Appendices

Appendix 1: The determination of unit-cell constants and their use in ascertaining the contents of the unit cell

Unit-cell dimensions

Unit-cell dimensions may be determined, with X rays of a known wavelength, from values of 2θ for Bragg reflections of known indices; 2θ is the deviation of the diffracted beam from the direct beam. The Bragg equation is then used, i.e., $n\lambda = 2d \sin \theta$; d_{hkl} = spacing between crystal planes (hkl).

Example

Monoclinic cell, $a = 23.033$ Å, $b = 7.670$ Å, $c = 9.928$ Å, $\alpha = \gamma = 90°$, $\beta = 100.12°$, $\sin \beta = 0.98445$, $\lambda = 1.5418$ Å [$a \sin \beta = 22.675 = d_{100}$, $c \sin \beta = 9.774 = d_{001}$].

Fig. A1.1 Unit cell with b perpendicular to the plane of the paper.

Experimental measurements

h	k	l	$2\theta(°)$	$\theta(°)$	$\sin \theta$	$n\lambda/2\sin\theta$(Å)		
20	0	0	85.68	42.84	0.67995	22.675	$\Big\} d_{100}$	$\Big\} a \sin \beta$
22	0	0	96.82	48.41	0.74791	22.676		
0	4	0	47.41	23.705	0.40203	7.670	d_{010}	b
0	0	10	104.14	52.07	0.78876	9.774	d_{001}	$c \sin \beta$

Conclusion: $a = 23.033$ Å, $b = 7.670$ Å, $c = 9.828$ Å, $\beta = 100.12°$.

Unit-cell contents

Let W = weight in grams of one gram-formula weight of the contents of the unit cell.
V = the unit-cell volume in cm^3 of this weight of the crystal.
$N_{Avog.}$ = Avogadro's number = number of molecules in a gram molecule = 6.02×10^{23}.
Unit-cell volume = 1726 Å^3 = 1726×10^{-24} cm^3.
Observed density (by flotation) = 1.34 g/cm^3.

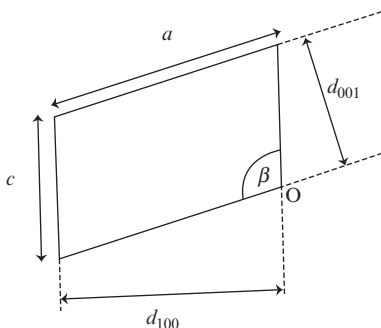If the density of a crystal is known (or guessed), it is possible to determine what is in the crystal. $N_{Avog.}$ unit cells occupy $1726 \times 10^{-24} \times 6.02 \times 10^{23}$ cm^3 = $V = 1039$ cm^3.

Crystal density = $W/V = W/1039$ g/cm^3 = 1.34 g/cm^3.

Therefore $W = 1392$.

But W also equals $(ZM + zm)$,

where Z is the number of molecules of the compound (molecular weight M) per unit cell, and z is the number of molecules of solvent of crystallization (molecular weight m) per unit cell. In this example, M is known to be 340 and m = 18 (for water).

$$(Z \times 340) + (z \times 18) = 1392.$$

The monoclinic symmetry of the unit cell suggests that Z is 4, or a multiple of 4, leading to the conclusion that $Z = 4$ and $z = 2$ ($W = 1396$) is the correct solution, and that the solution $Z = 3$ and $z = 20$ ($W = 1380$), which is equally probable from the calculated weight alone, is much less likely, because of the monoclinic symmetry.
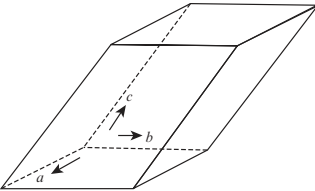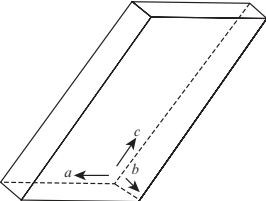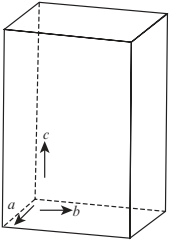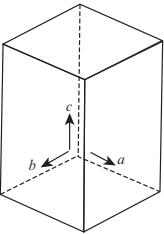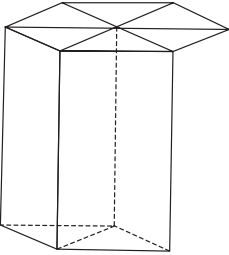
# Appendix 2: Some information about crystal systems and crystal lattices

There are seven crystal systems defined by the minimum symmetry of the unit cell. It is conventional to label the edges of the unit cell a, b, c and the angles between them α, β, γ, with α the angle between b and c, β that between a and c, and γ that between a and b. If the crystal lattice has six-fold symmetry, sometimes four axes of reference are used. These are x, y, u, z, where x, y, and u lie in one plane inclined at $120°$ to each other and with z perpendicular to them. The indices of Bragg reflections are then $hkil$ with the necessary condition that $i = -(h + k)$. We use the simpler cell here. For the seven crystal systems, the minimum symmetry and the diffraction symmetry are:

	Minimum point group symmetry of a crystal in this system	Diffraction symmetry (Laue symmetry)
1. Triclinic	None (one-fold rotation axis).	$\bar{1}$
2. Monoclinic	Two-fold rotation axis parallel to b.	$2/m$
3. Orthorhombic	Three independent mutually perpendicular two-fold rotation axes.	mmm
4. Trigonal/rhombohedral	Three-fold rotation axis parallel to $(a + b + c)$	$\bar{3}$ or $\bar{3}\,m$
5. Tetragonal	Four-fold rotation axis parallel to c.	$4/m$ or $4/mmm$
6. Hexagonal	Six-fold rotation axis parallel to c.	$6/m$ or $6/mmm$
7. Cubic	Four intersecting three-fold rotation axes along the cube diagonals.	$m3$ or $m3m$

Here a number, 1, 2, 3, 4, or 6, implies a rotation axis. If there is a line over it, such as $\bar{3}$, then it is an inversion axis. A mirror plane perpendicular to the rotation axis is n/m, but if the mirror plane is parallel to the rotation axis it is nm; see *International Tables*, Volume A (Hahn, 2005).

Diagrams of the unit cells are shown below, together with symmetry-imposed restrictions on the unit-cell dimensions.

Diagrams of unit cells	Crystal system	Rotational symmetry elements and cell-dimension restrictions
	Triclinic	No rotational symmetry. No restrictions on axial ratios or angles.
	Monoclinic	**b** chosen along the two-fold rotation axis.[a] Angles made by **b** with **a** and by **b** with **c** must be 90°.
	Orthorhombic	Three mutually perpendicular two-fold rotation axes chosen as **a**, **b**, **c** coordinate axes. No restrictions on axial ratios. All three angles must be 90°.
	Tetragonal	Four-fold rotation axis chosen as **c**. Two-fold rotation axes perpendicular to **c**. Lengths of **a** and **b** identical. All angles must be 90°.
	Hexagonal[b]	**c** is chosen along the six-fold axis. Two-fold rotation axes perpendicular to **c**. Angle between **a** and **b** must be 120°; other two angles must be 90°.
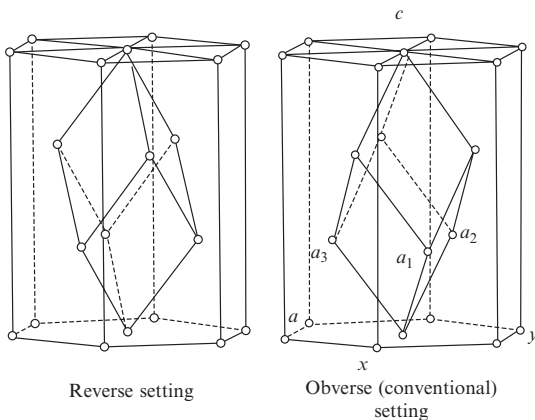
	Rhombohedral	Three-fold rotation axis along one body diagonal of unit cell. This makes all three axial lengths necessarily the same and all three interaxial angles also necessarily equal. There is no restriction on the value of the interaxial angle, a.

Reverse setting   Obverse (conventional) setting
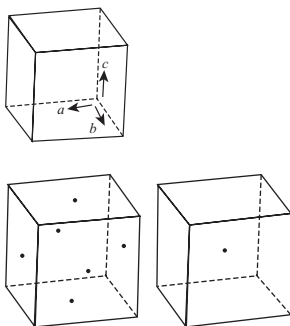
	Cubic	Three-fold rotation axes along all four body-diagonals of unit cell. Four-fold axes parallel to each crystal axis. Two-fold axes are also present. All axial lengths are identical by symmetry. All angles must be 90°.
	Face-centered (F) and body-centered (I)	Symmetry at each crystal lattice point is the same as for simple cubic. F has four crystal lattice points per cubic unit cell, the extra three being at face centers. I has two points per unit cell, the extra one being at the center of the cell.

[a] This means that if the cell is rotated $360°/2 = 180°$ about an axis parallel to **b**, the cell so obtained is indistinguishable from the original.
[b] The six-fold axis present in hexagonal crystal lattices is perhaps not evident from the shape of the unit cell, because the inclusion of the cell edges as solid lines in the diagram obscures the symmetry. If only the crystal lattice points are shown in a layer normal to the unique **c**-axis (one cell is outlined here on the right in dashed lines), the six-fold symmetry is apparent (ignoring the dotted lines). There is a six-fold rotation axis perpendicular to the plane of the paper at every crystal lattice point; it is indicated by the dashed lines drawn from one crystal lattice point.
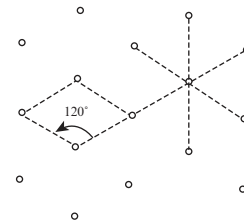
There are five additional Bravais lattices that are obtained by adding face-centering and body-centering to certain of the seven space lattices just listed. Face-centering involves a crystal lattice point at the center of opposite pairs of faces, and is designated F if all faces are centered and A, B, or C if only one pair of faces is centered. In body-centered unit cells, there is a crystal lattice point at the center of the unit cell; a body-centered cell is designated I. These centerings cause additional systematic absences in the measured Bragg reflections (h, k, l) as follows:

A $(k + l)$, odd, absent.
B $(l + h)$, odd, absent.
C $(h + k)$, odd, absent.
F $(h + k)$, $(k + l)$, $(l + h)$, all odd, absent.
I $(h + k + l)$, odd, absent.

The 14 Bravais lattices are:

Triclinic	*P*			
Monoclinic	*P*	*C*		
Orthorhombic	*P*	*C*	*F*	*I*
Tetragonal	*P*	*I*		
Hexagonal	*P*			
Rhombohedral	*P*			
Cubic	*P*	*F*	*I*	

(*C* in monoclinic can alternatively be *A* or *I*; *C* in orthorhombic can alternatively be *A* or *B*. *P* in rhombohedral is often called *R*.)

Addition of symmetry elements to these Bravais lattices give the 230 space groups. Some of these symmetry elements also cause systematic absences in the diffraction pattern. For example, for a two-fold screw axis parallel to **a**, *h* in the *h* 0 0 Bragg reflections is only even, and for a four-fold screw axis parallel to **a**, *h* in the *h* 0 0 reflections is only a multiple of 4. For a glide plane perpendicular to **a** with translation *b*/2 (which is a *b* glide), *k* in the 0*kl* reflections is only even. For more details, see *International Tables*, Volume A (Hahn, 2005), or *X-ray Crystallography* by M. J. Buerger, Chapter 4, pp. 82–90 (Buerger, 1942).

Appendix 3: The reciprocal lattice

The relation between the crystal lattice (real space) and the reciprocal lattice (reciprocal space) may be expressed most simply in terms of vectors. Some of the relationships between these two lattices are illustrated in Figure 3.7d. The point *hkl* in the reciprocal lattice is drawn at a distance $1/d_{hkl}$ from the origin and in the direction of the perpendicular between (*hkl*) lattice planes. If we denote the fundamental translation vectors of the crystal lattice by **a**, **b**, and **c**, and the volume of the unit cell by V_c, and then use the same symbols, starred, for the corresponding quantities of the reciprocal lattice, the relation between the two lattices is

$$\mathbf{a}^* = \frac{\mathbf{b}^* \times \mathbf{c}^*}{V_c}, \quad \mathbf{b}^* = \frac{\mathbf{c}^* \times \mathbf{a}^*}{V_c}, \quad \mathbf{c}^* = \frac{\mathbf{a}^* \times \mathbf{b}^*}{V_c} \tag{A3.1}$$

with $V_c = \mathbf{a} \cdot \mathbf{b} \times \mathbf{c} = 1/V_c^*$.

The vectors of the crystal lattice and the reciprocal lattice are thus oriented as follows: any fundamental translation of one lattice is perpendicular to the other two fundamental translations of the second lattice. Thus **a*** is perpendicular to both **b** and **c**, **b** is perpendicular to both **a*** and **c***, and so on. The vectors of the crystal lattice and the reciprocal lattice are therefore said to form an "adjoint set" in the sense that this term is used in tensor calculus; they satisfy the condition that the scalar product of any two corresponding fundamental translation vectors, one from each of the two lattices, is unity, and the scalar product of any two noncorresponding vectors of the two lattices is zero, because, as mentioned above, they are mutually perpendicular. This is expressed by

$$\mathbf{a}_i^* \cdot \mathbf{a}_j = \delta_{ij} \begin{cases} = 1, & \text{if } i = j \\ = 0, & \text{if } i \neq j \end{cases} \tag{A3.2}$$

That is,

$$\mathbf{a} \cdot \mathbf{a}^* = \mathbf{b} \cdot \mathbf{b}^* = \mathbf{c} \cdot \mathbf{c}^* = 1$$

and

$$\mathbf{b} \cdot \mathbf{a}^* = \mathbf{c} \cdot \mathbf{a}^* = \mathbf{c} \cdot \mathbf{b}^* = \mathbf{a} \cdot \mathbf{b}^* = \mathbf{a} \cdot \mathbf{c}^* = \mathbf{b} \cdot \mathbf{c}^* = 0$$

As stressed in Chapter 3, if a structure is arranged on a given lattice, its diffraction pattern is necessarily arranged on a lattice reciprocal to the first. The fact that any fundamental translation of the crystal lattice is perpendicular to the other two fundamental translations of the reciprocal lattice, and the converse, is an example of a quite general relation: *every reciprocal lattice vector is perpendicular to some plane in the crystal lattice and, conversely, every crystal lattice vector is perpendicular to some plane in the reciprocal lattice*. Furthermore, if the indices of a crystal lattice plane are (*hkl*) (in the sense defined in the caption of Figure 2.4), the reciprocal lattice vector $\mathbf{H}$ perpendicular to this plane is the vector from the origin of the reciprocal lattice to the reciprocal lattice point with indices *hkl*. It is expressed as

$$\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \tag{A3.3}$$

In a monoclinic unit cell,

$$d_{100} = a \sin \beta = \frac{1}{a^*}$$

We have the relation, for this Bragg reflection 100, where $h = 1$,

$$|\mathbf{H}| = |h\mathbf{a}^*| = h/d_{100} \tag{A3.4}$$

or

$$|\mathbf{H}_{100}| = |\mathbf{a}^*| = 1/d_{100}$$

A comparison with the Bragg equation for 100 with the appropriate values of d and θ,

$$h\lambda = 2d \sin \theta \quad \text{or} \quad h/d = \frac{2 \sin \theta}{\lambda} \tag{A3.5}$$

$$\lambda = 2d_{100} \sin \theta_{100} \quad \text{or} \quad 1/d_{100} = 2 \sin \theta_{100}/\lambda$$

indicates that in this case

$$|\mathbf{H}| = \frac{2 \sin \theta}{\lambda} \tag{A3.6}$$

This relation holds quite generally.

$$|\mathbf{H}_{100}| = 2 \sin \theta_{100}/\lambda \tag{A3.7}$$

$$|\mathbf{H}_{hkl}| = 2 \sin \theta_{hkl}/\lambda$$

The equations relating the real and reciprocal unit-cell dimensions are given in Buerger (1942) (Chapter 18, p. 360) and Stout and Jensen (1989) (p. 31). Some

of these are listed below:

$$a^* = bc \sin \alpha / V, \, b^* = ac \sin \beta / V, \, c^* = ab \sin \gamma / V$$

where

$$V = abc\sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$$

$$V^* = 1/V$$

$$\cos \alpha^* = (\cos \beta \cos \gamma - \cos \alpha)/ \sin \beta \sin \gamma$$

$$\cos \beta^* = (\cos \alpha \cos \gamma - \cos \beta)/ \sin \alpha \sin \gamma$$

$$\cos \gamma^* = (\cos \alpha \cos \beta - \cos \gamma)/ \sin \alpha \sin \beta$$

Appendix 4: The equivalence of diffraction by a crystal lattice and the Bragg equation

For simplicity we will consider diffraction by a two-dimensional orthogonal crystal lattice (a rectangular net), but the treatment can be generalized to three dimensions and to the nonorthogonal case. Suppose the crystal lattice has sides a and b for each unit cell and that X rays are incident upon the crystal lattice from a direction such that the incident beams make an angle ψ with the crystal lattice rows in the **a** direction. Consider the scattering (the diffracted beam) in the direction ψ' with respect to the **a** direction. Because a and b are crystal lattice translations, any atom in the structure will be repeated periodically with
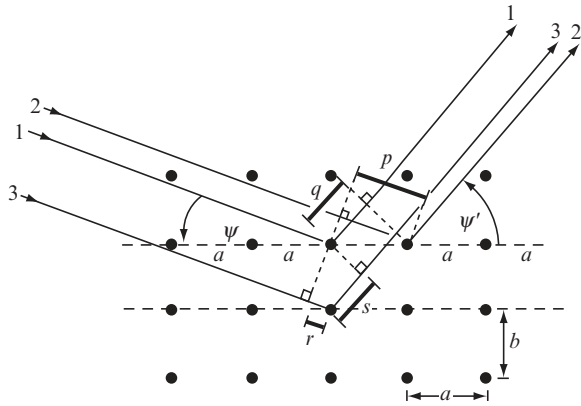
DIFFRACTION BY A CRYSTAL

Fig. A4.1

spacings a and b. Thus atoms may be imagined to be present at the crystal lattice points in Figure A4.1 (they will normally also be present at other points, lying between these crystal lattice points, but spaced identically in each unit cell). If scattering is to occur in the direction specified by ψ', then the radiation scattered in that direction from every crystal lattice point must be exactly in phase with that from every other crystal lattice point. (If scattering from any two crystal lattice points is somewhat out of phase, that from some other pair of crystal lattice points will be out of phase by a different amount, and the net sum over all crystal lattice points, considering the crystal to be essentially infinite, will consist of equal positive and negative contributions and thus will be zero.)

Consider waves 1 and 2, scattered by atoms separated by a (Figure A4.1). For these waves to be just in phase after scattering, the path difference (PD_1) must be an integral number (h) of wavelengths (ray 1 travels a distance q, while ray 2 travels a distance p):

$$PD_1 = p - q = a \cos \psi - a \cos \psi' = h\lambda \tag{A4.1}$$

Similarly, the path difference for waves 1 and 3, scattered by atoms separated by b, must also be an integral number of wavelengths (ray 3 travels a distance $r + s$ more than ray 1):

$$PD_2 = r + s = b \sin \psi + b \sin \psi' = k\lambda \tag{A4.2}$$

where k is some integer.

Both of these conditions must hold simultaneously. They are sufficient conditions to ensure that the scattering from all atoms in this two-dimensional net will be in phase in the direction ψ'. In three dimensions, another similar equation, corresponding to the spacing in the third (noncoplanar) direction, must be added. Each of these equations describes a cone. In three dimensions, the three cones intersect in a line corresponding to the direction of the diffracted beam, such that the conditions $h\lambda = PD_1$, $k\lambda = PD_2$, and $l\lambda = PD_3$ all are satisfied simultaneously. This is why, when a three-dimensional crystal diffracts, there are very few diffracted beams for any given orientation of the incident beam with respect to the (stationary) crystal. The chance that all three conditions will be satisfied at once is small.

Now let us see how this set of conditions can be related to the Bragg equation. Consider several parallel planes, I, II, and III, each passing through a set of crystal lattice points and making equal angles, θ, with the incident and scattered beams (Figure A4.2). The planes make an angle α with the a axis. The angles ψ and ψ' are defined as in Figure A4.1, and so

$$\theta = \psi + \alpha = \psi' - \alpha \tag{A4.3}$$

Substituting for ψ and ψ' from Eqn. (A4.3) into Eqns. (A4.1) and (A4.2), we find

$$h\lambda = 2a \sin \alpha \sin \theta \tag{A4.4}$$

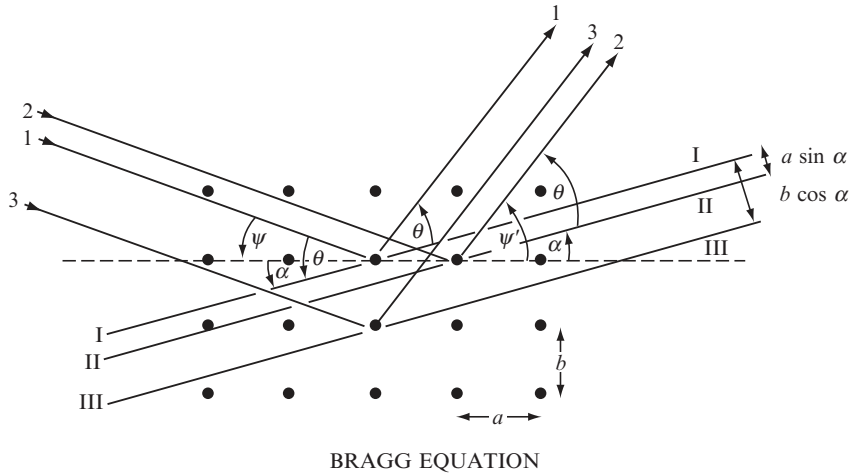$$k\lambda = 2b \cos \alpha \sin \theta \tag{A4.5}$$

BRAGG EQUATION

Fig. A4.2

or

$$\frac{2\sin\theta}{\lambda} = \frac{h}{a\sin\alpha} = \frac{k}{b\cos\alpha} \qquad (A4.6)$$

Now $a\sin\alpha$ is just the spacing between planes I and II, while $b\cos\alpha$ is just the spacing between planes I and III. If we let d_{hkl} represent the spacing between any two planes in a set of equidistant planes parallel to I, and let n be some integer, we can write Eqn. (A4.6) generally as

$$\frac{2\sin\theta}{\lambda} = \frac{n}{d_{hkl}} \qquad (A4.7)$$

which is the Bragg equation, $n\lambda = 2d\sin\theta$, Eqn. (3.1).

The indices $(H\ K)$ of the "reflecting planes," I, II and III, are determined, as described in the caption to Figure 2.4, by measuring the intercepts on the axes as fractions of the cell edges. From Figure A4.2 it can be seen that the intercepts along **b** and **a** are in the ratio $\tan\alpha$, whence

$$(b/K)/(a/H) = \tan\alpha \qquad (A4.8)$$

or

$$H/K = (a\tan\alpha)/b \qquad (A4.9)$$

Equation (A4.6) then shows the relation of H and K to the indices of the Bragg reflection $(h\ k)$,

$$\frac{H}{K} = \frac{a\sin\alpha}{b\cos\alpha} = \frac{h}{k} \qquad (A4.10)$$

That is, in conclusion, h and k, the indices of the Bragg reflection, are proportional to H and K, the indices of the reflecting plane.

Appendix 5: Some scattering data for X rays and neutrons

Element	Nuclide	X rays		Neutrons[a]	Neutrons normalized to ^{1}H as -1.00
		$\sin\theta/\lambda = 0$	$\sin\theta/\lambda = 0.5/\text{Å}$	$b/10^{-12}$ cm	
		(relative to scattering by one electron)			
H	^{1}H	1.0	0.07	-0.38	-1.00
	^{2}H = D	1.0	0.07	0.65	1.71
Li	^{6}Li	3.0	1.0	$0.18 + 0.025\text{i}$	$0.71 + 0.066\text{i}$
	^{7}Li	3.0	1.0	-0.25	-0.66
C	^{12}C	6.0	1.7	0.66	1.74
	^{13}C	6.0	1.7	0.60	1.58
O	^{16}O	8.0	2.3	0.58	1.53
Na	^{23}Na	11.0	4.3	0.35	0.92
Fe	^{54}Fe	26.0	11.5	0.42	1.11
	^{56}Fe	26.0	11.5	1.01	2.66
	^{57}Fe	26.0	11.5	0.23	0.61
Co	^{59}Co	27.0	12.2	0.25	0.66
Ni	^{58}Ni	28.0	12.9	1.44	3.79
	^{60}Ni	28.0	12.9	0.30	0.79
	^{62}Ni	28.0	12.9	-0.87	-2.29
U	^{238}U	92.0	53.0	0.85	2.24

[a] The quantity b is the neutron coherent scattering amplitude.

In the final column on the right of the table we have listed neutron scattering amplitudes arbitrarily normalized to a value of -1.0 (for ^{1}H) in order to illustrate more clearly the small range of amplitudes observed as compared with that observed for X-ray scattering. For the nuclides considered here, the range of scattering amplitudes for X rays is about 10^2 at $\theta = 0°$ and nearly 10^3 at sin $\theta/\lambda = 0.05\text{Å}^{-1}$, whereas for neutrons it is near 6, independent of scattering angle.

Appendix 6: Proof that the phase difference on diffraction is $2\pi(hx + ky + lz)$

The phase difference for the $h00$ Bragg reflection for diffraction by two atoms one unit cell apart is ($360h° = 2\pi h$ radians. However, if the atoms are only the fraction x of the cell length apart then the phase difference will be $2\pi hx$ radians. This may be extended to three dimensions to give $2\pi(hx + ky + lz)$ as the phase
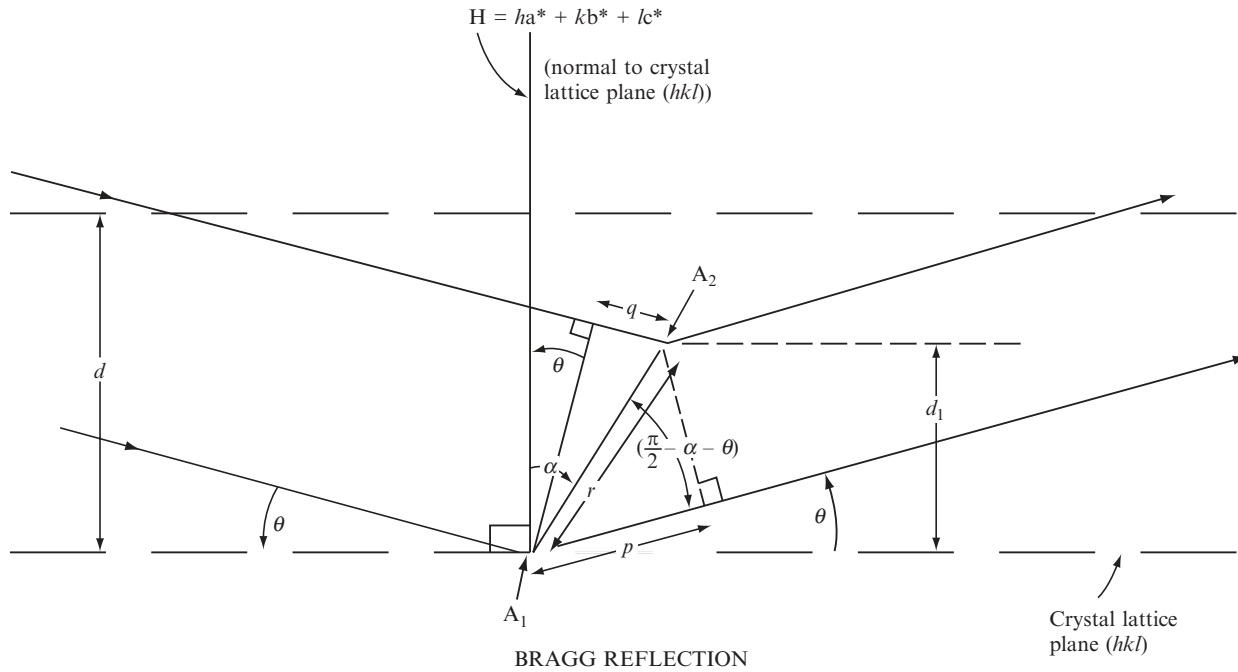
$\mathrm{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$

(normal to crystal lattice plane (*hkl*))

A_2

q

θ

d

d_1

$(\frac{\pi}{2} - \alpha - \theta)$

α

r

θ

θ

p

A_1

Crystal lattice plane (*hkl*)

BRAGG REFLECTION

Fig. A6.1

difference for the *hkl* Bragg reflection for two atoms, one at 0, 0, 0 and the other at *x*, *y*, *z*.

A proof is given below:

Let A_1 and A_2 be two scattering points (atoms) separated by a vector **r** (Figure A6.1). An inspection of the angles in the region of A_1 and A_2 shows that the phase difference for the beams scattered from these atoms at the angle θ is

$$2\pi \frac{p - q}{\lambda} \text{ radians}$$

where

$$p = |\mathbf{r}| \cos\left(\frac{\pi}{2} - \alpha - \theta\right) = |\mathbf{r}| \sin(\alpha + \theta)$$

$$= |\mathbf{r}| \sin\alpha\cos\theta + |\mathbf{r}| \cos\alpha\sin\theta \tag{A6.1}$$

$$q = |\mathbf{r}| \sin(\alpha - \theta) = |\mathbf{r}| \sin\alpha\cos\theta - |\mathbf{r}| \cos\alpha\sin\theta \tag{A6.2}$$

This leads to

$$p - q = 2|\mathbf{r}| \cos\alpha\sin\theta \tag{A6.3}$$

Therefore, from Eqn. (A6.3),

$$\frac{2\pi(p - q)}{\lambda} = 2\pi \frac{2\sin\theta}{\lambda} |\mathbf{r}| \cos\alpha \tag{A6.4}$$

But the reciprocal lattice vector (see Eqn. A3.7) is

$$\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* = l\mathbf{c}^* \qquad (A6.5)$$

and is normal to the crystal lattice plane (*hkl*).

$$|\mathbf{H}| = \frac{2\sin\theta}{\lambda} \qquad (A6.6)$$

Since α is the angle between $\mathbf{H}$ and $\mathbf{r}$, where $\mathbf{r} = \mathbf{a}x + \mathbf{b}y + \mathbf{c}z$, then, by Eqns. (A6.4) and (A6.6),

$$\frac{2\pi(p-q)}{\lambda} = 2\pi\,|\mathbf{H}|\,|\mathbf{r}|\cos(\text{angle between }\mathbf{H}\text{ and }\mathbf{r})$$

Therefore, the phase difference on diffraction is

$$\frac{2\pi(p-q)}{\lambda} = 2\pi\mathbf{H}\cdot\mathbf{r} = 2\pi(hx + ky + lz)$$

since

$$\mathbf{a}^*_i \cdot \mathbf{a}_j = \delta_{ij} \begin{cases} = 1,\ i = j \\ = 0,\ i \neq j \end{cases}$$

Appendix 7: The 230 space groups

Noncentrosymmetric space groups, chiral molecules (one hand only) in them. These are the 65 space groups that proteins and nucleic acids, which are chiral, crystallize in.

Triclinic (polar)	$P1$
Monoclinic (polar)	$P2$, $P2_1$, $C2$
Orthorhombic	$P222$, $P222_1$, $P2_12_12$, $P2_12_12_1$, $C222_1$, $C222$, $F222$, $I222$, $I2_12_12_1$
Tetragonal (polar)	$P4$, $P4_1$, $P4_2$, $P4_3$, $I4$, $I4_1$
Tetragonal	$P422$, $P42_12$, $P4_122$, $P4_12_12$, $P4_222$, $P4_22_12$, $P4_322$, $P4_32_12$, $I422$, $I4_122$
Trigonal (polar)	$P3$, $P3_1$, $P3_2$, $R3$
Trigonal	$P312$, $P321$, $P3_112$, $P3_121$, $P3_212$, $P3_221$, $R32$
Hexagonal (polar)	$P6$, $P6_1$, $P6_5$, $P6_2$, $P6_4$, $P6_3$
Hexagonal	$P622$, $P6_122$, $P6_522$, $P6_222$, $P6_422$, $P6_322$
Cubic	$P23$, $F23$, $I23$, $P2_13$, $I2_13$
Cubic	$P432$, $P4_232$, $F432$, $F4_132$, $I432$, $P4_332$, $P4_132$, $I4_132$

Noncentrosymmetric space groups, both enantiomers in them.

Monoclinic	Pm, Pc, Cm, Cc
Orthorhombic	$Pmm2$, $Pmc2_1$, $Pcc2$, $Pma2$, $Pca2_1$, $Pnc2$, $Pmn2_1$, $Pba2$, $Pna2_1$, $Pnn2$, $Cmm2$, $Cmc2_1$, $Ccc2$, $Amm2$, $Abm2$, $Ama2$, $Aba2$, $Fmm2$, $Fdd2$, $Imm2$, $Iba2$, $Ima2$
Tetragonal	$P\bar{4}$, $I\bar{4}$
	$P4mm$, $P4bm$, $P4_2cm$, $P4_2nm$, $P4cc$, $P4nc$, $P4_2mc$, $P4_2bc$, $I4mm$, $I4cm$, $I4_1md$, $I4_1cd$
	$P\bar{4}2m$, $P\bar{4}2c$, $P\bar{4}2_1m$, $P\bar{4}2_1c$, $P\bar{4}m2$, $P\bar{4}c2$, $P\bar{4}b2$, $P\bar{4}n2$, $I\bar{4}m2$, $I\bar{4}c2$, $I\bar{4}2m$, $I\bar{4}2d$
Trigonal	$P\bar{3}$, $R\bar{3}$
	$P3m1$, $P31m$, $P3c1$, $P31c$, $R3m$, $R3c$
Hexagonal	$P\bar{6}$
	$P6mm$, $P6cc$, $P6_3cm$, $P6_3mc$
	$P\bar{6}m2$, $P\bar{6}c2$, $P\bar{6}2m$, $P\bar{6}2c$
Cubic	$P\bar{4}3m$, $F\bar{4}3m$, $I\bar{4}3m$, $P\bar{4}3n$, $F\bar{4}3c$, $I\bar{4}3d$

Centrosymmetric space groups, both enantiomers in them.

Triclinic	$P\bar{1}$
Monoclinic	$P2/m$, $P2_1/m$, $C2/m$, $P2/c$, $P2_1/c$, $C2/c$
Orthorhombic	$Pmmm$, $Pnnn$, $Pccm$, $Pban$, $Pmma$, $Pnna$, $Pmna$, $Pcca$, $Pbam$, $Pccn$, $Pbcm$, $Pnnm$, $Pmmn$, $Pbcn$, $Pbca$, $Pnma$, $Cmcm$, $Cmca$, $Cmmm$, $Cccm$, $Cmma$, $Ccca$, $Fmmm$, $Fddd$, $Immm$, $Ibam$, $Ibca$, $Imma$
Tetragonal	$P4/m$, $P4_2/m$, $P4/n$, $P4_2/n$, $I4/m$, $I4_1/a$
	$P4/mmm$, $P4/mcc$, $P4/nbm$, $P4/nnc$, $P4/mbm$, $P4/mnc$, $P4/nmm$
	$P4/ncc$, $P4_2/mmc$, $P4_2/mcm$, $P4_2/nbc$, $P4_2/nnm$, $P4_2/mbc$, $P4_2/mnm$, $P4_2/nmc$, $P4_2/ncm$, $I4/mmm$, $I4/mcm$, $I4_1/amd$, $I4_1/acd$
Trigonal	$P\bar{3}1m$, $P\bar{3}1c$, $P\bar{3}m1$, $P\bar{3}c1$, $R\bar{3}m$, $R\bar{3}c$
Hexagonal	$P6/m$, $P6_3/m$
	$P6/mmm$, $P6/mcc$, $P6_3/mcm$, $P6_3/mmc$
Cubic	$Pm\bar{3}$, $Pn\bar{3}$, $Fm\bar{3}$, $Fd\bar{3}$, $Im\bar{3}$, $Pa\bar{3}$, $Ia\bar{3}$
	$Pm\bar{3}m$, $Pn\bar{3}n$, $Pm\bar{3}n$, $Pn\bar{3}m$, $Fm\bar{3}m$, $Fm\bar{3}c$, $Fd\bar{3}m$, $Fd\bar{3}c$, $Im\bar{3}m$, $Ia\bar{3}d$

The first letter shows the Bravais lattice type (P, A, B, C, R, I, F). Then follow the symmetry operation symbols. Monoclinic unit cells have **b** unique. The obverse setting is used for rhombohedral R space groups (listed in trigonal).

Appendix 8: The Patterson function

The Patterson function, deduced by A. L. Patterson in 1934, is a Fourier series, analogous to Eqn. (6.1), in which the coefficients of $|F|$ are replaced

by $|F|^2$:

$$P(uvw) = \frac{1}{V} \sum \sum \sum_{\text{all } h,k,l} |F|^2 \exp[-2\pi i(hu + kv + lw)] \qquad \text{(A8.1)}$$

This function was an extension from the suggestion of Zernike and Prins in 1927 that, because there may be local order in a liquid, there should be diffraction effects. For example, in a monatomic liquid such as mercury, the nearest neighbors of a given atom should never be at a distance less than two atomic radii, and seldom much more. There is more disorder for second nearest neighbors and, as the distance from the atom under consideration increases, the arrangement becomes random. Zernike and Prins showed that measurements of the diffraction pattern could be used to calculate the *average radial distribution* of matter in a liquid or powdered crystal (Zernike and Prins, 1927). The term "radial" is used because the distribution is averaged over all directions and depends only on the distance from its origin. The term "average" implies that the distribution function found represents the average of the distributions of neighbors around each of the atoms in the sample whose diffraction pattern has been used.

These ideas were extended to crystals by Patterson, who recognized the key fact that, because of the high degree of order in the crystal, the averaging over all directions could be eliminated and detailed information about both the *magnitudes* and the *directions* of the interatomic vectors (that is, both radial and angular information) could be obtained (Patterson, 1934, 1935).

It is easiest to consider first a one-dimensional case and then extend it to three dimensions. A one-dimensional electron density distribution map, $\rho(x)$, for a regularly repeating cell, length a, can be expressed by Eqn. (A8.2) and is illustrated in Figure A8.1:

$$\rho(x) = \frac{1}{a} \sum_{\text{all } h} F(h) \exp(-2\pi i h x) \qquad \text{(A8.2)}$$

Fig. A8.1

Consider the distribution of electron density about an arbitrary point, x, in the unit cell. The electron density at a point $+u$ from x is $\rho(x + u)$. Patterson defined the weighted distribution, WD, about the point x by allotting to the distribution about x a weight that was equal to $\rho(x)\,dx$, the total amount of scattering material in the interval between x and $x + dx$:

$$\text{WD} = \rho(x + u)\rho(x)\,dx \qquad \text{(A8.3)}$$

It can be seen that, for a given value of dx, the weighted distribution is large *only* if both $\rho(x)$ and $\rho(x + u)$ are large, and is thus small if either or both are small.

Values of weighted distributions are summed by integrating over all values of x in the cell, keeping u constant, so that the average weighted distribution of density, $P(u)$, is

$$P(U) = a \int_0^1 \rho(x)\rho(x + u)\,dx \qquad \text{(A8.4)}$$

$$= \frac{1}{a} \int_0^1 \left[\sum_{\text{all } h} F(h) \exp(-2\pi i h x) \right] \left[\sum_{\text{all } h'} F(h') \exp[-2\pi i h'(x + u)] \right] dx \qquad \text{(A8.5)}$$
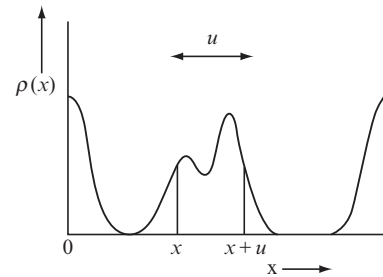
The properties of the complex exponential are such that the integral in Eqn. (A8.5) vanishes unless $h = -h'$; consequently, Eqn. (A8.5) leads to

$$P(u) = \frac{1}{a} \sum_{\text{all } h} F(h)F(-h) \exp(2\pi i h u)$$

$$= \frac{1}{a} \sum_{\text{all } h} |F(h)|^2 \exp(2\pi i h u) \tag{A8.6}$$

since $a(\bar{h}) = -a(h)$ and, by Eqn. (5.18), $F(h)F(-h) = |F|^2 e^{i\alpha} e^{-i\alpha} = |F|^2$.

This function, $P(u)$, may be visualized by imagining a pair of calipers set to measure a distance u. One point of the calipers is set on each point in the cell in turn; since the unit cell is repeated periodically, the situation at x is repeated at $x - 1, x + 1, x + 2, \ldots$ The sum of all the products of values of $\rho(x)$ at the two ends of the calipers then gives $P(u)$. As the electron density is nearly zero between atoms and is high near atomic centers, the positions of peaks in $P(u)$ correspond to vectors between atoms; in other words, large values of $\rho(x)\rho(x + u)$ give large contributions to $P(u)$.

These equations may be extended to three dimensions, letting V_c = the volume of the unit cell, so that from the definition

$$P(u, v, w) = V_c \int_0^1 \int_0^1 \int_0^1 \rho(x, y, z)\rho(x + u, y + v, z + w)\, dx\, dy\, dz \tag{A8.7}$$

after substitution of values for ρ and integration, most terms are zero, leaving

$$P(u, v, w) = \frac{1}{V_c} \sum \sum \sum_{\text{all } h,k,l} |F(hkl)|^2 \exp[2\pi i(hu + kv + lw)] \tag{A8.8}$$

This equation can easily be reduced to Eqn. (A8.9),

$$P(u, v, w) = \frac{F^2(000)}{V_c} + \frac{2}{V_c} \sum_{h \geq 0} \sum_{\text{all } k,l} \sum_{\text{excluding } F^2(000)} |F|^2 \cos 2\pi(hu + kv + lw) \tag{A8.9}$$

by noting that $|F|^2(hkl) = |F|^2(\bar{h}\bar{k}\bar{l})$ and

$$e^{i\phi} = \cos\phi + i \sin\phi \tag{A8.10}$$

and then grouping Bragg reflections in pairs, hkl and $\bar{h}\bar{k}\bar{l}$. For every such pair, the value of ϕ for hkl is equal in magnitude and opposite in sign to that for $\bar{h}\bar{k}\bar{l}$ for each point u, v, w and thus, since $\cos\phi = \cos(-\phi)$ while $\sin\phi = -\sin(-\phi)$, the sine terms in the expansion of Eqn. (A8.8) cancel when summed over each of these pairs of Bragg reflections.

To summarize, the importance of the Patterson function is that peaks in it occur at points to which vectors from the origin correspond very closely in direction and magnitude with vectors between atoms in the crystal and that no preliminary assumptions are needed because $|F|^2$ values are independent of phase and can be derived directly from the measured intensities.

Appendix 9: Vectors in a Patterson map

A certain derivative of vitamin B_{12} crystallizes in the space group $P2_12_12_1$ and contains Co, Cl, O, N, C, and H, with atomic numbers 27, 17, 8, 7, 6, and 1, respectively.

(a) The expected approximate relative heights of typical peaks in the Patterson map are

Co–Co	27×27	729
Co–Cl	27×17	459
Cl–Cl	17×17	289
Co–O	27×8	216
Co–C	27×6	162
O–O	8×8	64
H–H	1×1	1

(This map will then be dominated by Co–Co and Co–Cl vectors unless there are accidental overlaps of other peaks.)

(b) Derivation of the coordinates of vectors between symmetry-related positions of any atom (for example, Co) in terms of its atomic position parameters:

(i) Atomic positions:
   (1) x, y, z
   (2) $\frac{1}{2} - x, -y, \frac{1}{2} + z$
   (3) $\frac{1}{2} + x, \frac{1}{2} - y, -z$
   (4) $-x, \frac{1}{2} + y, \frac{1}{2} - z$

(ii) Interatomic vectors between symmetry-related atoms are expected at the following positions, corresponding to the differences in coordinates of the various atomic positions:

$u = 0$	$v = 0$	$w = 0$	(position 1 to position 1)
$u = \frac{1}{2} - 2x$	$v = -2y$	$w = \frac{1}{2}$	(position 2 to position 1)
$u = \frac{1}{2}$	$v = \frac{1}{2} - 2y$	$w = -2z$	(position 3 to position 1)
$u = -2x$	$v = \frac{1}{2}$	$w = \frac{1}{2} - 2z$	(position 4 to position 1)

(The vector between any other positions—for example, 2 to 4 or 4 to 3—either is identical to one of these, or is related by a two-fold axis or by a center of symmetry at the origin. Every Patterson map is centrosymmetric.)

(c) The actual Patterson map for this crystal shows peaks at, among other positions:

u	v	w
0.00	0.00	0.00
± 0.20	± 0.32	0.50
0.50	± 0.18	± 0.20
± 0.30	0.50	± 0.30

(d) A comparison of these observed peak positions with the general expectations in (b) above shows that a consistent set of coordinates for the Co

atom is $x = 0.15$, $y = 0.16$, $z = 0.10$. (See Hodgkin et al. (1957), p. 228 and Hodgkin et al. (1959), p. 306.)

Appendix 10: Isomorphous replacement (centrosymmetric structure)

$$F_T = F_M + F_R$$

M = replaceable atom or group of atoms

R = the rest of the structure

If the position of M is known, then F_M is known. If two isomorphous crystals are studied, it is assumed that the position of the remainder of the structure is the same in each. Then, for one crystal,

$$F_T = F_M + F_R$$

while for the second one,

$$F_{T'} = F_{M'} + F_R$$

* See Glusker et al.(1963).

The experimentally obtained data* consist of $|F_T|$ and $|F_{T'}|$ derived from the measured intensities. F_M and $F_{M'}$ are computed from the positions of M and M', found by an analysis of the Patterson map. The signs of F_T and $F_{T'}$ may then be obtained, as illustrated in the following table.

h	k	l	$\|F_T\|$	$\|F_{T'}\|$	$F_{Rb} - F_K$ (calculated from known metal position)	Sign of F for Rb computed	Sign of F for K computed
			Rb salt	K salt			
0	1	1	16	20	+33	+	−
0	1	3	132	78	−59	−	−
0	2	1	63	70	−11	+	+
0	2	2	56	31	+29	+	+
0	4	0	102	50	+61	+	+
0	4	1	6	12	+17	+	−
0	5	2	9	16	+21	+	−
0	5	3	38	9	−50	−	+

For example, for the 0 1 1 Bragg reflection it is known, from computed values of F_{Rb} and F_K, that the difference is approximately +33 between F_T for the rubidium salt (for which the experimental value is ±16) and F_T for the potassium salt (for which the experimental value is ±20). This is only possible if F_{Rb} is +16 and F_K is −20, an experimental difference ($F_{Rb} - F_K$) of +36. For the 0 1 3

Bragg reflection, the calculated value of $(F_{Rb} - F_K)$ is -59 and the experimental values are ±132 for F_{Rb} and ±78 for F_K. This difference of -59 indicates that F_{Rb} is -132 and F_K is -78, an experimental difference of -54. Some phases may be ambiguous, in which case they must then be omitted.

Appendix 11: Diffraction data showing anomalous scattering

The following values of $|F|$ for five pairs of reflections hkl and $\bar{h}\bar{k}\bar{l}$ from a crystal of potassium dihydrogen isocitrate[**] (Figure 10.6b), measured with chromium radiation, show the effect of anomalous scattering as a result of the presence of potassium ions in the structure. With these data the effect was sufficiently large that the absolute configuration of the sample could easily be determined. The $|F_c|$ values given here were calculated for the absolute configuration of the dihydrogen isocitrate ion given in Figure 10.6b; for the enantiomorphous form, the corresponding values for hkl and $\bar{h}\bar{k}\bar{l}$ would be reversed.

The effect of anomalous scattering on the electron density calculation was discussed by A. L. Patterson (Patterson, 1963). He showed how to correct the value of F so that the effect is removed, and in so doing, demonstrated that to use $F(\bar{h}\bar{k}\bar{l})$ or $F(hkl)$ to compute electron density is not correct when anomalous scattering is appreciable:

$$|F_\pm|^2 = A^2 + B^2 + (\delta_1^2 + \delta_2^2)(A_d^2 + B_d^2)$$
$$+2\delta_1(AA_d + BB_d) - 2\sigma\delta_2(AB_d - BA_d) \qquad \text{(A11.1)}$$

where A and B are the components of the structure factors for the normally scattering atoms and A_d and B_d are those for the anomalously scattering atoms. σ has a value of $+1$ for $F(hkl)$ and -1 for $F(\bar{h}\bar{k}\bar{l})$. $\delta_1 = f_d'/f_d$ and $\delta_2 = f_d''/f_d$. As a result two quantities were defined:

$$S = \tfrac{1}{2}\{|F_+|^2 + |F_-|^2\} = A^2 + B^2 + 2\delta_1(AA_d + BB_d) + (\delta_1^2 + \delta_2^2)(A_d^2 + B_d^2) \qquad \text{(A11.2)}$$

$$D = \tfrac{1}{2}\{|F_+|^2 - |F_-|^2\} = -2\delta_1(AB_d - BA_d) \qquad \text{(A11.3)}$$

Thus the average of the intensities of Bijvoet-related pairs of reflections (hkl and $\bar{h}\bar{k}\bar{l}$) may be computed by Eqn. (A11.2) and the differences may be computed by Eqn. (A11.3), provided the structure is known. If the sign of D is wrong, then the structure model has the wrong absolute configuration.

The term that should be used in computing an electron density map is

$$|F|_0 = \{S - 2\delta_1(AA_d + BB_d) - (\delta_1^2 + \delta_2^2)(A_d^2 + B_d^2)\} \qquad \text{(A11.4)}$$

Thus it is best, if accurate electron density maps are required, to measure diffraction data far from the absorption edge of any atom in the structure. Data measured near an absorption edge can be used to establish the absolute configuration.

[**] See van der Helm et al. (1968), p. 578.

h	k	l	$|F_o|$	$|F_c|$
1	3	1	19.0	19.2
−1	−3	−1	22.9	23.7
1	3	2	6.4	6.6
−1	−3	−2	11.7	11.7
1	3	3	26.3	25.7
−1	−3	−3	20.7	20.0
4	5	2	7.2	7.0
−4	−5	−2	2.5	2.7
7	1	2	9.2	9.0
−7	−1	−2	13.1	12.9

Appendix 12: Molecular geometry

Transformation from fractional coordinates to Cartesian coordinates

The fractional coordinates of atomic positions, x, y, z in a unit cell of dimensions a, b, c, α, β, γ, may be expressed in Cartesian coordinates, X, Y, Z (in units of Å), as follows:

$$X = xa + yb \cos \gamma + zc \cos \beta$$

$$Y = yb \sin \gamma + z\{c(\cos \alpha - \cos \beta \cos \gamma)/ \sin \gamma\}$$

$$Z = zcW/ \sin \gamma$$

where

$$W = \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$$

The orientation of the Cartesian axes relative to the crystallographic axes is:

A parallel to $\mathbf{a}$;
B in the $\mathbf{a}$, $\mathbf{b}$ plane perpendicular to $\mathbf{a}$;
C perpendicular to A and B.

Interatomic distances

Distance A–B:

$$d_{\text{A-B}} = \sqrt{(X_\text{A} - X_\text{B})^2 + (Y_\text{A} - Y_\text{B})^2 + (Z_\text{A} - Z_\text{B})^2}$$

$$= \sqrt{\Delta X_{\text{A-B}}^2 + \Delta Y_{\text{A-B}}^2 + \Delta Z_{\text{A-B}}^2}$$

Interbond angles

$$\text{Angle A–B–C} = \arctan(\sqrt{1 - c_\text{A}^2}/c_\text{A})$$

where

$$c_\text{A} = -(\Delta X_{\text{A-B}}\Delta X_{\text{B-C}} + \Delta Y_{\text{A-B}}\Delta Y_{\text{B-C}} + \Delta Z_{\text{A-B}}\Delta Z_{\text{B-C}})/d_{\text{B-C}}d_{\text{A-B}}$$

Torsion angles

$$\text{Torsion angle A–B–C–D} = \arctan(s_\text{T}/c_\text{T})$$

where

$$s_T = (\Delta X_{AB} v_1 + \Delta Y_{AB} v_2 + \Delta Z_{AB} v_3)/d_{AB}$$

and

$$c_T = u_1 v_1 + u_2 v_2 + u_3 v_3$$

where

$$u_1 = (\Delta Y_{AB} \Delta Z_{BC} - \Delta Z_{AB} \Delta Y_{BC})/(d_{AB} d_{BC})$$
$$u_2 = (\Delta Z_{AB} \Delta X_{BC} - \Delta X_{AB} \Delta Z_{BC})/(d_{AB} d_{BC})$$
$$u_3 = (\Delta X_{AB} \Delta Y_{BC} - \Delta Y_{AB} \Delta X_{BC})/(d_{AB} d_{BC})$$
$$v_1 = (\Delta Y_{BC} \Delta Z_{CD} - \Delta Z_{BC} \Delta Y_{CD})/(d_{BC} d_{CD})$$
$$v_2 = (\Delta Z_{BC} \Delta X_{CD} - \Delta X_{BC} \Delta Z_{CD})/(d_{BC} d_{CD})$$
$$v_3 = (\Delta X_{BC} \Delta Y_{CD} - \Delta Y_{BC} \Delta X_{CD})/(d_{BC} d_{CD})$$

Glossary

Absent Bragg reflections. (See Unobserved Bragg reflections.)

Absolute configuration. The structure of a crystal or molecule expressed in an absolute frame of reference. The configuration of a molecule or crystal is the relationship in space of the atoms within it. It is generally defined by atomic coordinates (see Atomic parameters) with respect to three independent axes, each of which has directionality; these axes provide an absolute frame of reference. Absolute configuration describes a real-space relationship and gives the actual three-dimensional structure as one would see it if it were lifted out of the viewing screen; we can immediately see it is "left handed" or "right handed." Bijvoet and co-workers, in 1951, used the difference between $I(hkl)$ and $I(\bar{h}\bar{k}\bar{l})$ for zirconium radiation in crystals showing anomalous scattering by rubidium ions to determine the absolute configuration of sodium rubidium (+)-tartrate.

Absolute scale, scale factor. Structure amplitudes are on an absolute scale when they are expressed relative to the amplitude of scattering by a single classical point electron under the same conditions. A scale factor is required to convert measured structure amplitudes (from experiment) to absolute values. This scale factor is generally found from a Wilson plot (q.v.) or by comparison with calculated values for a model structure.

Absorption correction. (See Linear absorption coefficient.)

Absorption edge. At absorption edges the plot of absorption versus X-ray wavelength shows an abrupt drop and then rises again. These sharp discontinuities, called absorption edges, occur at energies at which the incident X rays can excite a bound electron in a particular atom to a higher vacant orbital or can eject it altogether. The inner-shell vacancy left by this electron is then filled by another electron falling from an outer shell. The energy (and hence wavelength) of this process depends on the difference in energy of the levels that this second electron has moved between.

Accuracy. Deviation of a measurement from the value accepted as true (cf. Precision).

Amorphous solid. A material without a real or apparent crystalline nature; it contains no long-range ordering of atoms. Many substances that appear superficially to be amorphous may, in fact, be composed of many tiny crystals.

Amplitude. The height of a wave measured from its mean value. For a vertically symmetric wave (such as a sinusoidal wave), it is half the peak-to-valley (maximum to minimum) displacement. The square of the amplitude gives a measure of the intensity of the wave.

Angle of incidence. The angle that a ray of light that is impacting on a surface makes with a line perpendicular to (i.e., normal to) the surface at the point of incidence. The Bragg angle, θ, which is half the angle between the direct beam and a diffracted beam, is the complement of this, and the angle of incidence is $(90° - \theta)$.

Angle of reflection. The angle between a ray that is reflected by a surface and the normal to the surface at the point of reflection. (See Angle of incidence.)

Ångström unit. The unit of length used in crystal structure analyses, named after Anders J. Ångström, a Swedish spectroscopist. $1\,\text{Å} = 10^{-10}\,\text{m} = 10^{-8}\,\text{cm} = 10^{-7}\,\text{mm} = 10^{-4}\,\mu\text{m} = 0.1\,\text{nm} = 100\,\text{pm}$.

Anisotropic. Exhibiting physical properties that are non-spherical, that is, have different values when measured along axes with different directions.

Anomalous dispersion. "Dispersion" is the passage of light through a medium, such as glass in a prism or a crystal, so that the light is separated into its component parts, that is, beams of different (rainbow) colors. The refractive index of a material is the ratio of the velocity of light *in vacuo* to its velocity when it passes through this medium. Blue light (which is shorter in wavelength than red light and which has a larger refractive index than does red light) is bent more than red light when it enters a medium. This is "normal dispersion." If, however, the

wavelength of the light (or X rays) is near an absorption edge (q.v.) of one type of atom in the structure, there will be a large discontinuity in the curve of refractive index against wavelength. In a plot of wavelength versus refractive index the refractive index increases with wavelength and blue light is less refracted than red, the opposite of normal expectation. This is called "anomalous dispersion." All atoms scatter anomalously to some extent, but when the wavelength is near the absorption edge of a scattering atom, anomalous dispersion will be especially strong. It will cause a phase change on scattering other than the normal value of $180°$, and diffraction data will not obey Friedel's Law (q.v). In noncentrosymmetric crystals intensities of pairs of Bragg reflections $I(hkl)$ and $I(\bar{h}\bar{k}\bar{l})$, normally the same, will be different if a strong anomalous scatterer is present. These intensity differences can be used to determine the absolute configuration (q.v.) of the crystal and its constituent molecules.

Anomalous scattering. An effect caused by high absorption at wavelengths near an absorption edge (q.v.). In noncentrosymmetric crystals, Bragg reflections hkl and $\bar{h}\bar{k}\bar{l}$ from opposite faces (that is, in directions at $180°$ to one another) are caused to have different intensities, contrary to the requirement of Friedel's Law (q.v.). These differences in intensity ($I(hkl)$ versus $I(\bar{h}\bar{k}\bar{l})$) may be used to determine the absolute configuration (q.v.) of chiral crystals (see Anomalous dispersion).

Area detector. An electronic device, such as a charge-coupled device (q.v.), for measuring the intensities of a large number of Bragg reflections at one time. It gives information on the intensity and direction of each Bragg reflection and is equivalent to electronic film.

Asymmetric unit. The smallest portion of a crystal structure from which the entire structure can be generated from the space-group symmetry operations (including translations). The asymmetric unit may consist of part of a molecule, a whole molecule, or all or part of several molecules not related by crystallographic symmetry.

Atomic displacement parameters, displacement parameters. Displacements of atoms in the unit cell from their equilibrium positions as a result of atomic vibration or disorder. Because static displacements from one unit cell to another will simulate vibrations of an atom, the term "displacement parameters" is used unless it is clear that the displacements are caused by temperature effects only, and not by static disorder.

Atomic parameters or atomic coordinates. A set of numbers that specifies the position of an atom in a crystal structure with respect to a selected coordinate system, usually the crystal axes, and the extent of its vibration and disorder from unit cell to unit cell. Atomic coordinates are generally expressed as dimensionless quantities x, y, z (fractions of unit-cell edges, measured in directions parallel to these edges), but sometimes as lengths (with dimensions), with respect to either the axial directions of the crystal or an orthogonal Cartesian coordinate system (q.v.). Additional parameters include thermal or displacement parameters (one parameter if isotropic, six if anisotropic), and, for disordered structures, parameters that define the atomic occupancy factors.

Atomic scattering factor, scattering factor, form factor. The scattering power of an atom for X rays, f_i, is defined relative to the scattering of X rays by a single electron under the same conditions. It depends on the number of electrons in the atom (approximately the atomic number) and the angle of scattering 2θ. This scattering power, which is for an atom at rest, not vibrating, falls off as the scattering angle increases. By contrast, for neutron scattering this reduction in scattering power at higher scattering angles does not occur, because the scattering object, the atomic nucleus, is so small. Atomic scattering factors can be computed, usually as a function of the scattering angle, from theoretical wave functions for free atoms (neutral or charged). They are modified by anomalous scattering (q.v.), which occurs to some extent at all wavelengths. The value f_i is replaced by $f_i + f'_i + i f''_i$ (see Chapter 10). The effect is largest if the incident-beam wavelength is near an absorption edge of the scattering atom; at most other wavelengths it is often ignored.

Automated diffractometer. A computer-controlled instrument that automatically measures and records the intensities of the Bragg reflections. It may measure Bragg reflections sequentially or may have a detector that can measure large numbers of reflections at the same time. For sequential measurement, the mutual orientations of the crystal and of the detector with respect to the source of radiation are assessed by computer from some initial diffraction data on some 20–30 selected Bragg reflections. The computer then provides an orientation matrix that specifies the orientation of the crystal and detector with respect to the X-ray beam. Electromechanical devices under computer control then drive the gears that move the crystal orienter and detector to the desired angular settings for each Bragg reflection in turn, and scan and measure the intensity and scattering angle for each $I(hkl)$; they also open and close the X-ray shutter. The newer technology now involves the use of area detectors to record large numbers of Bragg reflections simultaneously through a continuum of angular rotations, while

the data are evaluated during the collection of the data or processed at a later time.

Avogadro's number. Named after Amedeo Avogadro, who, in 1811, proposed that equal volumes of all gases at the same pressure and temperature contain the same number of molecules. Avogadro's number is the number of molecules in a gram molecule of material (its molecular weight in grams), 6.022×10^{23} per mol.

Axial lengths and angles. These are the unit-cell lengths and angles, $a, b, c, \alpha, \beta, \gamma$. They are generally reported in Å and degrees.

Axial ratios. The ratios of the axial lengths, customarily expressed with the value of b equal to unity. These ratios may be deduced from measurements of the angles between faces on a crystal, and are useful in identifying the composition of crystals.

Axis of rotation or axis of symmetry, rotation axis. When an object can be rotated by $(360/n)°$ about an axis passing through it, and, as a result, give an object indistinguishable from the first, then the original object is said to possess an n-fold axis of rotation.

Azimuthal scan. The azimuth of a line is the angle between the vertical plane containing the line and the plane of the meridian. If you stood at the center of the earth, the north pole would be at an azimuthal angle of $0°$, and, measuring angles clockwise from the meridian (longitude through Greenwich), east at $90°$, south at $180°$, and west at $270°$. An azimuthal scan (also called a psi-scan or ψ-scan) of diffraction data is measured as the crystal rotates about the diffraction vector (q.v.). This scan is used to make an empirical absorption correction (q.v.) and to avoid possible errors due to double reflections (q.v.).

Bessel function. Bessel's differential equation arises in numerous problems, especially in polar and cylindrical coordinates. The solutions of this equation are called Bessel functions, named for Friedrich Bessel, a German mathematician and astronomer. These functions, which give graphs that look like damped cosine or sine waves, are available in computer mathematics libraries. They are used for structures that are best defined by polar or cylindrical coordinates, such as nucleic acids. They also appear in the probability theory that underlies direct methods.

Best plane. The plane through a group of atoms that satisfies the least-squares (see Method of least squares) criterion of planarity.

Bijvoet differences. In 1951 Johannes Martin Bijvoet and fellow crystallographers in the Netherlands demonstrated that it is experimentally possible to determine the absolute configuration of an optically active molecule in the crystalline state from the effects of anomalous dispersion. They showed that this information is available in the differences in intensity between Bragg reflections $I(hkl)$ and $I(\bar{h}\bar{k}\bar{l})$ when the incident X rays have a wavelength near the absorption edge (q.v.) of at least one (but not all) of the atoms in the asymmetric unit of the crystal.

Birefringence. Double refraction, that is, the separation of a ray of light on passing through a crystal into two unequally refracted, plane-polarized rays of orthogonal polarizations; these are called the "ordinary ray," which obeys the normal laws of refraction, and the "extraordinary ray," which does not. This effect occurs in crystals in which the velocity of light is not the same in all directions; that is, the refractive index is anisotropic. Uniaxial crystals, such as calcite or quartz, have one direction (the anisotropy axis or optic axis) along which double refraction does not occur, and are characterized by two refractive indices; biaxial crystals have two such axes of anisotropy and three refractive indices.

Body-centered unit cell. A unit cell having a lattice point at its center ($x = y = z = \frac{1}{2}$) as well as at each corner ($x = y = z = 0$ or 1).

Bragg. Father, William Henry Bragg, pioneered instrumental methods for measuring X-ray diffraction patterns. Son, William Lawrence Bragg, developed methods for analyzing the experimental data in terms of the atomic structure of the crystal. They shared the Nobel Prize in Physics in 1915 (W. L. Bragg then being only 25 years old).

Bragg reflection, reflection. Since diffraction by a crystal may be considered as reflection from a set of lattice planes (a view suggested by William Lawrence Bragg), the term "Bragg reflection" has come to be used to denote a diffracted beam. While this is correct, the term "reflection" (without the "Bragg") is also used. The more definitive term "Bragg reflection" is used in this book.

Bragg's Law or Bragg equation. Each diffracted beam is considered as a "Bragg reflection" from a family of parallel lattice planes, hkl. If the angle between the nth order of diffraction of X rays, wavelength λ, and the normal (perpendicular) to a set of crystal lattice planes is $(90° - \theta_{hkl})$, and the perpendicular spacing between successive lattice planes is d_{hkl}, then

$$n\lambda = 2d_{hkl} \sin \theta_{hkl} \quad \text{Bragg's Law}$$

When X rays strike a crystal *they will be diffracted when, and only when, this equation is satisfied*. With this equation, W. L. Bragg first identified the integers h, k, and l of the

Laue equations with the Miller indices of the lattice planes that cause that Bragg reflection.

Bravais lattice. One of the 14 possible arrays of points repeated periodically in three-dimensional space such that the arrangement of points surrounding any one of the points is identical in every respect to that surrounding any other point in the array. They are obtained by combining the seven crystal systems (q.v.) with one of the lattice centerings, that is, P = primitive, I = body-centered, F = face-centered, and A, B, or C = single-face-centered, and eliminating equivalent results (giving 14 rather than 42 Bravais lattices). They were studied by Auguste Bravais.

Bremsstrahlung. X rays (specifically "braking radiation") that are produced when accelerated electrons are suddenly decelerated by a collision with the electrical field of an atom in the metal target of an X-ray tube. This radiation has a continuous spectrum with respect to wavelength, and is generally considered background to characteristic X rays (q.v.).

Calculated phase angle or calculated phase. The phase angle, $\alpha(hkl)$, relative to a chosen origin, computed from the atomic positions (x, y, z) of a model structure. The equations that lead to its value are as follows:

$$A(hkl) = \Sigma f \cos 2\pi(hx + ky + lz) \text{ and}$$

$$B(hkl) = \Sigma f \sin 2\pi(hx + ky + lz) \text{ and}$$

$$F(hkl) = A(hkl) + iB(hkl) \text{ and}$$

$$|F(hkl)|^2 = [A(hkl)]^2 + [B(hkl)]^2$$

$$\alpha(hkl) = \tan^{-1}[B(hkl)/A(hkl)]$$

where f includes the scattering factor and displacement factor of the atom and each summation is over all atoms in the unit cell.

Cartesian coordinate system. The three-dimensional position of a point (x, y, and z) can be located by reference to three orthogonal (mutually perpendicular) axes with units of equal length (e.g., Å or cm) along these axes. The location is defined by distances from an origin, measured parallel to these axes. (Named after René Descartes, the mathematician and philosopher.)

Cauchy–Schwarz inequality. The square of the sum of the products of two variables (a and b here) for a particular range of values is less than or equal to the product of the sums of the squares of these two variables for the same range of values:

$$|\Sigma ab|^2 \leq \{|\Sigma a^2| \, |\Sigma b^2|\}$$

In this equation each sum Σ is over the same range, e.g., from 1 to N. This equation, the result of studies by Augustin Louis Cauchy, Viktor Yakovlevich Bunyakovsky, and Karl Hermann Amandus Schwarz, is used in direct methods of phase determination (see Chapter 8).

Center of symmetry or center of inversion. A point through which an inversion operation is performed, converting an object at x, y, z into its enantiomorph at $-x$, $-y$, $-z$ if the center of inversion is at 0, 0, 0 (see Inversion).

Centrosymmetric crystal structure. A crystal structure for which the space group, and therefore the arrangement of atoms, contains a center of symmetry. When the unit-cell origin is chosen at the center of symmetry, the phase angle for each Bragg reflection is either 0° or 180°.

Characteristic X rays. X rays of definite wavelength, characteristic of the target (generally a metal) and produced when that target is bombarded by fast electrons. Characteristic X rays are emitted when an electron that has been displaced from an inner shell of the atom being excited (an atom in the target material) is replaced by another electron that falls in from an outer shell. This gives radiation of a wavelength corresponding to the difference in the energies of the two shells in the target atom.

Charge-coupled device area detector, position-sensitive detector. A position-sensitive electronic device for measuring the intensities of a large number of diffracted intensities at one time. It gives information on the direction (exact point of impact on the detector) and intensity of each diffracted beam and behaves like electronic film. It is a photoelectric radiation sensor that acts, when hit by a photon, by generating electron–hole pairs. The electric charges so formed, which are proportional to the radiation intensity at that point in space, are collected in pixels (picture elements) formed by an array of gates, and transferred by application of a differential voltage across the gates.

Chiral. A chiral object or structure cannot be superimposed (with complete equivalence) upon its mirror image (Greek: *cheir* = hand). Left and right hands provide excellent examples of chiral objects.

Chi-square. The sum of the quotients obtained from the square of the difference between the observed (x_i) and mean or averaged ($\langle x \rangle$) values of a quantity when divided by the square of its standard uncertainty (s.u.), $\sigma(x_i)$. The relationship is $\chi^2 = \{\Sigma(x_i - \langle x \rangle)^2\}/\sigma(x_i)^2$.

Chi-square test. A test for the mathematical fit of the distribution of chi-square to a standard frequency

distribution. This gives the likelihood that an observed distribution arose from fluctuations of random sampling rather than from systematic error. Tables of probability values (likelihoods) are available.

Cleavage. The property of many crystals of splitting readily (usually upon impact) in one or more definite directions to give smooth surfaces, always parallel to actual or possible crystal faces.

Coherent scattering. Scattering in which the incoming radiation interacts with all the scatterers in a coordinated manner so that the scattered waves have definite relative phases and can interfere with each other. The energy of the scattered photon is the same as that of the incident photon. (See also Incoherent scattering.)

Collimator. A device for producing a parallel beam of radiation.

Complex number. An expression of the form $a + ib$, where a and b are real numbers and $i = \sqrt{-1}$. The word "complex" here implies that the number is composed of two or more separable parts, that is, a and ib.

Configuration. The configuration of a molecule consists of the relationships in space of the atoms within it.

Conformation. One of the likely shapes of a molecule. Generally applied to molecules for which there is a possibility for rotation about bonds. Different rotational positions about bonds are represented by torsion angles (q.v.).

Constraints. Constraints are limits on the values that parameters in a least-squares refinement may take. They reduce the number of parameters and are mathematically rigid with no standard uncertainty. A common constraint is a reduction in the number of parameters defining a group of atoms that is being refined. This simplifies the refinement. For example, a benzene ring may be constrained to six parameters, three defining position and three defining orientation in the unit cell. Atoms in special positions may also need to be constrained so that they do not move during refinement. Constraints remove parameters and restraints add data. (Think of a dog constrained in a cage in which he fits tightly and is not able to move.) (See Restraints.)

Contact goniometer. A device for measuring angles between faces of a crystal by making direct contact with the crystal faces with two straight edges and then measuring the angle between these straight edges.

Contour map. In crystal structure analysis, this is a map showing electron or nuclear density by means of contour lines drawn at regular intervals. It resembles a topographic map, with peaks representing areas of high electron or nuclear density. The map is drawn with contour lines at regular intervals of electron or nuclear density. (See Electron-density map.)

Convolution. One mathematical function folded with another. To calculate the convolution of the plots of two mathematical functions, we set the origin of the plot of the first function in turn on every point of the plot of the second function, multiply the value of the first function in each position by the value of the second at that point, and then the results are added together for all such possible operations. For two functions $A(x, y, z)$ and $B(x, y, z)$, the convolution of A and B at the point (u_0, v_0, w_0) is

$$c(u_0, v_0, w_0) =$$

$$\int\int\limits_{-\infty}^{+\infty}\int A(x, y, z)B(x + u_0, y + v_0, z + w_0)\,dx\,dy\,dz$$

Note that a crystal structure is the convolution of a crystal lattice and the contents of one unit cell.

Correlation of parameters. The extent to which two mathematical variables, such as atomic parameters, are dependent on each other. For example, position parameters of an atom that has been refined by least squares in an oblique coordinate system are correlated to an extent that is dependent upon the cosine of the interaxial angle. Parameters related by crystallographic symmetry are completely correlated. Displacement occupancy factors are often highly correlated, and this may be evident in the output of a least-squares refinement.

Crystal. A solid that contains a very high degree of long-range three-dimensional internal order of the component atoms, molecules, or ions.

Crystal class. (See Crystallographic point group.)

Crystal lattice. Crystals are solids composed of groups of atoms repeated at regular intervals in three dimensions with the same orientation. If each such group of atoms is replaced by a representative point, the collection of points so formed provides the space lattice, or crystal lattice. The meaning is specific for this arrangement of points, and the term "lattice" should not be used to denote the entire atomic arrangement.

Crystal morphology. (See Morphology.)

Crystal structure. The mutual arrangement of the atoms, molecules, or ions that are packed together in a regular way (on a crystal lattice) to form a crystal.

Crystal system. There are seven crystal systems, best classified in terms of their symmetry. They are: triclinic, monoclinic, orthorhombic, tetragonal, cubic, trigonal, and hexagonal. As a result of their symmetries they lead to the seven fundamental shapes for unit cells consistent with the 14 Bravais lattices (q.v.).

Crystallographic point group, crystal class. A point group is a group of symmetry operations that leave at least one point unmoved within an object when the symmetry operation is carried out. There are 32 crystallographic point groups (crystal classes) that contain rotation and rotatory-inversion axes ($n = 1, 2, 3, 4, 6$). The crystallographic point groups characterize the external symmetry of well-formed crystals.

Cubic unit cell. A unit cell in which there are threefold rotation axes along all four body diagonals. All axial lengths are therefore identical by symmetry, and all interaxial angles must be $90°$ ($a = b = c$, $\alpha = \beta = \gamma = 90°$).

Data reduction. Conversion of measured intensities, $I(hkl)$, to structure amplitudes $|F(hkl)|$ or to $|F^2(hkl)|$, by application of various factors including Lorentz, polarization, and absorption corrections (q.v.).

Database. A collection of data on a particular subject, such as atomic coordinates from crystal structure determinations. These data are readily retrievable by computer.

Defect. A crystal lattice imperfection. This may be due to impurities. A point defect is a vacancy or an interstitial atom. A line defect is a dislocation in the crystal lattice.

Deformation density. The difference between the experimental electron density in a molecule (with all its distortions as a result of chemical bonding) and the promolecule density (q.v.) (a model of the molecule with a spherical electron density around each isolated free atom). The deformation-density map contains information on chemical bonding, although this information is modified by errors in the phases and the measured intensities of the Bragg reflections and inadequacies in the calculated scattering factors of free atoms.

Deliquescence. The property that some crystals have of attracting and absorbing moisture from the surrounding atmosphere and dissolving gradually, eventually becoming a solution.

Density modification, solvent flattening. A computational method for improving phases, particularly when a unit cell contains a high proportion of solvent as do macromolecular crystals. When an electron-density map is calculated with $|F(hkl)|$ and an initial set of possible

relative phases, the map will probably be noisy if the relative phases are not very good. However, the outline of an "envelope," the protein–solvent boundary, may be evident. The overall density of atoms in aqueous areas of the crystal (involving oxygen–oxygen distances near 2.7 Å) is lower than in the interior of the molecule (involving C–C, C–O, and C–N distances near 1.4 Å). An "envelope" defining the approximate boundary of the molecule is determined from the electron-density map. All of the electron density outside this envelope, that is, the electron density in the solvent area, is then set to a single low value (the average for disordered water) and a new set of phases is then determined by Fourier inversion of this "solvent-flattened" map. The process is used to improve the phases and may be repeated, if necessary.

Difference synthesis or difference map. A Fourier map for which the input Fourier coefficients are the differences between measured structure factors and those calculated from a proposed structural model. Such a map will have peaks at positions in which there is not enough electron density in the trial structure, and troughs where too much is included. It is an exceedingly valuable tool both for locating missing atoms and for correcting the positions of those already present in the trial structure.

Differential synthesis. A method of refining parameters of an atom from a mathematical consideration of the slope and curvature of the difference synthesis (q.v.) in the region of each atom.

Diffraction. When radiation passes by the edges of an opaque object or through a narrow slit, the waves appear to be deflected and they produce fringes of parallel light and dark bands. This effect may best be explained as the interference of secondary waves generated in the area of the slit or the opaque object. These secondary waves, so generated, interfere with one another, and the intensity of the beam in a given direction is determined by a superposition of all the wavelets in that direction. When light passes through a narrow slit all the waves will be in phase in the forward direction. In any other direction, each secondary wave traveling in a given direction will be slightly out of phase with its neighbors by an amount that depends on the wavelength of the light and the angle of deviation from the direct beam. The shorter the wavelength, the more a wave is out of phase with its neighbor. In X-ray crystallography, the radiation is X rays and the slit is replaced by the electron clouds of atoms in a crystal which scatter the X rays. Because the crystal contains a regularly repeating atomic arrangement, the beams diffracted from one unit cell may be in phase with those from other unit cells and can reinforce each other to

produce a strong diffracted beam. The scattering from the arrangement of atoms within the unit cell will modify the intensities of these beams.

Diffraction grating. A series of close, equidistant parallel lines, usually ruled on a polished surface. Because of the regularity of the ruled lines, this grating can be used to produce diffraction spectra.

Diffraction pattern. The intensity pattern obtained when radiation is diffracted by an object that has a regular spacing with similar dimensions to that of the wavelength of the radiation.

Diffraction plane. The plane containing the incident beam, the location point of diffraction by the crystal, and the diffracted beam.

Diffraction symmetry. Symmetry in the intensities of Bragg reflections with indices (hkl) related by a change of sign (e.g., $-h$, $-k$, $-l$) or permutation (k, l, h). The diffraction symmetry must adhere exactly to one of the Laue groups; a small difference from Laue group symmetry is allowed when anomalous-dispersion effects are present.

Diffraction vector. A vector perpendicular to the lattice planes hkl causing a Bragg reflection. This vector bisects the directions of the incident and diffracted beams and lies in their plane. (See Diffraction plane.)

Diffractometer. An instrument for measuring the directions and intensities of Bragg reflections in the diffraction pattern of a crystal (see Automated diffractometer). For serial measurements, the required orientations of the crystal and detector with respect to the X-ray source are computed from initial data on some Bragg reflections. The orientations necessary for the measurement of all of the diffraction data are achieved by computer-directed commands to electromechanical devices that position the components of the instrument at the required settings. Alternatively, an area detector may be used that can measure many Bragg reflections at one time.

Diffuse scattering. Halos or streaks that appear around or between intense Bragg reflections and indicate the presence of disorder in the structure (static disorder), or high thermal motion of atoms (dynamic disorder).

Dihedral angle. The dihedral angle between two planes is the angle between the planes, often defined (with the same result) as the angle between the normals (perpendiculars) to these planes. If the planes, with an angle θ between them, have equations

$$a_1x + b_1y + c_1z + d_1 = 0 \text{ and } a_2x + b_2y + c_2z + d_2 = 0$$

then

$$\cos \theta = \frac{a_1a_2 + b_1b_2 + c_1c_2}{\sqrt{(a_1^2 + b_1^2 + c_1^2)(a_2^2 + b_2^2 + c_2^2)}}$$

Direct methods or direct phase determination. A method of deriving phases of Bragg reflections by consideration of probability relationships among the phases of the more prominent Bragg reflections. These relationships come from the conditions that the structure is composed of atoms (giving independent, isolated peaks in the electron-density map) and that the electron density must be positive or zero everywhere (not negative). Only specific values for the relative phases of Bragg reflections are consistent with these conditions.

Direct space. There are two types of lattices important in crystallography: the crystal lattice, commonly called the direct lattice, and the reciprocal lattice. Each of these two lattices can be thought of as existing in a space defined by its coordinate system. Direct space is the space where the atoms of the crystal structure reside. Reciprocal space is the space where the diffraction intensities reside.

Discrepancy index. (See *R* value.)

Dislocation. A discontinuity in the otherwise regularly periodic three-dimensional structure of a crystal resulting in a defect, often an imperfect alignment between lattice rows. There are two common varieties of dislocations: edge and screw dislocations. Edge dislocations form where only part of one plane of atoms or molecules exists in the crystal and, because atoms or molecules are missing, causes stress as a result of distortions of nearby planes. These dislocations can move through the crystal as a result of shear stress applied perpendicular to the dislocation line. On the other hand, screw dislocations also have a dislocation line, but a helical path is formed around it. This dislocation involves a displacement of rows of atoms or molecules along a plane.

Disordered crystal structure. Lack of regularity in the internal arrangement within a crystalline material. For example, there may not be an exact register of the contents of one unit cell with those of all others. Such disorder may be revealed by large displacement parameters in the least-squares refinement or by the presence of diffuse scattering, either as halos or streaks, around intense Bragg reflections.

Dispersion. Variation, as a function of wavelength, in the velocity of light in a material (such as a crystal) and hence variation in the refractive index (q.v.) of the medium. For example, the spreading of white radiation by a prism or

grating into a colored (rainbow-type) beam is due to dispersion of light. The variation of velocity with wavelength is usually smooth, but at strongly absorbed wavelengths of the incident radiation the curve may be discontinuous, leading to anomalous dispersion (q.v.).

Displacement parameters. (See Atomic displacement parameters.)

Distribution of intensities, intensity distribution. The number of intensities in selected ranges of the diffraction pattern and their overall variation. Intensities from a noncentrosymmetric crystal tend to be clustered more tightly around their mean value than do those from a centrosymmetric one. This forms the basis for one test for the presence or absence of a center of symmetry in the crystal.

Domain. A small region of a crystal containing a completely oriented structure.

Double reflection. X rays that are diffracted by one set of lattice planes may then be diffracted by another set of planes that, by chance, are in exactly the right orientation for this. The twice-reflected resultant beam emerges in a direction that corresponds to a single Bragg reflection from a third set of planes, whose Miller indices are the sums of the indices of the two sets of planes producing the Bragg reflection. This double reflection that is, by chance, traveling in the same direction as an original singly diffracted beam will enhance or weaken the intensity of the latter. The effect may even cause an ambiguity in the space group determination if a systematically absent Bragg reflection gains intensity by it. It can generally be eliminated by reorienting the crystal or by changing the wavelength of the incident X rays. The effect is also called the "Renninger effect" after its discoverer, Moritz Renninger.

Dynamical diffraction. Diffraction theory in which the modification of the primary beam on passage through the crystal is important. The mutual interactions of the incident and scattered beams are taken into account. This is important for perfect crystals and for electron diffraction by crystals.

E-map. A Fourier map (equivalent to an electron-density map) with phases derived by "direct methods" and normalized structure factors (q.v.) $|E(hkl)|$, replacing $|F(hkl)|$ in the Fourier summation. Since the $|E(hkl)|$ values correspond to sharpened atoms (with no fall-off as a function of $\sin\theta/\lambda$), the peaks on the resulting map are more easy to identify than those in an electron-density map computed with $|F(hkl)|$ values.

E-values. (See Normalized structure factors.)

Efflorescence. A change in the surface of a crystal that results in a powder as a result of loss of water (or some other solvent) of crystallization on exposure to air.

Elastic scattering. When radiation is scattered elastically, there is no exchange of energy or momentum between the incoming radiation and the scatterer, so that there is no change in wavelength between the incident (incoming) and scattered (outgoing) radiation. This is the type of scattering described in this book.

Electron density. The number of electrons per unit volume (usually per cubic Å).

Electron-density map. A representation of the electron density at various points in a crystal structure. Electron density is expressed as the concentration of electrons per unit volume (in electrons per cubic Å) and is highest near atomic centers. The map is calculated using a Fourier synthesis—that is, a summation of waves of known amplitude, frequency, and relative phase. The input consists of $|F(hkl)|$ and $\alpha(hkl)$. The three-dimensional map can be viewed and manipulated on a computer screen. Summation of the electron-density values (in electrons per cubic Å) over the volume expected to be occupied by one atom will give the atomic number (the total number of electrons in that volume) of the peak; this calculation, however, depends on good scaling and a near-perfect model.

Enantiomorph. A molecule or crystal that is not identical to its mirror image when superimposed on it.

Epitaxy. The oriented overgrowth of one crystalline material on the surface of another. Generally there is some match of periodicity between the two.

Epsilon factor, ε. This is a factor used in computing normalized structure factors (E-values, q.v.) that takes into account the fact that, depending on which of the 230 space groups the crystal belongs to, there may be certain groups of Bragg reflections in areas of the reciprocal lattice that will have an average intensity greater than that for the general Bragg reflections. The ε factor is used to correct for these differences.

Equivalent positions. The complete set of atomic positions produced by the operation of the symmetry elements of the space group upon any general position, x, y, z, in the unit cell.

Equivalent reflections. There are eight measurements for each h, k, l, of each Bragg reflection corresponding to combinations of positive or negative values of each h, k, l. Those that are equivalent by the symmetry of the crystal have (within experimental error) identical intensities. For high-symmetry crystals, other Bragg reflections

may also be equivalent, e.g., *hkl*, *klh*, and *lhk* for cubic crystals. In the absence of anomalous dispersion (q.v.), $|F(hkl)| = |F(\bar{h}\bar{k}\bar{l})|$.

Estimated standard deviation. (See Standard uncertainty.)

Euler's formula. $e^{i\theta} = \cos\theta + i\sin\theta$.

Eulerian angles. The three successive angles of rotation needed to transform one set of Cartesian coordinates into another or describe the orientation of a rigid body in terms of a defined set of axes. They are named after the Swiss mathematician Leonhard Euler.

Ewald sphere, sphere of reflection. A geometric construction for considering conditions for diffraction by a crystal in terms of its reciprocal lattice rather than its direct (real) crystal lattice. It is a sphere, of radius $1/\lambda$ (for a reciprocal lattice with dimensions $d^* = \lambda/d$), drawn with its diameter along the incident beam. The origin of the reciprocal lattice is positioned at the point at which the incident beam emerges from the Ewald sphere. The crystal (and its reciprocal lattice) can then be rotated. Whenever a reciprocal lattice point P touches the surface of the Ewald sphere, the conditions for a diffracted beam are satisfied. A Bragg reflection with the indices of that reciprocal lattice point P will result. Thus, for any orientation of the crystal relative to the incident beam, it is possible to predict which reciprocal lattice points, and thus which planes in the crystal, will be in a "reflecting position" (in the sense used by Bragg).

Extinction. An effect that reduces the intensity of a Bragg reflection to less than the expected value. This means that the X-ray beam has been weakened as it passes through the crystal. Extinction is evidenced by a tendency for $|F_o|$ to be systematically smaller than $|F_c|$ for very intense Bragg reflections. Primary extinction occurs when the incident beam passes through a single block of a perfect crystal. Part of the beam may be reflected twice so that it returns to its original direction but is out of phase with the main beam, thus reducing the intensity of the latter. However, when a crystal has a mosaic structure (q.v.), part of the incident beam will be diffracted by one mosaic block and therefore may not be available for diffraction by a following block. As a result the second block contributes less than expected to the diffracted beam. This is called secondary extinction. Extinction of this kind can sometimes be reduced by dipping the crystal in liquid nitrogen, thereby increasing its mosaicity.

Face-centered unit cell. A unit cell with a lattice point at the origin and at the center of a face. If all faces are centered, the designation is F; if only faces perpendicular to the *a* axis are centered, the description is A (in which case the face-centered atom lies in the *bc* plane). Analogous conditions pertain to B and C.

Faces of a crystal. The flat, smooth surfaces of a crystal that intersect with other faces giving sharp edges. They show symmetrical relationships that may reveal the point-group symmetry (see Point group) of the internal structure of the crystal.

Figure of merit. A numerical quantity used for indicating comparative effectiveness. In crystallographic studies it is used to indicate an estimate of the average precision in the selection of phase angles. It is particularly used in protein crystallography where phase angles are derived by isomorphous replacement methods.

Film scanner. A device for measuring the intensities of spots on an X-ray diffraction photograph. This is done by a light beam that is caused to scan the photograph systematically. The intensity of the beam transmitted through the film is recorded for each point on the film.

Filter. A semitransparent material that absorbs some or all of the radiation passing through it. It is possible to choose appropriate filters with different wavelength absorptivities to select a narrow wavelength range.

Focusing mirror system. Two bent metal mirrors that deflect the X-ray beam and produce a small, intense beam with a narrow angular divergence, a uniform beam profile, and a low background intensity. They are useful for experiments involving crystals with large unit cells.

Form factor. (See Atomic scattering factor.)

Fourier analysis. The breaking down of a periodic mathematical function into its component cosine and sine waves (harmonics), which have specific amplitudes and frequencies. The procedure was initiated by Jean Baptiste Joseph Fourier, a French mathematician and physicist.

Fourier map. A map computed for a periodic function by addition of waves of known amplitude, frequency, and relative phase. The term is generally used for an electron-density or difference electron-density map.

Fourier synthesis or Fourier series. A method of summing waves (such as scattered X rays) to obtain a periodic function (such as the representation of the electron density in a crystal). It is a mathematical function $f(t)$ that is periodic with a period T (so that $f(t + T) = f(t)$), and is represented by a sum of sine and cosine terms (an infinite

series) of the form

$$f(t) = a_0/2 + a_1 \cos 2\pi(t/T) + a_2 \cos 2\pi(2t/T)$$
$$+ \ldots + b_1 \sin 2\pi(t/T) + b_2 \sin 2\pi(2t/T) + \ldots$$

The Fourier theorem states that any periodic function may be resolved into cosine and sine terms involving known constants. Since a crystal has a periodically repeating internal structure, this can be represented, in a mathematically useful way, by a three-dimensional Fourier series, to give a three-dimensional electron-density map. In X-ray diffraction studies the magnitudes of the coefficients are derived from the intensities of the Bragg reflections; the periodicities of the terms are derived from the Miller indices h, k, l of the Bragg reflections, but the relative phases of the terms are rarely determined experimentally.

Fourier transform. A mathematical procedure used in crystallography to interrelate the electron density and the structure factors. In X-ray diffraction the structure factor, F, is related to the electron density, ρ, by

$$F = \int_{-\infty}^{\infty} \rho e^{i\phi} \, dV_c \text{ and, conversely, } \rho = (1/V_c) \, \Sigma \, F e^{-i\phi}$$

summing for all Bragg reflections. In these equations, $\phi = 2\pi(hx + ky + lz)$, and V_c is the volume of the unit cell. Summation replaces integration in the latter equation because the diffraction pattern of a crystal is observed only at discrete points. F is the Fourier transform of ρ, and ρ is the inverse Fourier transform (because of the negative sign) of F. (Note that $e^{ix} = \cos x + i \sin x$). See Glusker et al. (1994), p. 204, for a detailed worked-out example of a Fourier transform. Most such calculations are now done by computer.

Fractional coordinates. Coordinates of atoms expressed as fractions of the unit-cell lengths a, b, and c (see Atomic parameters).

Fraunhofer diffraction. Diffraction observed with parallel incident radiation, as in the diffraction by slits described in Chapter 3. Named after Joseph von Fraunhofer.

Friedel's Law. This law, named after Georges Friedel, states that $|F(hkl)|^2$ values of centrosymmetrically related Bragg reflections are equal (even for an acentric crystal structure): $|F(hkl)|^2 = |F(\bar{h}\bar{k}\bar{l})|^2$. This law holds only under conditions where anomalous scattering (q.v.) can be ignored.

Gaussian distribution. In many kinds of experiments repeated measurements follow a Gaussian or normal error distribution, which is a probability density function, named for Carl Friedrich Gauss, a German mathematician and scientist. It is a symmetrical bell-shaped curve of the form $y = A\exp(-x^2/B)$, where x is the deviation of a variable from its mean value and $\sigma^2 = B/2$ is its variance (the square of its standard uncertainty, s.u.). 68% of values lie within 1 s.u. of the mean, 95% lie within 2 s.u., and 99.7% within 3 s.u.

Geiger counter. A discharge tube filled with inert gas that can briefly conduct electricity if ions have been produced in the gas by ionizing radiation. The conduction is amplified by the gas tube and the amplified effect can then be detected electronically. This device, invented by Johannes (Hans) Wilhelm Geiger and improved with assistance from Walther Müller, can count radiation events but cannot provide the identities of the types of radiation being counted.

Glide plane. A glide plane involves reflection across the plane combined with translation in a direction parallel to the plane. It is designated by a, b, or c if the translation is, respectively, $a/2$, $b/2$, or $c/2$, by n if the translation is $(a + b)/2$, $(a + c)/2$, or $(b + c)/2$, i.e., halfway along one of the face diagonals, and by d if the translation is $(a + b)/4$, $(b + c)/4$, $(c + a)/4$, or $(a + b + c)/4$.

Goniometer. An instrument for measuring angles, such as those between the faces of a crystal. (See Contact goniometer and Reflecting goniometer.)

Goniometer head. A device for orienting (by movable arcs) and aligning (by translational motion) a crystal ready for diffraction studies. The crystal, mounted on the goniometer head, is adjusted so that it is always in the center of the collimated X-ray or neutron beam.

Group (mathematical). A collection or set of symmetry elements that obeys the following conditions. One element must be the identity element. The product of any two elements must also be an element. For every symmetry element in the group there must be another that is its inverse, so that when the two are multiplied together the identity element is obtained.

Habit of a crystal. The appearance of a crystal, as seen in the relative development of different faces.

Harker–Kasper inequalities, inequality relationships. Space-group-dependent inequalities among unitary structure factors (q.v.) that allow for the determination of the phases of certain intense Bragg reflections in a centrosymmetric crystal. These provided, in 1947, one of the earliest successful methods for solving the phase problem by direct methods. Named for David Harker and John Kasper.

Harker sections. Certain areas or projections of the Patterson map that contain many vectors between space-group-equivalent atoms. For example, if there are atoms at both x and $x + \frac{1}{2}$ then the Patterson map will contain information on them in the Harker section at $u = \frac{1}{2}$.

Heavy-atom derivative of a protein. The product of soaking a solution of a salt of a metal of high atomic number into a crystal of a protein. Many protein crystals contain aqueous channels that permit the interaction of a heavy-atom compound with functional groups of the protein. The heavy atom must be substituted in only one (or a few) ordered position(s) per molecule of protein, and the unmodified crystal and its heavy-atom derivative must be isomorphous. Then the isomorphous replacement method (q.v.) can be used to determine the phases of the Bragg reflections.

Heavy-atom method. A method of deriving phase angles in which the phases calculated from the position of a heavy atom are used to compute the first approximate electron-density map, from which further portions of the structure are recognizable as additional peaks in this map.

Hexagonal unit cell. A unit cell containing a six-fold rotation axis parallel to one axis (arbitrarily chosen as **c**) and also two-fold rotation axes perpendicular to **c**. These symmetry relations dictate that the lengths of a and b should be identical, that the angle between **a** and **b** is 120°, and that the other two angles are 90° ($a = b$, $\alpha = \beta = 90°$, $\gamma = 120°$).

Homometric structure. A crystal structure with a uniquely different arrangement of atoms from another crystal structure, but having the same sets of interatomic vectors, and hence the same Patterson map (see Patterson function).

Identity operation. A symmetry operation that leaves apparently totally unchanged anything upon which it operates.

Image plate. A detector surface that behaves like photographic film and can be used to store X-ray intensities as latent images in the form of color centers. The stored image is scanned by laser light to extract data. The image plate is erasable and can be used many times. It is more sensitive than photographic film and useful because intensities can be retrieved electronically.

Imperfect crystal. An ideally imperfect crystal is composed of small mosaic blocks that are small but are not precisely aligned with each other. An imperfect crystal ideally shows no primary and usually very little secondary extinction (see Extinction).

Improper symmetry operation, symmetry operation of the second kind. Any symmetry operation (q.v.) that converts a chiral object into its enantiomorph (that is, a right-handed object into a left-handed object). Such operations include mirror planes, glide planes, centers of symmetry, and rotation-inversion axes.

Incoherent scattering. Scattering in which the incoming radiation interacts independently with each scatterer. The scattered waves have random, unrelated phases.

Indices. Indices are used to describe the faces of a crystal and the orders of diffraction—that is, to refer to a specific crystal face or Bragg reflection (using indices h, k, l) (see Miller indices).

Inelastic scattering. With inelastic scattering of X rays by electrons or of neutrons by nuclei, there is an exchange of energy and momentum on impact, resulting in a small wavelength (energy) change for the X rays or neutrons.

Inequality. A mathematical statement that the value of one expression is not equal to the value of another expression. The expression that is greater is usually specified.

Inequality relationships. (See Harker–Kasper inequalities.)

Integrated intensity. The total intensity measured at the detector as a Bragg reflection is scanned. The intensity may be scanned over one, two, or three dimensions.

Intensity distribution. (See Distribution of intensities.)

Interference. The mutual effect of two waves traveling in the same direction on each other. If one wave is in phase with another, the second wave enhances the intensity of the first. The interference is then said to be "constructive." If they are partially or totally out of phase with each other, the intensity will be decreased and the interference will be described as "destructive."

Inversion. Conversion of an object into its enantiomorph by projecting it along a line through a center of symmetry (also called a center of inversion) and extending it an equal distance beyond this center. If the center of symmetry is at the origin $(0, 0, 0)$, every point x, y, z, after passing through this center, becomes $-x, -y, -z$.

Isomorphism. Similarity of crystal shape, unit-cell dimensions, and structure between two substances of similar (but not identical) chemical composition (for example, when one atom has a different atomic number in the two structures). Ideally, the substances are so closely similar that they can generally form a continuous series of solid solutions.

Isomorphous replacement method. A method for deriving phases by comparing the intensities of corresponding Bragg reflections from two or more isomorphous crystals (such as heavy-atom derivatives). If the locations in the unit cell of those atoms that vary between each isomorph have been found, for instance from a Patterson map, then the phase of each Bragg reflection can be assessed if a sufficient number of isomorphs is studied (at least two if the structure is noncentrosymmetric).

Isotropic. Exhibiting properties that are the same in all directions throughout a material of interest.

Isotropic displacement factor. An atomic displacement parameter (q.v.) that represents an equal amplitude of vibration or displacement in all directions through the crystal. At the beginning of a least-squares refinement of a structure, all atoms are considered to have isotropic displacement parameters but in the later stages, anisotropic displacement parameters are usually assigned to appropriate atoms.

Kinematical diffraction. Diffraction theory in which it is assumed that the incident beam only undergoes simple diffraction on its passage through the crystal. No further diffraction occurs that would change the beam direction after the first diffraction. This type of diffraction is considered in this book. (See Dynamical diffraction.)

Lagrange multiplier. An artificial variable used in least-squares calculations that is introduced in order to find the maximum or minimum of a function that is subject to constraints. Named after Joseph Louis Lagrange.

Lattice planes. Planes through at least three non-colinear crystal lattice points.

Laue class or Laue symmetry. Symmetry in the intensities of the diffraction pattern beyond that expected by Friedel's Law (q.v.), named for Max Theodor Felix von Laue, a German physicist. The Laue symmetry of the diffraction pattern of a crystal is the point-group symmetry of the crystal plus a center of symmetry. There are the 11 Laue groups, obtained by adding a center of symmetry (if absent) to the 32 crystallographic point groups (q.v.).

Laue equations. Equations that, like the Bragg equation, express the conditions for diffraction in terms of the path differences of the scattered waves. The path differences must be an integral number of wavelengths for diffraction (that is, reinforcement) to occur. This condition must be true simultaneously in three dimensions.

Laue photograph. Diffraction photograph produced by sending a beam of X rays that has a wide range of wavelengths ("white" X rays) along a principal axis of a stationary crystal. It demonstrates well the diffraction symmetry.

Law of Constancy of Interfacial Angles. In all crystals of a given type from a given compound, the angles between corresponding faces have a constant value. This law, of course, applies to only one particular form of a polymorphous crystalline material. Interfacial angles are measured with a goniometer (contact or reflecting) (q.v.).

Law of Rational Indices. A rational number is an integer or the quotient of two integers. The Law of Rational Indices, first proposed by Haüy in 1784, states that all of the faces of a crystal may be described, with references to three non-colinear axes, by three small whole numbers. (See Miller indices.)

Layer line. When a crystal is rotated or oscillated about a principal axis of a crystal, the diffraction spots on a cylindrical film surrounding the crystal are arranged in a series of straight lines called layer lines. They are perpendicular to the axis of rotation.

Least-squares method. (See Method of least squares.)

Libration. A form of rigid-body vibrational motion that may be described as a vibration along an arc rather than along a straight line.

Linear absorption coefficient, absorption correction. A factor to correct for the reduction in intensity of X rays as a result of absorption when the beam passes through a crystal. It is the ratio of the intensities of X rays entering and leaving a crystal of thickness t. This ratio is $\exp(\mu t)$, where μ is the linear absorption coefficient of the crystal (with units of cm^{-1}); it is a function of the atomic composition of the crystal and the wavelength of the X rays.

Linear equation. An equation that uses only constants or the product of a constant with the first power of a single variable, for example $y = ax + b$ or $d = ax + by + cz$.

Liquid crystal. A substance, such as *para*-azoxyanisole, that has observable optical anisotropy, as does a crystal, but behaves in other ways as a liquid. Thus the term refers to a state of matter with structural order intermediate between that of normal liquids and of crystalline solids.

Lorentz factor. A correction factor used in the reduction of intensity diffraction data to $|F(hkl)|^2$ values that takes into account the time that it takes for a given Bragg reflection (represented as a reciprocal lattice point with finite size) to pass through the surface of the Ewald sphere (q.v.). The value of this Lorentz factor depends on the scattering angle and on the geometry of the measurement of the

Bragg reflection. For a standard four-circle diffractometer the Lorentz factor is $(1/\sin 2\theta)$.

MAD phases. MAD = multiwavelength anomalous dispersion. A crystal containing highly anomalous scatterers, such as heavy atoms in a protein, is used to collect diffraction data at several carefully chosen X-ray wavelengths. The scattering factor for the heavy atom varies for data measured near and far from its absorption edge. As a result, sufficient information may be obtained from these data sets to determine phases and solve the crystal structure. The heavy atom may be a metal or metal complex. This method works well when, for example, sulfur is replaced by selenium in a protein structure.

Method of least squares, least-squares method. A statistical method for obtaining the best fit of a large number of observations to a given equation. This is done by minimizing the sum of the squares of the deviations of the experimentally observed values from those values calculated with the equation to be fitted. The individual terms in the sum are usually weighted to take into account their relative precision. In crystal structure analyses, atomic coordinates and other parameters are used to calculate values of $|F(hkl)|$, and these calculated values may be fitted by the least-squares method to the appropriate experimentally measured structure factors (so that the sum of the squares of their deviations is minimized). Ideally, there should be at least ten experimental measurements for each parameter to be determined. In a similar way, the least-squares criterion can be applied to the computation of a plane through a group of atoms and to many other geometrical problems.

Miller–Bravais indices. In the hexagonal lattice (c unique), there are three axes perpendicular to c inclined at 120° to each other. Therefore four indices, $hkil$, rather than the usual three Miller indices, hkl, are used in this hexagonal case, where $i = -(h + k)$.

Miller indices. A set of three integers (h, k, and l) that identifies a face of a crystal, a set of lattice planes, or a particular order of Bragg reflection from these planes. They are named for William Hallowes Miller, a British mineralogist. For sets of lattice planes with Miller indices h, k, and l, the plane nearest the origin makes intercepts a/h, b/k, and c/l with the unit-cell axes a, b, and c. The "Law of Rational Indices" (q.v.) states that the indices of the faces of a crystal are usually small integers, seldom greater than three. The importance of the Bragg equation is that it identifies the integers h, k, l that specify the "order" of diffraction in the Laue equations with the Miller indices of the lattice planes causing the "Bragg reflection."

Minimum function. A method of analyzing a Patterson map that involves setting the origin of the Patterson map in turn on the known positions of certain atoms, and then recording the minimum value throughout the map for all of these superpositions. The resulting three-dimensional map, a minimum-function map, should contain an indication of additional atoms in the crystal structure.

Mirror plane. A mirror plane converts an object into its mirror image. This image lies as far behind the mirror plane as the original object lies in front of it. If the mirror plane is perpendicular to b, it converts a chiral object at x, y, z into its enantiomorph (q.v.) at $x, -y, z$.

Modulated structure. A regular structure that is modified by a periodic or partially periodic perturbation. This is revealed by additional halos or spots around Bragg reflections in the diffraction pattern.

Molecular replacement method. The use of rotation and translation functions (q.v.), of noncrystallographic symmetry (q.v.), or of structural information from related structures to determine a protein crystal structure. The method is primarily used for macromolecules. It is used when a new investigation involves a protein or other large molecule that is similar to one for which the atomic coordinates are already available. The Patterson function is used to compare the relative orientations and positions of the two molecules, giving a rotation matrix and a translation vector between them. From these, a model of the new structure is available for refinement.

Monochromatic. Consisting of radiation of a single wavelength.

Monochromator. An instrument used to select radiation of a single wavelength. Some monochromators are crystals, such as graphite crystals, and an intense Bragg reflection from the crystal is selected as the new incident beam for diffraction studies. Gratings may also be used. Often monochromator crystals are bent or even doubly bent (for example, silicon crystals at a synchrotron source). The beam exiting the monochromator is the incident beam for diffraction studies.

Monoclinic unit cell. A unit cell in which there is a twofold rotation axis parallel to one unit-cell axis (usually chosen as **b**); as a result there are no restrictions on the axial ratios, but $\alpha = \gamma = 90°$.

Morphology, crystal morphology. The shape or form of a material. With crystals, a description of the crystal faces and the angles between them can often be used for identification.

Mosaic structure or mosaic spread. A measure of the degree of orientational inhomogeneity in a particular crystal. Bragg's Law (q.v.) implies that X-ray diffraction occurs only when the orientation of the crystal with respect to the incident beam exactly satisfies the Bragg equation, $n\lambda = 2d \sin\theta$. In practice, however, diffraction is appreciable over several tenths of a degree around the Bragg angle because the crystal is composed of a mosaic of tiny blocks of unit cells differing slightly in orientation. The misalignment of these blocks of unit cells is small, of the order of $0.2°$ to $0.5°$ for most crystals. (See Extinction.)

Mother liquor. The solution in which the crystals under study were grown. If the crystal is not stable in air, as for a protein, it is maintained in a capillary in contact with its mother liquor during data collection. An alternative to capillary mounting is freezing. Most protein data sets are now measured at $100\,\mathrm{K}$. This reduces radiation damage (q.v.) and keeps the mother liquor in place.

Multiple Bragg diffraction. Further diffraction of a Bragg reflection by a second set of lattice planes. This occurs when *two reciprocal lattice planes lie simultaneously on the surface of the Ewald sphere*. It affects the intensity of the Bragg reflection, and a detailed analysis of the effect can lead to some phase information. (See Double reflection.)

Multiple isomorphous replacement. When heavy-metal compounds are bound to a protein in a crystal they perturb the diffraction pattern. This gives information on possible values for the phase angle if at least two heavy-atom derivatives have been studied.

Neutron diffraction. Neutrons of wavelengths near $1\,\text{Å}$ can be used for diffraction by crystals. Neutrons are scattered by atomic nuclei, but their scattering factors are not a regular function of the atomic number of the scattering atom. Therefore their diffraction data give information that complements that from X-ray diffraction. The location of deuterium atoms (replacing some of the hydrogen atoms in a structure) by neutron diffraction is much more precise than for X-ray diffraction. This is because the neutron scattering of deuterium is similar to that of carbon, while, by contrast, the X-ray scattering of both hydrogen and deuterium is very small. Larger crystals are required currently for neutron diffraction than for X-ray diffraction studies.

Noncentrosymmetric structure. A crystal structure with no center of symmetry in its atomic arrangement. The phase angle of most Bragg reflections may have any value between $0°$ and $360°$ (0 and 2π radians). An electron-density map calculated with relative phases of a trial structure will generally show the features of the trial structure even if this structure is partially wrong. However, some features of the correct structure may also appear in the electron-density map.

Noncrystallographic symmetry. Local symmetry within the asymmetric unit of a crystal structure that is not accounted for by the space-group symmetry. For example, the asymmetric unit of a crystalline protein may contain a dimer whose two subunits may have identical molecular structures but, since they are not related by crystallographic symmetry, may have different environments. This noncrystallographic symmetry in macromolecules can be used as an aid in structure determination.

Nonlinear optics. In linear optics light, as it passes through a material, may be deflected or delayed but its wavelength remains unchanged. In nonlinear optics the dielectric polarization does not correspond linearly to the electric field of the light. Now that intense sources of light, such as lasers, are available, these effects are of technological use. An interesting effect is second-harmonic generation, or frequency doubling, in which light with half the wavelength is generated on passage through a noncentrosymmetric crystal. It can be used to test for a center of symmetry in the structure, in which case no frequency doubling is observed.

Normal equations. Any set of simultaneous equations involving experimental unknowns and derived from a larger number of observational equations in the course of a least-squares adjustment of observations. The number of normal equations is equal to the number of parameters to be determined.

Normalized structure factors, E-values. The ratio of the value of the structure amplitude, $|F(hkl)|$, to its root-mean-square expectation value. It is denoted by $|E(hkl)| = |F(hkl)|/(\varepsilon \Sigma f_j)^{1/2}$, where $(\Sigma f_j)^{1/2}$ is the root mean square scattering factor, corrected for thermal motion and disorder (see Epsilon factor for a definition of ε).

Nucleation of crystals. The action of a tiny seed crystal, dust particle, or other "nucleus" in starting a crystallization process. An example is provided in the seeding of a cloud with crystalline material (silver iodide, which has almost the same unit-cell dimensions as ice) so that ice crystals will be formed that may act as rainmakers.

Observational equation. An equation expressing a measured value as some function of one or more unknown quantities. Observational equations are reduced to normal equations during the course of a least-squares refinement.

Occupancy factor. A parameter that defines the partial occupancy of a given site by a particular atom. It is most frequently used to describe disorder in a portion of a

molecule, or for describing nonstoichiometric situations—for example, when a solvent molecule is being lost to the atmosphere.

Omit map. A difference map in which part of the structure in a specific area of the unit cell is omitted from the phasing calculation. The resulting electron-density map is then examined to check if the proposed structure can still be recognized in that area. This technique is generally used for large macromolecules such as proteins.

Optic axis. The direction in a birefringent crystal along which the ordinary and extraordinary rays travel at the same speed. Uniaxial crystals have one such axis; biaxial crystals have two.

Optical activity. The ability of a substance to rotate the plane of polarization of plane-polarized light.

Order of diffraction. An integer associated with a given interference fringe of a diffraction pattern. The diffraction is first order if it arises as a result of a radiation path difference of one wavelength. The nth order corresponds to a path difference of n wavelengths.

Orientation matrix. A matrix that provides a connection between the orientation of the diffractometer circles and the production of a Bragg reflection so that the indices hkl of the Bragg reflection can be related to the orientation of the chosen unit cell of the crystal, and the intensity of the Bragg reflection can then be measured.

Origin of a unit cell. The point in a unit cell (usually one corner), chosen by the investigator, from which x, y, and z axes originate. It is designated "0, 0, 0" for its values of x, y, and z.

Orthogonal system. Reference axes that are mutually perpendicular.

Orthorhombic unit cell. A unit cell in a lattice in which there are three mutually perpendicular two-fold rotation axes (parallel to the three reference axes a, b, and c); as a result, while there are no restrictions on axial ratios, all interaxial angles are necessarily equal to 90° ($\alpha = \beta = \gamma = 90°$).

Oscillation photograph. A photograph of the diffraction pattern obtained by oscillating the crystal through a small angular range.

Parallelepiped. A six-sided figure, each side of which is a parallelogram, and opposite sides of which are parallel to each other.

Parity group. A set of structure factors whose three Miller indices (h, k, and l) are odd (o) or even (e) in an identical way. There are eight parity groups for three indices (eee, eeo, eoe, eoo, oee, oeo, ooe, and ooo).

Path difference. This term is used in diffraction to describe the difference in distance that two beams travel when "scattered" from different points. As a result of such path differences, the two beams may or may not be in phase with each other.

Patterson function. A Fourier summation that has the squares of the structure factor amplitudes as coefficients and all phases zero. Because these values of $|F(hkl)|^2$ can be obtained (after some geometric corrections) directly from the diffraction intensities, the map can be computed directly with no phase information required.

$$P(uvw) = \frac{1}{V_c} \sum_{\text{all } h,k,l} \sum \sum |F(hkl)|^2 \cos 2\pi(hu + kv + lw)$$

Ideally, the positions of the maxima in the map represent the end points of vectors between atoms, all referred to a common origin. There is only one Patterson map for a given crystal structure, but the input may be enhanced to make the interpretation easier. If values of $|F(hkl)|^2$ are modified by an exponential or similar function that enhances those Bragg reflections with high values of $\sin \theta/\lambda$, the resulting interatomic vectors appear as sharper peaks. The map is named for Arthur Lindo Patterson, a physicist.

Perfect crystal. A crystal in which the unit cells and their contents are in perfect register.

Phase. The phase is the point to which the crest of a given wave has advanced in relation to a standard position, for example the origin of the unit cell. It is usually expressed as a fraction of the wavelength in angular measure, with one cycle or period being 2π radians or 360°; that is, if the crests differ by Δx for a wavelength λ, the phase difference is $\Delta x/\lambda$ or $2\pi \Delta x/\lambda$ radians or $360 \Delta x/\lambda$ degrees (see also Calculated phase). If two waves of the same wavelength travel in the same direction, their phase difference is the difference between the positions of crests (peaks) between the two. The relative phase of a structure factor is expressed relative to the phase of a wave scattered at the chosen origin of the unit cell (or some other defined position) in the same direction: $a(hkl) = \tan^{-1}(B(hkl)/A(hkl))$, where $A(hkl)$ and $B(hkl)$ are components of the structure factor $F(hkl)$. If the crystal structure is centrosymmetric and the origin is set at a center of symmetry, the phase is 0° or 180° (0 or π radians) according to a positive or negative sign of $A(hkl)$; $B(hkl) = 0$. When we use "relative phase" we remind the reader that its value depends on the chosen location of the origin of the unit cell; that is,

a structure factor does not usually have a fixed phase; its relative phase depends on where the unit-cell origin has been chosen to be.

Phase problem. The problem of determining the phase angle (relative to a chosen origin) for each Bragg reflection, so that an electron-density map may be calculated from a Fourier series with structure factors (including both amplitude and relative phase) as coefficients. "Solving a structure" requires determining phases.

Photometry. Measurement of the ratio of the intensity of a constant source of light to that of an equivalent beam of light after it has passed through a selected position on a piece of photographic film. In this way the intensity of a Bragg reflection that has been recorded on film can be measured.

Piezoelectric effect. The generation of a small potential difference across certain crystals when they are subjected to stress such as pressure (the direct effect), or the change in the shape of a crystal that accompanies the application of a potential difference across a crystal (the inverse effect). The effect is found only for noncentrosymmetric crystals; examples are provided by quartz and Rochelle salt.

Planck constant. The Planck constant (h), named after Max Planck, defines the size of a quantum of electromagnetic radiation. It is the proportionality constant between the energy of a photon (in joules) and the frequency (in oscillations per second) of the wave that it represents. $h = 6.626 \times 10^{-34}$ J s or kg m^2 s^{-1}.

Plane groups. The groups of symmetry elements that lead to those symmetry operations that produce regularly repeating patterns in two dimensions. There are 17 plane groups (listed in *International Tables*), meaning that there are 17 symmetry variations of wallpaper (if it has a two-dimensional repeating pattern).

Plane polarization. Electromagnetic radiation, such as visible light and X rays, contains electric vectors of its waves and if the radiation is plane-polarized, all of these are confined to a single plane.

Pleochroism. The property of certain crystals of appearing to have different colors when viewed from different directions under transmitted white light (dichroism if only two colors).

Point group. A group of symmetry operations that leave unmoved at least one point within the object to which they apply. Symmetry elements include simple rotation and rotatory-inversion axes; the latter include the center of symmetry and the mirror plane. Since one point remains invariant, all rotation axes must pass through this point and all mirror planes must contain it. A point group is used to describe isolated objects, such as single molecules or real crystals. (See Group (mathematical).)

Poisson distribution. A distribution of measurements applied to rare events in which the number of such events occurring in a fixed period of time depends only on the length of this time interval and is independent of previous events. The mean and variance of the distribution are equal so that the standard uncertainty is proportional to the square root of the measured value. The distribution is named after the French mathematician Siméon Denis Poisson.

Polar axis. An axis in a crystal that has different properties at its two ends (meaning that it has directionality, like an arrow). Such properties include crystal face development and charge accumulation.

Polarization factor. A correction factor for intensity data that takes into account the reduction in intensity of X-ray scattering due to the state of polarization of the incident beam. If the incident X rays are not polarized, the factor is $(1 + \cos^2 2\theta)/2$. It will be further modified if a monochromator was used to provide the incident radiation.

Polymorphism. Property of crystallizing in two or more forms with distinct structures (dimorphism if only two forms), generally depending on the conditions of crystallization. Polymorphs have different unit cells and different atomic arrangements within them.

Position-sensitive detector. (See Charge-coupled device area detector.)

Powder diffraction. Diffraction by a powder consists of lines or rings rather than separate diffraction spots. The diffraction pattern obtained is like that expected for a set of randomly oriented crystals. For diffraction studies the powder is either glued to a glass fiber, placed on a flat surface (e.g., a microscope slide), or, if it is unstable in air, put in a sealed capillary tube.

Precession photograph. A photograph of the diffraction pattern that is an undistorted magnified image of a given layer of the reciprocal lattice. The necessary camera and crystal motions involve the precession of one crystal axis about the direction of the direct beam. The film is continuously maintained in the plane perpendicular to this precessing axis. The photograph resulting from this complicated set of motions is simple to interpret, and the indices (h, k, l) of the diffraction spots may readily be found by inspection.

Precipitant. A chemical used to promote crystallization but not denaturation of a protein. Examples are highly soluble inorganic salts (ammonium sulfate or sodium chloride) and organic polyethers (polyethyleneglycols of a selected molecular weight range.)

Precipitation. The act of separation of a solid mass from solution. A precipitant (q.v.) will assist this.

Precision. A measure of the experimental uncertainty in a measured quantity, an indication of its reproducibility (cf. Accuracy).

Primitive unit cell. The unit cell of the smallest possible volume for a given space lattice. The term is used to differentiate this unit cell from a centered cell or other nonprimitive cells. When a primitive cell is chosen, the symbol P is included in the space-group designation.

Principal axes of thermal ellipsoids. Three mutually perpendicular directions, along two of which the amplitudes of vibration of an atom, represented by an ellipsoid, are at a maximum and at a minimum. Each axis is characterized by an amplitude and a direction.

Probability density function. The probability that a random variable will take on a particular value in an infinitesimal time interval, divided by the length of the interval.

Probability relationships. In crystallographic use, this term refers to equations that express the probability that a phase angle will have a certain value. Such equations are the basis of phase determination by direct methods.

Promolecule density. The electron density of spherically symmetrical free atoms without effects from chemical bonding or other factors that distort the electron density.

Proper symmetry operation. A symmetry operation that maintains the handedness of an object. Such operations include translations, rotation axes, and screw axes.

Proportional counter. A radiation detector that produces a measurable amplified voltage pulse of height proportional to the energy of photons hitting it; it gives a linear response at high counting rate.

Pyroelectric effect. The development of a small potential difference across certain crystals as the result of a temperature change.

R value or R factor, discrepancy index, residual. An index that gives a measure of the disagreement between observed and calculated structure amplitudes and therefore a crude (and sometimes misleading) measure of the correctness of a derived model for a crystal structure and the quality of the experimental data. It is defined as

$R = \Sigma|(|F_o| - |F_c|)|/\Sigma|F_o|$ and values of 0.02 to 0.06 are considered good for present-day small-molecule structure determinations. However, some partially incorrect structures have had R values below 0.10, and many basically correct but imprecise structures have higher R values.

Racemic mixture. A mixture composed of equal amounts of dextrorotatory and levorotatory forms (enantiomorphs) of the same compound. It displays no optical rotatory power.

Radiation damage. Damage caused by radiation. Since a crystal is constantly irradiated by X rays during a diffraction experiment, such damage can be an important source of error. As a result of such damage, molecules in the crystal may move, be ionized, form free radicals, or interact with other species in the crystal. Sometimes sets of three or more Bragg reflections are measured at regular intervals during intensity data measurement by a diffractometer in order to monitor any radiation damage. However, with area detector data, radiation (and other) damage is checked by average counts per image and any drop thereof. Radiation damage by X rays is dramatically reduced by low-temperature data collection. By contrast, neutrons do not generally damage a crystal.

Raw data. Diffraction data when they are first measured, before correction and other factors are applied to them.

Real space. (See Direct space.)

Real-space averaging. A computational method for improvement of phases, when there are two or more identical chemical units in the crystallographic asymmetric unit. In a trial electron-density map, the electron densities of the two identical units are averaged. Then a new set of phases is computed by Fourier transformation of the averaged structure, and, with these, a new electron-density map is synthesized with the observed $|F(hkl)|$ values. By iteration of this procedure, the electron-density map can be improved. This method is commonly used in refining large crystal structures.

Reciprocal lattice. The lattice defined by axes $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$, related to the crystal lattice or direct lattice (with axes $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$) in a reciprocal manner such that $\mathbf{a}^*$ is perpendicular to $\mathbf{b}$ and $\mathbf{c}$; $\mathbf{b}^*$ is similarly perpendicular to $\mathbf{a}$ and $\mathbf{c}$; and $\mathbf{c}^*$ is perpendicular to $\mathbf{a}$ and $\mathbf{b}$. The repeat distance, d^*, between points in a particular row of the reciprocal lattice is inversely proportional to the interplanar spacing, d, between the nets of the crystal lattice that are normal to this row of points ($d^* = \lambda/d$).

Refinement of a crystal structure. A process of improving the parameters of an approximate (trial) structure until the

best fit of calculated structure factor amplitudes to those observed is obtained. This is usually done by the method of least squares (q.v.). Since the dependence of the structure amplitudes on atomic parameters is not linear, the process involves a series of iterations until convergence is reached. To avoid falling into physically meaningless minima, it is important to start with a good set of initial parameters.

Reflecting goniometer. A device for measuring the angles between crystal faces by measuring the angle through which a crystal has to be rotated from a position at which one face reflects a narrow beam of light into a stationary detector to a position at which a second face reflects.

Reflection. (See Bragg reflection.)

Refraction. The change in direction that occurs when a beam of radiant energy passes from one medium into another in which its velocity is different. (See Refractive index.)

Refractive index. The ratio of the velocity of light *in vacuo* to its velocity as it passes through the material under study. It is evident when a stick is placed in a tumbler full of water. The stick appears bent at the surface of the water. When a colorless, clear object (such as a crystal) is immersed in a colorless medium of the same refractive index, the object becomes invisible.

Residual. (See *R* value.)

Resolution. The ability to distinguish adjacent parts of an object when examining it with radiation, that is, the process of distinguishing two adjacent objects (high resolution) as separate entities rather than as a single, blurred object (low resolution). Most X-ray structures of small molecules are determined to a "resolution" of 0.75–0.9 Å or better. At this resolution each atom is fairly distinct. The resolution improves with an increase in the maximum value of $\sin\theta/\lambda$ at which Bragg reflections are measured. Sometimes the quality of the crystal or the wavelength of the radiation limits the resolution that may be obtained experimentally.
A second use of this term is for the separation of enantiomorphs.

Restraints. Limits on the possible values that parameters may have. For example, additional observations, such as known bond distances and angles, can be added to the least-squares equations, and these must hold true for the results of the least-squares refinement. Restraints are used like data and one refines against them. They come with a standard uncertainty or elasticity that should be obeyed. Constraints remove parameters and restraints

add data. Constraints rigidly relate certain parameters or assign specific values to them, while restraints give ranges to target values for certain parameters. (Think of a dog restrained by a flexible leash of a selected length.) (See Constraints.)

Rhombohedral unit cell. A unit cell in which there is a three-fold rotation axis along one body diagonal of the unit cell. This symmetry requirement makes all three axial lengths necessarily the same and all three interaxial angles necessarily equal, although their values are not restricted ($a = b = c$, $\alpha = \beta = \gamma$). This is an alternative description of unit cells in trigonal space groups that are centered if they are drawn in the hexagonal representation. The difference between the trigonal and hexagonal systems is the symmetry; a hexagonal unit cell has a six-fold rotation axis, while a trigonal unit cell has only a three-fold axis. The rhombohedral unit cell, denoted R, is a third of the volume of the hexagonal representation. The hexagonal setting ($a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$), which has obverse and reverse settings (see Appendix 2), is, however, usually preferred.

Right-handed coordinate system. A system of three axes, x, y, and z, in which a rotation from x to y, coupled with a translation along z, corresponds to the action of a right-handed screw moving clockwise into a piece of wood (with x to y as the clockwise motion and z the direction into the wood). If the thumb, index finger, and middle finger of the right hand are extended in mutually perpendicular directions, then these digits point to the positive directions of x, y, and z, respectively.

Rigid-body model. A model of vibration that assumes a molecule (or a specific part of it) to be rigid, so that, during vibration, all its interatomic distances are constant and all atoms move in synchrony.

Rotating-anode generator. An X-ray tube in which an electron beam hits a wheel of target material rotating at high speed. The anode moves while the X-ray beam remains fixed, so that the heat generated during X-ray production is spread over a larger area than in a conventional sealed X-ray tube. This provides a higher intensity of X rays than obtained with a conventional sealed X-ray tube.

Rotation axis. (See Axis of rotation.)

Rotation function. A function that describes a measure of the degree of correspondence between (1) a set of interatomic vectors that has been calculated for a known structure and (2) the Patterson function of that crystal. It is expressed by a map of the rotation about the origin of one of these functions with respect to the other. Peaks in

this map define a likely orientation of the known fragment of the structure. The orientation of a known part of a structure may often be found through such comparison. In a self-rotation function, the Patterson map is compared with itself. Peaks in this function will indicate the relationship between molecules if there is more than one in the asymmetric unit.

Rotation photograph. A photograph of the diffraction pattern obtained by rotating a crystal continuously about a fixed axis, sometimes normal to some set of reciprocal lattice planes.

Rotatory-inversion axis. Rotation by $360°/n$ combined with inversion through a center of symmetry (on that axis) to give an enantiomorph of the original object.

SAD phases. SAD = single-wavelength anomalous dispersion. A single set of anomalous-dispersion data is measured with $CuK\alpha$ radiation for a crystal containing a heavy atom such as iodine or bromine. Alternatively, a sulfur-containing structure may be measured with $CrK\alpha$ radiation. In both cases the data can be collected in a laboratory (rather than at a synchrotron source), but the phase ambiguity persists (because only one data set was measured). This ambiguity is generally resolved by direct methods, such as by locating all the anomalously scattering atoms in the structure.

Salting out. Precipitating, coagulating, or separating a substance from a solution by the addition of a salt.

Saturated solution. A solution is saturated when the solute and solution are at equilibrium. This occurs when the maximum amount of solute has been dissolved in the solvent, and is usually dependent on the temperature and pressure.

Scale factor. (See Absolute scale.)

Scattering angle. The angle at which the scattered wave deviates from the direct beam. Conventionally, in X-ray diffraction, the direct X-ray beam is deviated by an angle $2\theta_{hkl}$.

Scattering factor. (See Atomic scattering factor.)

Scattering vector. The reciprocal lattice vector associated with (and perpendicular to) a set of reflecting crystal-lattice planes hkl,

$$H = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

Its magnitude is given by $H = 1/d_{hkl} = 2\sin\theta_{hkl}/\lambda$, where d_{hkl} is the interplanar spacing. The order of diffraction, n, is contained in the Miller indices hkl as a multiplying factor.

Scintillation counter. A device for measuring the intensity of an X-ray beam. It makes use of the fact that X rays cause certain substances to emit visible light by fluorescence. The intensity of this visible light is proportional to the intensity of the incident X-ray beam and is amplified by a photomultiplier and then counted. The substance generally used as the X-ray detector is a sodium iodide crystal, activated by a small amount of thallous ion.

Screw axis. A screw axis, designated n_r, is a symmetry operation that involves rotation about the axis by $360°/n = 2\pi/n$ coupled with a translation parallel to the axis by r/n of the unit-cell length in that direction. A two-fold screw axis through the origin of the unit cell and parallel to $\mathbf{b}$ converts an object at x, y, z to one at $-x, \frac{1}{2} + y, -z$. The translation component leads to the generation of an infinitely repeating periodic pattern in the direction of translation. The enantiomorphic identity remains the same if a screw axis is used.

Series-termination error. An effect in a periodic function that results from a truncation of the number of terms in a Fourier series. Ideally, an infinite amount of data is necessary for the calculation of a Fourier series. In practice, only a finite number of data are measured in a diffraction pattern. This leads to a truncation of the Fourier series so that peaks in the resulting Fourier syntheses may be surrounded by series of ripples, which are especially noticeable around a heavy atom. The use of difference syntheses (q.v.) obviates most of the effects of series-termination errors.

Sigma Two formula (Σ_2). A formula used in direct methods. It relates the phases of three intense Bragg reflections to each other.

Simulated annealing. Annealing is a method used to make steel or glass more soft and less brittle, and involves heating and then cooling. This process is simulated in crystallographic refinements by adjusting the parameters of a macromolecule to simulate "heating" of the molecule (by increasing the displacements or vibrations), and then "cooling" it so as to minimize the energy. In this way a global minimum may be more readily obtained than with other methods of refinement, such as least-squares methods, where a local minimum, but not the deepest minimum, may be the end point of a refinement.

Sinusoidal wave. A wave described by a function $y(t) = A\sin(\omega t + \theta)$, where A = amplitude, ω = angular frequency, and θ = phase. Sine and cosine functions are both sinusoidal waves, with different phases [$\cos x = \sin(x + \pi/2)$]. A sinusoidal wave retains its wave shape when added to another sinusoidal wave (see Fourier synthesis).

Small-angle scattering. The study of matter by analysis of the diffraction of X rays with diffraction angles smaller than a few degrees—that is, θ less than $1°$, for copper radiation. This scattering occurs when the sample is composed of particles with dimensions of the order of several hundred to several thousand Å. Measurement of the intensity distribution gives information on the low-resolution structure of the diffracting material; for example, it will give the radius of gyration of the particles, which is a measure of the size of the particle.

Solvent flattening. (See Density modification.)

Space group. A group of symmetry operations consistent with an infinitely extended, regularly repeating three-dimensional pattern. There are 230 such groups, which can be identified (although sometimes with some ambiguity) from the systematic absences in the diffraction pattern combined with the intensity data (see Distribution of intensities) and the Laue symmetry (see Laue class). A space group may be considered as the group of operations that converts one molecule or asymmetric unit into an infinitely extending pattern of such units. The 230 space groups are listed in detail in *International Tables for Crystallography*, Vol. A (Hahn, 2005).

Space group ambiguity. Sometimes more than one space group fits a set of systematic absences in the intensities of Bragg reflections for a given crystal. Other methods, such as information on the crystal contents and their possible symmetry or employing characteristics of the intensity distribution, may have to be used to determine the correct space group.

Spallation. Spallation is the ejection of material on impact. It can involve high-energy incident particles that bombard an atomic nucleus, ejecting particles such as neutrons. Neutrons are obtained when short bursts of high-energy pulsed protons are used to bombard a target of heavy nuclei (such as mercury, lead, or uranium) several times a second. Each proton produces several high-energy neutrons, which are slowed down by moderators to useful energies for diffraction studies.

Sphere of reflection. (See Ewald sphere.)

Standard uncertainty (s.u.). A measure of the precision of a quantity. If the distribution of errors is normal, then there is a 99% chance that a given measurement will differ by less than 2.7 s.u.. from the mean. A bond length 1.542(7) Å (1.542 Å with an s.u. of 0.007 Å) is, by the usual criteria, not considered significantly different from one measured as 1.528(7) Å (2 s.u. away). This term is sometimes called an "estimated standard deviation" (e.s.d.).

Stoichiometry. The quantitative relationship of constituents implied by a chemical formula or equation.

Structure factor. The structure factor $F(hkl)$ is the value, at a reciprocal lattice point, of the Fourier transform of the electron density in the unit cell. The wave scattered by the contents of the unit cell in the direction of the hkl Bragg reflection is described in amplitude and phase by the structure factor $F(hkl)$. The structure factor has both a magnitude (amplitude) and a phase (relative to the origin of the unit cell). The magnitude of the structure factor, $|F(hkl)|$, is the ratio of the amplitude of the radiation scattered in a particular direction by the contents of one unit cell to that scattered by a classical point electron at the origin of the unit cell under the same conditions. The structure factor depends on the chemical identities and arrangement in the unit cell of the constituent atoms, and on the direction of scattering with respect to the incident X-ray beam. For the relationship between structure factors and electron density, see Fourier transform.

Structure invariant. A linear combination of the phases of a particular set of Bragg reflections that does not change when the position of the origin of the unit cell is changed; that is, this linear combination of phases is totally independent of the choice of origin.

Structure seminvariant. Bragg reflections whose phases remains unchanged (except by an integral multiple of 2π radians) when the location of the origin is changed (provided this origin change is allowed by space-group symmetry constraints).

Superposition methods. Analysis of a Patterson map by setting the origin of the Patterson map in turn on the positions of certain atoms whose positions may already be known, and then recording those areas of the superposed maps in which peaks appear that are derived from both maps. The resulting map is called a vector superposition map and may contain information that allows one to derive the atomic arrangement.

Symbolic addition method. A direct-method procedure, in which phases for a few Bragg reflections are represented by algebraic symbols (such as a, b, or c) when needed during phase assignment. The meaning of the symbolic phases, such as + and − for $0°$ and $180°$ for a centrosymmetric structure, may then become evident during the subsequent analysis (for example, if the phase becomes a^2 which must be positive). Otherwise, electron-density maps with all possible values for the undetermined symbols must be computed, and hopefully one of these will be obvious as the correct structure.

Symmetry element. A point, a line, or a plane on or about which a particular symmetry operation is performed. The actual operation is a "symmetry operation" (q.v.).

Symmetry operation. In crystal structures (assumed infinite in extent), the possible symmetry operations include axes of rotation and rotatory inversion, screw axes, and glide planes, as well as lattice translations. Symmetry operations convert an object into a replica of itself. Translation and rotation are proper symmetry operations, while reflection and inversion are improper symmetry operations, which convert an object into the mirror image of itself.

Symmetry operation of second kind. (See Improper symmetry operation.)

Synchrotron radiation. Radiation emitted by very high-energy electrons, such as those in an electron storage ring, when their path is bent by a magnetic field. This radiation is characterized by a continuous spectral distribution (which can, however, be "tuned" by appropriate selection), a very high intensity, a pulsed time structure, and a high degree of polarization. Its high intensity makes it useful for rapid data collection on macromolecular crystals and its tunability makes it convenient for collecting anomalous scattering data.

Systematically absent reflections. Bragg reflections that are too weak to be observed by the method of measurement used and for which h, k, and l values are systematic in terms of evenness or oddness (for example, an absence of all Bragg reflections for which $h + k$ is odd, indicative of C-face centering in the unit cell). Systematic absences depend only upon symmetry in the atomic arrangement. There are two types of systematic absences: (1) those arising from translational symmetry elements, i.e., screw axes and glide planes, and (2) those that arise from a decision to use a nonprimitive unit cell, and are an artifact of the way we index Bragg reflections. Systematic absences are of great use in deriving the space group of a crystal.

Tangent formula. A formula used in direct methods of phase determination that allows the development of additional phases.

Taylor series. A power series that expresses a function as an infinite sum of terms that can be calculated from values of its derivatives at a single point. In this power series, the coefficients are the corresponding derivatives divided by the factorial of the order of the derivative. The higher the power in a term, the smaller its value. The series is named after Brook Taylor, an English mathematician, who followed the earlier work of James Gregory.

Temperature factor. An exponential expression by which the scattering of an atom is reduced as a consequence of vibration (or a simulated vibration resulting from static disorder). For isotropic motion the exponential factor is $\exp\left(-B_{\text{iso}}\sin^2\theta/\lambda^2\right)$, with B_{iso} called, loosely but commonly, the "isotropic temperature factor." B_{iso} equals $8\pi^2\langle u^2\rangle$, where $\langle u^2\rangle$ is the mean square displacement of the atom from its equilibrium position. For anisotropic motion the exponential expression contains six parameters, the anisotropic vibration or displacement parameters, which describe ellipsoidal rather than isotropic (spherically symmetrical) motion or average static displacements. (See Atomic displacement parameters.)

Tetragonal unit cell. A unit cell in which there is a four-fold rotation axis parallel to one axis (arbitrarily chosen as **c**); as a result, the lengths of a and b are identical and all interaxial angles are $90°$ ($a = b$, $\alpha = \beta = \gamma = 90°$).

Thermal diffuse scattering. Diffuse scattering results from a departure from the regular periodic character of a crystal lattice. It is evident as diffuse spots or blurs around normal diffraction spots. If it is a temperature-dependent effect, it is called thermal diffuse scattering. This can be analyzed to give information on the elastic properties of crystals and the force constants between their constituent atoms.

Thermal-motion corrections. Adjustments to intramolecular dimensions from a crystal structure determination for distortions arising from atomic vibrations, especially libration (q.v.). The appropriate corrections depend on a model for specifying the correlations between the motions of the several atoms.

Time-of-flight neutrons. Neutrons from a reactor arrive at a detector array at times determined by their energies. They come in pulses (as a result of the action of mechanical choppers) and their energies (and wavelengths) are determined from the time it takes for them to travel to and hit the detector. Their velocities v are related to the wavelength by $\lambda = h/mv = (h/m)(t/L)$, where h is Planck's constant, m is the mass of a neutron, and t is the time of flight for a path length L. This equation gives essential information for analysis of a Laue-type diffraction pattern. Time-of-flight detectors can record the different wavelengths one after the other.

Torsion angle (sometimes called "conformational angle"). The torsion angle (or angle of twist) about the bond B–C in a series of bonded atoms A–B–C–D is defined as the angle of rotation needed to make the projection of the line B–A coincide with the projection of the line C–D, when viewed along the B–C direction. The positive sense is clockwise.

If the torsion angle is $0°$ or $180°$, the four atoms lie in the same plane. Enantiomers have torsion angles of equal absolute value but opposite sign.

Translation. The word "translation" has two different meanings in crystallography. Generally it indicates the symmetry element (of one unit cell length) that is typical of lattices, or some fraction of that. It is also used when all atoms of a molecule move the same distance in the same direction along the same or parallel lines.

Translation function. A function that can be calculated in order to determine (with respect to the unit-cell axes) how a molecule, for which the orientation has been found (see Rotation function), is positioned with respect to the origin of the unit cell. This function is important in structure analysis in macromolecular crystallography.

Trial-and-error method. A method that involves postulating a structure (that is, assuming locations of the atoms in the unique part of the unit cell), calculating structure factors F_c, and comparing their magnitudes with the scaled observed values $|F_o|$. Since the number of trial structures that must be tested increases with the number of parameters, such methods have generally been applied in solving only the simplest structures.

Trial structure. A possible structure for a crystal (found by one of several methods), which is tested by a comparison of calculated and observed structure factors and by the results of an attempted refinement of the structure.

Triclinic unit cell. A unit cell in which there are no rotation axes or mirror planes. As a result there are no restrictions on axial ratios or interaxial angles.

Trigonal unit cell. (See Rhombohedral unit cell.)

Triple-product sign relationship. The sign relationship $s(h, k, l) \, s(h', k', l') \, s(-h - h', -k - k', -l - l') \approx +1$, where $\approx$ means "is probably equal to" and s means "the sign of."

Twin. A composite crystal built from two or more crystal specimens that have grown together in a specific relative orientation.

Unit cell. The basic building block of a crystal, repeated infinitely in three dimensions. It is characterized by three vectors, **a**, **b**, and **c**, that form the edges of a parallelepiped. The angles between these vectors are α (between **b** and **c**), β (between **a** and **c**), and γ (between **a** and **b**).

Unit-cell dimensions. The unit-cell dimensions a, b, c, α, β, γ, of a crystal structure.

Unitary structure factor. The ratio of the structure amplitude, $|F(hkl)|$, to its maximum possible value—that is,

the value it would have if all atoms scattered exactly in phase. It is denoted by U. $U(hkl) = |F(hkl)|/|\Sigma f_j|$, where f_j is the scattering factor of atom j at the $\sin\theta/\lambda$ value of $F(hkl)$.

Unobserved Bragg reflections, absent Bragg reflections. Bragg reflections that are too weak to be measured by the apparatus in use. The term is also used for Bragg reflections for which the intensity $I(hkl)$ is less than $n\sigma(I)$, where n is chosen (usually 2–3), and σ is the s.u. of $I(hkl)$.

Variance. The mean square deviation of a frequency distribution from its arithmetic mean. The variance is the square of the standard uncertainty σ. For a random variable x, the variance is $\Sigma[(x_i - x_m)^2/n]$, where x_m is the mean value of x, and n is the number of measurements.

Vector. A quantity that requires for its complete description a magnitude, direction, and sense. It is often represented by a line, the length of which specifies the magnitude of the vector, and the orientation of which specifies the direction of the vector. The sense of the vector is then indicated by an arrowhead at one end of the line. Two vectors may be added together by placing the second vector with its origin on the end (arrowhead) of the first. The resultant vector is the directed line from the origin of the first vector to the end of the second. This process of addition can be continued infinitely. The scalar product, $\mathbf{a} \cdot \mathbf{b}$, is $|a||b|\cos\gamma$, where γ is the angle from **a** to **b**. The vector product, $\mathbf{a} \times \mathbf{b}$, is a vector with direction normal to both a and b, and magnitude $|a||b|\sin\gamma$.

Wavefront. All points reached at a given instant in time by a series of waves as they move through any material.

Wavelength. The distance between two similar points on a wave system, for example, the crests of a cosine wave.

Weight of a measurement. A number assigned to express the relative precision of each measurement. In least-squares refinement the weight should be proportional to the reciprocal of the square of the standard uncertainty of the measurement. Other weighting schemes frequently are used.

Weissenberg camera. This is an oscillation camera in which the camera is translated (moved) as the crystal rotates so that Bragg reflections can be indexed more readily than for a simple oscillation photograph that lacks this simultaneous motion of camera and crystal. It is named after Karl Weissenberg, an Austrian physicist.

White radiation. Any radiation, such as X rays or sunlight, with a continuum of wavelengths.

Wilson plot. A plot of the logarithm of the average ratio of the observed Bragg intensities to the theoretical values expected for a random arrangement of the same (stationary) atoms in the unit cell, in successive ranges (shells) of $\sin^2\theta/\lambda^2$. Such a plot typically approaches a straight line, whose intercept yields the factor needed to place the observed intensities on an absolute scale (q.v.) and whose slope yields an average isotropic displacement parameter for the entire structure. The plot was designed by Arthur James Cochran Wilson, a crystallographer.

X-ray camera. A device for holding film in an appropriate manner to intercept and record an X-ray diffraction pattern.

X-ray tube. The basic parts of an X-ray tube are a source of electrons and a metal anode that emits the Xrays, enclosed in a glass envelope under vacuum. Tubes may be classified according to the nature of these parts.

X rays. Electromagnetic radiation of wavelength 0.1–100 Å, produced by bombarding a target (generally a metal such as copper or molybdenum) with fast electrons. It is found that X rays of definite wavelengths, characteristic of the target element (characteristic X rays, q.v.), plus a continuous background of X rays (bremsstrahlung, q.v.), are produced. Characteristic X rays are produced when electrons from the innermost shells (K or L) are ejected from atoms in the target material. When an electron from an outer shell falls back into the vacant shell, energy is emitted in the form of X rays with a specific wavelength. The spectrum of the emitted X rays has a maximum intensity at a few wavelengths characteristic of the target material.

References and further reading

Abbé, E. Beiträge zur Theorie des Mikroskops und der mikroskopischen Wahrnehmung. [Contributions to the theory of the microscope and microscopic observations.] *Archiv für Mikroskopische Anatomie* (*Archiv für Entwicklungsmechanik der Organismen*) **9**, 413–468 (1873).

Allen, F. H. The Cambridge Structural Database: A quarter of a million crystal structures and rising. *Acta Crystallographica* **B58**, 380–388 (2002).

Astbury, W. T. and Yardley, K. [Lonsdale] Tabulated data for the examination of the 230 space-groups by homogeneous X rays. *Philosophical Transactions of the Royal Society (London)* **A244**, 221–257 (1924).

Avrami, M. Direct determination of crystal structure from X-ray data. *Physical Review* **54**, 300–303 (1938).

Bacon, G. E. *Neutron Diffraction.* 1st edition (1955). 2nd edition (1962). 3rd edition, Oxford University Press: Oxford (1975).

Bacon, G. E., Curry, N. A., and Wilson, S. A. A crystallographic study of solid benzene by neutron diffraction. *Proceedings of the Royal Society (London)* **A279**, 98–110 (1964).

Banerjee, K. Determinations of the signs of the Fourier terms in complete crystal structure analysis. *Proceedings of the Royal Society (London)* **A141**, 188–193 (1933).

Barlow, W. Über die Geometrischen Eigenschaften homogener starrer Strukturen und ihre Anwendung auf Krystalle. [On the geometrical properties of homogeneous rigid structures and their application to crystals.] *Zeitschrift für Krystallographie und Mineralogie* **23**, 1–63 (1894).

Barlow, W. and Pope, W. J. The relation between the crystalline form and chemical constitution of simple inorganic substances. *Transactions of the Chemical Society (London)* **91**, 1150–1214 (1907).

Bentley, W. A. *Snow Crystals*. McGraw-Hill: New York (1931).

Bergerhoff, G. and Brown, I. D. Inorganic Crystal Structure Database. In: *Crystallographic Databases. Information Content, Software Applications, Scientific Applications*, Section 2.2, pp. 77–95. International Union of Crystallography: Bonn, Cambridge, Chester (1987).

Bergfors, T. M. (ed.). *Protein Crystallization: Techniques, Strategies, and Tips: A Laboratory Manual.* 1st edition (1999). 2nd edition, International University Line: La Jolla, CA (2009).

Bergman, T. Variae Crystallorum Formae a Spatho Orthae. [Various crystal shapes explained by the position of heavenly bodies.] *Nova Acta Regiae Societatis Scientiarum Upsaliensis* **1**, 150–155 (1773). English translation: Cullen, E. *Physical and Chemical Essays.* 3 volumes. J. Murray: London (1784).

Berman, H. M., Henrick, K., and Nakamura, H. Announcing the worldwide Protein Data Bank. *Nature Structural Biology* **10**, 980 (2003).

Bernal, J. D. Carbon skeleton of the sterols. *Chemistry and Industry* **51**, 466 (1932).

Bernal, J. D. and Crowfoot, D. X-ray photographs of crystalline pepsin. *Nature* **133**, 794–795 (1934).

Bernstein, F. C., Koetzle, T. F., Williams, G. J. B., Meyer, E. F. Jr, Brice, M. D., Rodgers, J. R., Kennard, O., Shimanouchi, T., and Tasumi M. The Protein Data Bank: A calculator-based archival file for macromolecular structures. *Journal of Molecular Biology* **112**, 535–542 (1977).

Bhat, T. N. Calculation of an OMIT map. *Journal of Applied Crystallograph*y **21**, 279–281 (1988).

Bhat, T. N. and Cohen, G. H. OMITMAP: An electron density map suitable for the examination of errors in a macromolecular model. *Journal of Applied Crystallography* **17**, 244–248 (1984).

Bijvoet, J. M., Kolkmeyer, N. H., and McGillavry, C. H. *X-ray Analysis of Crystals.* Interscience: New York; Butterworths: London (1951). Originally *Röntgenanalyse van Kristallen.* [X-ray Analysis of Crystals.] 2nd edition, revised. D. B. Centen: Amsterdam (1948).

Bijvoet, J. M., Peerdeman, A. F., and van Bommel, A. J. Determination of the absolute configuration of optically active compounds by means of X rays. *Nature* **168**, 271–272 (1951).

Blundell, T. L. and Johnson, L. N. *Protein Crystallography.* Academic Press: New York, 1976.

Bokhoven, C., Schoone, J. C., and Bijvoet, J. M. On the crystal structure of strychnine sulfate and selenate. III. [001] projection. *Proceedings of the Koninklijke Nederlandse Akademie van Wetenschappen* **52**, 120–121 (1949).

Bragg, W. L. The structure of some crystals as indicated by their diffraction of X rays. *Proceedings of the Royal Society (London)* **A89**, 248–277 (1913).

Bragg, W. H. IX Bakerian lecture. X-rays and crystal structures. *Transactions of the Royal Society (London) A215*, 253–274 (1915).

Bragg, W. H. and Bragg, W. L. The structure of the diamond. *Nature* **91**, 557 (1913).

Bravais, A. Mémoire sur les systèmes formés par des points distribués regulièrement sur un plan ou dans l'espace. *Journal de l'École Polytechnique (Paris).* **19** (cahier 33), 1–128 (1850). English translation: Shaler, A. J. On the system formed by points regularly distributed on a plane or in space. *Crystallographic Society of America Memoir # 1* (Monograph # 4), New York (1949).

Brock, C. P. and Dunitz, J. D. Temperature dependence of thermal motion in crystalline naphthalene. *Acta Crystallographica* **B38**, 2218–2228 (1982).

Brown, I. D. What factors determine cation coordination numbers? *Acta Crystallographica* **B44**, 545–553 (1988).

Brown, I. D. *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*, IUCr Monographs on Crystallography 12. Oxford University Press: Oxford (2006).

Brumberger, H. (ed.). *Modern Aspects of Small-Angle Scattering*, NATO Science Series C. Kluwer/Springer: New York (1994).

Buerger, M. J. *X-ray Crystallography.* Wiley: New York (1942).

Buerger, M. J. *The Precession Method in X-ray Crystallography.* Wiley: New York (1964).

Bunn, C. W. *Chemical Crystallography. An Introduction to Optical and X-ray Methods*. 1st edition (1946). 2nd edition, Oxford at the Clarendon Press: Oxford (1961).

Bürgi, H. B., Dunitz, J. D., and Shefter, E. Geometrical reaction coordinates. Nucleophilic addition to a carbonyl group. *Journal of the American Chemical Society* **95**, 5065–5067 (1973).

Burke, J. G. *Origins of the Science of Crystals.* University of California Press: Berkeley, Los Angeles (1966).

Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G., and Spagna, R. SIR2004: An improved tool for crystal structure determination and refinement. *Journal of Applied Crystallography* **38**, 381–388 (2005).

Cahn, R. S., Ingold, C. K., and Prelog, V. Specification of molecular chirality. *Angewandte Chemie International Edition* **5**, 385–415 (1966).

Caliandro, R., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., and Siliqi, D. Phasing at resolution higher than the experimental resolution. *Acta Crystallographica* **D61**, 556–565 (2005).

Caliandro, R., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., and Siliqi, D. Advances in the free lunch method. *Journal of Applied Crystallography* **40**, 931–937 (2007).

Carslaw, H. S. *Introduction to the Theory of Fourier's Series and Integrals*. 3rd edition. Macmillan and Company: London (1930).

Chadwick, J. The existence of a neutron. *Proceedings of the Royal Society (London)* **A136**, 692–708 (1932).

Chayen, N. E. Methods for separating nucleation and growth in protein crystallization. *Progress in Biophysics and Molecular Biology* **88**, 329–337 (2005).

Coppens, P. *X-ray Charge Densities and Chemical Bonding*, IUCr Texts on Crystallography 4. Oxford University Press: Oxford (1997).

Coster, D., Knol, K. S., and Prins, J. A. Unterschiede in der Intensität der Röntgenstrahlenreflexion an den beiden 111 Flächen der Zinkblende. [Difference in the intensities of X-ray reflection from the two sides of the 111 plane of zinc blende.] *Zeitschrift für Physik* **63**, 345–369 (1930).

Cotton, F. A. *Chemical Applications of Group Theory.* 2nd edition. Wiley-Interscience: New York, London, Sydney (1971).

Cox, E. G. and Smith, J. A. S. Crystal structure of benzene at −3°. *Nature* **173**, 75 (1954).

Crowther, R. A. and Blow, D. M. A method of positioning a known molecule in an unknown crystal structure. *Acta Crystallographica* **23**, 544–548 (1967).

Cullity, B. D. *Elements of X-Ray Diffraction.* 1st edition (1956). 2nd edition (1978). 3rd edition, with S. R. Stock, Addison-Wesley: Reading, MA (2001).

Curie, J. and Curie, P. Développment, par pression, de l'électricité polaire dans les cristaux hémièdres à faces inclinées. *Comptes Rendus de l'Académie des Sciences (Paris)* **91**, 294–295 (1880).

Dauter, Z. Phasing in iodine for structure determination. *Nature Biotechnology* **22**, 1239–1240 (2004).

Dauter, Z., Dauter, M., and Rajashankar, K. R. Novel approach to phasing proteins: Derivatization by short

cryo-soaking with halides. *Acta Crystallographica* **D56**, 232–237 (2000).

Davisson, C. and Germer, L. H. The scattering of electrons by a single crystal of nickel. *Nature* **119**, 558–560 (1927).

de Broglie, M. L. Radiations.—Ondes et quanta. [Radiation—waves or quanta.] *Comptes Rendus de l'Académie des Sciences (Paris)* **1177**, 507–510 (1923).

de Sénarmont, H., Verdet, E., and Fresnel, L. F. (eds.). *Œvres Complètes d'Augustin Fresnel*. Volume 1, pp. 129–170. Imprimerie Impériale: Paris (1866).

de Wolff, P. M. and Gruber, B. Niggli lattice characters: Definition and graphical representation. *Acta Crystallographica* **A47**, 29–36 (1991).

Debye, P. Interferenz von Röntgenstrahlen und Wärmebewegung. [X-ray interference and thermal motion.] *Annalen der Physik* **43**, 49–95 (1914). English translation in: *Collected Papers of Peter J. W. Debye*, pp. 3–39. Interscience: New York (1954).

DeLucas, L. J., Moore, K. M., and Long, M. M. Protein crystal growth and the International Space Station. *Gravitational and Space Biology Bulletin* **12**, 39–45 (1999).

Dianoux, A. J. and Lander, G. H. *Neutron Data Booklet*. 2nd edition. Institut Laue-Langevin, Old City Publishing: Philadelphia, London, Paris (2003).

Dickerson, R. E., Kopka, M. L., and Pjura, P. Base sequence, helix geometry, hydration, and helix stability in B-DNA. In: *Biological Macromolecules and Assemblies*, Volume 2, *Nucleic Acid and Interactive Proteins* (eds. F. Jurnak and A. McPherson). Chapter 2, pp. 38–126. Wiley: New York (1985).

Dittrich, B., Koritsanszky, T., Volkov, A., Mebs, S., and Luger, P. Novel approaches to the experimental charge density of vitamin B_{12}. *Angewandte Chemie, International Edition* **46**, 2935–2938 (2007).

Dodson, E. J. and Woolfson, M. M. ACORN2: New developments of the ACORN concept. *Acta Crystallographica* **D65**, 881–891 (2009).

Dougherty, J. P. and Kurz, S. K. A second harmonic analyzer for the detection of non-centrosymmetry. *Journal of Applied Crystallography* **9**, 145–158 (1976).

Drenth, J. *Principles of Protein X-ray Crystallography*. 1st edition (1994). 2nd edition (1999). 3rd edition, Springer-Verlag: New York (2007).

Duane, W. The calculation of the X-ray diffracting power at points in a crystal. *Proceedings of the National Academy of Sciences of the United States of America* **11**, 489–493 (1925).

Ducruix, A. and Giegé, R. (eds.). *Crystallization of Nucleic Acids and Proteins. A Practical Approach*. 1st edition (1992).

2nd edition, Oxford University Press: Oxford (1999).

Dunitz, J. D. *X-Ray Analysis and the Structure of Organic Molecules.* Cornell University Press: Ithaca, NY (1979). Revised edition, Wiley-VCH: New York (1996).

Dunitz, J. D., Schomaker, V., and Trueblood, K. N. Interpretation of atomic displacement parameters from diffraction studies of crystals. *Journal of Physical Chemistry* **92**, 856–867 (1988).

Emsley, P. and Cowtan, K. Coot: Model-building tools for molecular graphics. *Acta Crystallographica* **D60**, 2126–2132 (2004).

Ewald P. P. Zur Theorie der Interferenzen der Röntgentstrahlen in Kristallen. *Physikalische Zeitschrift*, **14**, 465–472 (1913). English translation: Cruickshank, D. W. J., Juretschke. H. J., and Kato, N. *P. P. Ewald and His Dynamical Theory of X-ray Diffraction*. International Union of Crystallography Monographs on Crystallography 2, pp. 114–123. Oxford University Press/International Union of Crystallography: Oxford (1992).

Ewald, P. P. Das "Reziproke Gitter" in der Strukturtheorie. Teil I: Das Reziproke eines einfachen Gitter. [The "reciprocal lattice" in the theory of structure. Part 1. The reciprocal of a primitive lattice.] *Zeitscrift für Kristallographie* **56**, 129–156 (1921).

Ewald, P. P. Introduction to the dynamical theory of X-ray diffraction. *Acta Crystallographica* **A25**, 103–108 (1969).

Fedorov, E. S. Simmetriia pravil'nykh sistem figur. [The symmetry of real systems of configurations.] *Zapiski Imperatorskogo S. Petersburgskogo Mineralogichesgo Obshchestva* [*Transactions of the Mineralogical Society of St. Petersburg*] **28**, 1–146 (1891). English translation: Harker, D. and Harker, K. *Symmetry of Crystals*, American Crystallographic Association Monograph No. 7, pp. 50–131. American Crystallographic Association: Buffalo, NY (1971).

Feynman, R. P., Leighton, R. B., and Sands, M. *The Feynman Lectures on Physics: Mainly Mechanics, Radiation and Heat.* Addison-Wesley: Reading, MA; Palo Alto, CA; London (1963).

Fischer, E. Synthesen in der Zuckergruppe. I. [Syntheses of sugars. I.] *Berichte der Deutschen Chemischen Gesellschaft* **23**, 2114–2141 (1890).

Fischer, E. Synthesen in der Zuckergruppe. II. [Syntheses of sugars. II.] *Berichte der Deutschen Chemischen Gesellschaft* **27**, 3189–3232 (1894).

Flack, H. D. On enantiomorph-polarity estimation. *Acta Crystallographica* **A39**, 876–881 (1983).

Fourier, J. B. J. *Théorie Analytique de la Chaleur.* Firmin Didot: Paris (1822). [English translation with notes: Freeman, A. *Analytical Theory of Heat*. Cambridge University

Press: London (1878); republication by Dover Phoenix Editions: New York (1955); digital version (2009).]

Franklin, R. E. and Gosling, R. G. Molecular configuration in sodium thymonucleate. *Nature* **171**, 740–741 (1953).

Frausto da Silva, J. J. R. and Williams, R. J. P. *The Biological Chemistry of the Elements: The Inorganic Chemistry of Life.* 2nd edition. Oxford University Press: New York (2001).

Friedel G. Sur les symétries cristallines que peut révéler la diffraction des rayons Röntgen. [Concerning crystal symmetry revealed by X-ray diffraction.] *Comptes Rendus de l'Académie des Sciences (Paris)* **157**, 1533–1536 (1913).

Friedrich, W., Knipping, P., and Laue, M. Interferenz-Erscheinungen bei Röntgenstrahlen [Interference phenomena with X rays.] *Sitzungberichte der mathematische-physikalischen Klasse der Königlichen Bayerischen Akademie der Wissenschaften zu München*, pp. 303–322 (1912). English translation: Stezowski, J. J. In: *Structural Crystallography in Chemistry and Biology* (ed. Glusker, J. P.), pp. 23–39. Hutchinson & Ross: Stroudsburg, PA (1981). [Max Laue became Max von Laue after his article was published].

Gabe, E. J., Taylor, M. R., Glusker, J. P., Minkin, J. A., and Patterson, A. L. The crystal structure of 2-keto-3-ethoxybutyraldehyde-bis(thiosemicarbazone). *Acta Crystallographica* **B25**, 1620–1631 (1969).

Germain, G., Main, P., and Woolfson, M. M. The application of phase relationships to complex structures. *Acta Crystallographica* **A27**, 368–376 (1971).

Gibbs, J. W. *Vector Analysis. A Text-book for the Use of Students of Mathematics and Physics. Founded upon the Lectures of J. Willard Gibbs, Ph.D., LL.D. Formerly Professor of Mathematical Physics in Yale University.* (By Wilson, E. B.) Yale University Press: New Haven, CT (1901).

Glasser, L. Fourier transforms for chemists. Part I. Introduction to the Fourier transform. *Journal of Chemical Education* **64**, A228–A233 (1987a).

Glasser, L. Fourier transforms for chemists. Part 2. Fourier transforms in chemistry and spectroscopy. *Journal of Chemical Education* **64**, A260–A268 (1987b).

Glusker, J. P., Patterson, A. L., Love, W. E., and Dornberg, M. L. X-ray crystal analysis of the substrates of aconitase. IV. The configuration of the naturally occurring isocitric acid as determined from potassium and rubidium salts of its lactone. *Acta Crystallographica* **16**, 1102–1107 (1963).

Glusker, J. P., van der Helm, D., Love, W. E., Dornberg, M. L., Minkin, J. A., Johnson, C. K., and Patterson, A. L. X-ray crystal analysis of the substrates of aconitase. VI. The structures of sodium and lithium dihydrogen citrates. *Acta Crystallographica* **19**, 561–572 (1965).

Glusker, J. P., van der Helm, D., Love, W. E., Minkin, J. A., and Patterson, A. L. The molecular structure of an azidopurine. *Acta Crystallographica* **B24**, 359–366 (1968).

Glusker, J. P., Minkin, J. A., and Patterson, A. L. X-ray crystal analysis of the substrates of aconitase. IX. A refinement of the structure of anhydrous citric acid. *Acta Crystallographica* **B25**, 1066–1072 (1969).

Glusker, J. P., Lewis, M., and Rossi, M. *Crystal Structure Analysis for Chemists and Biologists.* VCH: New York (1994).

Green, D. W., Ingram, V. M., and Perutz, M. F. The structure of haemoglobin. IV. Sign determination by the isomorphous replacement method. *Proceedings of the Royal Society(London)* **A225**, 287–307 (1954).

Grimaldi, F. M. *Physicomathesis de Lumine, Coloribus, et Iride, aliisque annexis.* [Physical insights into light, colors, and the spectrum (rainbow).] Vittoro Bonati: Bologna, Italy (1665).

Groth, P. H. R. von. *Chemische Kristallographie.* 5 volumes. Leipzig: Engelmann (1906–1919).

Guinier, A. and Fournet, G. *Small Angle Scattering of X-rays.* John Wiley: New York (1955).

Grzeskowiak, K., Yanagi, K., Privé, G. G., and Dickerson, R. E. The structure of B-helical C-G-A-T-C-G-A-T-C-G and comparison with C-C-A-A-C-G-T-T-G-C. The effect of base pair reversals. *The Journal of Biological Chemistry* **266**, 8861–8883 (1991).

Hahn, T. (ed.). *International Tables for Crystallography*, Volume A, *Space-group Symmetry.* Kluwer Academic (2005).

Hajdu, J., Machin, P. A., Campbell, J. W., Greenhough, T. J., Clifton, I. J., Zurek. S., Gover, S., Johnson, L. N., and Elder, M. Millisecond X-ray diffraction and the first electron density map from Laue photographs of a protein crystal. *Nature* **329**, 178–181 (1987).

Harburn, G., Taylor, C. A., and Welberry, T. R. *Atlas of Optical Transforms*. Bell and Sons: London (1975).

Harker, D. The application of the three-dimensional Patterson method and the crystal structures of proustite, Ag_3AsS_3, and pyrargyrite, Ag_3SbS_3. *Journal of Chemical Physics* **4**, 381–390 (1936).

Harker, D. The determination of the phases of the structure factors of non-centrosymmetric crystals by the method of double isomorphous replacement. *Acta Crystallographica* **9**, 1–9 (1956).

Harker, D. and Kasper, J. S. Phases of Fourier coefficients directly from crystal diffraction data. *Acta Crystallographica* **1**, 70–75 (1948).

Harp, J. M., Timm, D. E., and Bunick, G. J. Macromolecular crystal annealing: Overcoming increased mosaicity associ-

ated with cryocrystallography. *Acta Crystallographica* **D54**, 622–628 (1998).

Hartree, D. R. The wave mechanics of an atom with a non-Coulomb central field. Part I—Theory and methods. Part II—Some results and discussion. *Proceedings of the Cambridge Philosophical Society* **24**, 89–110, 111–132 (1928).

Hartshorne, N. H. and Stuart, A. *Crystals and the Polarising Microscope.* 2nd edition. Edward Arnold: London (1950).

Hauptman, H. On the identity and estimation of those cosine invariants, cos ($\psi_1 + \psi_2 + \psi_3 + \psi_4$), which are probably negative. *Acta Crystallographica* **A31**, 472–476 (1974).

Hauptman, H. A. and Karle, J. *Solution of the Phase Problem I. The Centrosymmetric Crystal*. American Crystallographic Association Monograph No. 3. The Letter Shop: Washington, DC (1953).

Häuy, R.-J. *Essai d'une théorie sur la structure des crystaux appliquée a plusieurs genres de substances crystallisées*. [Essay on a theory on the structure of crystals applied to various types of crystalline materials.] Gogué and Née de la Rochelle: Paris (1784).

Häuy, R, J. *Traité de Minéralogie.* [Treatise on Mineralogy.] 5 volumes. Chez Louis: Paris (1801).

Havighurst, R. J. The distribution of diffracting power in sodium chloride. *Proceedings of the National Academy of Sciences of the United States of America* **11**, 498–502 (1925).

Helliwell, J. R. *Macromolecular Crystallography with Synchrotron Radiation.* Cambridge University Press: Cambridge (1992).

Hendrickson, W. A. Determination of macromolecular structures from anomalous diffraction of synchrotron radiation. *Science* **254**, 51–58 (1991).

Hendrickson, W. A. and Teeter, M. M. Structure of the hydrophobic protein crambin determined directly from the anomalous scattering of sulfur. *Nature* **290**, 107–113 (1981).

Hirshfeld, F. Can X-ray data distinguish bonding effects from vibrational smearing? *Acta Crystallographica* **A32**, 239–244 (1976).

Hodgkin, D. C., Kamper, J., Lindsey, J., Mackay, M., Pickworth, J., Robertson, J. H., Shoemaker, C. B., White, J. G., Prosen, R. J., and Trueblood, K. N. The structure of vitamin B_{12}. I. An outline of the crystallographic investigations of vitamin B_{12}. *Proceedings of the Royal Society (London)* **A242**, 228–263 (1957).

Hodgkin, D. C., Pickworth, J., Robertson, J. H., Prosen, R. J., Sparks, R. A., and Trueblood, K. N. The structure of vitamin B_{12}. II. The crystal structure of a hexacarboxylic acid obtained by the degradation of vitamin B_{12}. *Proceed-*

ings of the Royal Society (London) **A251**, 306–352 (1959).

Holden, A. and Singer, P. *Crystals and Crystal Growing.* New York: Doubleday (1960).

Holmes, K. C. and Blow, D. M. The use of X-ray diffraction in the study of protein and nucleic acid structure. In *Methods in Biochemical Analysis* (ed. Glick, D.), Vol. 13, pp. 113–239. Wiley: New York (1965). Reprinted by Interscience: New York (1966).

Hooke, R. *Micrographia. Some Physiological Descriptions of Minute Bodies Made by Magnifying Glasses with Observations and Inquiries Thereupon.* J. Martyn and J. Allestry (for the Royal Society): London (1665).

Hoppe, W. and Gassmann, J. Phase correction, a new method to solve partially known structures. *Acta Crystallographica* **B24**, 97–107 (1968).

Hughes, E. W. The crystal structure of melamine. *Journal of the American Chemical Society* **68**, 1970–1975 (1946).

Hümmer, K. and Billy, H. Experimental determination of triplet phases and enantiomorphs of noncentrosymmetric structures. I. Theoretical considerations. *Acta Crystallographica* **A42**, 127–133 (1986).

Huygens, C. *Traité de la lumière*. [Treatise on light.] Pierre van der Aa: Leyden (1690). English translation: Thompson, S. P. *Treatise on Light*. Macmillan: London (1912).

James, R. W. *The Optical Principles of the Diffraction of X-Rays*. G. Bell and Sons: London (1948, 1950, 1954, 1962); Cornell University Press: Ithaca, NY (1965).

Jeffrey, G. A., Ruble, J. R., McMullan, R. K., and Pople, J. A. The crystal structure of deuterated benzene. *Proceedings of the Royal Society (London)* A**414**, 47–57 (1987).

Jenkins, R. and Snyder, R. *Introduction to X-ray Powder Diffractometry*. Wiley-Interscience: New York (1996).

Jenkins, F. A. and White, H. E. *Fundamentals of Optics.* 3rd edition. McGraw-Hill: New York (1957).

Johnson, C. K. *ORTEP: A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations.* ORNL Report #3794. Oak Ridge National Laboratory: Oak Ridge, TN (1965).

Johnson, C. K. Addition of higher cumulants to the crystallographic structure-factor equation: A generalized treatment for thermal-motion effects. *Acta Crystallographica* **A25**, 187–194 (1969).

Johnson, C. K., Gabe, E. J., Taylor, M. R., and Rose, I. A. Determination by neutron and X-ray diffraction of the absolute configuration of an enzymatically formed α-monodeuteroglycolate. *Journal of the American Chemical Society*, **87**, 1802–1804 (1965).

Jones, T. A., Zou, J. Y., Cowan, S. W., and Kjeldgaard, M. Improved methods for building protein models in electron density maps and the location of errors in these models. *Acta Crystallographica* **A47**, 110–119 (1991).

Judson, H. F. *The Eighth Day of Creation: Makers of the Revolution in Biology.* 1st edition, Simon and Schuster: New York (1979). 2nd edition, Cold Spring Harbor Laboratory Press: Cold Spring Harbor, NY (1996).

Kantardjieff, K. A. and Rupp, B. Matthews coefficient probabilities: Improved estimates for unit cell contents of proteins, DNA, and protein–nucleic acid complex crystals. *Protein Science* **12**, 1865–1871 (2003).

Karle, J. and Hauptman, H. The phases and magnitudes of the structure factors. *Acta Crystallographica* **3**, 181–187 (1950).

Karle, J. and Karle, I. L. The symbolic addition procedure for phase determination for centrosymmetric and noncentrosymmetric crystals. *Acta Crystallographica* **21**, 849–859 (1966).

Kasai, N. and Kakudo, M. *X-ray Diffraction by Macromolecules.* Kodansha: Tokyo, and Springer: Berlin, Heidelberg, New York (2005).

Kasper, J. S., Lucht, C. M., and Harker, D. The crystal structure of decaborane, $B_{10}H_{14}$. *Acta Crystallographica* **3**, 436–455 (1950).

Katz, A. K., Li, X., Carrell, H. L., Hanson, B. L., Langan, P., Coates, L., Schoenborn, B. P., Glusker, J. P., and Bunick, G. J. Locating active-site hydrogen atoms in D-xylose isomerase: Time-of-flight neutron diffraction. *Proceedings of the National Academy of Sciences* **103**, 8342–8347 (2006).

Kendrew, J. C., Dickerson, R. E., Strandberg, B. E., Hart, R. G., Davies, D. R., Phillips, D. C., and Shore, V. C. Structure of myoglobin. A three-dimensional Fourier synthesis at 2 Å resolution. *Nature* **185**, 422–427 (1960).

Kepler, J. *Strena seu de nive sexangula*. [The six-cornered snowflake]. Godefridum Tambach: Francofurti ad Moenum (1611). English translation: Hardie, C. *The Six-cornered Snowflake.* Clarendon Press: Oxford (1966).

Kitaigorodsky, A. I. *Molecular Crystals and Molecules.* Physical Chemistry Monographs Volume 29. Academic Press: London (1973).

Koch, M. H., Vachette, P., and Svergun, D. I. Small-angle scattering: A view on the properties, structures and structural changes of biological macromolecules in solution. *Quarterly Review of Biophysics* **36**, 147–227 (2003).

Ladd, M. F. C. and Palmer, R. A. *Structure Determination by X-ray Crystallography.* 4th Edition. Kluwer Academic/Plenum: New York (2003).

Lamzin, V. S., Perrakis, A., and Wilson, K. S. The ARP/wARP suite for automated construction and refinement of protein models. In: *International Tables for Crystallography*, Volume F: *Crystallography of biological macromolecules*. Rossmann, M. G. and Arnold, E. (eds.). Kluwer Academic: Dordrecht, pp. 720–722 (2001).

Langridge, R., Seeds, W. E., Wilson, H. R., Hooper, C. W., Wilkins, M. H. F., and Hamilton, L. D. Molecular structure of deoxyribonucleic acid (DNA). *Journal of Biophysical and Biochemical Cytology***3**, 767–778 (1957).

Le Bel, J. A. Sur les relations qui existent entre les formules atomiques des corps organiques, et le pouvoir rotatoire de leurs dissolutions. [On the relations which exist between the atomic formulas of organic compounds and the rotatory power of their solutions.] *Bulletin de la Société Chimique de France* **22**, 337–347 (1874). English translation: Benfy, O. T. In: *Classics in the Theory of Chemical Combinations*, pp. 151–171. Dover: New York (1963).

Legendre, A. M. Appendix. Sur la méthode des moindres quarrés. In: *Nouvelles Méthodes pour la Détermination des Orbites des Comètes*, pp. 72–75. Courcier: Paris (1805). English translation: Harvey, G. On the method of minimum squares, employed in the reduction of experiments, being a translation of the appendix to an essay of Legendre's entitled "Nouvelles Méthodes pour la Détermination des Orbites des Comètes," with remarks. *Edinburgh Philosophical Journal* **7**, 292–301 (1822).

Leslie, A. G. W. A reciprocal-space method for calculating a molecular envelope using the algorithm of B. C. Wang. *Acta Crystallographica* **A43**, 134–136 (1987).

Lima-de-Faria, J. (ed.). *Historical Atlas of Crystallography*. Kluwer Academic: Dordrecht, Boston, London (1990).

Lipscomb, W. N. Structures of the boron hydrides. *Journal of Chemical Physics* **22**, 985–988 (1954).

Lipson, H. and Cochran, W. *The Crystalline State*, Volume III, *The Determination of Crystal Structures.* Cornell University Press: Ithaca, NY; G. Bell and Sons: London (1966).

Lonsdale, K. The structure of the benzene ring. *Nature* **122**, 810 (1928).

Matthews, B. W. Solvent content of protein crystals. *Journal of Molecular Biology* 33, 491–497 (1968).

McPherson, A. *Preparation and Analysis of Protein Crystals*. Wiley: New York (1982).

McRee, D. E. *Practical Protein Crystallography.* 1st edition (1993). 2nd edition, Academic Press: San Diego (1999).

Miller, R., DeTitta, G. T., Jones. R., Langs, D. A., Weeks, C. M., and Hauptman, H. A. On the application of the

minimal principle to solve unknown structures. *Science* **259**, 1430–1433 (1993).

Miller, R., Gallo, S. M., Khalak, H. G., and Weeks, C. M. SnB: Crystal structure determination via shake-and-bake. *Journal of Applied Crystallography* **27**, 613–621 (1994).

Miller, W. H. *A Treatise on Crystallography.* Pitt Press (Deighton): Cambridge, and Parker: London (1839).

Mitchell, D. P. and Powers, P. N. Bragg reflection of slow neutrons. *Physical Review* **50**, 486–487 (1936).

Mitscherlich, E. Sur la relation qui existe entre la forme cristalline et les proportions chimiques. I. Mémoire sur les arseniates et les phosphates. [On the relationship that exists between crystal form and chemical proportions. I. Note on arsenates and phosphates.] *Annales des Chimie et des Physique* **19**, 350–419 (1822).

Moffat, K., Szebenyi, D., and Bilderback, D. X-ray Laue diffraction from protein crystals. *Science* **223**, 1423–1425 (1984).

Müller, P. Practical suggestions for better crystal structures. *Crystallography Reviews* **15**, 57–83 (2009).

Murshudov, G. N., Vagin, A. A., and Dodson, E. J. Refinement of macromolecular structures by the maximum-likelihood method. *Acta Crystallographica* **D53**, 240–253 (1997).

Niggli, P. *Krystallographische und Strukturtheoretische Grundbegriffe*, Volume 7, Part 1, pp. 108–176. Handbuch der Experimentalphysik. Akademische Verlagsgesellschaft: Leipzig, Germany (1928).

Nyburg, S. C. *X-ray Analysis of Organic Structures.* Academic Press: New York (1961).

Okaya, Y., Saito, Y., and Pepinsky, R. New method in X-ray crystal structure determination involving the use of anomalous dispersion. *Physical Review* **98**, 1857–1858 (1955).

Oldfield, T. J. Automated tracing of electron-density maps of proteins. *Acta Crystallographica* **D59**, 483–491 (2003).

Oszlányi, G. and Süto, A. Ab initio structure solution by charge flipping. II. Use of weak reflections. *Acta Crystallographica* **A61**, 147–152 (2005).

Ott, H. Zur Methodik der Strukturanalyses. [On a method of structure analysis.] *Zeitschrift für Kristallographie* **66**, 136–153 (1927).

Palatinus, L. and Chapuis, G. *SUPERFLIP*—a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. *Journal of Applied Crystallography* **40**, 786–790 (2007).

Pasteur, L. Mémoire sur la relation qui peut exister entre la forme cristalline et la composition chimique et sur la cause de la polarisation rotatoire. [Note on the relationship of crystalline form to chemical composition, and on the cause of rotatory polarization.] *Comptes Rendus de l'Académie des Sciences (Paris)* **26**, 535–538 (1848).

Patterson, A. L. A Fourier series method for the determination of the components of interatomic distances in crystals. *Physical Review* **46**, 372–376 (1934).

Patterson, A. L. A direct method for the determination of the components of interatomic distances in crystals. *Zeitschrift für Kristallographie* **90**, 517–542 (1935).

Patterson, A. L. Treatment of anomalous dispersion in X-ray diffraction data. *Acta Crystallographica* **16**, 1255–1256 (1963).

Patterson, T. S. and Buchanan, C. Historical and other considerations regarding the crystal form of sodium-ammonium *d*- and *l*-tartrate, potassium *d*- and *l*-tartrate, potassium-ammonium *d*- and *l*-tartrate, and potassium racemate. *Annals of Science* **5**, 288–295, 317–324 (1945).

Pauling, L. The principles determining the structure of complex ionic crystals. *Journal of the American Chemical Society* **51**, 1010–1026 (1929).

Perutz, M. F. Stereochemistry of cooperative effects in hæmoglobin. *Nature* **228**, 726–734 (1976).

Perutz, M. F., Muirhead, H., Cox, J. M., Goaman, L. C. G., Mathews, F. S., McGandy, E. L., and Webb, L. E. Three-dimensional Fourier synthesis of horse oxyhæmoglobin at 2.8 Å resolution: (I) X-ray analysis. *Nature* **219**, 29–32 (1968).

Peterson, S. W. and Levy, H. A. A single crystal neutron diffraction determination of the hydrogen position in potassium bifluoride. *Journal of Chemical Physics* **20**, 704–707 (1952).

Phillips, D. C. The three-dimensional structure of an enzyme molecule. *Scientific American* **215**, 78–90 (1966).

Phillips, F. C. *An Introduction to Crystallography*. 3rd edition, Longmans, Green: London (1963). 4th edition, Oliver and Boyd: Edinburgh (1971).

Planck, M. Über das Gesetz der Energieverteilung im Normalspektrum. [On the law of distribution of energy in the normal spectrum.] *Annalen der Physik* **4**, 553–563 (1901).

Pople, J. A. Nobel Lecture: Quantum chemical models. *Reviews of Modern Physics* **71**, 1267–1274 (1999).

Porter, A. B. On the diffraction theory of microscopic vision. *Philosophical Magazine* **11**, 154–166 (1906).

Ravelli, R. G. B., Leiros, H. K. S., Pan, B., Caffrey, M. and McSweeney S. Specific radiation damage can be used to solve macromolecular structures. *Structure* **11**, 217–224 (2003).

Renninger, M. "Umweganregung," eine bisher unbeachtete Wechselwirkungserscheinung bei Raumgitterinterferenzen. ["Detour-excitation," a hitherto unobserved interaction in space-lattice interference.] *Zeitschrift für Physik* **106**, 141–176 (1937).

Rietveld, H. M. A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography* **2**, 65–71 (1969).

Robertson, J. M. An X-ray study of phthalocyanines. Part II. Quantitative structure determination of the metal-free compound. *Journal of the Chemical Society* 1195–1209 (1936).

Romé de Lisle, J. B. L. *Essai de Cristallographie, ou Description des Figures Géométriques propres à Différens Corps du Règne Minéral, connus vulgairement sous le Nom de Cristaux.* [Essay on crystallography, or a description of geometric figures, characteristic of different materials in the mineral kingdom, known commonly under the name of crystals.] 1st edition. Didot, Knappen & Delaguette: Paris (1772).

Röntgen, W. C. Über eine neue Art von Strahlen. *Sitzungberichte der Würzburger Physikalischen-Medizinishen Gesellschaft*, pp. 132–141 (1895). English translation: Stanton, A. On a new kind of ray. *Science* **3**, 227–231 (1896); *Nature (London)* **53**, 274–276 (1896).

Rosenfield, R. E. Jr., Parthasarathy, R., and Dunitz, J. D. Directional preferences of nonbonded atomic contacts with divalent sulfur. 1. Electrophiles and nucleophiles. *Journal of the American Chemical Society* **99**, 4860–4862 (1977).

Rossmann, M. G. (ed.). *The Molecular Replacement Method*. Gordon and Breach: New York (1972).

Rossmann, M. G. and Blow, D. M. The detection of subunits within the crystallographic asymmetric unit. *Acta Crystallographica* **15**, 24–31 (1962). See also Tollin, P. and Rossmann, M. G. A description of various rotation function programs. *Acta Crystallographica* **21**, 53–57 (1966).

Rubin, B. H., Stallings, W. C., Glusker, J. P., Bayer, M. E., Janin, J., and Srere, P. A. Crystallographic studies of *Escherichia coli* citrate synthase. *Journal of Biological Chemistry* **258**, 1297–1298 (1983).

Sawaya, M. R. Characterizing a crystal from an initial native dataset. In: *Macromolecular Crystallography Protocols*, Volume 2, *Structure Determination*. Doublié, S. (ed.). Methods in Molecular Biology 364. Humana Press: Totowa, NJ (2007).

Sayre, D. The squaring method: A new method for phase determination. *Acta Crystallographica* **5**, 60–65 (1952).

Sayre, D. Report on a project on three-dimensional imaging of the biological cell by single-particle X-ray diffraction. *Acta Crystallographica* **A64**, 33–35 (2008).

Schneer, C.J. (ed.) *Crystal Form and Structure*. Dowden, Hutchinson and Ross. Stroudsburg, Pennsylvania (1977).

Schneider, T. R. and Sheldrick, G. M. Substructure solution with SHELXD. *Acta Crystallographica* **D58**, 1772–1779 (2002).

Schoenflies, A. *Krystallsysteme und Krystallstructur.* [Crystal systems and crystal structures.] B. G. Teubner: Leipzig (1891). 2nd edition (1923). Reprinted, Springer: Berlin (1984).

Schomaker, V. and Trueblood, K. N. On the rigid-body motion of molecules in crystals. *Acta Crystallographica* **B24**, 63–76 (1968).

Shapiro, D., Thibault, P., Beetz, T., Elser, V., Howells, M., Jacobsen, C., Kirz, J., Lima, E., Miao, H., Neiman, A. M., and Sayre, D. Biological imaging by soft X-ray diffraction microscopy. *Proceedings of the National Academy of the United States of America* **102**, 15343–15346 (2005).

Sheldrick, G. M. A short history of SHELX. *Acta Crystallographica* **A64**, 112–122 (2008).

Shen, Q. Solving the phase problem using reference-beam X-ray diffraction. *Physical Review Letters* **80**, 3268–3271 (1998).

Shmueli, U. *Theories and Techniques of Crystal Structure Determination*, IUCr Texts on Crystallography 9, International Union of Crystallography, Oxford Science Publications. Oxford University Press: New York (2007).

Snook, C. F., Purdy, M. D., and Wiener, M. C. Use of a crystallization robot to set up sitting-drop vapor-diffusion crystallization and in situ crystallization screens. *Journal of Applied Crystallography* **33**, 344–349 (2000).

Sommerfeld, A. Remarks in: *La Structure de la Matière.* [The structure of matter.] *Rapports et Discussions du Conseil de Physique tenu à Bruxelles du 27 au 31 Octobre 1913 sous les auspices de l'Institut International de Physique Solvay*, p. 131. [Publication delayed because of the Great War.] Gauthier-Villars: Paris (1921).

Spek, A. L. Single-crystal structure validation with the program PLATON. *Journal of Applied Crystallography* **36**, 7–13 (2003).

Squire, J. M. Fibre and muscle diffraction. In: *Structure and Dynamics of Biomolecules. Neutron and Synchrotron Radiation for Condensed Matter Studies.* Fanchon, E., Geissler, E., Hodeau, J.-L., Regnard, J.-R., and Timmins, P. A. (eds.), Chapter 14, pp. 272–301. Oxford University Press: New York (2000).

Steno [Stensen], N. *De Solido intra Solidum Naturaliter Contento. Dissertationis Prodromus.* [The prodromus to a

dissertation concerning solids naturally contained within solids.] *Ad Serenissimum Ferdinandum II. Magnum Erturiæ Ducem. Stellæ: Florentiæ* (1669). English translation: Oldenburgh, H. Published by J. G. Winter: London (1671).

Stewart, R. F., Davidson, E. R., and Simpson, W. T. Coherent X-ray scattering for the hydrogen atom in the hydrogen molecule. *Journal of Chemical Physics* **42**, 3175–3187 (1965).

Stigler, S. M. The epic story of maximum likelihood. *Statistical Science* **22**, 598–620 (2007).

Stoicheff, B. P. High resolution Raman spectroscopy of gases. II. Rotational spectra of C_6H_6 and C_6D_6 and internuclear distances in the benzene molecule. *Canadian Journal of Physics* **32**, 339–346 (1954).

Stout, G. H. and Jensen, L. H. *X-ray Structure Determination: A Practical Guide.* Macmillan: New York (1968). 2nd edition, Wiley-Interscience: New York (1989).

Stubbs, G., Warren, S., and Holmes, K. Structure of RNA and RNA binding site in tobacco mosaic virus from 4-Å map calculated from X-ray fibre diagrams. *Nature* **267**, 216–221 (1977).

Tanaka, Y., Ohtomo, N., and Katayama, M. A diffraction study of SiO_2 glass—an analysis of neutron and X-ray data by a liquid model. *Journal of the Physical Society of Japan* **54**, 967–976 (1985).

Taylor, C. A, and Lipson, H. *Optical Transforms: Their Preparation and Application to X-ray Diffraction Problems.* G. Bell and Sons: London (1964).

Templeton, D. H., Templeton, L. K., Phillips, J. C., and Hodgson, K. O. Anomalous scattering of X-rays by cesium and cobalt measured with synchrotron radiation. *Acta Crystallographica* **A36**, 436–442 (1980).

Terwilliger, T. C. Maximum-likelihood density modification. *Acta Crystallographica* **D56**, 965–972 (2000).

Thomson, J. J. *Conduction of Electricity through Gases*, p. 268 (1903). 2nd edition, p. 321 (1906). 3rd edition, with Thomson, G. P., in two volumes, Volume II, p. 256 (1928 and 1933). Merchant Books, Cambridge University Press: Cambridge.

Trueblood, K. N., Bürgi, H.-B., Burzlaff, H., Dunitz, J. D., Gramaccioli, C. M., Schulz, H. H., Shmueli, U., and Abrahams, S. C. Atomic displacement parameter nomenclature. Report of a subcommittee on atomic displacement parameter nomenclature. *Acta Crystallographica* **A52**, 770–781 (1996).

Usón, I., Stevenson, C. E., Lawson, D. N, and Sheldrick, G. M. Structure determination of the *O*-methyltransferase NovP using the "free lunch algorithm" as implemented in SHELXE. *Acta Crystallographica* **D63**, 1069–1074 (2007).

Vagin, A. A., Steiner, R. S., Lebedev, A. A., Potterton, L., McNicholas, S., Long, F., and Murshudov, G. N. REFMAC5 dictionary: Organisation of prior chemical knowledge and guidelines for its use. *Acta Crystallographica* **D60**, 2284–2295 (2004).

van der Helm, D., Glusker, J. P., Johnson, C. K., Minkin, J. A., Burow, N. E., and Patterson, A. L. X-ray crystal analysis of the substrates of aconitase. VIII. The structure and absolute configuration of potassium dihydrogen isocitrate isolated from *Bryophyllum calycinum*. *Acta Crystallographica* **B24**, 578–592 (1968).

van't Hoff, J. H. *Voorstel tot Uitbreiding der Tegenwoordige in de Scheikunde gebruikte Structuurformules in de Ruimte, benevens een daarmee samenhangende Opmerking omtrent het Verband tusschen Optisch Actief Vermogen en chemische Constitutie van Organische Verbindingen.* [Proposal for the extension of the structural formulae now in use in chemistry into space, together with a related note on the relation between the optical active power and the chemical constitution of organic compounds.] J. Greven: Utrecht (1874), and *Archives Néerlandaises des Sciences Exactes et Naturelles* **9**, 445–454 (1874). English translation: *Arrangement of Atoms in Space*. Longmans, Green: London (1898).

Verbist, J. J., Lehmann, M. S., Koetzle, T. F., and Hamilton, W. C. Direct methods in neutron crystallography: Structure of L-proline monohydrate by symbolic addition and tangent refinement. *Nature* **235**, 328–329 (1972).

Viterbo, D. Solution and refinement of crystal structures. In: *Fundamentals of Crystallography.* Giacovazzo, C. (ed.), Chapter 5, pp. 320–401. International Union of Crystallography, Oxford University Press (1992).

von Halban, H. and Preiswerk, P. Preuve experimentale de la diffraction des neutrons. (Experimental proof of the diffraction of neutrons.] *Comptes Rendus de l'Académie des Sciences (Paris)* **203**, 73–75 (1936).

Wahlstrom, E. E. *Optical Crystallography*. 5th edition. Wiley: New York, Chichester, Brisbane, Toronto (1979).

Waller, I. Zur Frage der Einwirkung der Wärmebewegung auf die Interferenz von Röntgenstrahlen. [On the question of the influence of heat motion on the scattering of Röntgen rays.] *Zeitschrift für Physik* **17**, 398–408 (1923).

Wang, B.-C. Resolution of phase ambiguity in macromolecular crystallography. *Methods in Enzymology* **115**, 90–112 (1985).

Warren, B. E. X-ray diffraction study of the structure of glass. *Chemical Reviews* **26**, 237–255 (1940).

Waser, J. Pictorial representation of the Fourier method of X-ray crystallography. *Journal of Chemical Education* **45**, 446–451 (1968).

Watson, J. D. and Crick, F. H. C. A structure for deoxyribose nucleic acid. *Nature* **171**, 737–738 (1953).

Weissenberg, K. Ein neues Röntgengoniometer. [A new X-ray camera.] *Zeitschrift für Physik* **23**, 229–238 (1924).

Willis, B. T. M. and Carlile, C. J. *Experimental Neutron Scattering.* Oxford University Press: Oxford (2009).

Willis, B. T. M. and Pryor, A. W. *Thermal Vibrations in Crystallography*. Cambridge University Press: Cambridge (1975).

Wilson, A. J. C. Determination of absolute from relative X-ray intensity data. *Nature* **150**, 151–152 (1942).

Wilson, A. J. C. The probability distribution of X-ray intensities. *Acta Crystallographica* **2**, 318–321 (1949).

Wilson, A. J. C. Largest likely values for the reliability index. *Acta Crystallographica* **3**, 397–398 (1950).

Wilson, C. *Single Crystal Neutron Diffraction from Molecular Materials*, Series on Neutron Techniques and Applications Volume 2. World Scientific: Singapore (2000).

Wilson, H. R. *Diffraction of X-rays by Proteins, Nucleic Acids and Viruses.* Arnold: London (1966).

Wood, E. A. *Crystals and Light: An Introduction to Optical Crystallography.* Van Nostrand: New York (1977).

Wyckoff, R. W. G. *The Analytical Expression of the Results of the Theory of Space Groups*. Publication 38. Carnegie Institution of Washington (1922). 2nd edition (1930).

Yang, C., Pflugrath, J. W., Courville, D. A., Stence, C. N., and Ferrara, J. D. Away from the edge: SAD phasing from the sulfur anomalous signal measured in-house with chromium radiation. *Acta Crystallographica* **D59**, 1943–1957 (2003).

Yao, J.-X., Woolfson, M. M., Wilson, K. S., and Dodson, E. J. A modified ACORN to solve protein structures at resolutions of 1.7 Å or better. *Acta Crystallographica* **D61**, 1465–1475 (2005).

Young, R. A. (ed.). *The Rietveld Method*. Oxford University Press: Oxford (1993).

Young, T. Lecture XXXIX. On the nature of light and colours. In: *A Course of Lectures on Natural Philosophy and the Mechanical Arts*, pp. 457–471 (1807).

Zachariasen, W. H. A new analytical method for solving complex crystal structures. *Acta Crystallographica* **5**, 68–73 (1952).

Zernike, F. and Prins, J. A. Die Beugung von Röntgenstrahlen in Flüssigkeiten als Effekt der Molekülanordnung. [The diffraction of X rays in liquids as an effect of the molecular arrangement.] *Zeitschrift für Physik* **41**, 184–194 (1927).

Acta Crystallographica **and other IUCr journals**

The international organization to which most crystallographers belong, through various national associations, is the International Union of Crystallography (IUCr), which holds congresses and symposia every three years and sponsors publications and compilations. The tables of data published by the IUCr provide not only useful information, but also an explanation of each area of crystallography that is referred to. The reader is urged to browse through *International Tables* (see below), particularly the plane groups in Volume A, and some of the details of the experimental methods that are clearly described in Volume C.

Some journals for crystallographers that are published by the International Union of Crystallography are: *Acta Crystallographica*, *Journal of Applied Crystallography*, and *Journal of Synchrotron Radiation.* Structure determinations are also reported in *Structure Reports*, *Zeitschrift für Kristallographie*, *Inorganic Chemistry*, *Journal of the American Chemical Society*, *Journal of the Chemical Society*, *Acta Chemica Scandinavica*, and *Helvetica Chimica Acta*, among others. *Acta Crystallographica* Sections E and F are online only; all other IUCr journals are available in print and online.

IUCr journals

Acta Crystallographica. ISSN 0365-110X, 1948–1967, http://journals.iucr.org/q/

Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography. ISSN 0567-7394, 1968–1982, http://journals.iucr.org/a/

Acta Crystallographica Section A: Foundations of Crystallography. Schwarzenbach, D. (ed.), ISSN 0108-7673, 1983–, http://journals.iucr.org/a/

Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry. ISSN 0567-7408, 1968–1982, http://journals.iucr.org/b/

Acta Crystallographica Section B: Structural Science. Brock, C. P. (ed.), ISSN 0108-7681, 1983–, http://journals.iucr.org/b/

Acta Crystallographica Section C: Crystal Structure Communications. Linden, A. (ed.), ISSN 0108-2701, 1983–, http://journals.iucr.org/c/

Acta Crystallographica Section D: Biological Crystallography. Baker, E. N. and Dauter, Z. (eds.), ISSN 0907-4449, 1993–, http://journals.iucr.org/d/

Acta Crystallographica Section E: Structure Reports Online. Harrison, W. T. A., Simpson, J., and Weil, M. (eds.), ISSN 1600-5368, 2001–, http://journals.iucr.org/e/

Acta Crystallographica Section F: Structural Biology and Crystallization Communications. Einspahr, H. M. and Weiss, M. S. (eds.), ISSN 1744-3091, 2005–, http://journals.iucr.org/f/

Journal of Applied Crystallography. Pyzalla, A. R. (ed.), ISSN 0021-8898, 1968–, http://journals.iucr.org/j/

Journal of Synchrotron Radiation. Ice, G. E., Kvick, Å., and Ohta, T. (eds.), ISSN 0909-0495, 1994–, http://journals.iucr.org/s/

International Tables for Crystallography (available as books or online)

International Tables for X-ray Crystallography, Volume 1, *Symmetry Groups.* Henry, N. F. M. and Lonsdale, K. (eds.). International Union of Crystallography, Kynoch Press: Birmingham, UK (1969).

(*International Tables for Crystallography* is available from Wiley.)

Volume A, *Space-group Symmetry.* Hahn, T. (ed.), ISBN 978-0-7923-6590-7 (2005), http://it.iucr.org/A/, IUCr/Springer.

Volume A1, *Symmetry Relations Between Space Groups.* Wondratschek, H. and Müller, U. (eds.), ISBN 978-1-4020-2355-2 (2004), http://it.iucr.org/A1/, IUCr/Springer.

Volume B, *Reciprocal Space*. Shmueli, U. (ed.), ISBN 978-1-4020-8205-4 (2008), http://it.iucr.org/B/, IUCr/Springer.

Volume C, *Mathematical, Physical and Chemical Tables.* Prince, E. (ed.), ISBN 978-1-4020-1900-5 (2004), http://it.iucr.org/C/, IUCr/Kluwer Academic.

Volume D, *Physical Properties of Crystals.* Authier, A. (ed.), ISBN 978-1-4020-0714-9 (2003), http://it.iucr.org/D/, IUCr/Kluwer Academic.

Volume E, *Subperiodic Groups*. Kopsk'y, V. and Litvin, D. B. (eds.), ISBN 978-1-4020-0715-6 (2002), http://it.iucr.org/E/, IUCr/Kluwer Academic.

Volume F, *Crystallography of Biological Macromolecules.* Rossmann, M. G. and Arnold, E. (eds.), ISBN 978-0-7923-6857-1 (2001), http://it.iucr.org/F/, IUCr/Kluwer Academic.

Volume G, *Definition and Exchange of Crystallographic Data.* Hall, S. R. and McMahon, B. (eds.), ISBN 978-1-4020-3138-0 (2005), http://it.iucr.org/G/, IUCr/Springer.

Useful books

All teachers of X-ray crystallography, including the present authors, have their favorite sources of information. We have chosen those that we consider to have a simple or clarifying approach. Those readers who wish to delve further into the subject should follow the bibliographies given in some of the books listed. We have tried to keep to a minimum the number of different books referred to, thus necessarily omitting some worthy ones. A few books are mentioned for the browser because they seem delightful, but they are not essential for those with limited time or budget. At the beginning of this book we stated that this is a book that tries to explain "why it is possible to do it," not "how to do it." There are many excellent texts listed here that address both, some concentrating on "how to do it."

The World Wide Web, Google, for example, contains almost everything you would want to know about X-ray and neutron diffraction and their use in structure determination. Many articles are available in full, even some of the historical articles listed in the text. However, the URLs of many informative teaching sites seem to change with time and therefore we have not included them.

Bentley, W. A. *Snow Crystals*. McGraw-Hill: New York (1931). See also Martin, J. B. *Snowflake Bentley*. Houghton-Mifflin: New York (1998).

Bijvoet, J. M., Burgers, W. G., and Hägg, G. (eds.). *Early Papers on Diffraction of X-rays by Crystals* (Volume I, Volume II). Published for the International Union of Crystallography by A. Oosthoek's Uitgeversmaatschappij N.V.: Utrecht (1969, 1972).

Blow, D. *Outline of Crystallography for Biologists*. Oxford University Press: Oxford (2002).

Bragg, W. L., Phillips, D. C., and Lipson, H. *The Development of X-ray Analysis.* New York: Dover (1992).

Clegg, W., Blake, A.J., Gould, R.O., and Main, P. *Crystal Structure Analysis Principles and Practice*. Oxford University Press: Oxford (2001).

Ewald, P. P. (ed.). *Fifty Years of X-ray Diffraction*. Published for the International Union of Crystallography by A. Oosthoek's Uitgeversmaatschappij N.V.: Utrecht (1962).

Giacovazzo, C., Monaco, H. L., Viterbo, D., Scordari, F., Gilli, G., Zanotti, G., and Catti, M. *Fundamentals of Crystallography.* 1st edition (1992). 2nd edition, IUCr and Oxford Science Publications: Oxford (2002).

Glusker, J. P. (ed.). *Structural Crystallography in Chemistry and Biology*. Benchmark Papers in Physical Chemistry and Chemical Physics. Hutchinson Ross: Stroudsburg, PA and Woods Hole, MA (1981).

Hammond, C. *The Basics of Crystallography and Diffraction*. International Union of Crystallography Texts on Crystallography 5. 1st edition (1997). 2nd edition (2001). 3rd edition, Oxford University Press: Oxford, New York (2009).

Jenkins, R. and Snyder, R. *Introduction to X-ray Powder Diffractometry*. Wiley-Interscience: New York (1996).

Lonsdale, K. *Crystals and X-rays.* D. van Nostrand: New York (1949).

Luger, P. *Modern X-ray Analysis on Single Crystals*. W. de Gruyter: Berlin, New York (1980).

Massa, W. *Crystal Structure Determination.* 2nd edition, Springer-Verlag: Berlin, Heidelberg, New York. (2004). Translated by Gould, R. O. Originally published in German as *Kristallstrukturbestimmung*, B. G. Teubner GbmH: Stuttgart, Leipzig, Wiesbaden (2002).

McPherson, A. *Introduction to Macromolecular Crystallography.* 2nd edition. Wiley: Hoboken, NJ (2009).

Müller, P., Herbst-Irmer, R., Spek, A. L., Schneider, T. R., and Sawaya, M. R. *Crystal Structure Refinement: A Crystallographer's Guide to SHELXL.* Oxford University Press: Oxford (2006).

Pecharsky, V. and Zavalij, P. *Fundamentals of Powder Diffraction and Structural Characterization of Materials.* Springer/Kluwer Academic: New York (2003).

Rhodes, G. *Crystallography Made Crystal Clear*. Academic Press: San Diego (2000).

Sands, D. E. *Introduction to Crystallography*. W. A. Benjamin (1969, 1975). Dover Publications: Mineola, NY (1975).

Schwarzenbach, D. *Kristallographie*. Springer: Berlin (2001).

Steadman, R. *Crystallography*. Van Nostrand Reinhold: Wokingham (1982).

Woolfson, M. M. *An Introduction to X-ray Crystallography*, Cambridge University Press: Cambridge (1997).

International Union of Crystallography Commission on Crystallographic Teaching teaching pamphlets

1. A non-mathematical introduction to X-ray diffraction. C. A. Taylor.
2. An introduction to the scope, potential and applications of X-ray analysis. M. Laing.
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Note: no dates listed for living persons.

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An italic entry is a Glossary definition of that specific entry.