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Unit cells, symmetry and space groups

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Contents

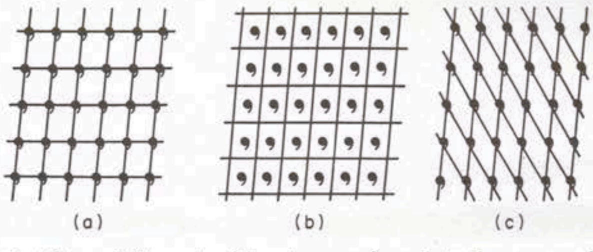
1 Unit Cells

1.1 Definition

The unit cell is defined as the smallest structural unit from which a crystal can be built up by only translational stacking of this unit in three dimensions. Smaller repeating structural entities may be found which are stacked by rotation, reflection or inversion, but these do not constitute a unit cell. The unit cell can be made up of these smaller entities, but, by definition, the 3-D structure can only be built up by translational stacking of unit cells.

For simplicity it is convenient to consider initially a 2-dimensional array. The nature of the array is illustrated below in Fig. 2.1 by the regular repetition of a simple motif by translation along two directions in the plane. The motif chosen in this case, a comma, can be thought of as a molecule, or group of molecules, in a real crystal. The array of commas can be overlaid by a lattice or grid system, such that each grid contains only one of the repeating units. The grid lines are drawn at equal intervals corresponding to the repeat distances of the array and, as a consequence, the surroundings of each grid line intersection, or lattice point, are identical. One unit of the grid, by the definition of the above paragraph, is the unit cell. Such a grid can be chosen in many different ways, as shown in Fig. 2.2, and all are equally valid, since they have equal areas. In practice, matters of convenience and convention usually dictate which choice is made.

Figure 2.1. Regular two-dimensional array.



(a) (b) (c)

Figure 2.2. Three different grid systems referred to the array of Fig. 2.1.

The unit cell may contain a whole unit of the repeating motif, as in Fig. 2.2b, or it may contain parts of several motifs as in Figs. 2.2a and c. Although the unit cells can differ in both shape and position they have the same area, or, in 3 dimensions, the same volume, as long as there is always the equivalent of one motif per unit cell. In real crystals, therefore, it is not necessary that a single molecule be entirely contained within a unit cell. If a molecule protrudes outside the chosen unit cell, then an identical neighbouring molecule will intrude into the other side of the unit cell by exactly the same amount.

It should be emphasised that the concept of a lattice and lattice points is purely imaginary; its main purpose being to function as a coordinate system to which the actual structure is referred. It is common practice to define lattice points as being at the corners of the unit cell, but they should not be confused with atoms. It is *not* necessary for an atom to lie at a lattice point. The important concept is that the relative positions and orientations of molecules about a given lattice point must be identical with that at every lattice point.

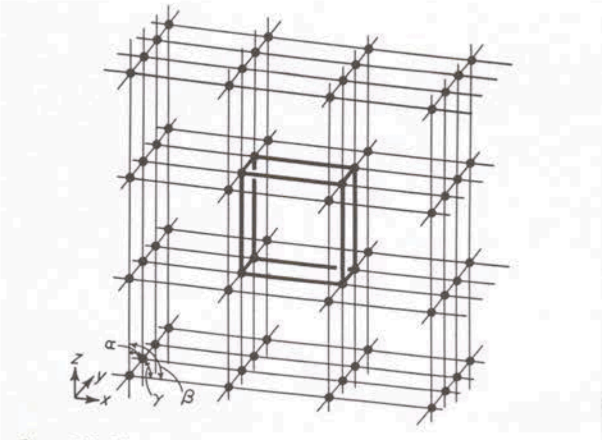


Figure 2.3. Three-dimensional lattice, showing unit cell (heavy lines).

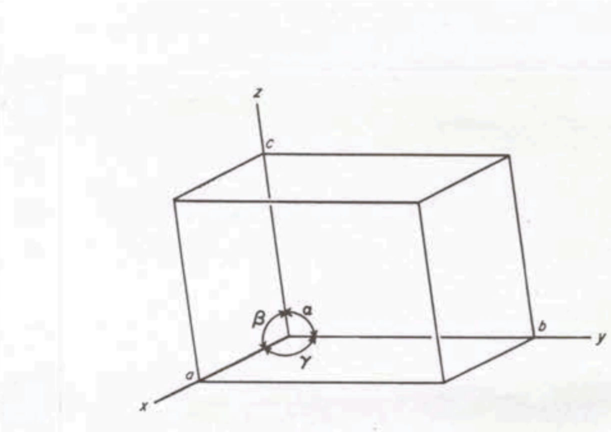


Figure 3.1. Unit cell.

The 2-dimensional example can easily be extended into 3 dimensions and a 3-dimensional lattice is shown in Fig. 2.3. By convention the directions of the grid lines joining the lattice points, and therefore the directions of the unit cell edges, are called the coordinate axes and are termed x, y, z. The lengths of the unit cell edges along the x, y, z axes are designated respectively a, b, c and the interaxial angles α, β, γ where α is the angle between b and c, β is between a and c, and γ is between a and b. It is not necessary for the coordinate axes to be an orthogonal system; they are, instead, referenced to the chosen shape for the unit cell.

1.2 Lattice planes

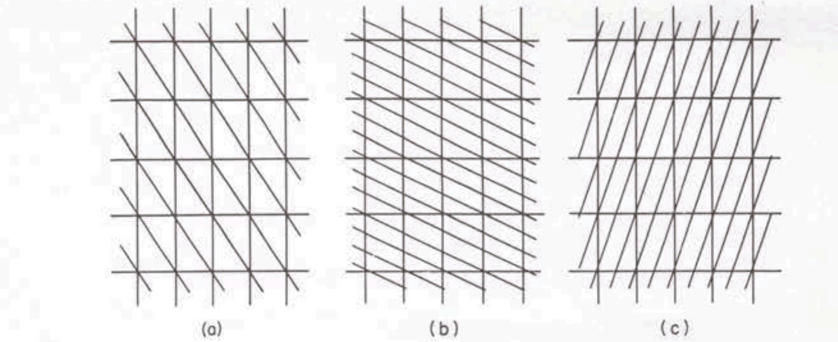


Figure 2.5 Three families of lattice "planes" in a two-dimensional lattice.

A set of lattice planes can be constructed so that for any given set of parallel planes every lattice point lies on one of the planes. Fig. 2.5 illustrates three examples of sets of lattice planes in the 2-dimensional case. A set of indices can be used to uniquely characterise each possible set of planes. These indices are obtained by considering some lattice point on one plane as the origin and proceeding along the axes until the next member of a given set of planes is reached. When the intercepts of the plane on the axes are expressed as fractions of the unit cell edges, the reciprocals of the fractions are the desired indices. Alternatively, these indices can be regarded as showing the number of planes of a given set that cut each axis of one unit cell. If the x-axis is across the page, and the y-axis is up the page, the indices of the planes in Figs. 2.5(a), (b) and (c) are (1,1), (1,3) and $(2,\bar{1})$ respectively. Fig. 2.6 shows a 3-dimensional example in which plane 1 has the indices (2,2,1). In the special case where a set of planes lies parallel to one or more of the axes, the intercept on the parallel axis is formally at infinity and the corresponding index is given as 0.

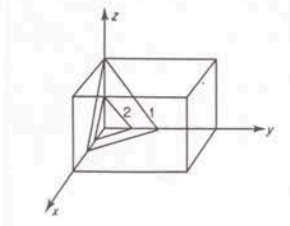


Figure 2.6. Example of a lattice plane and an interleaving plane.

The indices of these sets of parallel planes are known as Miller indices, and a general plane is indicated as having the Miller indices (*h*,*k*,*l*). We have already met Miller indices when talking about orders of diffraction. In the Bragg "reflection" theory of diffraction, diffracted X-rays are considered as having being "reflected" from a particular set of lattice planes (not planes of atoms!). Thus reflections, as we will now call diffracted X-ray beams, can be indexed using Miller indices to indicate which set of lattice planes each reflection comes from. In addition, faces of the unit cell can be given Miller indices, since each face is itself a member of a set of lattice planes.

Some notation is now important.

Miller indices can be used to designate a set of lattice planes, a particular member of the set, or the face of a crystal parallel to the set. Miller indices are always enclosed in parentheses. Thus (010) can represent the set of planes parallel to the *xz* plane and at $y = 0, b, 2b, 3b$...; or (010) can represent the particular plane at $y = 0$; or the crystal face parallel to these. In general Miller indices are written (*hkl*). Commas between the indices are optional, and usually only used to prevent confusion that would arise with indices greater than 9. We would write (12,1,3) rather than (1213), but (213) is clearly understood to mean (2,1,3).

A reflection that arises from a set of lattice planes is given Miller indices without the parentheses. Thus the reflection from (010) is referred to as the 010 reflection, that from the (*hkl*) set of planes is the *hkl* reflection.

In contrast, the notation [*x*,*y*,*z*] indicates the direction of a vector in the lattice from the origin to a point *x*,*y*,*z*. Do not confuse this with Miller indices. [100] is the vector, of length *a* along the *x* axis of the unit cell, while (100) is the *yz* plane.

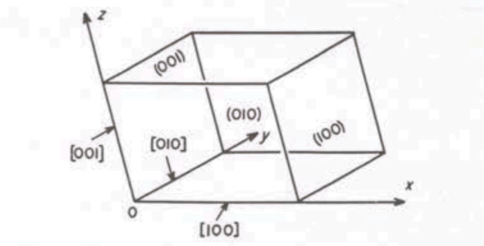


Figure 2.7. Unit cell showing bounding planes and edges.

A third notation, where the indices are enclosed by braces, is used to refer to a set of crystal faces that are equivalent by the symmetry of the crystal. This is known as the crystal form. For a cubic crystal, {100} includes the faces (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$ and $(0\bar{1}0)$, while for a triclinic crystal {100} refers only to the faces (100) and $(\bar{1}00)$.

It is usual practice to indicate a negative index by placing a minus sign above the index. Thus $(\bar{2}00)$ cuts the -*x* axis at -0.5 and lies parallel to the *y* and *z* axes.

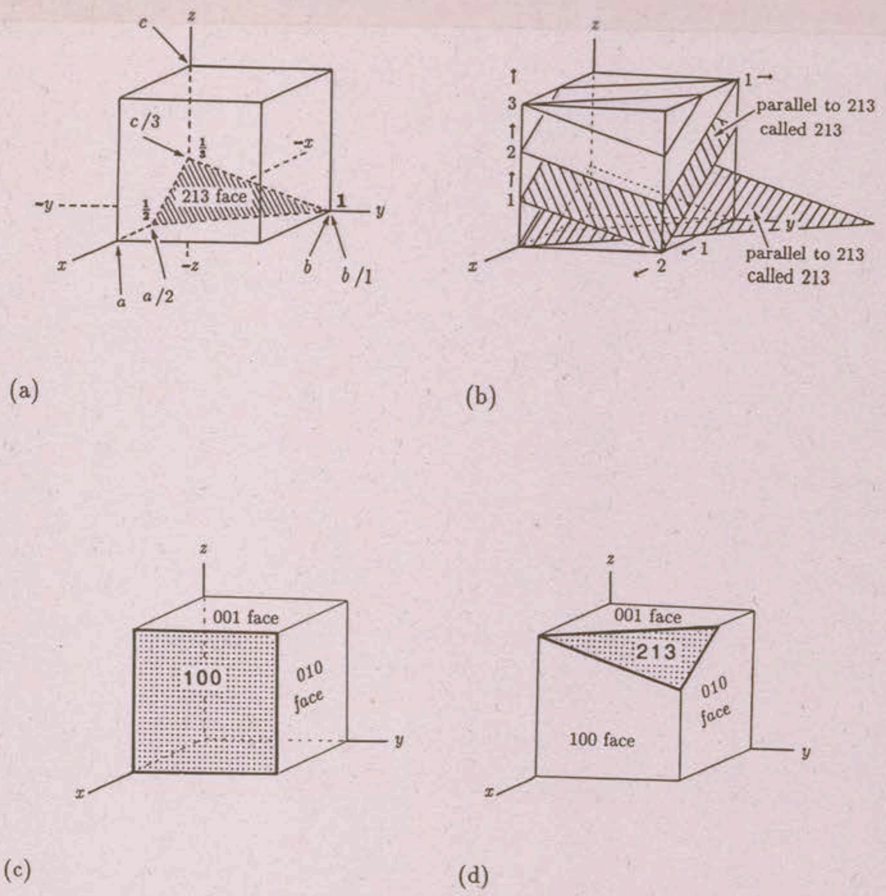


FIGURE 2.12. The indexing of crystal faces. (a) The derivation of the integers used to describe the crystal faces (Miller indices). The (213) face is marked as an example. It intersects the axes of the unit cell at $a/2$, $b/1$, and $c/3$. (b) Several parallel planes can be represented by these Miller indices. They intersect at, for example, a, $2b$, $2c/3$; $3a/2$, $3b$, c. (c) A crystal with its (100) face (stippled), intersecting the x axis at $x = a$ and the y and z axes at infinity (that is, parallel to them). (d) A crystal with a (213) face stippled.

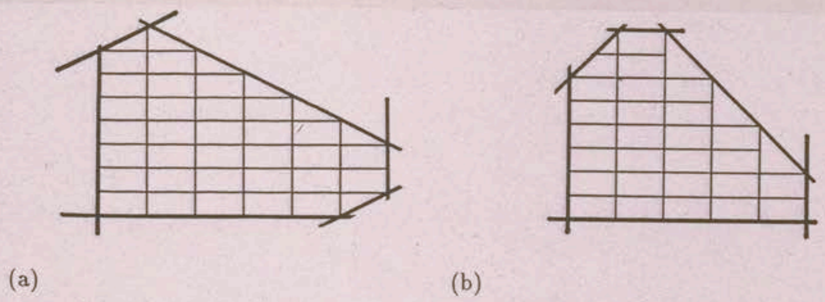
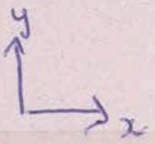


FIGURE 2.11. Diagrams showing the development of what amounts to crystal faces (shown with heavy lines) as unit cells build up. Each of these faces can be given a numerical indexing as shown in Figure 2.12.



1.3 Crystal systems

If we replace the repeating motif in the structure by a point we generate the crystal lattice, which is simply an infinite regular 3-dimensional arrangement of points related by a set of fundamental translations. Thus the lattice is the basic network of points on which the repeating unit (unit cell) may be imagined to be laid down so that the regularly repeating structure of the crystal is obtained.

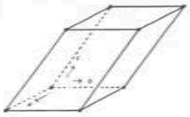
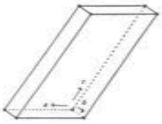
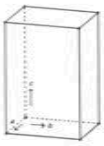
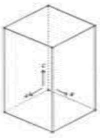
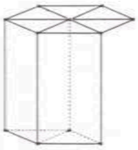
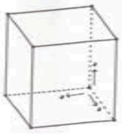
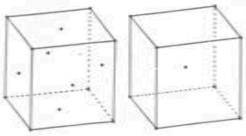
We have seen that for any given lattice it is possible to choose many shapes for the unit cell. How are we able to define a unique unit cell for a particular crystalline substance? In principle, a unit cell is chosen by examining the lattice of the crystal and choosing that cell whose shape displays the full symmetry of the lattice – rotational as well as translational. After that, the most convenient orientation is chosen, i.e. that which gives the shortest lengths of the edges of the unit cell (axial lengths) and interaxial angles as near to 90°.

Following these principles, it can be shown that there are 7 crystal systems which are defined by the rotational symmetry observed within the unit cell. This symmetry constrains the relationships between the unit cell edges and the angles between them. The seven crystal systems are given below. Convention dictates that monoclinic lattices are chosen such that b is usually the unique axis and β is obtuse. Similarly, the c axis is chosen to be the distinct axis for tetragonal and hexagonal lattices. If the lattice has 6-fold symmetry, sometimes four axes of reference are used, x, y, u, z, where x, y, u lie in one place and are inclined at 120° to one another and z is perpendicular to these. The indices of the corresponding reflections are then defined as *hkil* where $i = -(h+k)$.

Crystal system	**Constraints on unit cell dimensions**	**Rotational symmetry**	**Diffraction (Laue) symmetry**
Triclinic	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$	none	$\bar{1}$
Monoclinic	$a \neq b \neq c$; $\alpha = \gamma = 90°$; $\beta > 90°$	2-fold axis parallel to b	$2/m$
Orthorhombic	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$	3 perpendicular 2-fold axes parallel to a, b, c	mmm
Tetragonal	$a = b \neq c$; $\alpha = \beta = \gamma = 90°$	4-fold axis parallel to c; two 2-fold axes perpendicular to c	$4/m$ or $4/mmm$
Trigonal			
rhombohedral lattice	$a = b = c$; $\alpha = \beta = \gamma \neq 90°$	3-fold axis along body diagonal	$\bar{3}$ or $\bar{3}m$
hexagonal lattice	$a = b \neq c$; $\alpha = \beta = 90°$; $\gamma = 120°$	3-fold axis parallel to c	
Hexagonal	$a = b \neq c$; $\alpha = \beta = 90°$; $\gamma = 120°$	6-fold axis parallel to c; two 2-fold axes perpendicular to c	$6/m$ or $6/mmm$
Cubic	$a = b = c$; $\alpha = \beta = \gamma = 90°$	3-fold axes along all body diagonals; 4-fold axes parallel to each crystal axis	$m\bar{3}$ or $m\bar{3}m$

Always choose a unit cell of the most symmetrical crystal system that will display the full symmetry of the crystal lattice. For example, when the lattice points display relationships that correspond to three mutually perpendicular 2-fold axes, an orthorhombic unit cell should be chosen, rather than a monoclinic or a triclinic one which contains much lower symmetry. It should also be remembered that we are referring to the symmetry of the *lattice* here. The *structures* (molecules) arranged on these lattices do not necessarily display all of the symmetry of the lattice.

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

Diagrams of unit cells	Crystal systems	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, α.
	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*) cubic	Symmetry at each lattice point is the same as for simple cubic. *F* has four lattice points per 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.

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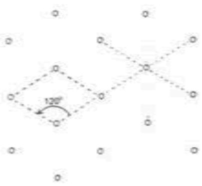
[a] This means that if the cell is rotated 360°/2 = 180° about an axis parallel to **b** the cell so obtained is indistinguishable from the original.

[b] The six-fold axis present in hexagonal 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 lattice points are shown in a layer normal to the unique **c**-axis (one cell is outlined here 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 lattice point; this is indicated by the dashed lines drawn from one lattice point.



The lengths of the unit cell axes and the interaxial angles are only a guide for suggesting the likely crystal system. Although they are a reliable prediction of the crystal system in the majority of cases, the symmetry must always be checked to see if it is consistent with the chosen system. For instance, some structures with monoclinic symmetry have been found with $\beta = 90°$. On the other hand do not assume that because the unit cell dimensions suggest a certain crystal system, that there is not a higher system indicated by the symmetry, which would be revealed by a suitable transformation of the unit cell dimensions.

The correct choice of crystal system is sometimes a problem with unit cell indexing programs on diffractometers, which might produce a triclinic unit cell on the first attempt, but for which a higher crystal system is evident after examining the crystal symmetry and performing a unit cell transformation. Modern diffractometers automatically check for this possibility, but can make mistakes, especially with poor crystals. Twinned crystals can also lead to unreasonably large unit cells because the software attempts to find a cell consistent with the positions of all found reflections from both twin domains. The crystallographer needs to be constantly alert for such problem, since the correct choice of unit cell is a crucial step towards having a correct crystal structure analysis.

1.4 Bravais lattices

The simple lattices in each of the 7 crystal systems have lattice points only at the corners of the unit cell; there is the equivalent of one lattice point per unit cell. In other words, each unit cell contains only one of the structural units that makes up the lattice by translation only. Such lattices are termed primitive and are designated by the letter P in space group symbols (except in the rhombohedral lattice, where R is used).

It can be shown that there are a total of 14 distinct arrangements of lattices. These are known as the Bravais lattices. The additional 7 non-primitive lattices contain two or more lattice points per unit cell and can be considered as the combination of a primitive lattice with one or more offset identical copies of itself. Diagrams of the 14 Bravais lattices are shown on the following page.

A non-primitive lattice with a pair of lattice points centered on opposite faces of the unit cell is designated A, B or C, depending on whether the *bc*, *ac* or *ab* faces are centered. By convention the unit cell is usually oriented so that the C lattice is defined. A unit cell with a lattice point at its body centre is designated I (inner). If all faces have lattice points at their centres, the designation is F (face-centered). The Bravais lattices are then as follows:

Triclinic	P				
Monoclinic	P	C			(C may also be A or I; C is chosen by convention)
Orthorhombic	P	C	F	I	(C may also be A or B)
Tetragonal	P	I			
Hexagonal	P				
Rhombohedral	P	(usually designated R)			
Cubic	P	F	I		

The non-primitive Bravais lattices are such that the origin of the unit cell can be moved to any of the offset lattice points and the arrangement of lattice points on the unit cell will still look the same.

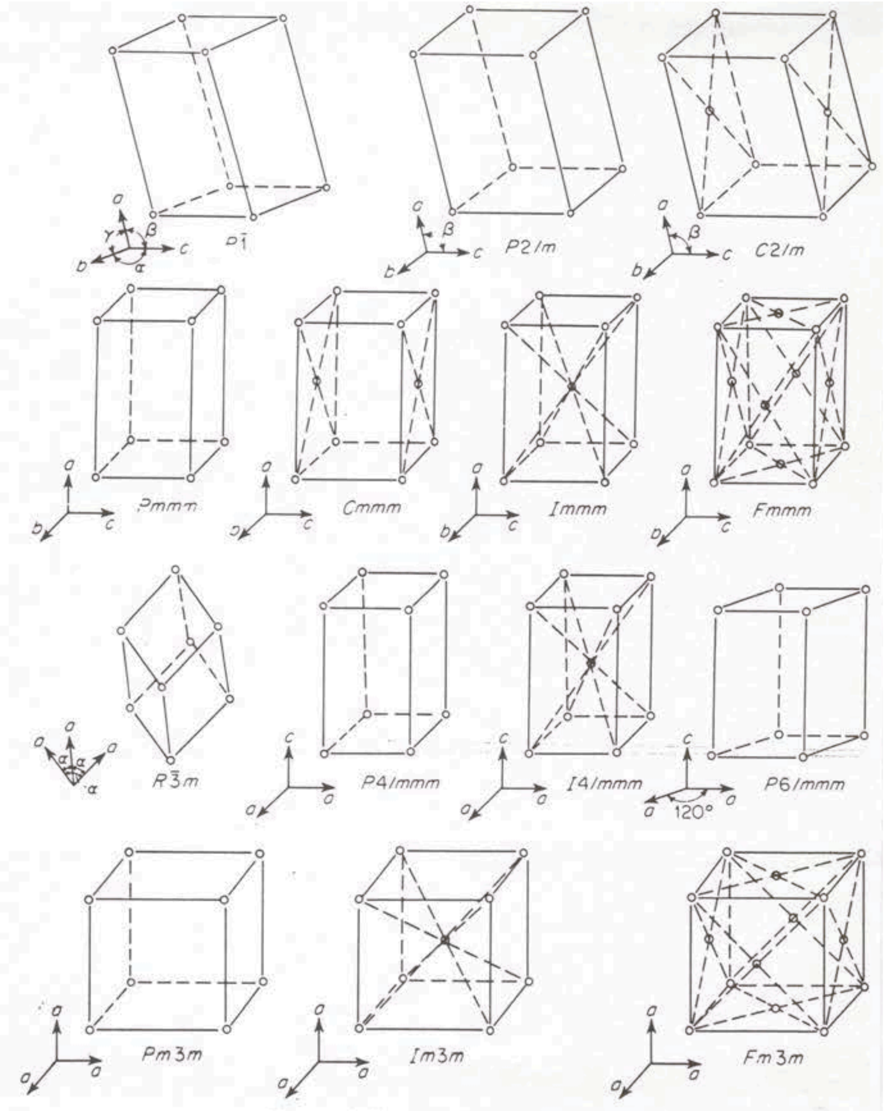


Figure 3.13. The 14 Bravais lattices.

This is, of course, inherent in the definition of a lattice point! The non-primitive lattices may appear to be a contradiction of the concept that the unit cell should be chosen to enclose the smallest structural unit that can be used to build the crystal from translation only. The non-primitive lattices contain translation symmetry, and thus are clearly not the smallest possible unit. It is always possible to draw a smaller primitive unit cell, usually of a lower crystal system, to connect the lattice points, however, the cardinal rule when choosing the unit cell is to choose in such a way that the unit cell displays fully the actual symmetry present in the way the structural components are built up.

Thus, when choosing the correct unit cell in which to describe a structure, not only must the crystal system be determined, but the correct Bravais lattice so that the full symmetry of the structure can be utilised in the unit cell description. The Bravais lattice is always indicated by the first letter of the space group symbol (i.e. P2/*m* is a primitive lattice, C2/*c* is centered on the *ab* faces and F*m*3*m* is a face centered lattice). The remaining parts of the space group symbol will be discussed in the next section.

The correct choice of Bravais lattice also serves to simplify the description of the basic structural unit from which the structure is built by all types of symmetry. Always let the symmetry build the total structure from the absolutely smallest fragment. This basic unit, in which there is no symmetry whatsoever, is known as the asymmetric unit. Once the structure and contents of the asymmetric unit are known, the whole structure of the crystal is known.

2 Symmetry

2.1 The basic symmetry operators

Non-translational symmetry has been mentioned several times already. The details are now presented.

There are three basic symmetry operators which can be combined to produce all possible types of symmetry. These are **translation, rotation and reflection**.

Translation is obtained by adding a constant to one or more of the coordinate axes, x, y or z. We have already seen that the crystal lattice is built up from translations of the unit cell by integer multiples of the axial lengths. Any translation is possible, although in space group symmetry, simple fractional translations of $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$ and $\frac{1}{6}$ are the only ones found. For example, in the body centered space groups, the body centered lattice point is related to the lattice point at the unit cell origin by the translational operator $(x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2})$.

Rotation is necessarily about an axis, and is designated n-fold if, on rotation of an arrangement by $360°/n$, the resulting arrangement is indistinguishable from the original one. Such an operator is designated n. A 4-fold axis is shown below. A rotation of $360°/4 = 90°$ about the 4-fold axis leaves the set of four points in a position indistinguishable from the initial position. In normal crystals it is only possible to have 1-, 2-, 3-, 4- and 6-fold axes.

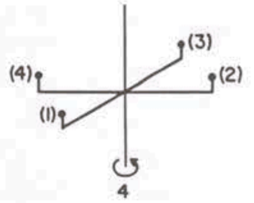


Figure 3.2. A 4-fold rotation axis.

If a plane exists in a structure such that every part on one side of the plane is related to a part on the other side as if reflected in the plane, the structure is said to possess a plane of symmetry or **mirror plane**. Such a plane is designated by the letter m. An example of two points related by a mirror is shown below. Mirror planes convert a left-handed molecule into a right-handed one.

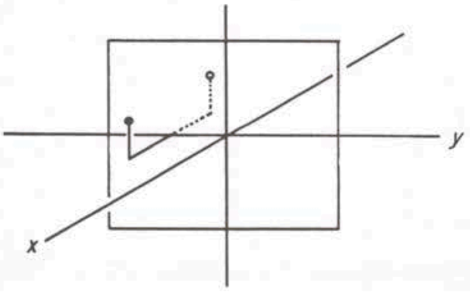


Figure 3.3. A mirror plane.

Any isolated object, such as a molecule, or a box of matches, can possess **point symmetry**. This means that the object must have at least one point within the object that remains fixed after the symmetry operation. On the other hand, an infinite array, such as a lattice, possesses **translational symmetry**. A translation leaves no point unchanged, since all points are moved an equal distance along parallel vectors. Translational symmetry is an example of a **space symmetry** operation.

It is not necessary that a crystal be built up from objects that possess point symmetry, but objects within the crystal can be related by a point of symmetry. It is necessary that the entire lattice can be built up from objects by symmetry operations that lead to a regular and complete packing of space. For this reason it is not possible to have 5-fold or 8-fold rotation axes within a crystal, since it is not possible to pack pentagons or octagons in a regularly repeating way such that they completely fill a plane. This does not mean that a molecule cannot possess a 5-fold axis. However, the molecule possesses only local 5-fold symmetry. Crystallographic 5-fold axes cannot exist.

2.2 Point symmetry operators

We have already met two point symmetry operators, ***n*-fold rotation axes** and **mirror planes**. An object that possesses one of these operators has one point that remains in the same location after the operation. The combination of these two operators can be used to generate more complex types of point symmetry.

The combination of a 2-fold axis with a mirror plane perpendicular to it results in a very commonly occurring point symmetry; that is, **inversion**. In the diagram below point (1) is rotated 180° about the z axis to give point (2) and then reflected in the xy plane to give point (3). Points (1) and (3) are said to be related by a centre of inversion or to be centrosymmetrically related. The symmetry point is known as the inversion centre or centre of symmetry. Whether the reflection or rotation operation is performed first is unimportant, the same effect results from the combination of the two. If the origin of a unit cell is a centre of inversion, any atom with coordinates x, y, z will also exist at $-x$, $-y$, $-z$.

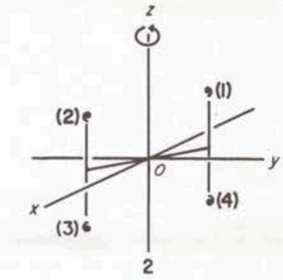


Figure 3.4. Center of symmetry produced by a 2-fold axis combined with reflection.

Another point symmetry is the ***n*-fold rotary inversion axis**. This operation is the result of performing a rotation of 360°/n followed by inversion (or 180° + 360°/n rotation + reflection). Again, n is restricted to 1, 2, 3, 4 or 6. An object that possesses this type of point symmetry will appear unchanged after the rotary inversion operation. The n-fold rotary inversion axis is designated $\bar{n}$. Note that the inversion operation itself, $\bar{1}$, is actually a special case of this symmetry operation. A 4-fold rotary inversion axis ($\bar{4}$) is shown below.

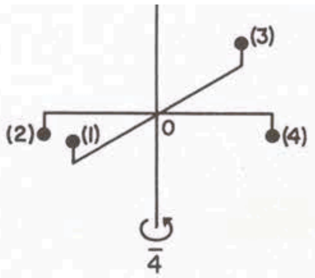


Figure 3.5. A 4-fold rotary inversion axis.

An important point is that, since a mirror reverses the handedness of an object, it is not possible for a solution containing a single enantiomer of a molecule to crystallise in a space group which possesses mirror, inversion or rotary inversion symmetry elements. Of course, racemic mixtures of chiral molecules may crystallise in space groups with these symmetry elements.

2.3 Point groups

The point symmetry operators listed above (1, 2, 3, 4, 6, $\bar{1}$, $\bar{2}$ = m, $\bar{3}$, $\bar{4}$, and $\bar{6}$) can be combined in just 32 ways in three dimensions to form the 32 3-dimensional **crystallographic point groups**. As said earlier, there are other local point groups appropriate to isolated molecules, e.g. 5-fold axes, but there are only 32 point groups whose symmetries can extend throughout a crystal lattice, so that any point in the lattice has a corresponding identical point related by one of the point group operators.

2.4 Space symmetry

Combination of the various point symmetry operations with translations gives rise to various kinds of space-symmetry operations in addition to the pure translations.

***n*-fold screw axes** result from the combination of translation and pure rotation and are symbolised n_r. They involve a rotation of 360°/*n* and a translation parallel to the rotation axis by the fraction *r*/*n* of the unit cell repeat length along that axis. The translation must always be in the ratio *r*/*n*, since, after translation of a distance corresponding to one complete unit cell the object must be in the identical orientation to its original orientation (by definition of unit cells) and thus must have undergone a complete 360° rotation. Screw axes preserve the chirality of an object.

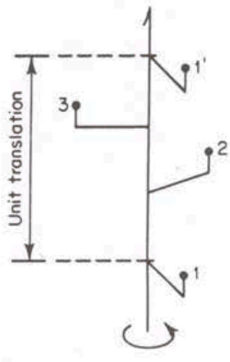


Figure 3.20. Screw axis 3_1.

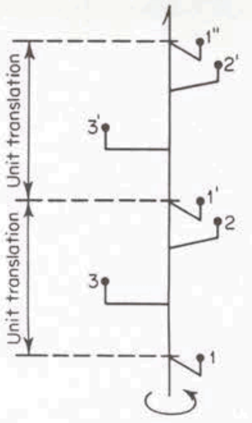


Figure 3.21. Screw axis 3_2.

Glide planes result from the combination of translation with the mirror operation. The glide must be parallel to some lattice vector, namely a unit cell axis, face diagonal or, for F and I cells only, a body diagonal. Glide planes parallel to a unit cell edge are designated *a*, *b* or *c*. Glides parallel to a face diagonal are *n* and those along a body diagonal are diamond glides, *d* (very rare). It is characteristic of glide planes that after two glide operations (or 4 for *d* glides) the position of the point laid down is identical to that of the initial point plus unit translations on one or two axes.

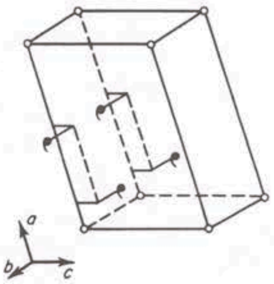


Figure 3.22. Glide plane *a*.

It is worth considering how various symmetry operations affect the positions of objects or atoms within a structure. If an atom exists at the point *x*, *y*, *z* in the unit cell and some symmetry operation exists within the unit cell, an identical atom with the same environment will also exist at a point *x*', *y*', *z*' related specifically by the symmetry operator. These symmetry related positions are called **equivalent positions**. Some examples are in the following table.

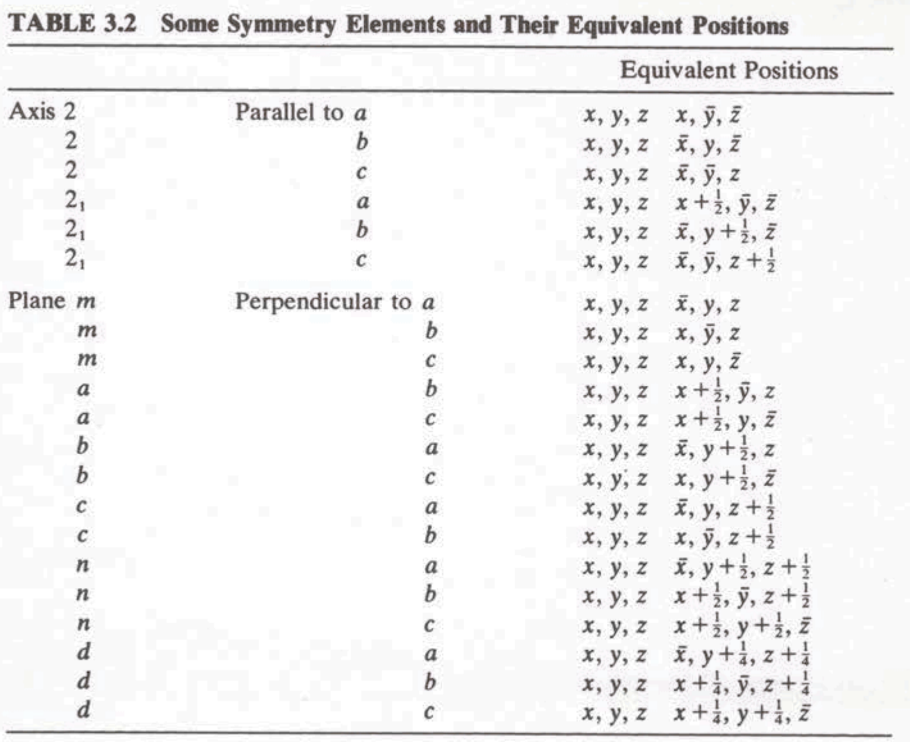


TABLE 3.2 Some Symmetry Elements and Their Equivalent Positions

		Equivalent Positions	
Axis 2	Parallel to *a*	x, y, z	$x, \bar{y}, \bar{z}$
2	*b*	x, y, z	$\bar{x}, y, \bar{z}$
2	*c*	x, y, z	$\bar{x}, \bar{y}, z$
2_1	*a*	x, y, z	$x+\frac{1}{2}, \bar{y}, \bar{z}$
2_1	*b*	x, y, z	$\bar{x}, y+\frac{1}{2}, \bar{z}$
2_1	*c*	x, y, z	$\bar{x}, \bar{y}, z+\frac{1}{2}$
Plane *m*	Perpendicular to *a*	x, y, z	$\bar{x}, y, z$
m	*b*	x, y, z	$x, \bar{y}, z$
m	*c*	x, y, z	$x, y, \bar{z}$
a	*b*	x, y, z	$x+\frac{1}{2}, \bar{y}, z$
a	*c*	x, y, z	$x+\frac{1}{2}, y, \bar{z}$
b	*a*	x, y, z	$\bar{x}, y+\frac{1}{2}, z$
b	*c*	x, y, z	$x, y+\frac{1}{2}, \bar{z}$
c	*a*	x, y, z	$\bar{x}, y, z+\frac{1}{2}$
c	*b*	x, y, z	$x, \bar{y}, z+\frac{1}{2}$
n	*a*	x, y, z	$\bar{x}, y+\frac{1}{2}, z+\frac{1}{2}$
n	*b*	x, y, z	$x+\frac{1}{2}, \bar{y}, z+\frac{1}{2}$
n	*c*	x, y, z	$x+\frac{1}{2}, y+\frac{1}{2}, \bar{z}$
d	*a*	x, y, z	$\bar{x}, y+\frac{1}{4}, z+\frac{1}{4}$
d	*b*	x, y, z	$x+\frac{1}{4}, \bar{y}, z+\frac{1}{4}$
d	*c*	x, y, z	$x+\frac{1}{4}, y+\frac{1}{4}, \bar{z}$

The next table shows some of the symbols used to denote various symmetry operators.

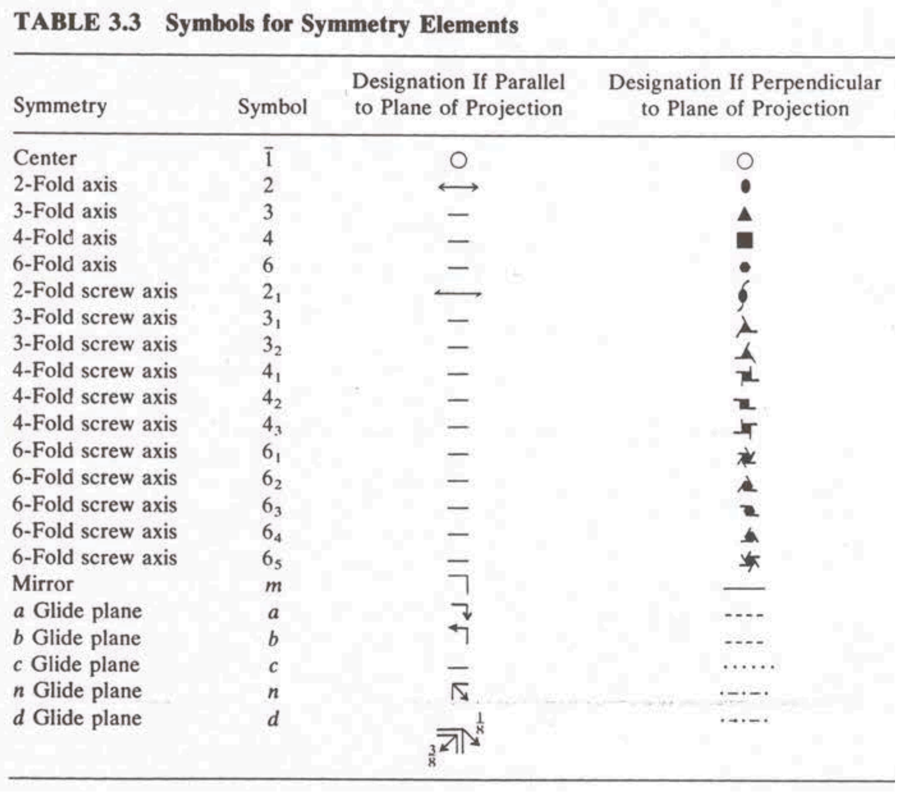


TABLE 3.3 Symbols for Symmetry Elements

Symmetry	Symbol	Designation If Parallel to Plane of Projection	Designation If Perpendicular to Plane of Projection
Center	$\bar{1}$	○	○
2-Fold axis	2	⟷	●
3-Fold axis	3	—	▲
4-Fold axis	4	—	■
6-Fold axis	6	—	⬢
2-Fold screw axis	2_1	⟷	●
3-Fold screw axis	3_1	—	▲
3-Fold screw axis	3_2	—	▲
4-Fold screw axis	4_1	—	■
4-Fold screw axis	4_2	—	■
4-Fold screw axis	4_3	—	■
6-Fold screw axis	6_1	—	⬢
6-Fold screw axis	6_2	—	⬢
6-Fold screw axis	6_3	—	⬢
6-Fold screw axis	6_4	—	⬢
6-Fold screw axis	6_5	—	⬢
Mirror	*m*	⌉	——
a Glide plane	*a*	⌉↓	- - - -
b Glide plane	*b*	↰⌉	- - - -
c Glide plane	*c*	—	······
n Glide plane	*n*	↘	-·-·-
d Glide plane	*d*	↗⌉↘ $\frac{1}{8}$ $\frac{3}{8}$	-·→-·→

3 Space Groups

3.1 Space group symbols

It is possible to combine the various rotations, mirrors, rotary inversions, screw axes and glide planes with each other and the 14 Bravais lattices in 230 ways, and only 230 ways, compatible with the geometrical requirements of 3-dimensional lattices. There are thus 230 3-dimensional space groups, ranging from that with no symmetry other than the identity translation operation, (symbolised P1, P implying a primitive lattice) to those with the highest symmetry, such as $Fm\bar{3}m$, a face-centred cubic space group. These 230 space groups represent the only ways in which identical objects (such as molecules) can be packed in an infinite 3-dimensional lattice so that the contents of one unit cell are arranged in exactly the same way as in every other unit cell, and that space is completely filled with these objects (no discontinuous holes as would be found when trying to pack pentagons of octagons).

The properties of all 230 space groups are listed in detail in *International Tables for Crystallography, Volume A*, which is a standard reference for crystallographers found in every X-ray laboratory. Once the space group has been determined only the contents of the asymmetric unit, not the entire unit cell, need be determined. The contents of the rest of the unit cell, and of the entire crystal, are then known by application of the symmetry operations of the space group.

The space group symbol, which is reported for every crystal structure analysis, is just an indicator of the symmetry present in a unit cell for that particular crystalline species. The symbol is designated by a capital letter identifying the lattice type (P, C, R, I, F) followed by the point group symbols necessary to uniquely define the symmetry; one position in the symbol for each symmetry direction in the lattice. Where a symmetry axis (rotation or screw) is perpendicular to a plane of symmetry (mirror or glide), the two symbols are combined with a slash, as in $2/m$ or $6_3/m$.

Redundant symmetry elements, generated by the presence of other symmetry operators, are omitted from the symbol. Further, if a space group contains less than three symmetry directions (as in triclinic, monoclinic and rhombohedral lattices), the symbols are only given for the symmetry directions. Symmetry directions that do not contain symmetry are represented by the symbol 1, but such entries can be omitted if they fall at the end of a symbol and no ambiguity is possible. A few examples:

P6/*m* is a primitive lattice containing a 6-fold axis perpendicular to a mirror plane. The term is a shortened form of P6/*m* 1 1, but the trailing 1's can be omitted. For P3*m*1 the trailing 1 is retained to help distinguish it from P31*m*, which is a different space group.

P6/*mmm* should be thought of as P (6/*m*) *m m* rather than P6/(*mmm*).

$P2_1/c$ is a primitive lattice with a 2-fold screw axis perpendicular to a glide plane. The full symbol can be given as $P1\ 2_1/c\ 1$, but since the *a* and *c* axes in a monoclinic unit cell for which *b* is the unique axis are not symmetry directions, the symbol can be shortened. This space group is the one most commonly observed for centrosymmetric (or racemic) compounds.

$P2_12_12_1$ is a primitive lattice with three mutually perpendicular non-intersecting 2-fold screw axes. This is a common space group for organic compounds containing a single enantiomer.

3.2 Equivalent positions

An equivalent position has been defined earlier. If an atom exists at the point *x*, *y*, *z* in the unit cell and some symmetry operation exists within the unit cell, an identical atom with the same environment will also exist at a point *x*', *y*', *z*' related specifically by the symmetry operator. Diagrams showing the equivalent positions for some of the low symmetry space groups are given below. Those interested should read Chapter 3 of Stout and Jensen for a detailed description.

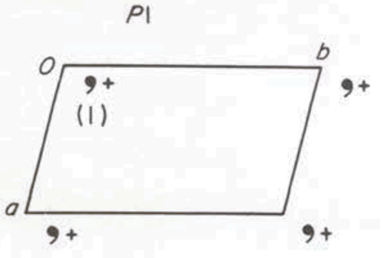


Figure 3.23. $P1$, equivalent positions x, y, z.

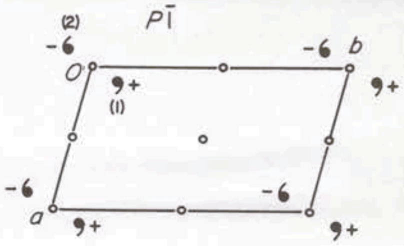


Figure 3.24. $P\bar{1}$, equivalent positions (1) x, y, z; (2) $\bar{x}, \bar{y}, \bar{z}$.

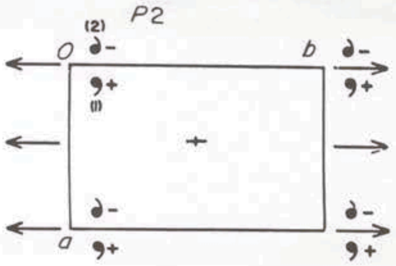


Figure 3.25. $P2$, equivalent positions (1) x, y, z; (2) $\bar{x}, y, \bar{z}$.

You may recall that the definition of the unit cell allowed the origin of the cell to be placed anywhere, as long as the unit cell contained the basic repeating unit. However, as a requirement that the unit cell display the full symmetry of the crystal packing it is necessary that the choice of position for the origin of the unit cell be restricted in one, two or three dimensions. If the crystal packing contains a centre of inversion, then the unit cell as a whole will not exhibit a centre of inversion unless the inversion point is at the origin (and consequently in the centre of the unit cell, the centre of each face and each edge, as in Figs. 3.24 and 3.6). Similarly, a structure exhibiting a crystallographic mirror plane requires that the plane lies either in one of the unit cell faces (and also necessarily at the mid point of the unit cell parallel to the original plane, as in Fig. 3.29) or at $\frac{1}{4}$ and $\frac{3}{4}$ of the distance along one unit cell edge as in Fig. 3.35, however, the choice of origin in the other two directions remains arbitrary.

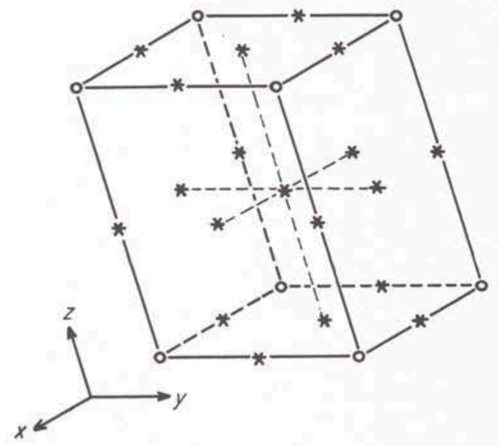


Figure 3.6. Triclinic unit cell showing centers of symmetry at corners of the unit cell (○) and between them (*).

Below are some more examples of how space group symmetry can be built up from the combination of symmetry elements, and the equivalent positions thereby generated.

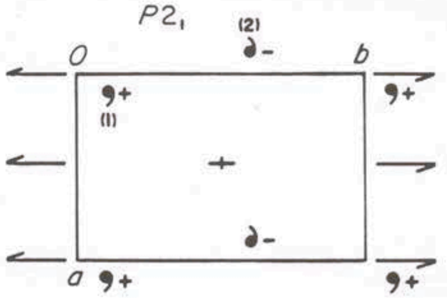


Figure 3.26. $P2_1$, equivalent positions (1) x, y, z; (2) $\bar{x}, y+\frac{1}{2}, \bar{z}$.

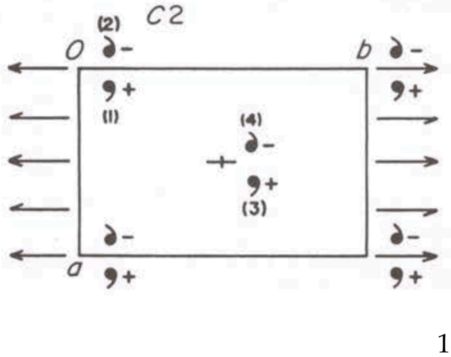


Figure 3.27. $C2$, equivalent positions (1) x, y, z; (2) $\bar{x}, y, \bar{z}$; (3) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (4) $\bar{x}+\frac{1}{2}, y+\frac{1}{2}, \bar{z}$.

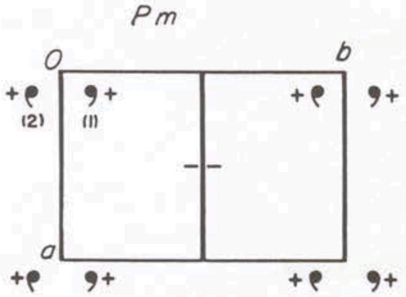


Figure 3.29. *Pm*, equivalent positions (1) x, y, z; (2) $x, \bar{y}, z$.

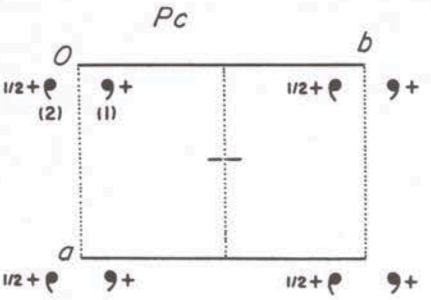


Figure 3.30. *Pc*, equivalent positions (1) x, y, z; (2) $x, \bar{y}, z+\frac{1}{2}$.

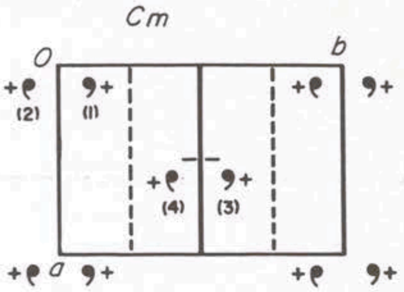


Figure 3.31. *Cm*, equivalent positions (1) x, y, z; (2) $x, \bar{y}, z$; (3) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (4) $x+\frac{1}{2}, \bar{y}+\frac{1}{2}, z$.

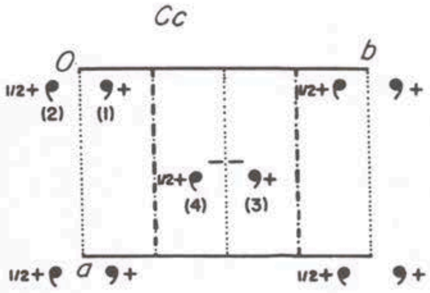


Figure 3.32. *Cc*, equivalent positions (1) x, y, z; (2) $x, \bar{y}, z+\frac{1}{2}$; (3) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (4) $x+\frac{1}{2}, \bar{y}+\frac{1}{2}, z+\frac{1}{2}$.

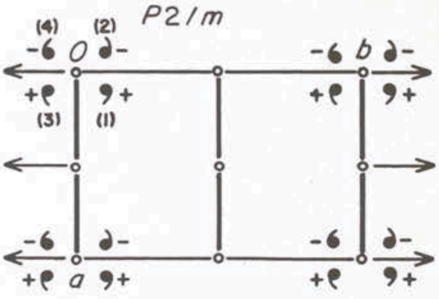


Figure 3.33. *P*2/*m*, equivalent positions (1) x, y, z; (2) $\bar{x}, y, \bar{z}$; (3) $x, \bar{y}, z$; (4) $\bar{x}, \bar{y}, \bar{z}$.

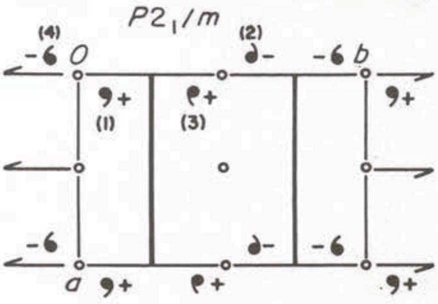


Figure 3.35. $P2_1/m$, equivalent positions (1) x, y, z; (2) $\bar{x}, y+\frac{1}{2}, \bar{z}$; (3) $x, \bar{y}+\frac{1}{2}, z$; (4) $\bar{x}, \bar{y}, \bar{z}$.

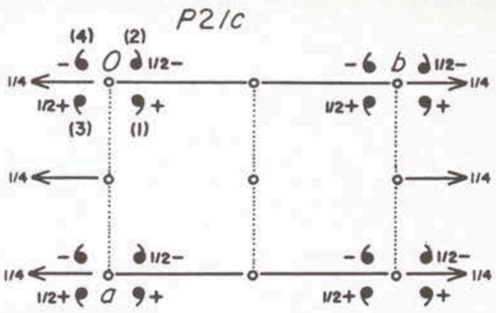


Figure 3.36. *P*2/*c*, equivalent positions (1) x, y, z; (2) $\bar{x}, y, \bar{z}+\frac{1}{2}$; (3) $x, \bar{y}, z+\frac{1}{2}$; (4) $\bar{x}, \bar{y}, \bar{z}$.

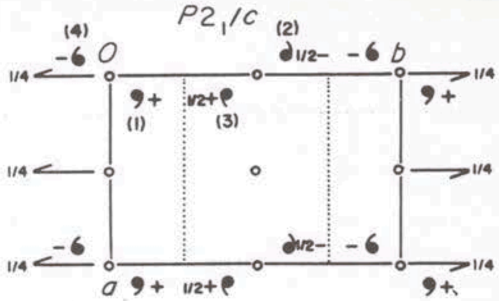


Figure 3.37. *P*2_1/*c*, equivalent positions (1) x, y, z; (2) $\bar{x}, y+\frac{1}{2}, \bar{z}+\frac{1}{2}$; (3) $x, \bar{y}+\frac{1}{2}, z+\frac{1}{2}$; (4) $\bar{x}, \bar{y}, \bar{z}$.

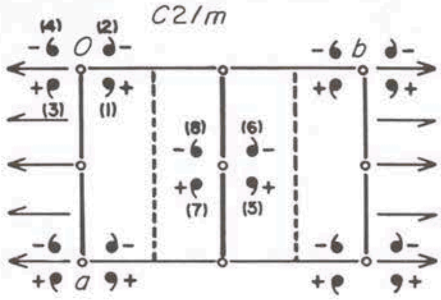


Figure 3.38. *C*2/*m*, equivalent positions (1) x, y, z; (2) $\bar{x}, y, \bar{z}$; (3) $x, \bar{y}, z$; (4) $\bar{x}, \bar{y}, \bar{z}$; (5) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (6) $\bar{x}+\frac{1}{2}, y+\frac{1}{2}, \bar{z}$; (7) $x+\frac{1}{2}, \bar{y}+\frac{1}{2}, z$; (8) $\bar{x}+\frac{1}{2}, \bar{y}+\frac{1}{2}, \bar{z}$.

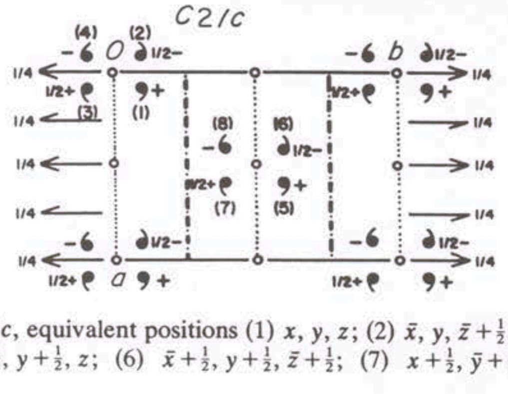


Figure 3.39. *C*2/*c*, equivalent positions (1) x, y, z; (2) $\bar{x}, y, \bar{z}+\frac{1}{2}$; (3) $x, \bar{y}, z+\frac{1}{2}$; (4) $\bar{x}, \bar{y}, \bar{z}$; (5) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (6) $\bar{x}+\frac{1}{2}, y+\frac{1}{2}, \bar{z}+\frac{1}{2}$; (7) $x+\frac{1}{2}, \bar{y}+\frac{1}{2}, z+\frac{1}{2}$; (8) $\bar{x}+\frac{1}{2}, \bar{y}+\frac{1}{2}, \bar{z}$.

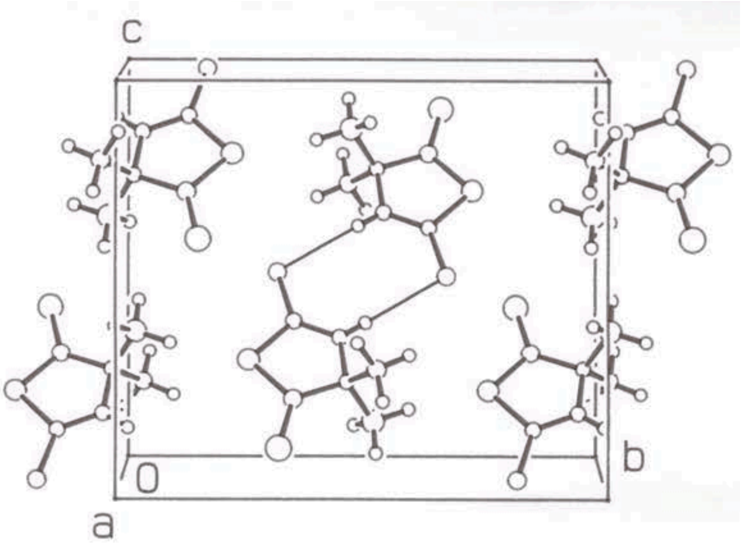
International Tables for Crystallography, Volume A lists the equivalent positions for each space group. An object is said to lie in a general position unless it lies exactly on a symmetry element, when it is said to lie on a special position. The general position is always given as x, y, z and all the equivalent positions are expressed in terms of the coordinates of the initial position. If an atom or molecule lies in a general position, the number of general positions for a space group determine how many identical atoms, or molecules, there are in the unit cell.

For organic molecules, an asymmetric unit usually contains one molecule, but asymmetric units sometimes contain two (or, in rare cases, more) molecules. Multiple molecules in an asymmetric unit are termed symmetry independent molecules because there is no symmetry relationship between them which permits the choice of a smaller asymmetric unit. Symmetry independent molecules may be a consequence of variations in the conformation of the molecule, so that two or more conformations exist in the same crystal (this can also result in disorder, which will be discussed later), or it may be a consequence of restrictions in molecular packing. Molecules which appear to be identical may not be crystallographically identical; that is, not related perfectly by symmetry.

Atoms or molecules that contain a symmetry element, such as a centre of inversion or a mirror plane, may lie with that element on a crystallographic special position. In such a case the number of molecules in the unit cell is reduced to just the number of non-identical positions generated by application of all the equivalent position generators on the special position's coordinates. The coordinates and multiplicity of special positions are also listed with each space group in *International Tables*.

As an example of the information for each space group contained in *International Tables, Volume A*, the details for the space group $P2_1/c$ is given on the following page.

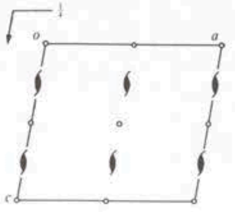
The packing diagram of a "real" structure is shown below. The space group is $P2_1/c$, viewed down the *a* axis. The inversion centre is easily seen. Look for the 2-fold screw axis and the glide plane and compare this with Fig. 3.37 above. Hydrogen bonding may play an important part in the symmetry adopted in the crystal packing of this compound. What is the asymmetric unit for this crystal?

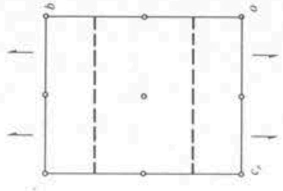


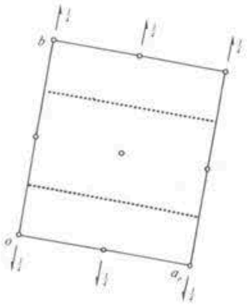
$P\,2_1/c$ $\quad C_{2h}^5$ $\quad 2/m$ Monoclinic

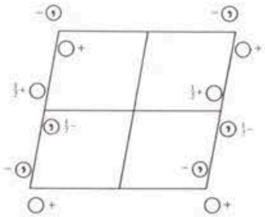
No. 14 $\quad P\,1\,2_1/c\,1$ Patterson symmetry $P\,1\,2/m\,1$

UNIQUE AXIS b, CELL CHOICE 1









Origin at $\bar{1}$

Asymmetric unit $\quad 0\le x\le 1;\quad 0\le y\le \frac{1}{4};\quad 0\le z\le 1$

Symmetry operations

(1) 1 $\quad$ (2) $2(0,\frac{1}{2},0)\ \ 0,y,\frac{1}{4}$ $\quad$ (3) $\bar{1}\ \ 0,0,0$ $\quad$ (4) $c\ \ x,\frac{1}{4},z$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3)

Positions

Multiplicity, Wyckoff letter, Site symmetry	Coordinates	Reflection conditions
		General:
4 e 1	(1) x,y,z (2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$ (3) $\bar{x},\bar{y},\bar{z}$ (4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$	$h0l$: $l=2n$ $0k0$: $k=2n$ $00l$: $l=2n$
		Special: as above, plus
2 d $\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$ $\quad \frac{1}{2},\frac{1}{2},0$	hkl : $k+l=2n$
2 c $\bar{1}$	$0,0,\frac{1}{2}$ $\quad 0,\frac{1}{2},0$	hkl : $k+l=2n$
2 b $\bar{1}$	$\frac{1}{2},0,0$ $\quad \frac{1}{2},\frac{1}{2},\frac{1}{2}$	hkl : $k+l=2n$
2 a $\bar{1}$	$0,0,0$ $\quad 0,\frac{1}{2},\frac{1}{2}$	hkl : $k+l=2n$

Symmetry of special projections

Along [001] $p\,2gm$	Along [100] $p\,2gg$	Along [010] $p\,2$
$\mathbf{a}'=\mathbf{a}_p$ $\quad \mathbf{b}'=\mathbf{b}$	$\mathbf{a}'=\mathbf{b}$ $\quad \mathbf{b}'=\mathbf{c}_p$	$\mathbf{a}'=\frac{1}{2}\mathbf{c}$ $\quad \mathbf{b}'=\mathbf{a}$
Origin at $0,0,z$	Origin at $x,0,0$	Origin at $0,y,0$

Maximal non-isomorphic subgroups

I $\quad [2]P\,1\,2_1\,1\,(P\,2_1)$ $\quad$ 1; 2
$[2]P\,\bar{1}$ $\quad$ 1; 3
$[2]P\,1\,c\,1\,(P\,c)$ $\quad$ 1; 4

IIa none

IIb none

Maximal isomorphic subgroups of lowest index

IIc $[3]P\,1\,2_1/c\,1\,(\mathbf{b}'=3\mathbf{b})(P\,2_1/c)$; $[2]P\,1\,2_1/c\,1\,(\mathbf{a}'=2\mathbf{a}$ or $\mathbf{a}'=2\mathbf{a},\mathbf{c}'=2\mathbf{a}+\mathbf{c})(P\,2_1/c)$

Minimal non-isomorphic supergroups

I $\quad [2]P\,n\,n\,a$; $[2]P\,m\,n\,a$; $[2]P\,c\,c\,a$; $[2]P\,b\,a\,m$; $[2]P\,c\,c\,n$; $[2]P\,b\,c\,m$; $[2]P\,n\,n\,m$; $[2]P\,b\,c\,n$; $[2]P\,b\,c\,a$; $[2]P\,n\,m\,a$; $[2]C\,m\,c\,a$

II $\quad [2]C\,1\,2/c\,1\,(C\,2/c)$; $[2]A\,1\,2/m\,1\,(C\,2/m)$; $[2]I\,1\,2/c\,1\,(C\,2/c)$; $[2]P\,1\,2_1/m\,1\,(2\mathbf{c}'=\mathbf{c})(P\,2_1/m)$; $[2]P\,1\,2/c\,1\,(2\mathbf{b}'=\mathbf{b})(P\,2/c)$

It is not necessary that a molecule which contains internal symmetry occupies a position in a unit cell which displays the same crystallographic symmetry. The PF_6^- anion in the ideal case has $\bar{3}$ symmetry, so that only the positions of the P-atom and one F-atom need to be known; symmetry generates the rest of the anion. However, it is not very often that the anion crystallises in a space group that displays full $\bar{3}$ symmetry. This is usually because the cation does not possess $\bar{3}$ symmetry, and cannot be arranged in general positions around a $\bar{3}$ axis without there being 6 cations for every anion. In such cases the anion would probably occupy a general position in a lower symmetry space group and all of the P-F bonds would be crystallographically independent. In a similar way, a molecule with apparent C_2 symmetry does not always crystallise in a space group with a corresponding 2-fold axis. The molecule can then be said to contain a local or pseudo-2-fold axis.

3.3 Determining the space group

Choosing the correct space group from 230 possibilities may seem an arduous task, but in most cases it is a relatively simple procedure. Life is made easy since about 60% of all organic structures fall into one of 6 space groups, the centrosymmetric ones being $P\bar{1}$ (triclinic), $P2_1/c$, $C2/c$ (both monoclinic) and $Pbca$ (orthorhombic), while the non-centrosymmetric space groups are $P2_1$ (monoclinic) and $P2_12_12_1$ (orthorhombic). In the Linden lab in Zurich, of 206 structures, 91% were in these 6 space groups, and the remainder cover just 10 additional space groups. One learns very quickly to recognise the features representative of the more commonly observed space groups.

As a first step one must determine the crystal system. This immediately reduces the possibilities. There are 2 triclinic space groups, 13 monoclinic, 59 orthorhombic, 68 tetragonal, 25 trigonal (including rhombohedral), 27 hexagonal and 36 cubic. As a first guide the relationships within the unit cell dimensions can help to suggest the crystal system, but as we have seen, this is not an infallible rule as they could suggest a higher system than the true one.

To really be sure of the crystal system, the lattice symmetry or Laue class must be determined. The Laue class can be determined by studying the intensities of certain reflections. Since reflections are the result of diffraction from lattice planes within the crystal, and the intensity of a given reflection is proportional to the number of atoms in the structure that fall on that lattice plane, it follows that if there is a symmetry element in the lattice, those planes that are related by the symmetry element will contain equivalent atoms and the intensities of the reflections from the related planes will be equal. Such reflections are known as equivalent reflections. From an examination of such equivalences we can deduce the lattice (or Laue) symmetry of the crystal.

For example, a 2-fold axis parallel to the unique b-axis of a monoclinic unit cell will transform an atom at x, y, z to the position $-x, y, -z$. This means that lattice planes (hkl) and ($\bar{h}k\bar{l}$) will have the same atomic contents and thus the reflections hkl and $\bar{h}k\bar{l}$ will have equal intensities (within the statistical limits of detector measurements and allowing for absorption, which will be discussed later).

We can also assume that the intensity of a reflection from a set of lattice planes will be equivalent to that from the "back" of these planes (Friedel's Law) and therefore reflections of the type hkl and $\bar{h}\bar{k}\bar{l}$ will always be equivalent in intensity. Again, there are exceptions caused by anomalous scattering, but the effect is usually weak and can generally be ignored at this stage of the analysis.

Combining the above two conditions, we can see that for a monoclinic lattice there are four sets of equivalent reflections, namely hkl, $\bar{h}k\bar{l}$, $\bar{h}\bar{k}\bar{l}$, and $h\bar{k}l$. The Friedel (centrosymmetrically) related pairs will always be equivalent for all crystal systems, but if the intensities for any other pairing of these four conditions are measured for 10-20 reflections, it will clearly be seen whether or not the monoclinic lattice is present.

In a similar manner it can be shown that for an orthorhombic lattice, any reflection hkl will be equal in intensity to reflections having all combinations of signs for h, k and l; i.e. $\pm h \pm k \pm l$, giving 8 equivalent reflections. For the cubic lattice with Laue class F$m\bar{3}m$, reflections having all permutations of hkl, together with the sign combinations, have equal intensities, giving 48 equivalent reflections for just one hkl value!

Determination of the Laue class enables us to determine the crystal system and therefore reduce the number of possible choices for the space group. In fact, crystal systems higher in symmetry than orthorhombic have two Laue classes, the distinction between which further reduces the possible space groups.

As a consequence of the principle of equivalent reflections, it is not necessary to measure the intensities for all possible reflections during the data collection. One needs to measure only those reflections that arise from the asymmetric unit of the unit cell. In this way the measuring time for a sample can be considerably reduced; only one eighth of the total data needs to be measured for an orthorhombic unit cell; one quarter for a monoclinic unit cell.

The next step in determining the space group is to examine the **systematically absent reflections**. It can be shown mathematically that the presence of any translational symmetry elements (screw axes, glide planes, face- or body-centering) in the structure of a crystal results in reflections with particular combinations of indices being forbidden from containing any diffracted intensity; that is, these forbidden reflections are unobserved. This is merely a consequence of the superposition of waves as discussed earlier. The conditions under which reflections are observed in each space group are listed in *International Tables, Volume A*, and a copy of this listing is included at the end of this section.

Refer to the table of systematic absences for the orthorhombic crystal system. The column $h00$ is interpreted to mean all those reflections for which h can have any value, but k and l are always zero. The column $hk0$ refers to all reflections with l restricted to 0 and the column hkl refers to any general reflection. An entry of h under the $hk0$ column means that the only reflections of this category that are observed are those with h a multiple of 2; the reflection is observed when $h = 2n$ and unobserved when $h = 2n+1$. An entry of $h+k$ under the same column means that the condition $h+k = 2n$ must be satisfied for the reflection to be observed; that is, the sum of the two indices must be even. The entry h, k means that *both* $h = 2n$ and $k = 2n$ are required for the reflection to be observed. In some cases the index must be a multiple of 3, 4 or 6 for the reflection to be observed. This is always stated explicitly in the tables.

For general reflections hkl, no entry under the heading indicates that the lattice is P; $h+k$ indicates a C-centred unit cell; $h+k+l$ (sum of all three is even) indicates a body centred I unit cell and $h+k$, $h+l$, $k+l$ (sum of any two indices is even) indicates a face centred F unit cell.

As an exercise find which orthorhombic space groups exhibit the following conditions under which reflections are observed:

1: $h00$, $h=2n$; $0k0$, $k=2n$

2: $0kl$, $k=2n$; $h0l$, $l=2n$; $hk0$, $h+k=2n$;
$h00$, $h=2n$; $0k0$, $k=2n$; $00l$, $l=2n$

3: hkl, $h+k=2n$; $0kl$, $k,l=2n$; $h0l$, $h,l=2n$ $hk0$, $h+k=2n$,
$h00$, $h=2n$; $0k0$, $k=2n$; $00l$, $l=2n$

4: hkl, $h+k=2n$, $h+l=2n$, $k+l=2n$;
$0kl$, $k,l=2n$; $h0l$, $h,l=2n$ $hk0$, $h,k=2n$,
$h00$, $h=2n$; $0k0$, $k=2n$; $00l$, $l=2n$

It is necessary to look at a range of reflections to determine the full pattern of systematic absences. Therefore, this is not usually done until after the data collection is completed, so that all possible combinations of reflection conditions are available for scrutiny. However, if it is suspected that the lattice is non-primitive, this should be confirmed before starting the data collection, because, once confidently determined, it is not necessary to collect the systematically absent reflections. For a non-primitive lattice the omission of the systematic absences can reduce the number of reflections to be measured by at least 50%. Non-primitive lattices are usually predictable after the initial stages of measurement on the diffractometer, because the initial unit cell will be a primitive one which the program decides to convert to a non-primitive unit cell of a higher crystal system with a corresponding doubling (or more) or the unit cell volume. We will discuss this in more detail in the section on data collection.

From the examination of systematic absence conditions the possible choice of space group will be narrowed to 1-3 possibilities for orthorhombic or lower crystal systems, although up to 8 possibilities remain in higher symmetries. If we are lucky, the pattern of systematic absences will be consistent with just one space group, as with $P2_1/c$, and we can be confident of our choice. In other cases we have to make some decisions based on chemical knowledge. For example, a pure enantiomer will not crystallise in a centrosymmetric space group and, as long as we are *absolutely certain* it is not a racemic mixture, we can utilise this fact to eliminate the centrosymmetric space groups. An analysis of intensity statistics can also help to distinguish between centrosymmetric and non-centrosymmetric space groups. A comparison of the volume of the unit cell with the size of the expected molecule can also help in the elimination of some space groups, since the the presence of too much symmetry may require too many molecules to fit into a given volume. If there is still ambiguity, attempt to solve the structure using each of the remaining choices of space group. Usually a sensible structure will appear in only one of these trials.

Space group determination is one of the fundamental steps of a crystal structure analysis. Get it wrong and you will probably be unable to either solve or refine the structure, or you will see an unexpected molecular fragment or strange geometry. In all cases of difficulty check the space group assignment first. It could save you hours of worry. Problems often arise from the incorrect interpretation of the pattern of systematic absences.

Very weak intensities observed for reflections which should be systematically absent according to the chosen space group may mean that the reflections are not absent at all, and thus the choice of space group is incorrect. There is always a danger that this could be overlooked initially. This is particularly a danger with structures of compounds that contain a heavy element, when the arrangement of the heavy atoms considered alone leads to a higher symmetry than the structure exhibits when all atoms are considered. Such structures are said to have a super-lattice. Reflections to which the heavy atoms contribute will be intense, while those resulting from only the lighter atoms will be very weak. When super-lattice effects are present, the pattern of the intense reflections will conform to the symmetry of the super-lattice and the very weak reflections will be exactly those expected to be systematically absent in the super-lattice symmetry. If the very weak reflections are ignored, the space group corresponding to the super-lattice could be chosen instead of the space group corresponding to the entire structure.

The super-lattice problem can also lead to an initial choice of unit cell that is too small and is something to watch out for, particularly when using automated diffractometers. If the initial reflections from which the unit cell dimensions are calculated do not contain any of the very weak reflections, the calculated unit cell will be just that of the super-lattice. This problem can often be detected by comparing the calculated unit cell volume and the predicted symmetry with the expected molecular volume of the compound. If the comparison causes suspicion, each axis of the unit cell, in turn, should be doubled and the intensities of reflections of the type $h00$, $0k0$, $00l$ (axial reflections) with odd values for the indices should be measured and examined. If significant intensities are found for reflections in one or more of these classes, then the doubling of the corresponding unit cell axis is justified and the data collection can continue with the new larger unit cell. Generating unwarping or reciprocal lattice layer reconstruction images which contain reciprocal lattice layers or axial reflections can be a convenient and very sensitive means of checking for the possible presence of a larger unit cell.

Conversely, disorder in a structure, or a poor quality crystal can give one or two weakly observed reflections in reflection classes where they should all be unobserved, thus leading to the incorrect choice of space group. You need to remain aware of all the possibilities. In all structure determinations do not forget to check the chemical sense of the results you obtain. Always question unusual features before you try to find a chemical explanation for them. They may be an artefact of an error in the structure analysis somewhere. Do not blindly accept your results. Crystallographic referees take great delight in shooting holes in a publication if the structure analysis is incorrectly done.

You have been provided with a document which contains the listings of the conditions under which reflections are observed for each space group in *International Tables for Crystallography, Volume A*.