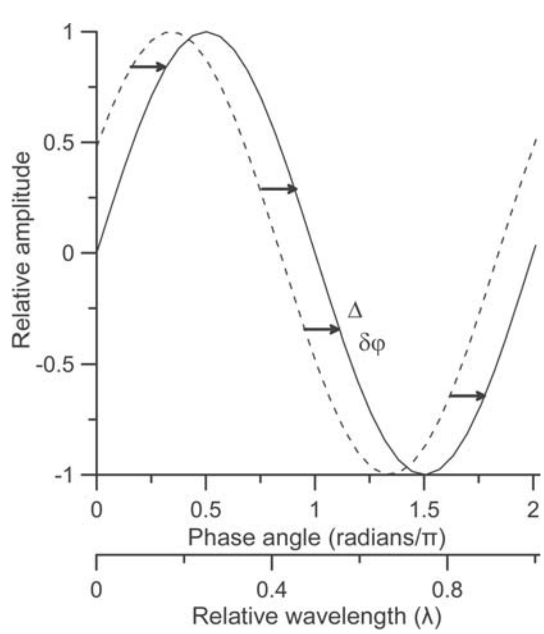

Figure 1.1.14
Graphical illustration of the phase shift between two sine waves of equal amplitude. [Reproduced from Dinnebier & Billinge (2008) with permission from the Royal Society of Chemistry.]

1.1.13, and a one-dimensional scan will give arbitrary intensities for the reflections. To check for this in a conventional measurement it is possible to measure a rocking curve by keeping the detector positioned so that the Bragg condition for a reflection is satisfied and then taking measurements while the sample is rotated. If the powder is ideal, *i.e.* it is uniform and fine-grained enough to sample every orientation uniformly, this will result in a constant intensity as a function of sample angle, while large fluctuations in intensity will suggest a poor powder average. To improve powder statistics, powder samples may be rotated during a single measurement exposure, both for conventional point measurements and for measurements with two-dimensional detectors. Additional averaging of the signal also occurs during the azimuthal integration in the case of two-dimensional detectors. Outlier intensities can be identified and excluded from the integration. On the other hand, the intensity variation around the rings can give important information about the sample, such as preferred orientation of the crystallites or texture.

The *d*-spacings that are calculated from a powder diffraction pattern will include measurement errors, and it is important to minimize these as much as possible. These can come from uncertainty in the position of the sample, the zero point of 2θ, the angle of the detector or the angle of a pixel on a two-dimensional detector, uncertainties in the wavelength and so on. These effects will be dealt with in detail in later chapters. These aberrations often have a well defined angular dependence which can be included in fits to the data so that the correct underlying Bragg-peak positions can be determined with high accuracy.

1.1.3. The peak intensity

1.1.3.1. *Adding phase-shifted amplitudes*

Bragg's law gives the *positions* at which diffraction by a crystal will lead to sharp peaks (known as Bragg peaks) in diffracted intensity. We now want to investigate the factors that determine the intensities of these peaks.

X-rays are electromagnetic (EM) waves with a much shorter wavelength than visible light, typically of the order of 1 Å (= 10^{-10} m). The physics of EM waves is well understood and excellent introductions to the subject are found in every textbook on optics. Here we briefly review the results that are most important in understanding the intensities of Bragg peaks.

Classical EM waves can be described by a sine wave of wavelength λ that repeats every 2π radians. If two identical waves are not coincident, they are said to have a phase shift, which is either measured as a shift, Δ, on a length scale in units of the wavelength, or equivalently as a shift in the phase, $\delta\varphi$, on an angular scale, such that

$$\frac{\Delta}{\lambda} = \frac{\delta\varphi}{2\pi} \Rightarrow \delta\varphi = \frac{2\pi}{\lambda}\Delta. \qquad (1.1.50)$$

This is shown in Fig. 1.1.14.

The detected intensity, I, is proportional to the square of the amplitude, A, of the sine wave. With two waves present that are coherent and can interfere, the amplitude of the resultant wave is not just the sum of the individual amplitudes, but depends on the phase shift $\delta\varphi$. The two extremes occur when $\delta\varphi = 0$ (constructive interference), where $I \simeq (A_1 + A_2)^2$, and $\delta\varphi = \pi$ (destructive interference), where $I \simeq (A_1 - A_2)^2$. In general, $I \simeq [A_1 + A_2 \exp(i\delta\varphi)]^2$. When more than two waves are present, this equation becomes