

3.2. The physics of diffraction from powders

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3.2.1. Introduction

The term powder is used here as a label for polycrystalline samples, but they may not be powdery at all, *e.g.*, metallurgical samples or chocolate. The central premise of powder diffraction is that the sample consists of a sufficiently large number of independent particles (Smith, 2001). In that case, the diffraction pattern will consist of a series of peaks corresponding to the Bragg reflections from each component of the sample. This chapter starts with an idealized description of the data collected in a powder-diffraction measurement and how it relates to the physical properties of the sample and the diffractometer. In real experiments, many of the idealizations of this description are not satisfied, and the influence of those deviations from simple model behaviour are discussed in turn. To a greater or lesser extent, those confounding factors are under the control of the experimenter, and so it is important to understand how they can be optimized or avoided in the experimental design, as well as how to deal with situations where they cannot be (or have not been) avoided and deal with them in real data that have been collected.

The diffraction probes discussed here are X-rays and neutrons. Bragg's equation, $\lambda = 2d \sin \theta$, relates properties of the measurement (wavelength of the diffracted radiation λ and scattering angle 2θ) with a property of the sample (the d -spacing of the particular reflection observed). Data may be collected with radiation of fixed wavelength as a function of angle, or as energy-dispersive measurements at fixed angle. The former case is perhaps the most familiar, exemplified by a laboratory powder diffractometer using characteristic radiation from an X-ray tube, but it is frequently performed with X-rays or neutrons from a continuum source (*e.g.*, storage ring or nuclear reactor) selected by a suitable monochromator. Energy-dispersive X-ray experiments are performed by illuminating the sample with a continuum spectrum from a synchrotron source or *Bremsstrahlung* from an X-ray tube, whereas time-of-flight methods are in use at pulsed spallation neutron sources. Convenient conversions are that X-rays of energy E (keV) have wavelength λ (Å) = 12.398/ E , and neutrons with a speed v (m s⁻¹) have wavelength λ (Å) = 3956/ v .

3.2.2. Idealized diffraction from powders

From an experimental measurement, powder-diffraction data generally consist of detected intensity *versus* an experimental parameter (angle, time of flight, photon energy), where the latter can be related to the d -spacing of a Bragg reflection in the sample. Unless the sample is severely disordered, these data takes the form of a series of peaks which may or may not be distinctly separated. (In a severely disordered sample, the concept of a discrete set of Bragg peaks may not be applicable, and the Debye scattering equation, mentioned in Section 3.2.4 and more thoroughly covered in Chapters 3.6, 5.6 and 5.7, may be more appropriate.) The attributes of those peaks are their positions, integrated intensities and shapes. Their positions will depend on the dimensions of the crystal lattice, their relative

intensities will depend on the crystallographic structure factors of the reflections, and their shapes will depend on aspects of the sample (*e.g.* grain size and internal strain) and on the configuration of the instrument on which the pattern is measured. We consider each of these in turn in the following sections.

In addition, there is generally a relatively smooth background (Riello *et al.*, 1995) due to a number of effects, such as fluorescence (X-rays), thermal diffuse scattering, multiple scattering within the sample, incoherent scattering, small-angle scattering, parasitic scattering from the atmosphere, the sample holder and/or the windows of environmental chambers, *etc.*

3.2.2.1. Peak positions

Starting with a single crystal, the lattice is described by non-coplanar translation vectors \mathbf{a} , \mathbf{b} and \mathbf{c} , with magnitudes a , b and c , respectively, and angles α between \mathbf{b} and \mathbf{c} , β between \mathbf{c} and \mathbf{a} , and γ between \mathbf{a} and \mathbf{b} . Diffraction peak positions are governed by the reciprocal lattice, spanned by vectors $\mathbf{a}^* = \mathbf{b} \times \mathbf{c} / (\mathbf{a} \cdot \mathbf{b} \times \mathbf{c})$ and cyclic permutations. These have the property that $\mathbf{a}^* \cdot \mathbf{a} = 1$, $\mathbf{b}^* \cdot \mathbf{a} = 0$ *etc.* (This is the 'crystallographic' convention; the scattering community usually defines reciprocal-lattice vectors as larger by a factor of 2π .) The reciprocal lattice is indexed by Miller indices (hkl), so that each vector in the reciprocal lattice is given by $\mathbf{G} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$.

Incoming and diffracted radiation are described by wave vectors \mathbf{k}_i and \mathbf{k}_f , both of magnitude $1/\lambda$, and separated by the angle 2θ . The condition for a particular Bragg reflection to be observed is $\mathbf{G}_{hkl} = \mathbf{k}_f - \mathbf{k}_i$. Note that this requires that the diffracting crystal be correctly oriented relative to the incident beam. For a given reflection \mathbf{G}_{hkl} , the d -spacing between reflecting planes is given by $d = 1/|\mathbf{G}|$. (Again, in the scattering convention, incident and diffracted beams have wave vectors of magnitude $2\pi/\lambda$, and $d = 2\pi/|\mathbf{G}|$.) In either case, this allows the Bragg condition to be written in the scalar form $\lambda = 2d \sin \theta$.

If the sample is a powder instead of a single crystal, some large number of crystallites will be aligned to meet the (vector) Bragg condition with the incident radiation, and then the diffracted radiation will take the form of a cone of opening half-angle 2θ .

It is often convenient to work with equations written for scalars, *viz.*

$$\begin{aligned} a^* &= bc \sin \alpha / V, \\ \sin \alpha^* &= V / (abc \sin \beta \sin \gamma) \text{ or equivalently} \\ \cos \alpha^* &= \frac{\cos \beta \cos \gamma - \cos \alpha}{\sin \beta \sin \gamma}, \end{aligned}$$

with cyclic permutations. Here the unit-cell volume is given by

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

Note that the volume of the reciprocal cell is $V^* = 1/V$, and that the equations above are valid upon exchanging starred and unstarred variables.

For powder samples, using only scalars, the Bragg condition may be written as