

## 1.1. OVERVIEW AND PRINCIPLES

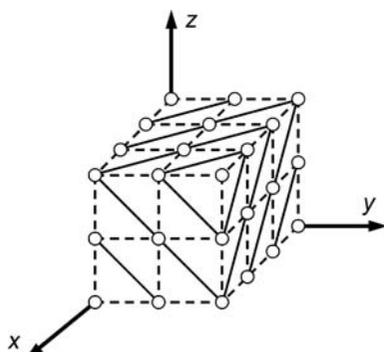
is infinitely thin, but still goes through the same set of points (the cube corners). What we see is that there is not just a single plane, but a series of equivalent planes: for example, between the top and second layers, the second and third layers, and so on. Each plane is parallel to the others and subsequent planes are separated by the same distance (the height of the cube). This is a set of lattice planes. We can also envisage inserting the trays in other ways. For example, we could place the trays vertically rather than horizontally and running from the left side to the right side of the stack of cubes, or alternatively running from the front of the stack to the back of the stack. Each of these is a different set of lattice planes (Fig. 1.1.2), although in this case they have the same layer spacing, or periodicity. If we were able to insert the tray at different angles to the cubes, for example at  $45^\circ$ , we could find other sets of parallel planes that, when we force them to go through some well defined subset of the points defining the lattice, will have well defined layer spacings or periodicities. Bragg's law showed that the diffraction pattern could be understood in terms of X-rays reflecting specularly off subsequent planes in each of these sets of planes and emerging in phase. (In reality, the actual effect is not specular reflection of light from an abstract plane, but a diffraction effect. However, the combination of diffraction and periodicity results in a selection rule that intense scattering only occurs when this particular specular-reflection condition holds.)

There are actually an infinite number of lattice planes in an infinite lattice, and it is important to have a way of labelling them, which is commonly done using the triplet of indices  $hkl$ , called Miller indices, where  $h$ ,  $k$  and  $l$  are integers, and the separation of the planes is denoted by the distance  $d_{hkl}$ . When  $h$ ,  $k$  and  $l$  have small values the planes are said to be 'low-order' planes. Low-order planes have the largest interplanar separations, and for a particular symmetry of the lattice there is a direct relationship between the Miller indices and  $d_{hkl}$ .

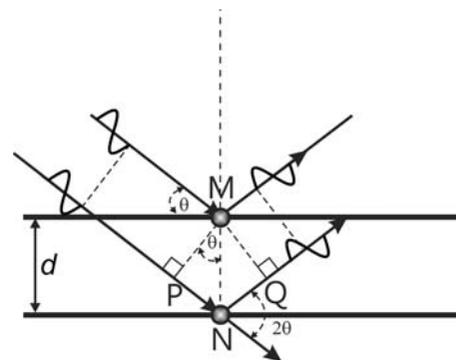
The Bragg equation gives the condition that must hold for specular reflection from subsequent planes in a set to be perfectly in phase, as illustrated in Fig. 1.1.3. It is evident in Fig. 1.1.3 that the wave reflecting off the lower plane travels a longer distance (by  $PN$  before and  $NQ$  after reflection occurs) than the wave reflecting off the upper plane. The two waves are in phase, resulting in constructive interference, only when  $\Delta = |PN| + |NQ|$  is a multiple  $n = 0, 1, 2, \dots$  of the wavelength  $\lambda$ ,

$$\Delta = n\lambda. \quad (1.1.1)$$

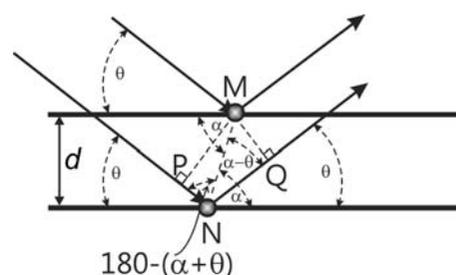
In all other cases, destructive interference results, since it is always possible to find a deeper plane,  $p$ , for which the relation



**Figure 1.1.2**  
Schematic drawing of a set of parallel lattice planes (111) passing through all points of the cubic lattice.



**Figure 1.1.3**  
Illustration of the geometry used for the simplified derivation of Bragg's law. [Reproduced from Dinnebier & Billinge (2008) with permission from the Royal Society of Chemistry.]



**Figure 1.1.4**  
Illustration of the geometry in the general case where scattering takes place at the position of atoms in consecutive planes. [Reproduced from Dinnebier & Billinge (2008) with permission from the Royal Society of Chemistry.]

$p\Delta = n\lambda + 1/2$  exactly holds, giving rise to perfect destructive interference. Thus, when a narrow beam of X-rays impinges on a crystalline sample, sharp peaks in the intensity of the scattered X-rays are seen only at the angles for which equation (1.1.1) holds, with no intensity observed at other angles. As can easily be seen from Fig. 1.1.3, geometrically,

$$\Delta = 2d \sin \theta, \quad (1.1.2)$$

where  $d$  is the interplanar spacing of the parallel lattice planes and  $2\theta$  is the diffraction (or 'scattering') angle, the angle between the incoming and outgoing X-ray beams. The angle  $\theta = 2\theta/2$  is often called the Bragg angle. Combining equations (1.1.1) and (1.1.2) we get

$$n\lambda = 2d \sin \theta, \quad (1.1.3)$$

which is the Bragg equation (Bragg, 1913).

This simplified derivation of the Bragg equation is often reproduced in textbooks. Although it leads to the correct solution, it has a serious drawback. In reality the X-rays are not reflected by planes, but are scattered by electrons bound to the atoms in the sample. The planes within a crystal are not like shiny optical mirrors, but contain discrete atoms separated by regions of much lower electron density and, in general, the atoms in one plane will not lie exactly above atoms in the plane below as implied by Fig. 1.1.3. How is it then that the simplified picture shown in Fig. 1.1.3 gives the correct result? A more general description shows that equation (1.1.3) is also valid if the atom in the lower lattice plane in Fig. 1.1.3 is shifted by an arbitrary amount within the plane (Fig. 1.1.4).

The phase shift can immediately be deduced from Fig. 1.1.4 as

$$\begin{aligned} n\lambda &= MN \cos[180^\circ - (\alpha + \theta)] + MN \cos(\alpha - \theta) \\ &= MN[-\cos(\alpha + \theta) + \cos(\alpha - \theta)]. \end{aligned} \quad (1.1.4)$$