$$\frac{1}{d_{hkl}} = \frac{1}{V}\left\{\left[h^2b^2c^2\sin^2\alpha + k^2a^2c^2\sin^2\beta + l^2a^2b^2\sin^2\gamma + 2hkabc^2(\cos\alpha\cos\beta - \cos\gamma) + 2kla^2bc(\cos\beta\cos\gamma - \cos\alpha) + 2hlab^2c(\cos\alpha\cos\gamma - \cos\beta)\right]\right\}^{1/2}, \quad (1.1.48)$$

for the triclinic case. Equation (1.1.48) simplifies considerably with symmetry to, for example,

$$\frac{1}{d_{hkl}} = \frac{\sqrt{h^2 + k^2 + l^2}}{a} \quad (1.1.49)$$

for the cubic case.

1.1.2.4. *The Ewald construction and Debye–Scherrer cones*

The Bragg equation shows that diffraction occurs when the scattering vector equals a reciprocal-lattice vector. The scattering vector depends on the geometry of the experiment, whereas the reciprocal-lattice vectors are determined by the orientation and the lattice parameters of the crystalline sample. Bragg's law shows the relationship between these vectors in a scattering experiment. Ewald developed a powerful geometric construction that combines these two concepts in an intuitive way (Ewald, 1921). A sphere of radius 1/λ is drawn following the recipe below. The Bragg equation is satisfied and diffraction occurs whenever a reciprocal-lattice point coincides with the surface of the sphere.

The recipe for constructing Ewald's sphere[2] is as follows (Fig. 1.1.9):

(1) Draw the incident wave vector $\mathbf{s}_0$. This points in the direction of the incident beam and has length 1/λ.
(2) Draw a sphere centred on the tail of this vector with radius 1/λ. The incident wave vector $\mathbf{s}_0$ defines the radius of the sphere. The scattered wave vector $\mathbf{s}$, also of length 1/λ, points in the direction from the sample to the detector. This vector is also drawn starting from the centre of the sphere and also terminates at a point on the surface of the sphere. The scattering vector $\mathbf{h} = \mathbf{s} - \mathbf{s}_0$ completes the triangle from the tip of $\mathbf{s}$ to the tip of $\mathbf{s}_0$, both of which lie on the surface of the sphere. Thus the surface of the sphere defines the locus of points in reciprocal space where the scattering vector in our experiment may possibly lie.
(3) Draw the reciprocal lattice with the origin lying at the tip of $\mathbf{s}_0$.
(4) Find all the places on the surface of the sphere where reciprocal-lattice points lie. This gives the set of points in reciprocal space where the expression $\mathbf{h} = \mathbf{h}_{hkl}$ may possibly be satisfied in our experiment.

This construction places a reciprocal-lattice point at one end of $\mathbf{h}$. The other end of $\mathbf{h}$ lies on the surface of the sphere by definition. Thus, Bragg's law is only satisfied when another reciprocal-lattice point coincides with the surface of the sphere. Diffraction can be envisaged as beams of X-rays emanating from the sample in these directions. In order to detect the intensity of these diffracted beams, one simply moves the detector to the right position. Any vector between two reciprocal-lattice points has the potential to produce a Bragg peak. The Ewald-sphere construction indicates which of these possible reflections are experimentally accessible.

[2] For practical reasons, plots of the Ewald 'sphere' are circular cuts through the sphere and the corresponding slice of reciprocal space.

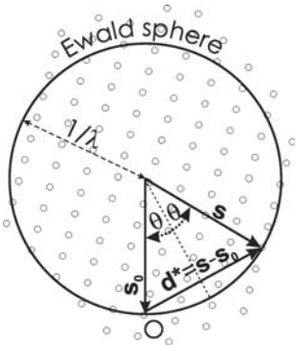

Figure 1.1.9
Simplified representation of the Ewald-sphere construction as a circle in two dimensions. O marks the origin of reciprocal space. The vectors are defined in the text. [Reproduced from Dinnebier & Billinge (2008) with permission from the Royal Society of Chemistry.]

Changing the orientation of the crystal reorients the reciprocal lattice, bringing different reciprocal-lattice points onto the surface of the Ewald sphere. In a single-crystal experiment it is necessary to repeatedly reorient the crystal to bring new reciprocal-lattice points onto the surface of the Ewald sphere, and then to reorient the detector in such a way as to measure the scattering from each particular reflection on the surface. This is done in a highly automated fashion these days. Once a diffraction pattern has been indexed so that the lattice vectors and the orientation matrix (the relation of the lattice vectors to the laboratory coordinate frame) are found, then all of the diffractometer settings that are required to collect all the Bragg peaks are fully determined and this process can be accomplished automatically.

In this chapter we are considering scattering from powders. An ideal powder contains individual crystallites in all possible orientations with equal probability. The powder experiment is equivalent to placing a detector at a fixed position and rotating a single crystal through every orientation, spending an equal amount of time in each orientation. The first powder experiment was reported by Debye & Scherrer in 1916, and independently by Hull in 1917. In the Ewald construction, this is the same as

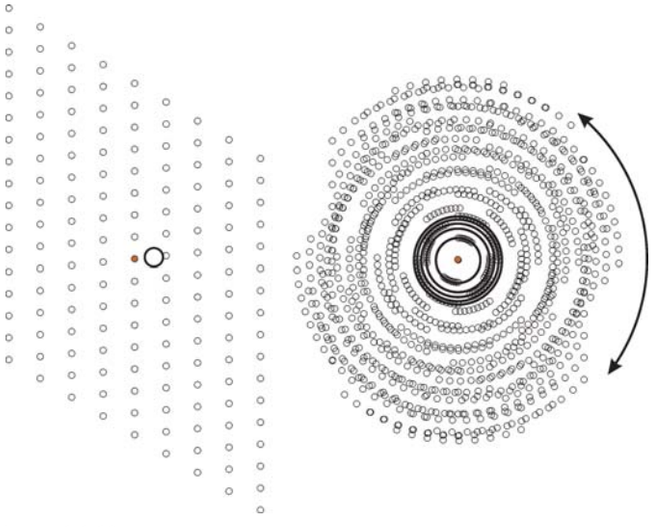

Figure 1.1.10
Illustration of the reciprocal lattice associated with a single-crystal lattice (left) and a large number of randomly oriented crystallites (right). A real powder consists of so many grains that the dots of the reciprocal lattice form into continuous lines. [Reproduced from Dinnebier & Billinge (2008) with permission from the Royal Society of Chemistry.]