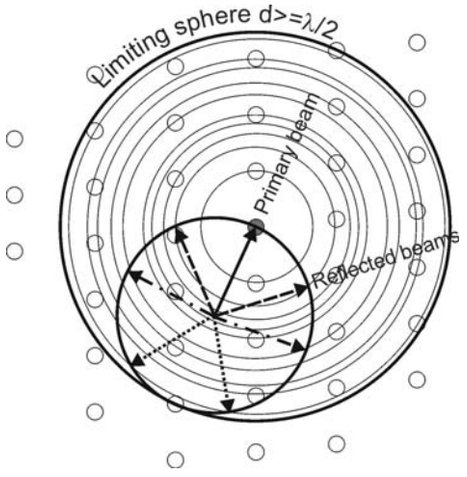

Figure 1.1.11
Simplified representation of the Ewald-sphere construction as a circle in two dimensions. Illustration of the region of reciprocal space that is accessible in a powder diffraction experiment. The smaller circle represents the Ewald sphere. As shown in Fig. 1.1.10, a powder sample has crystallites in all possible orientations, which is modelled by rotating the reciprocal lattice to sample all orientations. An equivalent operation is to rotate the Ewald sphere in all possible orientations around the origin of reciprocal space. The volume swept out is the region of reciprocal space accessible in the experiment. [Reproduced from Dinnebier & Billinge (2008) with permission from the Royal Society of Chemistry.]

smearing out every reciprocal-lattice point over the surface of a sphere centred on the origin of reciprocal space. This is illustrated in Fig. 1.1.10. The orientation of the $\mathbf{d}^*_{hkl}$ vector is lost and the three-dimensional vector space is reduced to one dimension with the independent variable being the modulus of the vector $\left|\mathbf{d}^*_{hkl}\right| = 1/d$.

These spherical shells intersect the surface of the Ewald sphere in circles. A two-dimensional projection is shown in Fig. 1.1.11. Diffracted beams can be envisaged as emanating from the sample in, and only in, the directions where the thin circles from the smeared reciprocal lattice intersect the thick circle of the Ewald sphere. A few representative diffraction beams are indicated by the dashed, dotted and dash-dotted arrows.

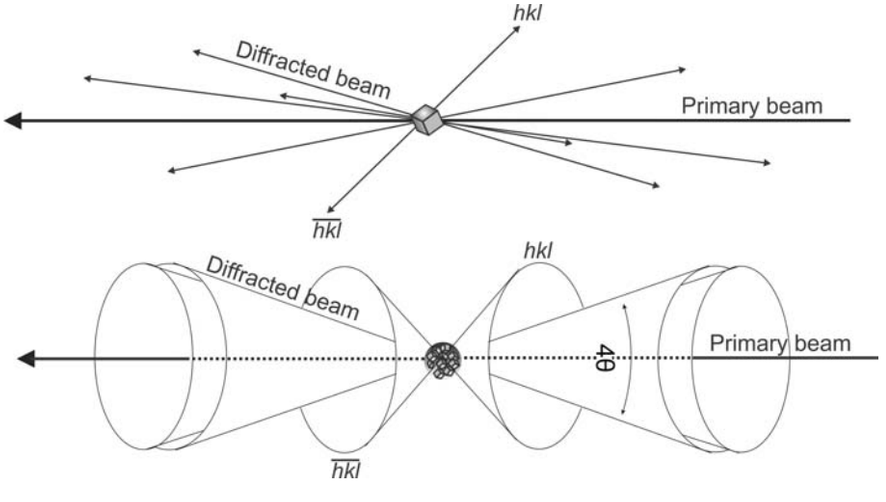

Figure 1.1.12
Comparison between the scattered beams originating from a single crystal (top) and a powder (bottom). For the latter, some Debye–Scherrer cones are drawn in reciprocal space. [Reproduced from Dinnebier & Billinge (2008) with permission from the Royal Society of Chemistry.]

The reflections from planes with the smallest d-spacing that are accessible in the experiment are determined by the diameter of the Ewald sphere, which is $2/\lambda$. In order to increase the number of reflections that can be detected, one must decrease the incident wavelength. In the case of an energy-dispersive experiment such as a time-of-flight neutron powder diffraction experiment, which makes use of a continuous distribution of wavelengths from λ_{min} to λ_{max} at fixed angle, all reflections that lie in the cone-shaped region of reciprocal space between the two limiting Ewald spheres at $2/\lambda_{min}$ and $2/\lambda_{max}$ will be detected.

As mentioned above, in a powder the reciprocal-lattice points get smeared into a spherical surface, which intersects the Ewald sphere as a circle. This means that, in three dimensions, the resulting diffracted radiation associated with the reflection hkl forms a cone emanating from the sample on an axis given by the direct beam, the so-called Debye–Scherrer cone. Different reciprocal-lattice points, at different values of $1/d_{hkl}$, give rise to coaxial cones of scattering. This is illustrated in Fig. 1.1.12.

The smearing of reciprocal space in a powder experiment makes the measurement of a powder diffraction pattern easier than the measurement of a set of single-crystal data, because the sample does not have to be repeatedly re-oriented, but this comes at the cost of a loss of information. At first sight the loss of information seems to be the directional information about the points in the reciprocal lattice. However, once the lattice is indexed (*i.e.* its basis vectors are known) the directional information in the pattern can be recovered without difficulty, which is why three-dimensional structures can be determined from the one-dimensional diffraction information in a powder pattern. The loss of information comes from the fact that reflections from lattice planes whose vectors lie in different directions but which have the same d-spacing overlap. These reflections cannot be resolved by the measurement and so the intensity in each of the peaks is not known. The peak-overlap problem becomes increasingly worse with increasing scattering angle as the number of diffraction planes in a particular d-spacing range increases and their separation decreases.

Some of these overlaps are dictated by symmetry (systematic overlaps) and others are accidental. Systematic overlaps are less problematic because the number of equivalent reflections (the multiplicity) is known from the symmetry, and, by symmetry, each of the overlapping peaks has the same intensity. For highly crystalline samples, the number of accidental overlaps can be reduced by making measurements with higher resolution, since this allows similar but not identical d-spacings to be separated.

To obtain the maximum amount of information, a spherical-shell detector would be desirable, although this is currently impractical. Often, a flat two-dimensional detector, either film, an image plate or a charge-coupled device (CCD), is placed perpendicular to the direct beam, or offset to one side to increase the angular range of the data collected. In this case, the Debye–Scherrer cones appear as circles, as shown in Fig. 1.1.13, or as ellipses if the detector is at an angle to the direct beam.

For an ideal powder, the intensity distribution around the rings is uniform. In a traditional powder diffraction experiment using a point detector, for example a scin-

references