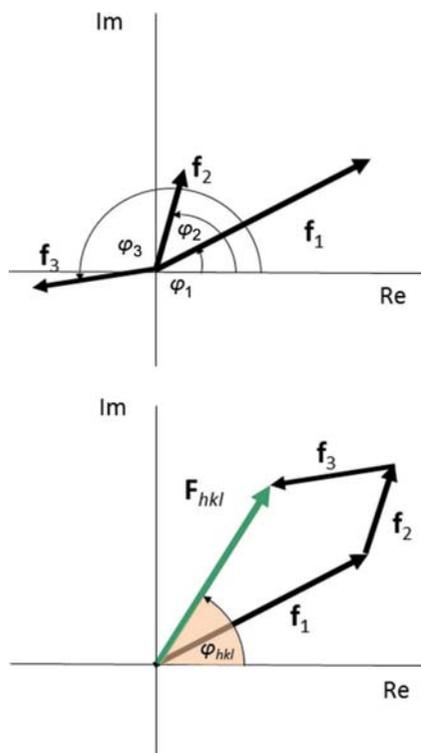1.1. OVERVIEW AND PRINCIPLES

Figure 1.1.16
Graphical illustration of the summation of scattered wave amplitudes $\mathbf{f}_t$ in the complex plane, accounting for the phase shifts coming from the different positions of the atoms in the unit cell.

Figure 1.1.17
Schematic illustration of the projection of the reciprocal $\mathbf{a}^*\mathbf{c}^*$ plane (representing the three-dimensional reciprocal-lattice space) into the one-dimensional powder pattern.

lattice points (directions of the Bragg peaks), and their intensities are multiplied by a factor, the crystallographic structure factor,

$$F_{hkl} = \sum_{t=1}^{m} f_t(h)\exp(2\pi i\mathbf{h}\cdot\mathbf{u}_t). \tag{1.1.56}$$

If we write each term as a complex number denoted $\mathbf{f}_t$, we can represent this complex sum as a vector sum in the complex plane, as illustrated in Fig. 1.1.16, where the $\varphi_t = 2\pi\mathbf{h}\cdot\mathbf{u}_t$. The intensity of the Bragg peak depends only on the length of the $\mathbf{F}_{hkl}$, not its direction. However, its length depends on both the lengths *and the phases* of each contribution, which in turn depend on the positions of the atoms within the unit cell. This is the phase information that is 'lost' in a diffraction experiment. Given a structure, we can directly calculate all the Bragg-peak intensities (the 'forward problem'). However, given all the Bragg-peak intensities, we cannot directly calculate the structure (the 'inverse problem'). Structure determination uses the measured intensities and reconstructs the lost phase information using various iterative methods and algorithms.

In fact, the intensity of a Bragg reflection *hkl* is given by the squared absolute value of the structure-factor amplitude F_{hkl},

$$\left|F_{hkl}\right|^2 = \sum_{t,t'=1}^{m} f_t(h)f_{t'}^*(h)\exp\left(2\pi i\mathbf{h}\cdot(\mathbf{u}_t-\mathbf{u}_{t'})\right), \tag{1.1.57}$$

where * indicates the complex conjugate. This analysis shows that the *positions* of the Bragg peaks determine the geometry of the periodic lattice (the size and shape of the unit cell, for example), but the *intensities* of the Bragg peaks are determined by the relative positions of atoms within the unit cell, scaled by their respective scattering power. To solve the internal structure of the structural motif within the unit cell, it is necessary to measure quantitatively the intensities of many Bragg peaks and use some kind of iterative procedure to move the atoms within the cell until
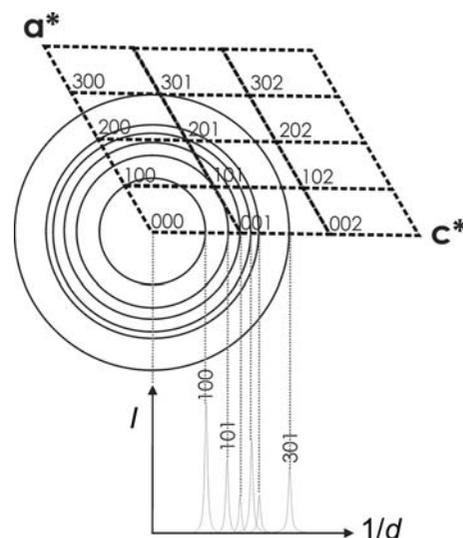
the calculated structure factors self-consistently reproduce the intensities of all the measured Bragg peaks.

The situation is not fundamentally different in a powder diffraction experiment from the single-crystal case, except that the Bragg peaks in three-dimensional reciprocal space are projected into one dimension, as shown in Fig. 1.1.17.

'Indexing' is the term used for deriving the lattice parameters from the positions of the Bragg peaks (see Chapter 3.4). Once the size and shape of the reciprocal lattice is determined, Miller indices can be assigned to each of the Bragg peaks in a one-dimensional powder pattern. If it is possible to extract the intensities of those peaks from the pattern, diffraction data from a powder can be used to reconstruct the three-dimensional structure in exactly the same way as is done with data from a single crystal. This process is known as structure solution from powder diffraction, and is often successful, although it is less well automated than structure solution from data from single crystals. As mentioned above, the main problem with powder data is a loss of information due to systematic and accidental peak overlap, but this can often be overcome.

There are various methods for extracting quantitative peak intensities from indexed powder patterns by computer fitting of profiles to the Bragg peaks at their known positions. Two of the most common are Pawley refinement (Pawley, 1981) and Le Bail refinement (Le Bail *et al.*, 1988), as discussed in Chapter 3.5.

In general, the intensities of the Bragg reflections must be corrected by the product K_{hkl} of various correction factors. Some common correction factors are given by

$$K_{hkl} = M_{hkl}\mathrm{Abs}_{hkl}\mathrm{Ext}_{hkl}\mathrm{LP}_{hkl}\mathrm{PO}_{hkl}\ldots, \tag{1.1.58}$$

where M_{hkl} is the multiplicity, Abs_{hkl} is an absorption correction, Ext_{hkl} is an extinction correction, LP_{hkl} is the geometrical Lorentz–polarization correction and PO_{hkl} is a correction for preferred orientation (see Chapter 4.7).

If there is more than one crystalline phase present in the sample, and the structures of all the crystalline phases are known, then we can find a scale factor for each phase in the mixture which reproduces the data. This is then a way of determining the proportion of each phase in the sample. This is called quantitative phase analysis (see Chapter 3.9).

references