vector **d**:

$$\mathbf{d}^*_{hkl} = \frac{\mathbf{d}}{d^2}, \tag{1.1.28}$$

which gives

$$\mathbf{d}^*_{hkl} = \frac{\mathbf{d}_{hkl}}{d^2} = h\mathbf{a} + k\mathbf{b} + l\mathbf{c}, \tag{1.1.29}$$

or written in terms of the reciprocal basis

$$\mathbf{d}^*_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*, \tag{1.1.30}$$

which was obtained using

$$\begin{aligned}\mathbf{d}^*_{hkl}\cdot\mathbf{a}^* &= h\mathbf{a}\cdot\mathbf{a}^* + k\mathbf{b}\cdot\mathbf{a}^* + l\mathbf{c}\cdot\mathbf{a}^* = h,\\ \mathbf{d}^*_{hkl}\cdot\mathbf{b}^* &= h\mathbf{a}\cdot\mathbf{b}^* + k\mathbf{b}\cdot\mathbf{b}^* + l\mathbf{c}\cdot\mathbf{b}^* = k,\\ \mathbf{d}^*_{hkl}\cdot\mathbf{c}^* &= h\mathbf{a}\cdot\mathbf{c}^* + k\mathbf{b}\cdot\mathbf{c}^* + l\mathbf{c}\cdot\mathbf{c}^* = l.\end{aligned} \tag{1.1.31}$$

Comparing equation (1.1.30) with equation (1.1.11) proves the identity of $\mathbf{d}^*_{hkl}$ and the reciprocal-lattice vector $\mathbf{h}_{hkl}$. Bragg's equation, (1.1.24), can be re-stated as

$$\mathbf{h} = \mathbf{h}_{hkl}. \tag{1.1.32}$$

In other words, diffraction occurs whenever the scattering vector **h** equals a reciprocal-lattice vector $\mathbf{h}_{hkl}$. This powerful result is visualized in the useful Ewald construction, which is described in Section 1.1.2.4.

Useful equivalent variations of the Bragg equation are

$$|\mathbf{h}| = \left|\mathbf{s} - \mathbf{s}_0\right| = \frac{2\sin\theta}{\lambda} = \frac{1}{d} \tag{1.1.33}$$

and

$$|\mathbf{Q}| = \frac{4\pi\sin\theta}{\lambda} = \frac{2\pi}{d}. \tag{1.1.34}$$

The vector **Q** is the physicist's equivalent of the crystallographer's **h**. The physical meaning of **Q** is the momentum transfer on scattering and it differs from the scattering vector **h** by a factor of 2π.

1.1.2.3. *The Bragg equation from the Laue equation*

Another approach for describing scattering from a material was first described by Laue (von Laue, 1912). The Laue equation can be derived by evaluating the phase relation between two wavefronts after hitting two scatterers that are separated by the vector **r**. The path-length difference $\Delta = |\mathrm{CD}| - |\mathrm{BA}|$ between the two scattered waves introduces a phase shift between the two outgoing waves (Fig. 1.1.8). From Fig. 1.1.8 one immediately sees that the path-length difference is given by

$$\Delta = r\cos\varepsilon - r\cos\varepsilon_0. \tag{1.1.35}$$

This path-length difference gives rise to a phase shift

$$\varphi = 2\pi\frac{\Delta}{\lambda} = 2\pi\left(\frac{r}{\lambda}\cos\varepsilon - \frac{r}{\lambda}\cos\varepsilon_0\right). \tag{1.1.36}$$

The term in parentheses is

$$\mathbf{s}\cdot\mathbf{r} - \mathbf{s_0}\cdot\mathbf{r} = (\mathbf{s} - \mathbf{s_0})\cdot\mathbf{r} = \mathbf{h}\cdot\mathbf{r}. \tag{1.1.37}$$

The amplitude of the scattered wave at a large distance away in the direction of the vector **s** is

$$A(\mathbf{h}) = \exp(2\pi i 0) + \exp(2\pi i\mathbf{h}\cdot\mathbf{r}) \tag{1.1.38}$$

When we generalize the idea laid out above to n scatterers, we get

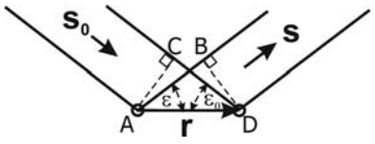

Figure 1.1.8
Scattering from an object consisting of two scatterers separated by **r**.

$$A(\mathbf{h}) = \sum_{j=1}^{n}\exp\left(2\pi i\mathbf{h}\cdot\mathbf{r}_j\right). \tag{1.1.39}$$

For simplicity, consider the case of an infinite one-dimensional crystal of scatterers that are equally spaced by distance a_i. In this case, $r_j = aj$ and

$$A(h) = \sum_{j=-\infty}^{\infty}\exp(2\pi i h a j). \tag{1.1.40}$$

Using the definition for a periodic delta function,

$$\lim_{n\to\infty}\sum_{j=-n}^{n}\exp(2\pi i h a j) = \sum_{k=-\infty}^{\infty}\delta(k - ha) \tag{1.1.41}$$

and

$$A(h) = \sum_{k=-\infty}^{\infty}\delta(k - ha), \tag{1.1.42}$$

which is a periodic array of delta functions at positions $h = k/a$. This means that sharp peaks of intensity will only appear when this expression holds, which are the reciprocal-lattice points. This is the same result as given by the Bragg equation (1.1.3) in one dimension. Extending to three dimensions, equations (1.1.40) and (1.1.42) become

$$\begin{aligned}A(\mathbf{h}) = &\sum_{j=-\infty}^{\infty}\exp\left(2\pi i(\mathbf{h}\cdot\hat{\mathbf{a}})aj\right)\sum_{k=-\infty}^{\infty}\exp\left(2\pi i(\mathbf{h}\cdot\hat{\mathbf{b}})bk\right)\\ &\times\sum_{l=-\infty}^{\infty}\exp\left(2\pi i(\mathbf{h}\cdot\hat{\mathbf{c}})cl\right),\end{aligned} \tag{1.1.43}$$

where $\hat{\mathbf{a}} = \mathbf{a}/a$, and

$$A(\mathbf{h}) = \sum_{\mu,\nu,\eta=-\infty}^{\infty}\delta[\mu - (\mathbf{h}\cdot\hat{\mathbf{a}})a]\delta[\nu - (\mathbf{h}\cdot\hat{\mathbf{b}})b]\delta[\eta - (\mathbf{h}\cdot\hat{\mathbf{c}})c]. \tag{1.1.44}$$

Equation (1.1.44) has the same meaning in three dimensions, where intensity appears only when all three delta functions are non-zero. This occurs for the conditions

$$\mathbf{h}\cdot\hat{\mathbf{a}} = \frac{\mu}{a},\ \ \mathbf{h}\cdot\hat{\mathbf{b}} = \frac{\nu}{b}\ \text{and}\ \mathbf{h}\cdot\hat{\mathbf{c}} = \frac{\eta}{c}, \tag{1.1.45}$$

where μ, ν and η are integers. From this follows

$$\mathbf{h}\cdot\mathbf{a} = \mu,\ \ \mathbf{h}\cdot\mathbf{b} = \nu\ \text{and}\ \mathbf{h}\cdot\mathbf{c} = \eta. \tag{1.1.46}$$

These conditions are met when

$$\mathbf{h} = \mu\mathbf{a}^* + \nu\mathbf{b}^* + \eta\mathbf{c}^* = \mathbf{d}^*_{\mu\nu\eta}. \tag{1.1.47}$$

This is exactly Bragg's equation in the form given in equation (1.1.30).

For practical purposes including the indexing of powder patterns and refinement of a structural model, given a set of lattice parameters a, b, c, α, β, γ, the positions for all possible reflections hkl can be calculated according to

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

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 $1/\lambda$ 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 $1/\lambda$.
(2) Draw a sphere centred on the tail of this vector with radius $1/\lambda$. The incident wave vector $\mathbf{s}_0$ defines the radius of the sphere. The scattered wave vector $\mathbf{s}$, also of length $1/\lambda$, 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.

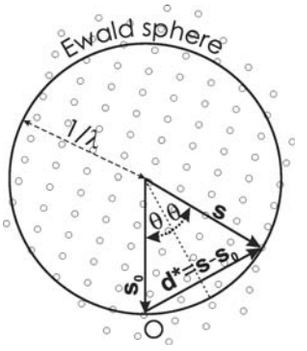

Figure 1.1.9
Simplified representation of the Ewald-sphere construction as a circle in two dimensions. O marks the origin of reciprocal space. The vectors are defined in the text. [Reproduced from Dinnebier & Billinge (2008) with permission from the Royal Society of Chemistry.]

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

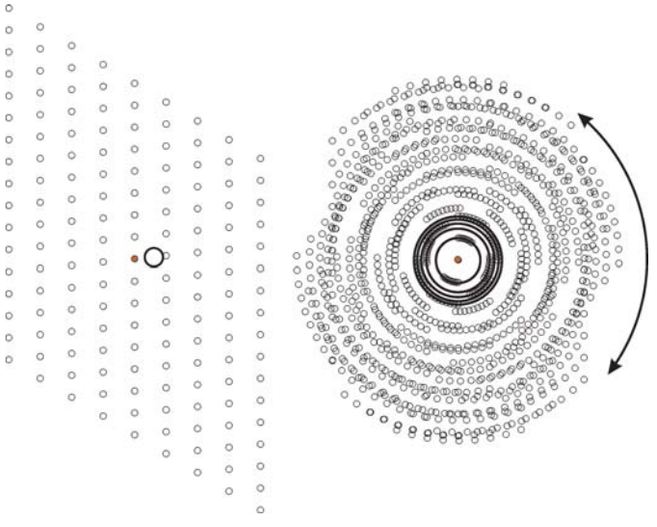

Figure 1.1.10
Illustration of the reciprocal lattice associated with a single-crystal lattice (left) and a large number of randomly oriented crystallites (right). A real powder consists of so many grains that the dots of the reciprocal lattice form into continuous lines. [Reproduced from Dinnebier &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

references