1. INTRODUCTION

Using the standard trigonometric results

$$\cos(\alpha + \theta) = \cos\alpha\cos\theta - \sin\alpha\sin\theta,$$
$$\cos(\alpha - \theta) = \cos\alpha\cos\theta + \sin\alpha\sin\theta, \qquad (1.1.5)$$

equation (1.1.4) becomes

$$n\lambda = \mathrm{MN}(2\sin\alpha\sin\theta) \qquad (1.1.6)$$

with

$$d = \mathrm{MN}\sin\alpha, \qquad (1.1.7)$$

which may be substituted to yield the Bragg equation:

$$n\lambda = 2d\sin\theta. \qquad (1.1.8)$$

The Bragg equation holds for any radiation or particle that is used to probe the structure of the sample: X-rays, neutrons or electrons. Another equivalent, and highly useful, form of the Bragg equation for the particular case of X-rays is

$$Ed = \frac{6.199}{\sin\theta} \ \text{ with } \lambda = \frac{12.398}{E}, \qquad (1.1.9)$$

where the energy E of the X-rays is in keV and λ is in ångströms.

The Bragg law results in narrow beams of high intensity that emerge from the crystal in specific directions given by the Bragg equation, resulting in sharp spots on the detector, and there is a one-to-one correspondence between these Bragg spots (often referred to as Bragg reflections) and each set of crystallographic planes. Each Bragg spot is therefore labelled with the same set of Miller indices, hkl, as the set of planes that gave rise to it.

It is possible to construct a 'reciprocal space' where the axes of the space are in units of inverse length. The reference coordinate frame of the reciprocal space is defined by a set of basis vectors whose directions are perpendicular to the plane normals of the (100), (010) and (100) planes of the crystal. Thus, a *point* in this reciprocal space corresponds to a *direction* in direct space and every allowed reflection according to the Bragg law is represented by a point in reciprocal space. The set of points arising from the Bragg law forms a lattice in reciprocal space, which is called the 'reciprocal lattice', and each single crystal has its own reciprocal lattice. [See *International Tables for Crystallography* Volume B (Shmueli, 2008) for more details.]

To derive the Bragg equation, we used an assumption of specular reflection, which is borne out by experiment: for a crystalline material, destructive interference eliminates scattered intensity in all directions except where equation (1.1.3) holds. Strictly this holds only for crystals that are infinite in extent and which the incident X-ray beam can penetrate without loss of intensity. This does not sound like a particularly good approximation, but in practice it holds rather well. Even a fairly low energy X-ray beam that only penetrates, say, a micrometre into the material will still probe $\sim$10 000 atomic layers. The condition is not strictly obeyed in the presence of defects and disorder in the material. In such materials the Bragg peaks are modified in their position, their width and their shape, and there is also an additional component of the diffracted intensity that may be observed in all directions, away from reciprocal-lattice points, known as diffuse scattering.

1.1.2.2. *The Bragg equation from the reciprocal lattice*

Here we develop in more detail the mathematics of the reciprocal lattice. The reciprocal lattice has been adopted by crystallographers as a simple and convenient representation of the physics of diffraction by a crystal. It is an extremely useful tool
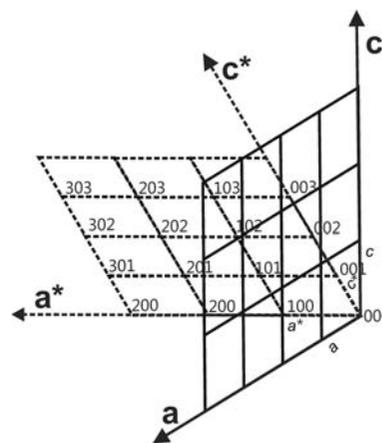

Figure 1.1.5
A two-dimensional monoclinic lattice and its corresponding reciprocal lattice. [Adapted from Dinnebier & Billinge (2008) with permission from the Royal Society of Chemistry.]

for describing all kinds of diffraction phenomena occurring in powder diffraction.

Consider a 'normal' crystal lattice with lattice vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$, which have lengths a, b and c, respectively, and angles α between $\mathbf{b}$ and $\mathbf{c}$, β between $\mathbf{a}$ and $\mathbf{c}$ and γ between $\mathbf{a}$ and $\mathbf{b}$. The unit-cell volume is given by V. A second lattice with lattice parameters a^*, b^*, c^*, α^*, β^*, γ^* and unit-cell volume V^* with the same origin exists such that

$$\mathbf{a}\cdot\mathbf{b}^* = \mathbf{a}\cdot\mathbf{c}^* = \mathbf{b}\cdot\mathbf{c}^* = \mathbf{a}^*\cdot\mathbf{b} = \mathbf{a}^*\cdot\mathbf{c} = \mathbf{b}^*\cdot\mathbf{c} = 0,$$
$$\mathbf{a}\cdot\mathbf{a}^* = \mathbf{b}\cdot\mathbf{b}^* = \mathbf{c}\cdot\mathbf{c}^* = 1. \qquad (1.1.10)$$

This is known as the reciprocal lattice[1] (Fig. 1.1.5), which exists in so-called reciprocal space. As mentioned above, we will see that it turns out that the points in the reciprocal lattice are related to the vectors defining the crystallographic plane normals. There is one point in the reciprocal lattice for each set of crystallographic planes, (hkl), separated by distance d_{hkl}, as discussed below. For now, just consider h, k and l to be integers that index a point in the reciprocal lattice. A reciprocal-lattice vector $\mathbf{h}_{hkl}$ is the vector from the origin of reciprocal space to the reciprocal-lattice point for the plane (hkl),

$$\mathbf{h}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*, \quad h,k,l \in \mathbb{Z}. \qquad (1.1.11)$$

where $\mathbb{Z}$ is the set of all integers.

The length of the reciprocal basis vector $\mathbf{a}^*$ is defined according to

$$\mathbf{a}^* = x(\mathbf{b}\times\mathbf{c}), \qquad (1.1.12)$$

where the scale factor x can easily be deduced, using equations (1.1.12) and (1.1.10), as

$$\mathbf{a}^*\cdot\mathbf{a} = x(\mathbf{b}\times\mathbf{c}\cdot\mathbf{a}) = xV \Rightarrow x = \frac{1}{V}, \qquad (1.1.13)$$

leading to

$$\mathbf{a}^* = \frac{1}{V}(\mathbf{b}\times\mathbf{c}), \quad \mathbf{b}^* = \frac{1}{V}(\mathbf{c}\times\mathbf{a}), \quad \mathbf{c}^* = \frac{1}{V}(\mathbf{a}\times\mathbf{b}) \qquad (1.1.14)$$

and, *vice versa*,

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[1] The reciprocal lattice is a commonly used construct in solid-state physics, but with a different normalization: $\mathbf{a}\cdot\mathbf{a}^* = 2\pi$.

$$\mathbf{a} = \frac{1}{V^*}(\mathbf{b}^* \times \mathbf{c}^*), \quad \mathbf{b} = \frac{1}{V^*}(\mathbf{c}^* \times \mathbf{a}^*), \quad \mathbf{c} = \frac{1}{V^*}(\mathbf{a}^* \times \mathbf{b}^*).$$
(1.1.15)

The relationship between the reciprocal and the real lattice parameters expressed geometrically rather than in the vector formalism used above is

$$a^* = \frac{bc \sin \alpha}{V},$$

$$b^* = \frac{ac \sin \beta}{V},$$

$$c^* = \frac{ab \sin \gamma}{V},$$

$$\cos \alpha^* = \frac{\cos \beta \cos \gamma - \cos \alpha}{\sin \beta \sin \gamma},$$

$$\cos \beta^* = \frac{\cos \alpha \cos \gamma - \cos \beta}{\sin \alpha \sin \gamma},$$

$$\cos \gamma^* = \frac{\cos \alpha \cos \beta - \cos \gamma}{\sin \alpha \sin \beta},$$

$$V = abc\sqrt{1 + 2\cos \alpha \cos \beta \cos \gamma - \cos^2\alpha - \cos^2\beta - \cos^2\gamma}.$$
(1.1.16)

Equation (1.1.16) is the most general expression for non-orthogonal lattices. The expressions simplify considerably for higher-symmetry crystal systems.

We now re-derive Bragg's law using the vector notation introduced above (Fig. 1.1.6). The wave vectors of the incoming and outgoing beams are given by $\mathbf{s}_0$ and $\mathbf{s}$, respectively. They point in the direction of propagation of the wave and their length depends on λ. For elastic scattering (for which there is no change in wavelength on scattering), $\mathbf{s}_0$ and $\mathbf{s}$ have the same length.

We define the scattering vector as

$$\mathbf{h} = (\mathbf{s} - \mathbf{s}_0),$$
(1.1.17)

which for a specular reflection is always perpendicular to the scattering plane. The length of $\mathbf{h}$ is given by

$$\frac{h}{s} = 2 \sin \theta.$$
(1.1.18)

Comparison with the formula for the Bragg equation (1.1.3),

$$\frac{n\lambda}{d} = 2 \sin \theta,$$
(1.1.19)

gives

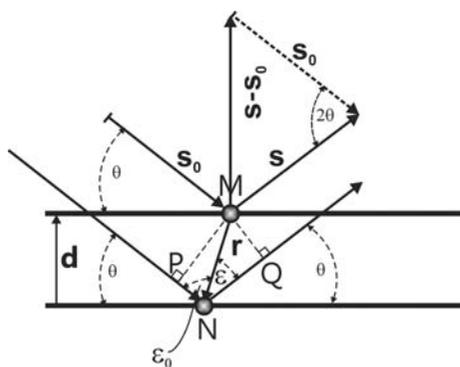$$\frac{n\lambda}{d} = \frac{h}{s}.$$
(1.1.20)

Figure 1.1.6
Illustration of the important wave and scattering vectors in the case of elastic Bragg scattering. [Reproduced from Dinnebier & Billinge (2008) with permission from the Royal Society of Chemistry.]
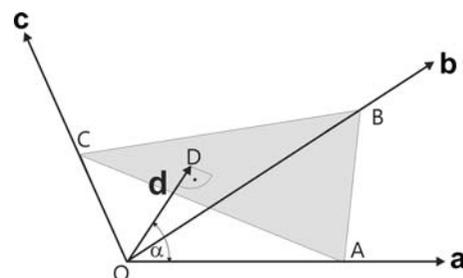

Figure 1.1.7
Geometrical description of a lattice plane in terms of real-space basis vectors. The arc and dot below the letter D indicate a right angle. [Reproduced from Dinnebier & Billinge (2008) with permission from the Royal Society of Chemistry.]

Setting the magnitude of $\mathbf{s}$ to $1/\lambda$, we get the Bragg equation in terms of the magnitude h of the scattering vector,

$$h = \frac{n}{d}.$$
(1.1.21)

This shows that diffraction occurs when the magnitude of the scattering vector is an integral number of reciprocal-lattice spacings $1/d$. We define a vector $\mathbf{d}^*$ perpendicular to the lattice planes with length $1/d$. Since $\mathbf{h}$ is perpendicular to the scattering plane, this leads to

$$\mathbf{h} = n\mathbf{d}^*.$$
(1.1.22)

Diffraction can occur at different scattering angles 2θ for the same crystallographic plane, giving the different orders n of diffraction. For simplicity, the number n will be incorporated in the indexing of the lattice planes, where

$$d^*_{nh,nk,nl} = nd^*_{hkl},$$
(1.1.23)

e.g., $d^*_{222} = 2d^*_{111}$, and we get an alternative expression for Bragg's equation:

$$\mathbf{h} = \mathbf{d}^*_{hkl}.$$
(1.1.24)

The vector $\mathbf{d}^*_{hkl}$ points in a direction perpendicular to a real-space lattice plane. We would like to express this vector in terms of the reciprocal-space basis vectors $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$.

First we define $\mathbf{d}_{hkl}$ in terms of the real-space basis vectors $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$. Referring to Fig. 1.1.7, we can define

$$\mathbf{OA} = \frac{1}{h}\mathbf{a}, \quad \mathbf{OB} = \frac{1}{k}\mathbf{b}, \quad \mathbf{OC} = \frac{1}{l}\mathbf{c}$$
(1.1.25)

with h, k and l being integers, as required by the periodicity of the lattice.

The plane-normal vector $\mathbf{d}_{hkl}$ originates on one plane and terminates on the next parallel plane. Therefore, $\mathbf{OA} \cdot \mathbf{d} = (OA)d \cos \alpha$. From Fig. 1.1.7 we see that, geometrically, $(OA) \cos \alpha = d$. Substituting, we get $\mathbf{OA} \cdot \mathbf{d} = d^2$. Combining this with equation (1.1.25) leads to

$$\frac{1}{h}\mathbf{a} \cdot \mathbf{d} = d^2$$
(1.1.26)

and consequently

$$h = \mathbf{a} \cdot \frac{\mathbf{d}}{d^2}, \quad k = \mathbf{b} \cdot \frac{\mathbf{d}}{d^2}, \quad l = \mathbf{c} \cdot \frac{\mathbf{d}}{d^2}.$$
(1.1.27)

By definition, h, k and l are divided by their largest common integer to be Miller indices. The vector $\mathbf{d}^*_{hkl}$, from Bragg's equation (1.1.24), points in the plane-normal direction parallel to $\mathbf{d}$ but with length $1/d$. We can now write $\mathbf{d}^*_{hkl}$ in terms of the

vector $\mathbf{d}$:

$$\mathbf{d}_{hkl}^* = \frac{\mathbf{d}}{d^2}, \qquad (1.1.28)$$

which gives

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

or written in terms of the reciprocal basis

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

which was obtained using

$$\mathbf{d}_{hkl}^* \cdot \mathbf{a}^* = h\mathbf{a} \cdot \mathbf{a}^* + k\mathbf{b} \cdot \mathbf{a}^* + l\mathbf{c} \cdot \mathbf{a}^* = h,$$
$$\mathbf{d}_{hkl}^* \cdot \mathbf{b}^* = h\mathbf{a} \cdot \mathbf{b}^* + k\mathbf{b} \cdot \mathbf{b}^* + l\mathbf{c} \cdot \mathbf{b}^* = k,$$
$$\mathbf{d}_{hkl}^* \cdot \mathbf{c}^* = h\mathbf{a} \cdot \mathbf{c}^* + k\mathbf{b} \cdot \mathbf{c}^* + l\mathbf{c} \cdot \mathbf{c}^* = l. \qquad (1.1.31)$$

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

$$\mathbf{h} = \mathbf{h}_{hkl}. \qquad (1.1.32)$$

In other words, diffraction occurs whenever the scattering vector $\mathbf{h}$ 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

$$|\mathbf{h}| = |\mathbf{s} - \mathbf{s}_0| = \frac{2 \sin \theta}{\lambda} = \frac{1}{d} \qquad (1.1.33)$$

and

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

The vector $\mathbf{Q}$ is the physicist's equivalent of the crystallographer's $\mathbf{h}$. The physical meaning of $\mathbf{Q}$ is the momentum transfer on scattering and it differs from the scattering vector $\mathbf{h}$ 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 $\mathbf{r}$. The path-length difference $\Delta = |CD| - |BA|$ 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

$$\Delta = r \cos \varepsilon - r \cos \varepsilon_0. \qquad (1.1.35)$$

This path-length difference gives rise to a phase shift

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

The term in parentheses is

$$\mathbf{s} \cdot \mathbf{r} - \mathbf{s}_0 \cdot \mathbf{r} = (\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{r} = \mathbf{h} \cdot \mathbf{r}. \qquad (1.1.37)$$

The amplitude of the scattered wave at a large distance away in the direction of the vector $\mathbf{s}$ is

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

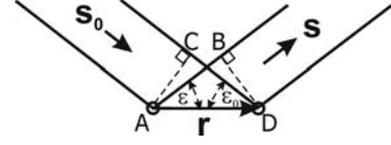When we generalize the idea laid out above to n scatterers, we get

Figure 1.1.8
Scattering from an object consisting of two scatterers separated by $\mathbf{r}$.

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

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

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

Using the definition for a periodic delta function,

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

and

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

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

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

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

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

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

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

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

$$\mathbf{h} \cdot \mathbf{a} = \mu, \quad \mathbf{h} \cdot \mathbf{b} = \nu \text{ and } \mathbf{h} \cdot \mathbf{c} = \eta. \qquad (1.1.46)$$

These conditions are met when

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

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