

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

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$$\frac{4 \sin^2 \theta}{\lambda^2} = d^{-2} = Ah^2 + Bk^2 + Cl^2 + Dkl + Ehl + Fhk, \quad (3.2.1)$$

where $A = a^{*2}$, $B = b^{*2}$, $C = c^{*2}$, $D = 2b^*c^* \cos \alpha^*$, $E = 2c^*a^* \cos \beta^*$ and $F = 2a^*b^* \cos \gamma^*$. Crystal symmetries higher than triclinic lead to significant simplifications in the above, e.g. in the orthorhombic system, $a^* = 1/a$, $A = 1/a^2$ etc., $\alpha^* = \beta^* = \gamma^* = 90^\circ$, and $D = E = F = 0$. See Chapter 1.1, *Reciprocal space in crystallography*, in Volume B of *International Tables for Crystallography* for more details.

3.2.2.2. Diffraction peak intensities

3.2.2.2.1. X-rays

Consider a polycrystalline sample of randomly oriented grains of a single crystalline phase, containing a total number of atoms N , illuminated by an X-ray beam of wavelength λ . Each reciprocal-lattice vector with magnitude $|\mathbf{G}| < 2/\lambda$ will produce a cone of diffracted radiation with opening half-angle $2\theta = 2 \sin^{-1}(\lambda|\mathbf{G}|/2)$. Regarding the diffraction lines as perfectly sharp delta-functions, the differential cross section for one powder Bragg peak is (Marshall & Lovesey, 1971)

$$\frac{d\sigma}{d\Omega} = \frac{N\lambda^3 r_e^2}{16\pi V \sin \theta \sin 2\theta} |A_{hkl}|^2 \delta\left(2\theta - 2 \sin^{-1} \frac{\lambda}{2d}\right). \quad (3.2.2)$$

In this equation, $r_e = 2.82 \times 10^{-15}$ m is the classical electron radius and V is the unit-cell volume; the polarization factor P , multiplicity m_{hkl} and structure factor A_{hkl} are discussed below. Finite crystallite size, strain and other factors discussed below will broaden the peak, but the integrated intensity of each peak will be given by the factors before the delta-function.

Before continuing, note that this result is correct within the approximation that the entire sample is uniformly bathed in radiation (i.e., there is no absorption) and the kinematic approximation that the scattering power is very weak, so that further interaction of the scattered radiation with the sample may be neglected. The latter is equivalent to the Born approximation of elementary quantum mechanics, and its failure is referred to as extinction; it is discussed below in Section 3.2.3.6. It should also be noted here that equation (3.2.2) refers only to diffraction in Bragg peaks, and not to thermal diffuse scattering or scattered radiation due to static distortions from an ideal crystal lattice (Huang scattering; Krivoglaз, 1969).

Returning to the terms in equation (3.2.2), for X-rays the polarization factor P accounts for the polarization dependence of the Thomson scattering cross section from a free electron. For a completely polarized incident beam: $P = 1$ for S polarization (polarization perpendicular to the scattering plane); $P = \cos^2 2\theta$ for P polarization (in the scattering plane). For unpolarized X-rays (no monochromator), $P = (1 + \cos^2 2\theta)/2$. For horizontally polarized X-rays from a synchrotron-radiation source, diffracted vertically, the polarization factor is very close to unity, and so P can generally be taken as 1. If there is a crystal monochromator (deflection angle $2\theta_m$) coplanar with the diffractometer and an unpolarized source, $P = (1 + \cos^2 2\theta_m \cos^2 2\theta)/(1 + \cos^2 2\theta_m)$. If there is a polarization-sensitive analyser crystal following the sample, its relative transmission of X-rays polarized within or perpendicular to its plane of scattering must also be taken into account.

The multiplicity factor m_{hkl} accounts for the number of symmetry-equivalent reflections in the crystal structure, i.e., the number of distinct reflections that have the same structure factor. Note that the equivalence of Bragg reflections depends on the

Laue group of the sample. For example, in the cubic space group $Fm\bar{3}m$, reflections (hkl) and (khl) are equivalent, whereas they are not in space group $Fm\bar{3}$. If the atomic scattering factors are purely real or the structure is centrosymmetric, the intensities of Friedel pairs hkl and $h\bar{k}\bar{l}$ are equal. However, in an acentric structure with significant imaginary component of any of the atomic scattering factors (see below), Friedel pairs cannot be treated as symmetry equivalent.

The (dimensionless) X-ray structure factor is given by

$$\begin{aligned} A_{hkl} &= \sum_n f_n \exp(2\pi i \mathbf{G}_{hkl} \cdot \mathbf{r}_n) \exp(-W_n) \\ &= \sum_n f_n \exp[2\pi i(hx_n + ky_n + lz_n)] \exp(-W_n), \end{aligned} \quad (3.2.3)$$

where the sum runs over all atoms in the unit cell. In the first form of this equation, \mathbf{r}_n is the vector from the origin of the unit cell to the n th atom; in the second form, x_n , y_n and z_n are fractional coordinates of the n th atom in the unit cell such that $\mathbf{r}_n = x_n \mathbf{a} + y_n \mathbf{b} + z_n \mathbf{c}$.

The term $\exp(-W_n)$ is called the Debye–Waller factor, and it accounts for random dynamical motion of the n th atom away from its equilibrium position. This may be due to thermal fluctuations or (at low temperature) the quantum zero-point motion. If the atomic motion is isotropic, this term takes the form

$$W_n = B \sin^2 \theta / \lambda^2 = 8\pi^2 U_n \sin^2 \theta / \lambda^2, \quad (3.2.4)$$

where $U_n = \langle u_n^2 \rangle$ is the mean-square fluctuation of the atom's distance from its equilibrium position (in three dimensions). Observed values of B are generally in the range of 0.5 to 1 Å² for inorganic crystals, and as large as 5 Å² for organic crystals.

A more general treatment of the Debye–Waller factor considers the probability density of the centre of the atom to be a three-dimensional ellipsoidal Gaussian function. Then for a given diffraction peak, it takes the form

$$\begin{aligned} W &= 2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 \\ &\quad + 2U_{12}a^*b^*hk + 2U_{23}b^*c^*kl + 2U_{13}a^*c^*hl). \end{aligned} \quad (3.2.5)$$

The parameters U_{ij} that define the displacement ellipsoid are constrained to match the point symmetry of the site. For example, an atom that lies on a site of mmm symmetry will have the cross terms $U_{12} = U_{23} = U_{13} = 0$.

In equation (3.2.3), f_n is the atomic scattering factor, which arises because X-rays interact with the electrons in the sample, and the strength of that interaction depends both on the magnitude of the scattering vector and the X-ray frequency (wavelength). The electrons are distributed around the nucleus, and so their scattering power decreases with increasing magnitude of the scattering vector. There is also a dependence of the phase and amplitude of the scattering factor on the X-ray energy, which is especially significant near resonance with atomic transition energies. These factors are gathered into the atomic scattering factor f_n , which is commonly written as

$$f_n = f_n^0(\sin \theta / \lambda) + f'(\lambda) + if''(\lambda). \quad (3.2.6)$$

f^0 is the Fourier transform of the electron number density, so that $f^0(0)$ is equal to the number of electrons in the atom or ion. These factors are tabulated in *International Tables for Crystallography*, Volume C, Chapter 6.1 and <https://physics.nist.gov/PhysRefData/FFast/html/form.html> and http://henke.lbl.gov/optical_constants/asf.html. Values of atomic scattering factors are normally incorporated into data-analysis programs that require them, so the user does not often have to worry about them.