

# Crystallographic Fundamentals – Glossary of Terms

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## Symmetry

Property of physical and mathematical objects. After a *symmetry operation*, a symmetrical object and its transformed copy are indistinguishable. *Proper* symmetry involves pure rotation. *Improper* symmetry combines rotation with reflection; in particular, improper *symmetry elements* include center of inversion ( $\bar{1}$ ), mirror plane ( $m$ ), and four-fold inversion axis ( $\bar{4}$ ). Proper symmetry leaves the object unchanged, improper symmetry converts it into its mirror image. Consequently, chiral objects are incompatible with improper symmetry. (However, a *pair* of enantiomers can have improper symmetry between them.) An important, but trivial, operation corresponds to  $0^\circ$  (or  $360^\circ$ ) rotation (identity transformation). In classical crystallography, only the following rotations are compatible with the periodic nature of crystal lattices: 1, 2, 3, 4, and 6-fold. Symmetry transformations of finite objects (e.g. crystals) must leave at least one point stationary, and are governed by *point symmetry* elements. In infinite periodic objects (such as crystal lattices) this requirement is not necessary, and symmetry transformations may include (a fraction of lattice-) translation. In particular, screw axes are possible. Some of them are right-handed ( $3_1$ ,  $4_1$ ,  $6_1$ ,  $6_2$ ), some left-handed ( $3_2$ ,  $4_3$ ,  $6_4$ ,  $6_5$ ), and some neutral ( $2_1$ ,  $4_2$ ,  $6_3$ ).

## Crystal system

All crystals are divided into seven groups, called crystal systems, according to their principal symmetry. In another definition, this principal symmetry itself may be identified with the crystal system. From the lowest to the highest symmetry, the crystal systems are: *triclinic*, *monoclinic*, *orthorhombic*, *tetragonal*, *trigonal*, *hexagonal*, *cubic*. In yet another definition, the term "crystal system" refers to the system of coordinates that most conveniently describes objects with given symmetry. In general, those coordinate systems are non-cartesian, i.e. can have axial units  $a$ ,  $b$ ,  $c$ , of any length and at any (not necessarily orthogonal) inclination  $\alpha$ ,  $\beta$ ,  $\gamma$ , but must be compatible with the underlying symmetry.

## Point group

Symmetry usually comes in bunches, i.e. a symmetrical object usually has more than one symmetry element. Those symmetry elements must form consistent sets, called groups. For finite objects, those groups are called point groups (or *crystal classes* with reference to crystals). The term "group" is used in strict mathematical sense, i.e. it means that (i) combination of any two symmetry elements is another element of the group, (ii) for each symmetry transformation there is an inverse operation, (iii) the group includes a null (or identity) element (1). There are 32 three-dimensional crystallographic point groups. Only 11 of them do not include improper symmetry. An international (Hermann-Mauguin) symbol of a point group lists the symmetry of the essential directions in each crystal system. For instance, 2 is a monoclinic point group (two-fold axis in the **b** direction), 222 is an orthorhombic point group (three mutually perpendicular two-fold axes), and 432 is a cubic point group.

## Lattice

A collection of nodes, i.e. points with integral coordinates. In crystallography, a lattice is an abstract representation of a crystal structure: it is periodic and infinite, and the real structure can be reconstructed by associating with each lattice point the concrete structural motif (molecule, cluster of ions, cluster of molecules) which it symbolically represents. Strictly speaking, lattices with points at integral coordinates are called primitive (P) lattices. To preserve the maximal internal crystal symmetry, crystallography allows in some cases nodes

with special combinations of "half-integral" (i.e.  $\frac{1}{2}$ ) coordinates, resulting in the so-called centered lattices. Each lattice point has exactly the same environment.

### Unit cell

The smallest parallelepiped in the lattice whose translation (repetition) in the three lattice directions (vectors) **a**, **b**, **c** (which form its edges) recreates the entire crystal structure. From many possible choices, a conventional unit cell should be compatible with the symmetry of the space group. The smallest fragment, from which the entire unit cell can be recreated by symmetry, is called the *asymmetric unit* (ASU).

### Bravais lattice

In some cases, non-primitive unit cells have to be chosen in order to make the symmetry of the unit cell compatible with the symmetry of the entire lattice. Non-primitive lattices, derived mathematically by Auguste Bravais, can have the following centering nodes:  $\frac{1}{2} \frac{1}{2} \frac{1}{2}$  (I),  $\frac{1}{2} \frac{1}{2} 0$  (C), or  $0 \frac{1}{2} \frac{1}{2}$ ,  $\frac{1}{2} 0 \frac{1}{2}$ ,  $\frac{1}{2} \frac{1}{2} 0$  (F). Convention and symmetry considerations lead to 14 Bravais lattices: triclinic P; monoclinic P, C; orthorhombic P, I, C, F; tetragonal P, I; trigonal R; hexagonal and trigonal P; cubic P, I, F. The rhombohedral (R) unit cell represents a special case; it has nodes only at its vertices but has a three-fold axis along its body diagonal. In consequence, it has a unique shape with  $a=b=c$  and  $\alpha=\beta=\gamma$  (not necessarily  $90^\circ$ ).

### Space group

Analogously to point groups, space groups are defined as consistent sets of symmetry elements of three-dimensional lattices. A Hermann-Mauguin space-group symbol is formed by specifying the Bravais lattice and a list of symmetry directions, as in a point-group symbol. For instance,  $P2_12_12_1$ , is an orthorhombic space group, with primitive lattice and two-fold screw axes parallel to **a**, **b**, and **c**. There are 230 space groups. Only 65 of them do not include improper symmetry.

### Miller indices

A set of *lattice planes* is a family of parallel and equidistant planes which pass through lattice points. The number of divisions into which a plane set cuts the axial vectors **a** (*h*), **b** (*k*), and **c** (*l*) is known as Miller indices (*hkl*) of this set of lattice planes. The characteristic interplanar spacing is denoted  $d_{hkl}$ .

### Reciprocal lattice

A lattice, i.e. collection of nodal points, derived mathematically from the real (or direct) lattice using a "reciprocal" relationship. To derive a single reciprocal lattice (r.l.) point (with coordinates *hkl*), one starts with the (*hkl*) set of lattice planes in the direct lattice. Next, a line perpendicular (normal) to this set is constructed, and the *hkl* r.l. point is found on this line at a distance of  $1/d_{hkl}$  from the origin. Conveniently, three r.l. points generated by the (100), (010), and (001) lattice planes, define the reciprocal lattice axial vectors, **a\***, **b\***, **c\***, respectively. They have inverse vectorial relationship to the corresponding direct lattice vectors **a**, **b**, **c**. For instance,  $\mathbf{a}^* \cdot \mathbf{a} = 1$ , etc., while  $\mathbf{a}^* \cdot \mathbf{b} = 0$ ,  $\mathbf{a}^* \cdot \mathbf{c} = 0$ , etc. The latter "zero-value" scalar products indicate, that a given r.l. axial vector is perpendicular to "the other" two vectors in the direct lattice. A lattice reciprocal to the r.l. is again the direct lattice. Planes of r.l. points are called *layers*. As in direct lattice, there is also a r.l. unit cell, with reciprocal volume ( $V^* = 1/V$ ). The reciprocal and direct lattice vectors are also related by vector products, e.g.  $\mathbf{c}^* = \mathbf{a} \times \mathbf{b} / V$ , etc.

### **Laue condition**

A beam of parallel X-rays, impinging at an angle  $\alpha_1$  on a crystal axis with a repeat period  $a$ , can emerge from that axis reinforced at a new angle  $\alpha_2$ , provided the optical-path-difference between rays diffracted on adjacent lattice nodes is an integral ( $h$ ) multiple of the wavelength  $\lambda$ . This situation, corresponding to constructive interference, is described by the mathematical relationship  $h\lambda = a(\cos\alpha_2 - \cos\alpha_1)$ , known as the Laue condition. If the experimental parameters  $a$ ,  $\lambda$ ,  $\alpha_1$  are set, then the Laue condition defines the  $\alpha_2$  angle of a *Laue cone* of order  $h$  around the axis  $\mathbf{a}$ . In three dimensions, three Laue conditions, one for each crystal axis, have to be fulfilled simultaneously if constructive interference (of orders  $h$ ,  $k$ , and  $l$ ) is to take place. For this reason, this elegant Laue condition is awkward in practical applications.

### **Bragg's Law**

In Bragg's interpretation, the phenomenon of diffraction is viewed as reflection from the lattice planes ( $hkl$ ). The incident and reflected beams make the same angle ( $\theta$ ) with the reflecting plane, and the two beams and the plane normal are coplanar, as in geometrical optics. The difference, however, is that this is *selective reflection*, which can occur only at  $\theta$  angles selected by the Bragg's Law:  $n\lambda = 2d_{hkl}\sin\theta$ . This is because the rays reflected from consecutive planes of a plane-set must be in phase, i.e. must form an optical-path-difference equal to  $n\lambda$ .  $n$  is the order of reflection from the set of lattice planes ( $hkl$ ) with interplanar spacing  $d_{hkl}$ . Sometimes the equation is rewritten as  $\lambda = 2d\sin\theta$ , with  $d = d_{hkl}/n$ . The new (smaller)  $d$  value corresponds to an artificial set of planes which is  $n$ -times denser, and has artificial (non-Miller) indices  $n$ -times larger ( $nh$   $nk$   $nl$ ). Those new indices, without brackets, are used as *reflection indices*. They are equal to the  $h$ ,  $k$ ,  $l$  orders of diffraction in the corresponding Laue conditions. Note that the easy-to-measure angle between the incident and reflected beam is  $2\theta$ .

### **Ewald construction**

In Ewald construction the equivalence of the diffraction pattern and the reciprocal lattice is demonstrated. The diffracting crystal is placed at the center of a (Ewald) sphere of radius  $1/\lambda$ , which sets the X-ray wavelength. The point of exit of the primary beam from the Ewald sphere defines the origin of the reciprocal lattice,  $0^*$ . If at a given orientation of the crystal, a set of planes ( $hkl$ ) fulfills the Bragg's Law, then the point at which the reflected beam leaves the Ewald sphere coincides with the r.l. point  $hkl$ . Reorienting the crystal will bring other r.l. points into coincidence with the surface of the Ewald sphere, defining when and where the corresponding Bragg reflections will arise.

### **Friedel Law**

In non-resonant situations (no special phenomena effected by the X-ray quanta in the electronic clouds of the atoms in a crystal), X-rays are reflected in the same fashion from both sides of a set of lattice planes. In effect, the diffraction pattern is centrosymmetric (identical reflection intensities on both sides of the origin). This is expressed by the equation  $I(hkl) = I(\bar{h}\bar{k}\bar{l})$ , known as the Friedel Law. The Friedel Law is violated in the presence of atoms that scatter the given wavelength anomalously.

### **Laue class**

Because of the Friedel Law, there are fewer (11) classes possible for the symmetry of the diffraction pattern than the number of crystal classes or point groups (32). The point groups possible as symmetry groups of diffraction patterns are all centrosymmetric and are known as the Laue classes.

### Systematic absences

The most dramatic manifestation of lattice translations in the diffraction pattern is its discrete nature: the endlessly repeating scattering motif directs the diffracted beams into infinitely narrow and discrete angles while scattering in all other directions is extinguished. However, additional elements of translational symmetry in the space group cause further extinctions among the Bragg reflections. They are called systematic absences (or extinctions). Non-primitive lattice centering wipes out all reflections with certain index categories. For instance, I-centering systematically extinguishes all reflections with  $h+k+l$  odd, leaving only those for which  $h+k+l=2n$  ( $n$  – any integer). The reflections present with C-centering are  $h+k=2n$ , and with F-centering only those are left for which all three indices,  $h$ ,  $k$ ,  $l$ , have the same parity. Screw axes extinguish reflections on axes running in the reciprocal-lattice direction corresponding to the direction of the screw, but the extinction rule depends on the order of the axis and its pitch (but it does not depend on the handedness of the screw). For instance  $2_1$  screw along  $\mathbf{b}$  affects reflection on the  $0k0$  axis, leaving only those with  $k=2n$ .  $6_1$  (and  $6_5$ ) screw along  $\mathbf{c}$  affects reflections on the  $00l$  axis, leaving only those with  $l=6n$  (multiple of 6). The analogous rule for  $6_2$  (and  $6_4$ ) is  $00l$  with  $l=3n$ , and for  $6_3$  –  $00l$  with  $l=2n$ .

### Structure factor

The physical quantity representing the amplitude (and phase) of the wave scattered by a crystal as reflection  $hkl$  is called the structure factor  $F(hkl)$  and is calculated by adding up the contributions of all scattering atoms in the unit cell with a proper exponential ("phase") factor accounting for the phase differences of the partial wavelets:  $F(hkl)=\sum f_j \cdot \exp[2\pi i(hx_j+ky_j+lz_j)]$ . Those phase (or optical-path) differences result from the spatial distribution of the scattering atoms.  $f_j$  is called the *atomic scattering factor* (or *formfactor*). It is obvious that, in general,  $F$  is a complex quantity as it contains the imaginary unit  $i$  ( $=\sqrt{-1}$ ). This is why it can express both the amplitude ("length" or modulus of  $F$ ,  $|F|$ ) and phase (direction, or inclination angle of the vector  $F$  in the Argand diagram) of the scattered wave. It is also obvious that the structure factor contains information about the atomic structure of the crystal, as its calculation depends on the coordinates  $x_j$ ,  $y_j$ ,  $z_j$  of all atoms in the unit cell. Mathematically, the structure factor is the *Fourier Transform* of the electron density in the crystal. The intensity of reflection  $hkl$  is proportional to the square of the amplitude, i.e.  $I(hkl)=|F(hkl)|^2$  (scale neglected).

### Fourier Transform

In Fourier Theory, a function defined as  $F(h)=\sum f(x) \cdot \exp[2\pi i(hx)]$  has its nearly-identical twin companion,  $f(x)=\sum F(h) \cdot \exp[-2\pi i(hx)]$  (scale neglected). In simple applications, these formulas (or Fourier transforms) can be interpreted as trigonometric Fourier series. The existence of this pair of Fourier transforms means, that if we have a recipe (+i transform) for calculating  $F$  expressed as a Fourier series in  $f$ , then automatically  $f$  can be calculated as a Fourier series in  $F$  (-i transform).

### Phase problem

To be able to calculate electron density distribution in the crystal [ $\rho(xyz)$ ] from the diffraction pattern using the Fourier transform  $\rho(xyz)=(1/V)\sum F(hkl) \cdot \exp[-2\pi i(hx+ky+lz)]$ , one would need to know the complete information, i.e. the magnitude and the phase, of each structure factor. However, since experimentally only reflection intensities, or squares of structure factor amplitudes, are measured, the information about the phases is not available. For this reason the simple Fourier transform above cannot be used until the Phase Problem has been solved, i.e. until the phases have been obtained in one way or another.

### **Atomic scattering factor**

The atomic scattering factor (or formfactor)  $f_j$  is the Fourier transform of the electron density (electron "cloud") of a free atom of element  $j$ . For scattering of X-rays, it falls-off very quickly with the scattering angle, or  $\sin\theta/\lambda$ . At  $\theta=0$ ,  $f$  is equal to the atomic number (number of electrons). In normal (non-resonant) scattering of X-rays by electrons,  $f$  is real ( $f_0$ ). In resonant scattering,  $f$  becomes complex, which is expressed by the formula  $f = f_0 + f' + if''$ , where  $f'$  is called the dispersive (real) and  $f''$  absorptive (imaginary) correction.

### **Temperature factor**

Atoms in crystals are never motionless, they oscillate around their equilibrium positions (other effects, e.g. static and dynamic disorder, are also frequent, especially in protein crystals). Those oscillations smear the electron density and make atomic scattering less efficient, especially at high angles, and this effect increases with temperature. To account for this, the atomic scattering factor  $f_j$  must be multiplied by an exponential "temperature" factor which takes the form  $\exp[-B_j(\sin\theta/\lambda)^2]$ . Sometimes the parameter  $B$  itself is called the temperature factor (the more correct term is atomic displacement parameter, or ADP).  $B$  is related to the displacement from the equilibrium position,  $u$ , in the following way:  $B = 8\pi^2 \langle u^2 \rangle$ . Isotropic thermal model assumes the same (spherical) oscillation amplitude in all direction. This is not correct for bonded atoms, but the model is useful because it introduces only one parameter per atom (Biso). The more adequate anisotropic model requires as many as six parameters per atom to define the general ellipsoid that describes the atomic motion. In protein models, it can only be used when atomic-resolution data are available.

### **Electron density**

Distribution of electrons, in the form of electron density ( $e/\text{\AA}^3$ ), usually drawn as a map, represents the chemical constituents of the crystal interior. Electron density maps are the primary product of crystal structure determination by X-ray crystallography, and atomic models represent their chemical interpretation. This is so because the X-rays, which are used to "probe" the crystal structure by diffraction, are scattered by electrons.

### **Patterson function**

Before the Phase Problem is solved, the elegant Fourier transform based on the structure factors  $F(hkl)$  cannot be used to calculate the electron density map  $\rho(xyz)$ . However, when only the values of  $|F(hkl)|^2$  are available, a similar Fourier transform can be calculated, called the Patterson map  $P(uvw) = (1/V) \sum |F(hkl)|^2 \cdot \exp[-2\pi i(hu + kv + lw)]$ . Mathematically,  $P(uvw)$  represents an autocorrelation function, or convolution of the structure with its centrosymmetric image. Therefore, while  $\rho(xyz)$  represents the distribution of atoms,  $P(uvw)$  represents the distribution of all possible interatomic vectors, all drawn from the origin. For large structures (many atoms  $N$ ), it contains a large number of peaks ( $N^2$ ) and is not amenable to straightforward interpretation, but anyway it does contain information about the crystal structure and can help in its solution because each pair of atoms has a unique peak whose height is proportional to the product of the atomic numbers. The Patterson function is always centrosymmetric and contains (Harker) sections with accumulation of peaks corresponding to rotation-related atoms.

### **Resolution**

In principle, faithful reconstruction of an image (crystal structure) would require the use of all (infinite number)  $F(hkl)$  terms in the Fourier summation. This is impossible not only because of theoretical considerations (maximum  $\theta$  or minimum  $d_{hkl}$  limitation in the Bragg's Law), but also for practical reasons, as the  $2\theta$  angle has technical limitations and, especially, as protein

crystals do not scatter X-rays to high angles. The minimum d-spacing corresponding to the highest  $\theta$  angle at which measurable diffraction has been recorded, is known as the resolution of the diffraction pattern. The resolution in reciprocal lattice has immediate interpretation in the direct space, where the structural image is reconstructed from effects observed using less (low resolution) or more (high resolution) closely spaced reflecting planes. Geometrical considerations show that the resolution of the structural image obtained (i.e. the ability to distinguish points  $d$  Å apart) is roughly equal to the minimum d-spacing in the diffraction pattern.