

1. INTRODUCTION

$$I \simeq \left[\sum_j A_j \exp(i\varphi_j) \right]^2, \quad (1.1.51)$$

where the sum is over all the sine waves present and the phases, φ_j , are measured with respect to some origin.

Measuring X-ray diffraction involves the measurement of the intensity of X-rays scattered from electrons bound to atoms. Waves scattered by atoms at different positions arrive at the detector with a relative phase shift. Therefore, the measured intensities yield information about the relative atomic positions.

In the case of X-ray diffraction, the Fraunhofer approximation is valid. This is a far-field approximation, where the distances L_1 from the source to the place where scattering occurs (the sample) and L_2 from the sample to the detector are much larger than the separation, D , of the scatterers. This is an excellent approximation, since in this case $D/L_1 \simeq D/L_2 \simeq 10^{-10}$. The Fraunhofer approximation greatly simplifies the mathematics. The incident X-rays come from a distant source and form a wavefront of constant phase that is a plane wave. X-rays scattered by single electrons are outgoing spherical waves, which again appear as plane waves in the far field. This allows us to express the intensity of the diffracted X-rays using equations (1.1.51) and (1.1.39).

This is the origin of equation (1.1.39), which gives the amplitude of the scattered radiation in terms of the scattering vector, $\mathbf{h} = \mathbf{s}_0 - \mathbf{s}$, and the atomic positions, \mathbf{r}_j . In fact, the amplitude of the scattered radiation is only proportional to this expression. The actual intensity depends on the amplitude of the incident wave and also on the absolute scattering power of the scatterers. If we neglect for now the incident intensity and assume that our measured intensities are normalized to the incident beam intensity, we get

$$A(\mathbf{h}) = \sum_{j=1}^n f_j(h) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j), \quad (1.1.52)$$

where $f_j(h)$ is the atomic form factor and $h = |\mathbf{h}|$ is the magnitude of the scattering vector, and is described in more detail in *International Tables for Crystallography*, Volume C, Part 6. This is a measure of the strength of scattering from the j th atom. At $h = 0$, scattering is in the forward direction with all electrons scattering in phase. As a result, $f_j(0)$ equals the number of electrons bound to the atom (in units of the Thomson scattering cross section for an electron), usually taken to be the atomic number of the atomic species at the j th site. An additional h -dependent reduction of the amplitude comes from positional disorder of the atoms. A Gaussian blurring is used with a width that is often falsely called the ‘temperature factor’, but is more correctly known as the atomic displacement parameter (ADP). The Gaussian is known as the Debye–Waller factor, which is discussed below. More information can be found in Chapter 4.7.

The crystal structure consists of periodic arrangements of atoms. The simplest structures have one atom in a periodically repeated unit cell. However, in general, there is a well defined group of atoms that forms a structural motif that is periodically repeated. This motif can range from one atom to thousands of atoms in complex protein structures. Solving the crystal structure consists of finding the unit-cell parameters and determining the positions in the unit cell of the atoms in the structural motif. In this sense, the structure of the infinite crystal can be thought of mathematically as a convolution of the periodic lattice that we discussed above with the structural motif. This results in a perfect, orientationally ordered copy of the structural motif in every unit cell translated in three-dimensional space.

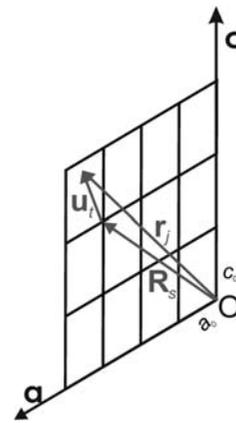


Figure 1.1.15

The position vector of the j th atom \mathbf{r}_j can be decomposed into a vector \mathbf{R}_s from the origin of the crystal to the origin of the unit cell containing the j th atom, and the vector \mathbf{u}_j from the unit cell origin to the j th atom.

As we discussed above, the direct-space lattice has a reciprocal lattice associated with it which determines the positions of the Bragg peaks, or allowed delta functions of scattered intensity. The reciprocal lattice is actually a Fourier transform of the periodic lattice in direct space. The convolution theorem of Fourier transforms tells us that a convolution of two functions in direct space will result in a product of the Fourier transforms of those functions in the Fourier space. Since the structure is a convolution of the direct-space lattice with the structural motif, the reciprocal lattice will be *multiplied* by the Fourier transform of the structural motif. This Fourier transform of the structural motif is called the crystallographic structure factor, F_{hkl} .

This result can be readily derived from equation (1.1.52). In this equation \mathbf{r}_j is the vector from the (arbitrary but fixed) origin to the j th atom in the material. If we now think of the crystal as consisting of n identical cells, each containing an identical structural motif consisting of m atoms, we can write \mathbf{r}_j as a sum of two vectors: a vector that goes from the origin to the corner of the s th unit cell that contains the j th atom, and a second vector that goes from the corner of the s th cell to the position of the j th atom. This is illustrated in Fig. 1.1.15.

Equation (1.1.52) can then be written as

$$A(\mathbf{h}) = \sum_{s=1}^n \sum_{t=1}^m f_t(h) \exp(2\pi i \mathbf{h} \cdot (\mathbf{R}_s + \mathbf{u}_t)), \quad (1.1.53)$$

where it is readily seen that the first sum is taken over all the cells in the crystal and the second sum is taken over the m atoms in the structural motif. The equation is readily factored as follows:

$$A(\mathbf{h}) = \sum_{s=1}^n \exp(2\pi i \mathbf{h} \cdot \mathbf{R}_s) \sum_{t=1}^m f_t(h) \exp(2\pi i \mathbf{h} \cdot \mathbf{u}_t). \quad (1.1.54)$$

Taking n to infinity, we immediately recognise the first sum as the lattice sum of equation (1.1.43), and we can therefore rewrite equation (1.1.54) as

$$\begin{aligned} A(\mathbf{h}) &= \sum_{t=1}^m f_t(h) \exp(2\pi i \mathbf{h} \cdot \mathbf{u}_t) \\ &\quad \times \sum_{\mu, \nu, \eta = -\infty}^{\infty} \delta[\mu - (\mathbf{h} \cdot \hat{\mathbf{a}})a] \delta[\nu - (\mathbf{h} \cdot \hat{\mathbf{b}})b] \delta[\eta - (\mathbf{h} \cdot \hat{\mathbf{c}})c], \\ A(\mathbf{h}) &= F_{hkl} \sum_{\mu, \nu, \eta = -\infty}^{\infty} \delta[\mu - (\mathbf{h} \cdot \hat{\mathbf{a}})a] \delta[\nu - (\mathbf{h} \cdot \hat{\mathbf{b}})b] \delta[\eta - (\mathbf{h} \cdot \hat{\mathbf{c}})c]. \end{aligned} \quad (1.1.55)$$

The delta functions determine the positions of the reciprocal-