Basics of diffraction: theory and practice W. Clegg, University of Newcastle upon Tyne and Daresbury Laboratory

Main headings, tables, equations and figures

Fundamentals of the crystalline state

Translation symmetry is essential; other symmetry (rotation, reflection, inversion) may also be present. Translation symmetry is characterised by a *lattice*, and its basic repeat unit is the *unit cell*; geometry is specified by 3 lengths and 3 angles, some of which take special values/relationships if rotation/reflection symmetry is present.



Space group: the collection of all symmetry operations for a crystal structure. Symbol is a combination of letters and numbers, indicating the symmetry present. There are 230 space groups.

Asymmetric unit: the unique part of the structure (a fraction of a unit cell). Operation of symmetry except for pure translation generates the unit cell, then operation of translation symmetry generates the complete crystal structure.

Crystal systems

For the essential symmetry, each type of rotation axis is generic; it could be a proper or improper rotation or a screw axis, and mirrors can also be glide planes. The lattice types shown in parentheses can be converted into standard types not in parentheses by a different choice of axes, but are used in some cases in order to satisfy other conventions or conveniences regarding symmetry and geometry.

Crystal system	Essential symmetry	Unit cell restrictions	Lattice types
triclinic	none	none	Р
monoclinic	2 and/or <i>m</i> for one axis	α=γ=90°	P, C(I)
orthorhombic	2 and/or <i>m</i> for three axes	α=β=γ=90°	P, C (A), I, F
tetragonal	4 for one axis	<i>a=b</i> ; α=β=γ=90°	P, I
trigonal	3 for one axis	<i>a=b</i> ; α=β=90°, γ=120°	P(R)
hexagonal	6 for one axis	<i>a=b</i> ; α=β=90°, γ=120°	Р
cubic	3 for four directions	<i>a=b=c</i> ; α=β=γ=90°	P, I, F

Any line, and any plane (or set of regularly spaced parallel planes) in a 3D lattice (crystal structure) can be specified by 3 numbers; for lines joining lattice points, and sets of planes passing through lattice points, these numbers are integers. For planes, they are called *Miller indices*, represented by the letters h,k,l.

Crystals and their diffraction patterns

X-rays are used because their wavelengths are comparable to the sizes of atoms and molecules, giving rise to diffraction effects by crystals.

The diffraction pattern is the *Fourier transform* of the crystal structure, and the crystal structure is the *Fourier transform* of the diffraction pattern. Any given X-ray beam is characterised by its *wavelength* λ (usually a known single value in most diffraction experiments), *amplitude* |F| (*intensity* $I \propto |F|^2$), and *phase* ϕ (0–360°) relative to other beams (important for interference effects when waves are added together).



Geometry of diffraction pattern (positions of spots on film/detector, directions of diffracted beams) is related to unit cell (lattice) geometry.

Symmetry of diffraction pattern is related to symmetry of crystal structure (space group).

Intensities of diffraction pattern are related to nature and positions of atoms within the asymmetric unit.

Diffraction by crystals (geometry): the reciprocal lattice, Bragg equation, and Ewald sphere

Direct lattice (crystal structure lattice) is defined by three vectors: **a**, **b**, **c**. Define a reciprocal lattice ($\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$), such that

$$\mathbf{a}^* = (\mathbf{b} \times \mathbf{c}) / V \qquad \mathbf{b}^* = (\mathbf{c} \times \mathbf{a}) / V \qquad \mathbf{c}^* = (\mathbf{a} \times \mathbf{b}) / V$$
$$V = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = \mathbf{b} \cdot (\mathbf{c} \times \mathbf{a}) = \mathbf{c} \cdot (\mathbf{a} \times \mathbf{b})$$
Hence:
$$\mathbf{a} \cdot \mathbf{a}^* = \mathbf{b} \cdot \mathbf{b}^* = \mathbf{c} \cdot \mathbf{c}^* = 1$$
and
$$\mathbf{a} \cdot \mathbf{b}^* = \mathbf{a} \cdot \mathbf{c}^* = \mathbf{b} \cdot \mathbf{a}^* = \mathbf{b} \cdot \mathbf{c}^* = \mathbf{c} \cdot \mathbf{a}^* = \mathbf{c} \cdot \mathbf{b}^* = 0$$

This means that \mathbf{a}^* is perpendicular to both \mathbf{b} and \mathbf{c} , etc. If every set of parallel lattice planes is represented by a point such that its distance from the origin is 1/d (the reciprocal of the spacing between planes) and the direction is perpendicular to the planes, then all the possible points lie at reciprocal lattice points, and the coordinates of each point (counting from the origin in three dimensions) are the Miller indices of the plane: $(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* = \mathbf{d}^*_{hkl}, \mathbf{a}$ vector with length $1/d_{hkl}$). As a consequence of the Bragg equation (below), the reciprocal lattice is a convenient representation for the geometry of the diffraction pattern, and every diffracted beam (X-ray reflection) is labelled by the three indices h,k,l, specifying the associated lattice planes.



Diffraction in one dimension (left): for rays scattered by two adjacent points in the row

path difference = $a \sin \psi_i + a \sin \psi_d = h\lambda$

where Ψ_i and Ψ_d are the angles of the incident and diffracted beams as shown, λ is the wavelength, *a* is the one-dimensional lattice spacing, and *h* is an integer (positive, zero, or negative). For a given value of Ψ_i (a fixed incident beam), each value of *h* corresponds to an observed diffraction maximum and the equation can be used to calculate the permitted values of Ψ_d , the directions in which intensity is observed. The result is a set of bright fringes.

Using vector notation: if s and s_0 are unit vectors along the directions of the diffracted and incident beams, and a is the lattice translation vector, then

$$\mathbf{a} \cdot (\mathbf{s} - \mathbf{s}_0) = h\lambda$$

There are three such equations, one for each dimension, and all must be satisfied simultaneously (Laue equations); this requires three integers h, k, l and reference to all three lattice vectors **a**, **b**, **c**.

Alternative representation for three dimensions (right): for rays reflected by two adjacent planes

path difference =
$$2d_{hkl} \sin\theta = (n) \lambda$$

Using vector notation: if d_{hkl}^* is the reciprocal lattice vector for the reflecting planes, then this vector is parallel to $s - s_0$ and

$$(\mathbf{s} - \mathbf{s}_0)/\lambda = \mathbf{d}_{hkl}^* = h\mathbf{a}^* + k\mathbf{b}^* + \mathbf{l}\mathbf{c}^*$$

The Ewald sphere construction is a way of showing how rotation of a crystal (and its reciprocal lattice with it) leads to the Bragg equation being satisfied in certain orientations, generating observed diffracted beams. A sphere of radius $1/\lambda$ is centred on the crystal, with the incident beam in a fixed direction. The origin of the reciprocal lattice is placed on the sphere opposite the incident beam, and the crystal rotates. Whenever a reciprocal lattice point touches the surface of the sphere, the Bragg equation is satisfied for this set of lattice planes, and a Bragg reflection occurs; the direction of the diffracted beam is from the centre of the sphere to the reciprocal lattice point. This allows us to predict both where and when diffraction will occur, if the lattice parameters and crystal orientation are known.



Diffraction by crystals (symmetry)

To a first approximation, all diffraction patterns have inversion symmetry; the point group symmetry of the pattern is related to the space group of the crystal and is called the Laue group. There are 11 possible Laue groups. Other aspects of the space group symmetry are revealed in 'systematic absences', special subsets of the data that systematically have zero intensity.

Diffraction by crystals (intensities)

Intensities of diffracted X-rays are due to interference effects of X-rays scattered by all the different atoms in the structure. The diffraction pattern is the Fourier transform of the crystal structure, corresponding to the pattern of waves scattered from an incident X-ray beam by a single crystal; it can be measured by experiment (only partially, because the amplitudes are obtainable from the directly measured intensities via a number of corrections, but the relative phases of the scattered waves are lost), and it can be calculated (giving both amplitudes and phases) for a known structure. In turn, the crystal structure is the Fourier transform of the diffraction pattern and is expressed in terms of electron density distribution concentrated in atoms; it can not be measured by direct experiment, because the scattered X-rays can not be refracted by lenses to form an image as is done with light in an optical microscope, and it can not be obtained directly by calculation, because the required relative phases of the waves are unknown.

The forward Fourier transform (diffraction experiment or calculation from known structure):

$$F(hkl) = \sum_{j=1}^{N} f_{j} \exp[2\pi i (hx_{j} + ky_{j} + lz_{j})]$$

The reverse Fourier transform (calculation, requiring a knowledge of phases somehow):

$$\rho(xyz) = \frac{1}{V} \sum_{hkl} F(hkl) \exp[-2\pi i(hx + ky + lz)]$$

These form the basis of crystal structure determination by X-ray crystallography.

Example of a section through an electron density map (reverse Fourier transform), showing a largely planar structure.





Crystal structure determination in outline

Some references

International Tables for Crystallography, Volume A, 5th edition, Kluwer, 2002 (comprehensive compilation for symmetry and space groups)

W. Clegg, *Crystal Structure Determination*, OUP, 1998 (brief account at undergraduate level in Oxford Chemistry Primer series)

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