

Crystal Lattices and Crystal Symmetry

Davide Viterbo

Department of Inorganic, Physical and Materials Chemistry, University of Torino, via Giuria 7, I-10125 Torino, Italy

June 4, 1996

Summary. The basic concepts of the geometrical representation of crystalline solids and of their symmetry are outlined. The combination of periodic translational symmetry (describing crystal lattices) with other symmetry elements (rotation axes, mirror planes, inversion centers, etc.) is described as the basis of the space group theory.

Key words: Crystal Lattice – Translational Symmetry – Unit Cell – Crystal Structure – Crystallographic Rows and Planes – Metric Tensor – Reciprocal Lattice – Symmetry Operators – Symmetry Elements – Point Groups – Symmetry Classes – Laue Classes – Crystal Systems – Bravais Lattices – Space Groups

1. Lattice geometry

1.1. Lattices

Crystalline solids, as confirmed by evidence from several experiments (the anisotropy of their physical properties, diffraction, etc.), may be described as ordered repetitions of atoms or groups of atoms in three dimensions. Translational periodicity in crystals may be conveniently studied by focusing our attention on the geometry of the repetition rather than on the repeating motif. In an ideal crystal, all repeating units are identical and we may say that they are related by translational symmetry operations, corresponding to the set of vectors:

$$\mathbf{T} = u \mathbf{a} + v \mathbf{b} + w \mathbf{c} \quad (1)$$

where u , v and w are three integers ranging from minus infinity to plus infinity, zero included, and \mathbf{a} , \mathbf{b} and \mathbf{c} are three non-coplanar vectors defining the basis of the three-dimensional space. Real crystals may present more or less marked

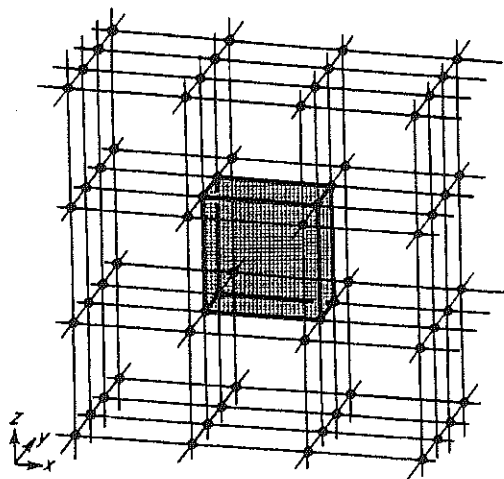


Figure 1. A three-dimensional lattice, showing a unit cell (heavy lines).

deviations from this ideal, perfect order. The set of points at the ends of all the translation vectors \mathbf{T} forms a three-dimensional lattice and the points are called *lattice nodes* (Figure 1). The three integers u , v and w defining a given vector, are the corresponding coordinates of the node in the reference system defined by \mathbf{a} , \mathbf{b} and \mathbf{c} . The parallelepiped formed by these three basis vectors is called the *unit cell* and their directions define the *crystallographic axes*: X , Y and Z . The lattice constants are the three moduli a , b and c and the three angles, α , β and γ between the vectors (α between \mathbf{b} and \mathbf{c} , β between \mathbf{a} and \mathbf{c} and γ between \mathbf{a} and \mathbf{b}).

A two-dimensional example will serve to illustrate these concepts. In Figure 2(a), a given "three-atom" motif is repeated at intervals \mathbf{a} and \mathbf{b} . If we replace each motif by a point at its centre of gravity we obtain the lattice of Figure 2(b). The same lattice is obtained if the point is located on any other position of the motif and the position of the lattice with respect to the motif is completely arbitrary. If any lattice point is chosen as the origin of the lattice, any other point in Figure 2(b) is uniquely defined by the vector:

$$\mathbf{T} = u\mathbf{a} + v\mathbf{b} \quad (2)$$

where u and v are integers and the unit cell is defined by the vectors \mathbf{a} and \mathbf{b} . The choice of the basis vectors is rather arbitrary, as shown in Figure 2(b), where four different choices are illustrated, all of which are consistent with relation (2) with u and v being integers. These cells contain only one lattice point, since the four points at the corners of each cell are each shared by a total of four cells. They are called *primitive* cells. Nevertheless, we are allowed to choose different types of unit cells, such as those shown in Figure 2(c), which contain two or more lattice points. Also in this case, each lattice point will satisfy (2) but u and

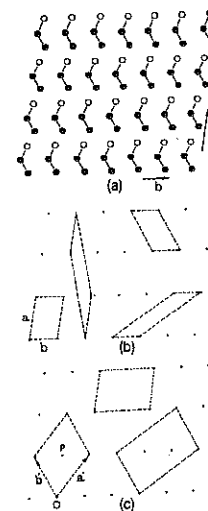


Figure 2. (a) Repetition of a graphical motif as an example of a two-dimensional crystal; (b) the corresponding lattice with some examples of primitive cells; (c) the same lattice with some examples of multiple cells.

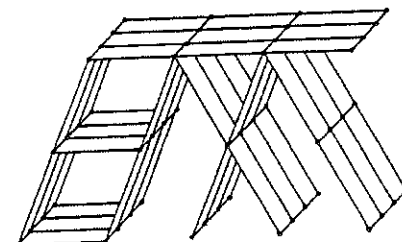


Figure 3. Lattice rows and planes.

v are no longer restricted to integer values (in Figure 2(c), point P is related to the origin and to the basis vectors \mathbf{a}' and \mathbf{b}' by a vector with $u = \frac{1}{2}$, $v = \frac{1}{2}$). These cells are called *multiple* or *centred* cells.

1.2. Crystal structure

The periodic repetition of the structural motif (atoms, groups of atoms or molecules) by the infinite set of vectors (1) yields the *crystal structure*, which is completely determined once the lattice constants and the coordinates, x , y and z , of all the atoms in the unit cell are known. These coordinates are the components of the vectors:

$$\mathbf{r}_j = x_j\mathbf{a} + y_j\mathbf{b} + z_j\mathbf{c} \quad (j = 1, 2, \dots, N) \quad (3)$$

linking the cell origin to the nucleus of the j -th atom. For all N atoms inside the chosen unit cell, the coordinate values are in the interval 0 to 1. They are therefore called *fractional coordinates* and are given by:

$$x = X/a \quad y = Y/b \quad z = Z/c$$

1.3. Crystallographic rows and planes

Since crystals are anisotropic, it is necessary to identify, in a simple way, directions or planes in which specific physical properties are observed. Directions defined by two lattice nodes, and planes defined by three lattice points are called *crystallographic directions* and *planes*, respectively. A *lattice row* is defined by two lattice points and the *identity period*, separating the infinite number of nodes along the row is the minimum distance between two points. The lattice translations will then generate an infinite number of parallel and equally spaced, identical rows (Figure 3). Therefore, in a lattice with a primitive cell, the vector $\mathbf{T} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$ linking the origin with the nearest point on a given crystallographic direction, may be used to represent a given row together with the infinite number of rows parallel to it. The three values u , v and w are the *indices* of the row, which is then represented by the symbol $[uvw]$. The three integers u , v and w have no common factor since they correspond to the coordinates of the point nearest to the origin along the row. The three rows corresponding to the base vectors \mathbf{a} , \mathbf{b} , and \mathbf{c} will have symbols $[100]$, $[010]$ and $[001]$, respectively.

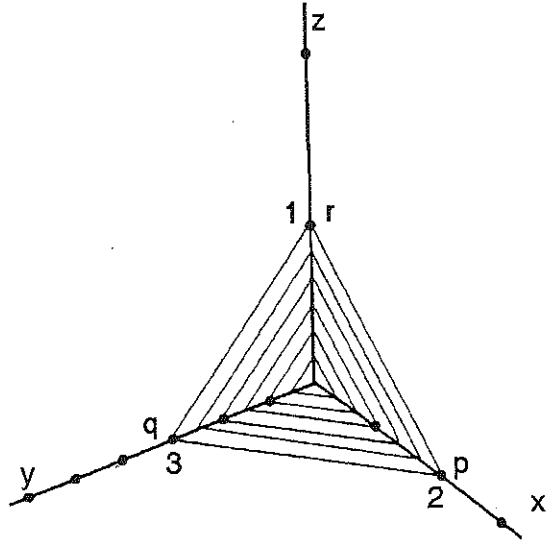


Figure 4. Some lattice planes of the set (236).

Three lattice points define a crystallographic plane. Let us consider a plane intersecting the three crystallographic axes, X , Y and Z , at the three lattice points $(p, 0, 0)$, $(0, q, 0)$ and $(0, 0, r)$ with integer values for p , q and r (Figure 4). Suppose that the largest common factor of p , q and r is 1 and that $m = pqr$ is their least common multiple. Then the equation of the plane is:

$$X/(pa) + Y/(qb) + Z/(rc) = 1 \quad (4)$$

If we introduce the fractional coordinates, $x = X/a$, $y = Y/b$ and $z = Z/c$, the equation of the plane becomes:

$$x/p + y/q + z/r = 1 \quad (5)$$

Multiplying both sides by the product pqr we obtain:

$$qrx + pry + pqz = pqr$$

which can be rewritten as:

$$hx + ky + lz = m \quad (6)$$

where $h = qr$, $k = pr$ and $l = pq$ are also integers with largest common factor equal to 1 and $m = pqr$. We can therefore generate a *family* of planes parallel to the plane (6) by varying m over all integers from $-\infty$ to $+\infty$. These will all be crystallographic planes since each of them is bound to pass through at least three lattice points. Each lattice plane is identical to any other within the family through a lattice translation. For a given triplet h , k and l , the plane with $m = 0$ will pass through the origin, while the plane with $m = 1$, that is:

$$hx + ky + lz = 1 \quad (7)$$

will be the closest to it. The intercepts of plane (7) on X , Y , Z are $1/h$, $1/k$ and $1/l$, while those of plane (6) are m/h , m/k and m/l . It is then clear that the distance of plane (6) from the origin is m times that of plane (7). The three indices, h , k and l , define the family of identical and equally spaced crystallographic planes, and are called the *Miller indices*. The symbol of a family of planes is (hkl) . A simple interpretation of the Miller indices can be deduced from (6) and (7). In fact, they indicate that the planes of the family divide \mathbf{a} into h parts, \mathbf{b} into k parts and \mathbf{c} into l parts. Crystallographic planes parallel to one of the three axes, X , Y or Z , are defined by indices $(0kl)$, $(h0l)$ or $(hk0)$ respectively. Planes parallel to the YZ (face A), XZ (face B) and XY (face C) planes are of type $(h00)$, $(0k0)$ or $(00l)$ respectively.

1.4. The metric tensor

In matrix notation, the set of basis vectors chosen to define a lattice may be written as:

$$|\mathbf{e}\rangle = \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix} \quad (8)$$

and a lattice vector with indices u , v and w , is written as:

$$|\mathbf{T}\rangle = \langle \mathbf{u} | \mathbf{e} \rangle \quad \text{with} \quad \langle \mathbf{u} | = (u \ v \ w) \quad (9)$$

The modulus of this vector is obtained from the scalar product of the vector by its transpose:

$$\langle \mathbf{T} | \mathbf{T} \rangle = \langle \mathbf{u} | \mathbf{e} \rangle \langle \mathbf{e} | \mathbf{u} \rangle = \langle \mathbf{u} | \mathbf{G} | \mathbf{u} \rangle \quad (10)$$

where $\mathbf{G} = |\mathbf{e}\rangle \langle \mathbf{e}|$ is a square matrix:

$$\mathbf{G} = \begin{pmatrix} \mathbf{a} \cdot \mathbf{a} & \mathbf{a} \cdot \mathbf{b} & \mathbf{a} \cdot \mathbf{c} \\ \mathbf{b} \cdot \mathbf{a} & \mathbf{b} \cdot \mathbf{b} & \mathbf{b} \cdot \mathbf{c} \\ \mathbf{c} \cdot \mathbf{a} & \mathbf{c} \cdot \mathbf{b} & \mathbf{c} \cdot \mathbf{c} \end{pmatrix} \quad (11)$$

which is known as the *metric tensor* or *matrix* and allows the calculation of all geometrical features of the lattice.

1.5. The reciprocal lattice

In metric calculations and in the interpretation of many physical properties of crystals (diffraction, conductivity, etc.), it is very useful to introduce the so-called *reciprocal lattice*. Given the basis of a lattice (called here a *direct lattice*) as defined by (8), we can associate with it the basis $\{\mathbf{e}^*\}$ of a new lattice, defined by the vectors \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* , satisfying the condition $\mathbf{I} = |\mathbf{e}^*\rangle\langle\mathbf{e}|$ or explicitly:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \mathbf{a}^* \cdot \mathbf{a} & \mathbf{a}^* \cdot \mathbf{b} & \mathbf{a}^* \cdot \mathbf{c} \\ \mathbf{b}^* \cdot \mathbf{a} & \mathbf{b}^* \cdot \mathbf{b} & \mathbf{b}^* \cdot \mathbf{c} \\ \mathbf{c}^* \cdot \mathbf{a} & \mathbf{c}^* \cdot \mathbf{b} & \mathbf{c}^* \cdot \mathbf{c} \end{pmatrix} \quad (12)$$

from which:

$$\begin{aligned} \mathbf{a}^* \cdot \mathbf{a} &= 1 & \mathbf{b}^* \cdot \mathbf{b} &= 1 & \mathbf{c}^* \cdot \mathbf{c} &= 1 \\ \mathbf{a}^* \cdot \mathbf{b} &= 0 & \mathbf{a}^* \cdot \mathbf{c} &= 0 \\ \mathbf{b}^* \cdot \mathbf{a} &= 0 & \mathbf{b}^* \cdot \mathbf{c} &= 0 \\ \mathbf{c}^* \cdot \mathbf{a} &= 0 & \mathbf{c}^* \cdot \mathbf{b} &= 0 \end{aligned} \quad (13)$$

The last three lines of equations (13) suggest that \mathbf{a}^* is normal to the plane (\mathbf{b}, \mathbf{c}) , \mathbf{b}^* to the plane (\mathbf{a}, \mathbf{c}) and \mathbf{c}^* to the plane (\mathbf{a}, \mathbf{b}) . The modulus and direction of \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* are fixed by relations (13). According to the second row of (13), we can write:

$$\mathbf{a}^* = p (\mathbf{b} \wedge \mathbf{c}) \quad (14)$$

where p is a constant. Scalar multiplication of both sides of (14) by \mathbf{a} , will give:

$$\mathbf{a}^* \cdot \mathbf{a} = 1 = p (\mathbf{b} \wedge \mathbf{c}) \cdot \mathbf{a} = p V \quad (15)$$

from which $p = 1/V$ (V is the volume of the unit cell). Equation (14) and its analogues obtained from the third and fourth row of (13) may then be written as:

$$\mathbf{a}^* = (\mathbf{b} \wedge \mathbf{c})/V ; \quad \mathbf{b}^* = (\mathbf{c} \wedge \mathbf{a})/V ; \quad \mathbf{c}^* = (\mathbf{a} \wedge \mathbf{b})/V \quad (16)$$

giving the reciprocal basis vectors in terms of the direct unit cell. Equations (13) also suggest that the roles of direct and reciprocal space may be interchanged: i.e. the reciprocal of the reciprocal lattice is the direct lattice. It may be easily seen that a reciprocal lattice vector:

$$\mathbf{T}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad (h, k, l \text{ integers}) \quad (17)$$

is perpendicular to the family of direct lattice planes (hkl) . For the reciprocal lattice, we can also define a metric matrix \mathbf{G}^* :

$$\mathbf{G}^* = \begin{pmatrix} \mathbf{a}^* \cdot \mathbf{a}^* & \mathbf{a}^* \cdot \mathbf{b}^* & \mathbf{a}^* \cdot \mathbf{c}^* \\ \mathbf{b}^* \cdot \mathbf{a}^* & \mathbf{b}^* \cdot \mathbf{b}^* & \mathbf{b}^* \cdot \mathbf{c}^* \\ \mathbf{c}^* \cdot \mathbf{a}^* & \mathbf{c}^* \cdot \mathbf{b}^* & \mathbf{c}^* \cdot \mathbf{c}^* \end{pmatrix} \quad (18)$$

and it may be verified that:

$$\mathbf{G}^{**} = \mathbf{G}^{-1} \quad (19)$$

Finally, it is worth pointing out that the "1's" in equations (12) and (13) are sometimes substituted by a constant, such as 2π : the resulting reciprocal lattice is simply scaled by a factor equal to the constant.

2. Symmetry operations and symmetry elements

2.1. Isometric transformations

In order to understand the periodic and ordered nature of crystals, it is also necessary to know all other operations, besides translation, by which the repetition of the basic motif may be obtained. Given two identical objects, placed in random positions and orientations, we must know which operations should be performed to superimpose one object onto the other. The existence of enantiomeric molecules also requires that we know how to superimpose two objects of opposite handedness (*enantiomorphic objects*). The objects are said to be congruent if each point on one object corresponds to a point on the other and if the distance between two points on one object is equal to that between the corresponding points on the other. As a consequence, the angles formed by three related points will also be equal in absolute value and the correspondence is called *isometric*. The congruence may either be *direct* or *opposite* according to whether the corresponding angles have the same or opposite signs. The study of operations relating congruent objects is the goal of the theory of *isometric transformations*, of which we will only consider the most useful results (more detailed accounts may be found in references [1]-[9]). For a direct congruence, the *movements* by which two objects are brought to coincidence, may be: a) a *translation*, which we have already considered; b) a *rotation* of $2\pi/n$ around an axis (an axis of order n or an n -axis); c) a *rototranslation* or *screw* movement, which may be considered as the combination (product) of a rotation around an axis and a translation along the axial direction. For an opposite congruence, which relates enantiomorphic objects, these may be brought to coincidence by the following operations: a) an *inversion* with respect to a point; b) a *reflection* with respect to a plane; c) a *rotoinversion*, the product of a rotation around an axis by an inversion with respect to a point on that axis (an \bar{n} -axis); d) the product of a reflection by a translation parallel to the reflection plane: the plane is then called a *glide plane*; e) a *rotoreflexion*, the product of a rotation by a reflection with respect to a plane perpendicular to the axis. As is well known, the description of the chemical and physical properties of molecules may be greatly simplified when their symmetry is taken into account and the symmetry operations which are considered are among those listed above.

2.2. Symmetry restrictions imposed by lattice periodicity

Suppose now that the isometric operations not only bring to coincidence a pair of congruent objects, but act on the entire space. If all the properties of the space remain unchanged after the operation has been performed, the operation will be a *symmetry operation* and *symmetry elements* are the points, axes or planes with respect to which symmetry operations are carried out.

When, as in the case of ideal crystals, the space is filled by the periodic repetition of a motif, we have seen that it may be described by a lattice. In this case, not all symmetry elements are compatible with the periodic nature of the space, which requires the repetition of these elements also. Without losing generality, let us assume that a rotation axis of order n passes through the origin O of the lattice. Since all lattice points are identical, there will be an

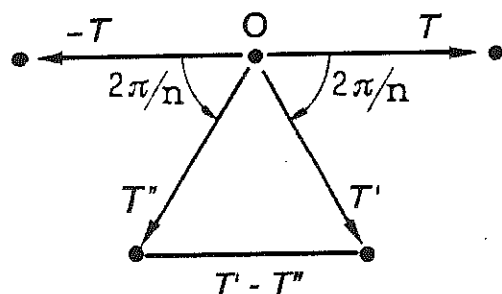


Figure 5. Lattice points in a plane normal to the symmetry axis n passing through O .

n axis passing through each and every lattice point, parallel to that passing through the origin. Each symmetry axis will lie along a lattice row and will be perpendicular to a crystallographic plane. In Figure 5, T is the period vector of a row passing through O and normal to n . Lattice points at $-T$, T' and T'' will also be present, and the vector $T' - T''$, parallel to T , will have to be a lattice vector. This imposes the condition that $T' - T'' = mT$, m being an integer; in a scalar form:

$$2 \cos(2\pi/n) = m \quad (m \text{ integer}) \quad (20)$$

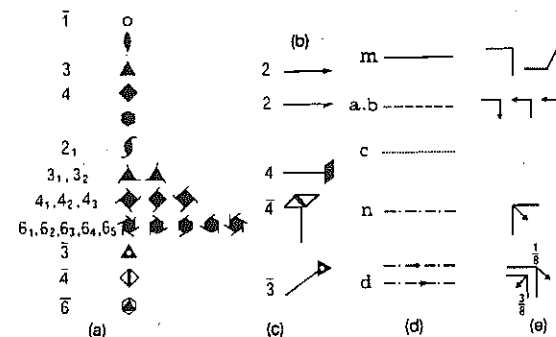
which is only verified for $n = 1, 2, 3, 4, 6$. Axes with $n = 5$ or $n > 6$ are not allowed in crystals. This is the reason why it is impossible to pave a room only with pentagonal tiles. The same restrictions apply to rotoinversion axes (\bar{n} axes) and to screw axes. For the latter, the possible values of the translational component t are also restricted by periodicity: for an axis of order n , the translational component is repeated n times, and, because of lattice periodicity, we must have $nt = pT$, with p integer and $0 \leq p < n$, or:

$$t = (p/n)T \quad (21)$$

Thus, for a screw axis of order 4, the allowed translational components will be $(0/4)T$, $(1/4)T$, $(2/4)T$ and $(3/4)T$. A normal n axis may be thought of as a special screw with $t = 0$ and the properties of a screw axis are completely defined by the symbol n_p .

Reflection planes are indicated by the symbol m and must be parallel to the crystallographic planes. For glide planes, the periodicity requires that the translational component t must be either $t = 0$ (mirror plane) or $t = \frac{1}{2}T$. Glide planes with translational components equal to $a/2$, $b/2$ and $c/2$ will be indicated by the symbols a , b and c respectively, while the diagonal glides with translational components: $(a+b)/2$, $(a+c)/2$, $(b+c)/2$ and $(a+b+c)/2$, are indicated by the symbol n . As we have seen, in a non-primitive cell, T is a vector with rational components and t may assume other values: in this case, the symbol d is used for the glide plane.

Table 1. Graphical symbols for symmetry elements: (a) axes normal to the plane of projection; (b) axes 2 and 2_1 parallel to the plane of projection; (c) axes parallel or inclined to the plane of projection; (d) symmetry planes normal to the plane of projection; (e) symmetry planes parallel to the plane of projection.



Of the five rotoinversion axes, only $\bar{3}$, $\bar{4}$, and $\bar{6}$ are independent, while $\bar{1}$ and $\bar{2}$ are equivalent to an inversion point and to a mirror plane, m , perpendicular to the axis, respectively. Finally, it can be shown that all the rotoreflection axes are equivalent to rotoinversion axes and these symmetry operations will no longer be considered separately.

The graphic symbols of all independent symmetry elements compatible with a crystal lattice, used in the *International Tables for Crystallography* [1], are shown in Table 1, while their effects on the space are illustrated in Figure 6, where, following international notation, an object is represented by a circle with a + or a - sign next to it indicating whether it is above or below the plane of the page; its enantiomorph is indicated by a comma inside the circle and, when both object and enantiomorph fall one on top of each other in the drawing plane, they are represented by a single circle divided into two halves (each with its appropriate sign), one of which contains a comma.

Symmetry operations relating objects through a direct congruence are called *proper*, while those relating objects through an opposite congruence are called *improper*.

3. Point groups and symmetry classes

In crystals more symmetry axes, both proper and improper, with or without translational components, may coexist. Let us first consider the combinations of symmetry operators which do not imply translations, i.e. the combinations of proper and improper axes intersecting in a point. These are called *point groups*, since the operators form a mathematical *group* and leave one point fixed. The set of crystals having the same point group is called *crystal class* and its symbol

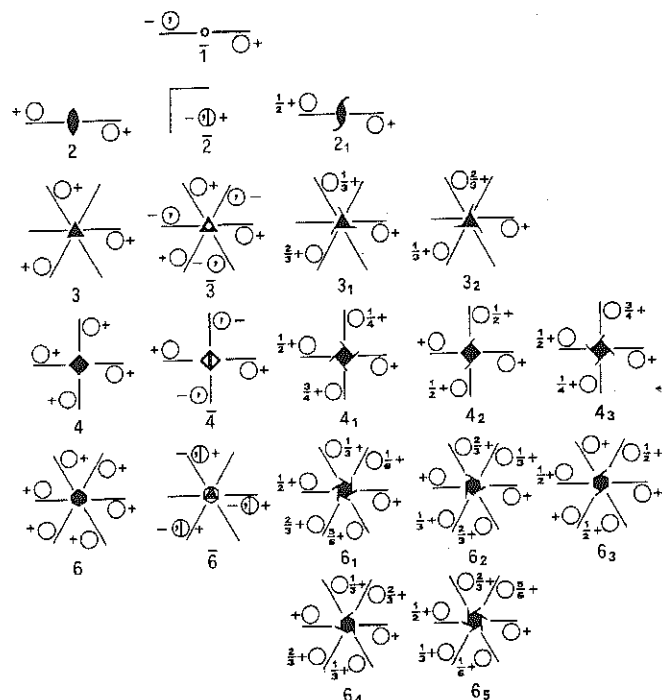


Figure 6. Arrangements of symmetry-equivalent objects, showing the effect of rotation, inversion and screw axes.

is that of the point group. In three dimensions, there are 32 possible crystallographic point groups. The simplest groups are those with only one symmetry axis. As we have seen, there are 5 possible proper (P) axes and 5 improper (I) axes giving rise to 10 point groups. We must also consider the cases where both a proper and an improper axis are simultaneously present along the same direction; these give rise to 3 new groups indicated by the symbol n/\bar{n} . In the remaining 19 groups, more axes coexist. We will not consider the rules governing the combinations of different axes (see references [1]-[9]), but simply list, in Table 2, the conventional symbols of the resulting groups, together with those of the 13 single-axis point groups. It may be noted that crystals with inversion symmetry operators which have an equal number of 'left' and 'right' moieties, each being the enantiomorph of the other. It is important to note that there is no direct relation between the crystal symmetry classes and the molecular symmetry of the individual molecules forming the crystals, in the sense that molecules which have a molecular symmetry not allowed in crystals (for instance with a 5 axis) may well form crystals. Of course, the symmetry of the crystal will belong to one of the 32 point groups.

3.1. Point groups in one and two dimensions

In a one-dimensional lattice, there are only two possible point groups: 1 and $\bar{1}$. In two dimensions, instead of reflection with respect to a plane, we have reflection with respect to a line and rotoinversion axes are not used. The following 10 point groups result: 1, 2, 3, 4, 6, m , $2mm$, $3m$, $4mm$ and $6mm$.

4. Laue classes and crystal systems

4.1. The eleven Laue classes

It is also very important to understand how the symmetry of the physical properties of a crystal relates to its point group. Of basic relevance to this is a postulate of crystal physics, known as the *Neumann principle*: "the symmetry elements of any physical property must include the symmetry elements of the crystal point group". In keeping with this principle, the physical properties may present a higher, but not a lower, symmetry than the point group. As a consequence physical experiments do not normally reveal the true symmetry of the crystal. Some of them, such as diffraction, always add an inversion centre and point groups differing only by the presence of such a centre will not be differentiated by these experiments. When these groups are collected in classes they form the 11 *Laue classes* also listed in Table 2.

Table 2. List of the 32 point groups.

Crystal Systems	Point groups		Laue Classes	Lattice point groups
	Non-centrosymmetric	Centrosymmetric		
Triclinic	1	$\bar{1}$	$\bar{1}$	$\bar{1}$
Monoclinic	2	m	$2/m$	$2/m$
Orthorhombic	222	mmm	mmm	mmm
Tetragonal	4	$\bar{4}$	$4/m$	$4/mmm$
	422	$4mm, \bar{4}2m$	$4/mmm$	$4/mmm$
Trigonal	3	$\bar{3}$	$\bar{3}$	$\bar{3}m$
	32	$3m$	$\bar{3}m$	$\bar{3}m$
Hexagonal	6	$\bar{6}$	$6/m$	$6/mmm$
	622	$6mm, \bar{6}2m$	$6/mmm$	$6/mmm$
Cubic	23	$m\bar{3}$	$m\bar{3}$	$m\bar{3}m$
	432	$\bar{4}3m$	$m\bar{3}m$	$m\bar{3}m$

4.2. The seven crystal systems

If the crystal periodicity is only compatible with axes of order 1, 2, 3, 4 and 6, the presence of these different types of axes will in turn impose some restrictions

on the geometry of the lattice. It is therefore convenient to group together the symmetry classes with common lattice features which may be described by unit cells of the same type. In turn, the cells will be chosen in the most suitable way to show the symmetry actually present. Seven different groups may be identified, which are listed in the first column of Table 2. They are known as the *seven crystal systems*.

Triclinic system - Point groups 1 and $\bar{1}$ have no symmetry axes and therefore there are no constraints on the unit cell: the ratios $a : b : c$ and the angles α, β, γ can assume any value.

Monoclinic system - Point groups 2, $\bar{2} \equiv m$ and $2/m$ all present a two-fold axis. Conventionally, this axis is assumed to coincide with the b axis of the unit cell (y -axis *unique*) and then a and c can be chosen on the lattice plane normal to b . We will then have $\alpha = \beta = 90^\circ$ and γ unrestricted and the axial ratio $a : b : c$ also unrestricted.

Orthorhombic system - Classes 222, $mm2$ and mmm all have three mutually orthogonal two-fold axes. If we assume these as reference axes we will obtain a unit cell with angles $\alpha = \beta = \gamma = 90^\circ$ and with unrestricted $a : b : c$ ratio.

Tetragonal system - The 7 point groups: 4, $\bar{4}$, $4/m$, 422 , $\bar{4}2m$, $4mm$ and $4/mmm$, all have a single four-fold axis which is chosen to coincide with the c axis. Then the a and b axes become symmetry equivalent on the plane normal to c . The cell angles will be $\alpha = \beta = \gamma = 90^\circ$ and the axial ratio $a : b : c = 1:1:c$.

Trigonal and hexagonal systems - 3, $\bar{3}$, 32, $3m$, $\bar{3}m$, 6, $\bar{6}$, $6/m$, 622 , $6mm$, $\bar{6}2m$ and $6/mmm$ all have a single three-fold or six-fold axis which is assumed to coincide with the c axis. Axes a and b become symmetry equivalent on the plane normal to c . Both systems are characterized by a unit cell with angles $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ and ratio $a : b : c = 1:1:c$.

Cubic system - 23, $m\bar{3}$, 432, $\bar{4}3m$ and $m\bar{3}m$ all have four three-fold axes directed along the diagonals of a cube and can be referred to orthogonal unit cell axes coinciding with the cube edges. The presence of the three-fold axes ensures that these directions are symmetry equivalent. The chosen unit cell will have $\alpha = \beta = \gamma = 90^\circ$ and axial ratio $a : b : c = 1 : 1 : 1$.

5. Bravais Lattices

As we have seen, each crystal system can be associated with a primitive cell compatible with the point groups belonging to that system. Each of these primitive cells defines a lattice type, but there are other types of lattices, based on non-primitive cells, which are also compatible with some of the crystal systems but cannot be related to those already seen. In this section, we will describe the 5 possible plane lattices and the 14 possible space lattices based on both primitive and non-primitive cells. These are called *Bravais lattices*, after Auguste Bravais who first listed them in 1850.

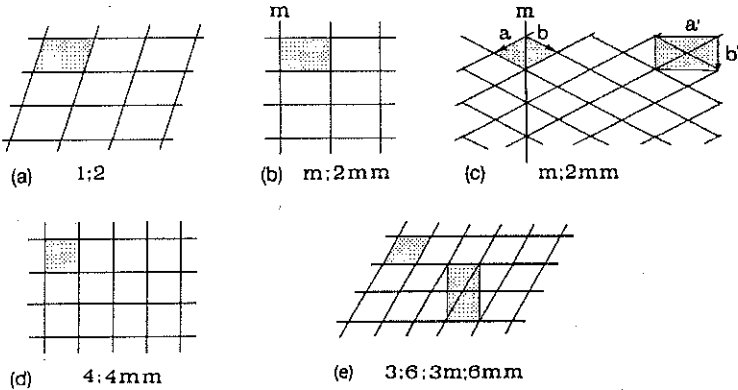


Figure 7. The five plane lattices and the corresponding two-dimensional point groups.

5.1. Plane lattices

As may be seen in Figure 7(a), an oblique cell is compatible with the presence of axes 1 and 2 normal to the cell. This cell is primitive and has point group 2. If the row indicated by m in Figure 7(b) is a reflection line, the cell must be rectangular. It is primitive and compatible with the point groups, m and $2mm$. The lattice shown in Figure 7(c) with $a = b$ and $\gamma \neq 90^\circ$, is also compatible with m .

Table 3. The five plane lattices.

Cell	Type of cell	Point group of the net	Lattice parameters
Oblique	p	2	a, b, γ
Rectangular	p, c	$2mm$	$a, b, \gamma = 90^\circ$
Square	p	$4mm$	$a = b, \gamma = 90^\circ$
Hexagonal	p	$6mm$	$a = b, \gamma = 120^\circ$

Even though this lattice has an oblique primitive cell, each lattice point has $2mm$ symmetry and therefore, the lattice must be compatible with a rectangular system. This can be seen by choosing the rectangular centred cell, defined by the unit vectors: a' and b' . The choice of an orthogonal cell is more convenient because it is more simply related to the symmetry of the lattice. It is important to note that the two lattices shown in Figures 7(b) and (c) are of different types, even though they are compatible with the same point groups. In Figure 7(d), a plane lattice is represented, which is compatible with the presence of a 4 axis. The square cell is primitive and compatible with the point groups 4 and $4mm$. Finally, in Figure 7(e), a plane lattice is shown, compatible with the presence of a 3 or a 6 axis. A primitive unit cell with a rhombus shape and angles of

60° and 120° (an hexagonal cell) may be chosen. This is compatible with the point groups 3, 6, $3m$ and $6mm$. A centred rectangular cell can also be selected, but such a cell, which is not as simply related to the lattice symmetry, is less convenient. The basic features of the five plane lattices are listed in Table 3.

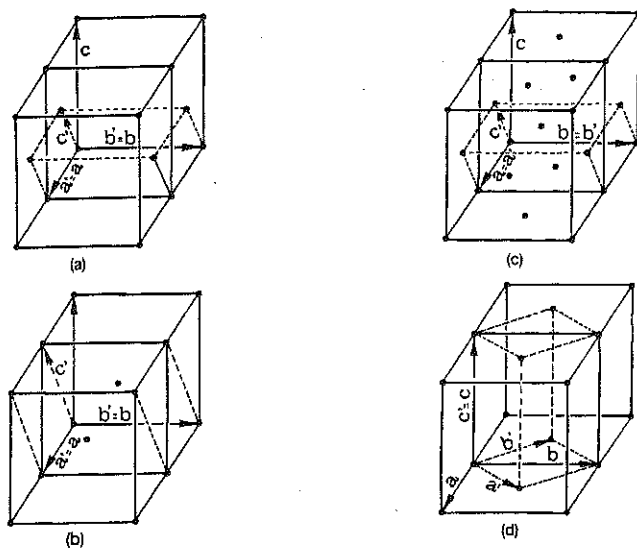


Figure 8. Monoclinic lattices: (a) reduction of a B-centred cell to a P cell; (b) reduction of an I-centred to an A-centred cell; (c) reduction of an F-centred to a C-centred cell; (d) reduction of a C-centred to a P non-monoclinic cell.

5.2. Space lattices

In Table 4, the different types of cells are described. The positions of the additional lattice points define the minimal translational components which will move an object onto an equivalent one. For instance, in an A-type cell, an object at (x, y, z) is repeated by translation into $(x, y + v/2, z + w/2)$, with v and w integers; the shortest translation from the original position will be $(0, 1/2, 1/2)$.

Let us now examine the different types of three-dimensional lattices grouped in the appropriate crystal systems.

Triclinic lattices - Even though non-primitive cells can always be chosen, the absence of axes of order greater than one makes such choices inconvenient. The simplest choice is that of the primitive cell described in section 4.2.

Monoclinic lattices - In the same section, we have described the conventional primitive monoclinic cell as having $\alpha = \beta = 90^\circ$ with γ and $a:b:c$ unrestricted. Figure 8(a) shows a B-centred monoclinic cell with unit vectors a, b and c . Choosing unit vectors, so that $a' = a, b' = b, c' = (a+c)/2$, gives the primitive cell shown by the dotted line, which is also monoclinic (c' lies on the ac plane

Table 4. The conventional types of unit cell.

Symbol	Type	Positions of additional lattice points	Number of lattice points per cell
P	primitive		1
I	body-centred	$(1/2, 1/2, 1/2)$	2
A	A face-centred	$(0, 1/2, 1/2)$	2
B	B face-centred	$(1/2, 0, 1/2)$	2
C	C face-centred	$(1/2, 1/2, 0)$	2
F	all faces centred	$(1/2, 1/2, 0), (1/2, 0, 1/2), (0, 1/2, 1/2)$	4
R	rhombohedrally centred (description with "hexagonal axes")	$(1/3, 2/3, 2/3), (2/3, 1/3, 1/3)$	3

and only the value of β will change). A B-type monoclinic cell can therefore always be reduced to the conventional primitive cell. With similar arguments, it may be shown that an I cell can be reduced to an A cell [Figure 8(b)] (since the a and c axes can always be interchanged, an A cell is equivalent to a C cell), and an F cell may become a C cell [Figure 8(c)]. However, a C cell is not reducible to a monoclinic P cell, as may be seen in Figure 8(d), where the primitive cell, shown by the dotted line with: $a' = (a+b)/2, b' = (-a+b)/2, c' = c$, no longer has the features of a monoclinic cell, since $\gamma' \neq 90^\circ, |a'| = |b'| \neq |c'|$ and the 2 axis lies along the diagonal of a face. It is worth noting that the choice of the C cell becomes necessary if we want to preserve the symmetry features of the monoclinic lattice in the cell geometry. The P cell shown by the dotted line is an allowed, but less convenient, reference system, which is seldom used to describe crystal structures. Nevertheless, in some cases, the choice of a P cell may become more convenient from a computational point of view and then an appropriate transformation must be performed from the conventional C cell to the corresponding primitive one. All transformation matrices, which allow passage from a centred cell to the corresponding primitive one and vice versa, are given in Table 5. It can therefore be concluded that there are two distinct monoclinic lattices, conventionally described by P and C cells, which are not interchangeable.

Orthorhombic lattices - With arguments similar to those used for monoclinic lattices, it can be verified that there are four different types of orthorhombic lattice, which are conventionally described in terms of P, C, I and F cells.

Tetragonal lattices - As a result of the four-fold axis, an A cell will always be equivalent to a B cell and therefore, to an F cell; indeed, the combination of the two lattice translations $(0, 1/2, 1/2)$ and $(1/2, 0, 1/2)$ gives the third translation $(1/2, 1/2, 0)$ of the F cell (see Table 4). The latter is then transformable to a tetragonal I cell. A C cell is interchangeable with another tetragonal P cell. Thus only two different tetragonal lattices, P and I, are found.

Table 5. Transformation matrices, M , conventionally used to generate centered from primitive lattices, and vice versa, according to the relationship: $A' = M A$.

$I \rightarrow P$	$P \rightarrow I$	$R_h \rightarrow R_{obv}$	$R_{obv} \rightarrow R_h$
$\begin{pmatrix} -\frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} \frac{2}{3} & \frac{1}{3} & \frac{1}{3} \\ -\frac{1}{3} & \frac{2}{3} & \frac{1}{3} \\ -\frac{1}{3} & -\frac{1}{3} & \frac{2}{3} \end{pmatrix}$	$\begin{pmatrix} 1 & -1 & 0 \\ 0 & 1 & -1 \\ 1 & 1 & 1 \end{pmatrix}$
$R_h \rightarrow R_{rev}$	$R_{rev} \rightarrow R_h$	$F \rightarrow P$	$P \rightarrow F$
$\begin{pmatrix} \frac{1}{3} & -\frac{1}{3} & \frac{1}{3} \\ -\frac{1}{3} & \frac{1}{3} & \frac{1}{3} \\ \frac{1}{3} & \frac{1}{3} & -\frac{1}{3} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & -1 \\ -1 & 1 & 0 \\ 1 & 1 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{pmatrix}$
$A \rightarrow P$	$P \rightarrow A$	$B \rightarrow P$	$P \rightarrow B$
$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{1}{2} \\ 0 & \frac{1}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 1 \\ 0 & 1 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & 0 & \frac{1}{2} \\ 0 & -1 & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 1 \end{pmatrix}$
$C \rightarrow P$	$P \rightarrow C$		
$\begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{1}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$		

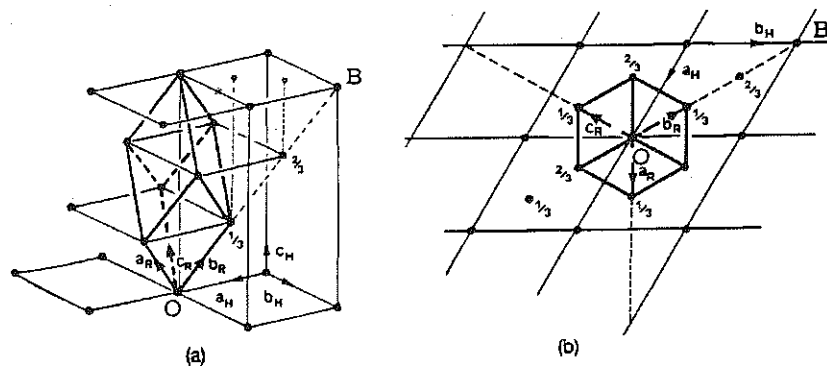


Figure 9. The rhombohedral lattice. The basis of the rhombohedral cell is labelled a_h , b_h and c_h (numerical fractions are calculated in terms of the c_h axis). (a) Obverse setting; (b) the same figure as in (a), projected along c_h .

Cubic lattices - For cubic lattices, symmetry requires that an A-type (or B or C) cell is also an F cell. There are three independent cubic lattices, P, I and F.

Hexagonal lattices - Only the P hexagonal Bravais lattice exists and is described in terms of the conventional primitive cell ($\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ and ratio $a : b : c = 1 : 1 : c$) described in section 4.2.

Trigonal lattices - As in the case of the hexagonal lattices, all centred cells are transformable to the conventional P trigonal cell. As may be seen in Figure 9, due to the presence of a three-fold axis, some lattices can exist which may be described by a primitive cell of rhombohedral shape, with unit vectors a_R , b_R , c_R , such that $a_R = b_R = c_R$, $\alpha_R = \beta_R = \gamma_R$, and the three-fold axis lies along the $a_R + b_R + c_R$ direction. Such lattices may also be described by the three triple hexagonal cells with basis vectors:

$$a_H = a_R - b_R; b_H = b_R - c_R; c_H = a_R + b_R + c_R \quad \text{or}$$

$$a_H = b_R - c_R; b_H = c_R - a_R; c_H = a_R + b_R + c_R \quad \text{or}$$

$$a_H = c_R - a_R; b_H = a_R - b_R; c_H = a_R + b_R + c_R$$

which are said to be in *obverse setting*. Three further triple hexagonal cells, said to be in *reverse setting*, can be obtained by changing a_H and b_H into $-a_H$ and $-b_H$. In conclusion, some trigonal lattices may be described by a hexagonal P cell, others by a triple hexagonal cell. In the first case, the nodes lying on the different lattice planes normal to the three-fold axis will lie exactly on top of each other. In the second case, these planes are shifted with respect to each other, in such a way that the n th plane will be superimposed on the $(n+3)$ th plane (see Figure 9).

The 14 Bravais lattices are illustrated in Figure 10 by means of their conventional unit cells. Each of these lattices will have a corresponding reciprocal lattice. It may be easily verified that the reciprocal of each type of crystal system will be a lattice of the same crystal system: the reciprocal of an F lattice is an I lattice and vice versa.

5.3. Wigner-Seitz cells and Brillouin zones

Other cells may also be used to describe the 14 Bravais lattices. If we regard the conventional cells, which are parallelepipeds, as particular types of polyhedra, we can find several families of polyhedra with which we can fill up space by translation. A very important type of space filling is obtained through the *Dirichlet construction*. Each lattice point is connected with a line to its nearest neighbours and then, through the mid-points of all these segments, the planes perpendicular to them are traced. These intersecting planes will delimit a region of space which is called the *Dirichlet region*, *Wigner-Seitz cell* or *Voronoi cell*. An example in two dimensions is given in Figure 11(a), and two three-dimensional examples are shown in Figure 11(b). The Wigner-Seitz cell is always primitive and coincides with the Bravais cell when this is both rectangular and primitive. A construction identical to the Wigner-Seitz cell delimits in reciprocal space a

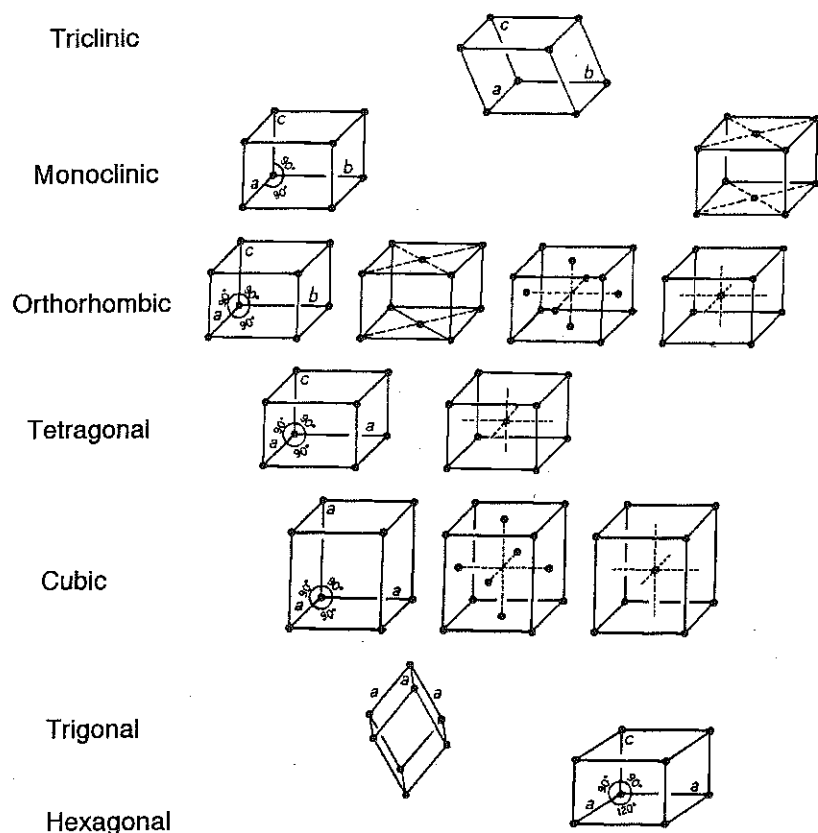


Figure 10. The 14 three-dimensional Bravais lattices.

cell conventionally known as the *first Brillouin zone*. There will be 14 first Brillouin zones corresponding to the 14 reciprocal Bravais lattices and that of an I lattice will look like a Wigner-Seitz cell of an F lattice and vice versa. As will be shown in the rest of this book, the Brillouin zones are very important in the study of lattice dynamics and in the band theory of solids.

6. Space groups

In section 3, we have seen that 32 combinations of either simple rotation or rotoinversion axes are compatible with the periodic nature of crystals. By combining the 32 point groups with the 14 Bravais lattices, 73 space groups are obtained. Furthermore, if we also consider symmetry operations with translational components, such as screw axes and glide planes, the total number of possible combinations, i.e. of *crystallographic space groups*, becomes 230. Note, however, that when such combinations have more than one axis, the restriction

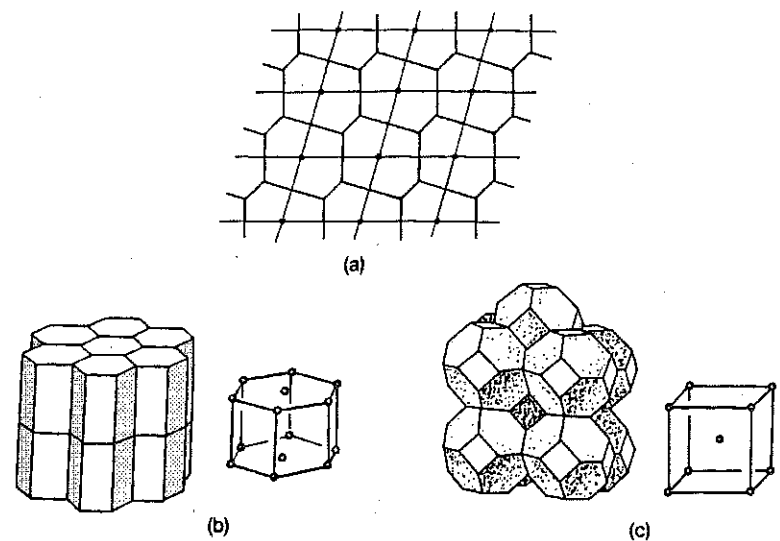


Figure 11. Examples of Wigner-Seitz cells.

that all symmetry elements must intersect in a point no longer applies. As a consequence of the presence of symmetry elements, several symmetry-equivalent objects (groups of atoms or molecules) will coexist within the unit cell. We will call the smallest part of the unit cell an *asymmetric unit*, which will generate the whole cell contents when the symmetry operations of the space group are applied to it. The asymmetric unit is not usually uniquely defined and can be chosen with some degree of freedom. It is, nevertheless, obvious that when rotation or inversion axes are present, they must lie at the borders of the asymmetric unit. We can, therefore, define as a crystallographic space group, the set of symmetry operations which, in a three-dimensional periodic medium, convert a given asymmetric unit into all its equivalent units. The space groups were first independently derived by the mathematicians Fedorov (1890) and Schoenflies (1891) and are listed in Table 6.

Here, we will simply introduce the main terms of the space group language, following the international notation of Herman-Mauguin, used in the *International Tables for Crystallography* [1]. Indeed, the aim of this section is to introduce the reader to the use of these tables, which are an essential tool for the study of solid-state physics and chemistry. Each space group symbol consists of a letter (P, A, B, C, I, F, R), which indicates the type of centring in the conventional cell, followed by a set of characters indicating the symmetry elements. Such a set is organized according to the following rules:

1. For triclinic groups, no symmetry directions are needed and only two space groups exist: P1 and $\bar{P}1$.
2. For monoclinic groups, only one symbol is needed, which gives the nature of the unique dyad (two-fold) axis (proper and/or inversion). Two *settings* are used: *y*-axis unique or *z*-axis unique.

Table 6. The 230 three-dimensional space groups arranged by crystal systems and point groups.

Crystal system	Point group	Space groups
Triclinic	1	P1
	1	P $\bar{1}$
Monoclinic	2	P2, P2 ₁ , C2
	m	Pm, Pc, Cm, Cc
	2/m	P2/m, P2 ₁ /m, C2/m, P2/c, P2 ₁ /c, C2/c
Orthorhombic	222	P222, P222 ₁ , P2 ₁ 2 ₁ 2, P2 ₁ 2 ₁ 2 ₁ , C222 ₁ , C222,
	mm2	F222, I222, I2 ₁ 2 ₁ 2 ₁ Pmm2, Pmc2 ₁ , Pcc2, Pma2 ₁ , Pca2 ₁ , Pnc2 ₁ , Pmn2 ₁ , Pba2, Pna2 ₁ , Pnn2, Cmm2, Cmc2 ₁ , Ccc2, Amm2, Abm2, Ama2, Aba2, Fmm2, Fdd2, Imm2, Iba2, Ima2
	mmm	Pmmm, Pnnn, Pccm, Pban, Pmma, Pnna, Pmna, Pcca, Pbam, Pccn, Pbcm, Pnrm, Pmra, Pben, Pbca, Pnma, Cmcm, Cmca, Cmmm, Cccm, Cmma, Ccca, Fmmm, Fddd, Immm, Ibam, Ibca, Imma
Tetragonal	4	P4, P4 ₁ , P4 ₂ , P4 ₃ , I4, I4 ₁
	$\bar{4}$	P $\bar{4}$, I $\bar{4}$
	4/m	P4/m, P44 ₂ /m, P4/n, P4 ₂ /n, I4/m, I4 ₁ /a
	422	P422, P42 ₁ 2, P4 ₁ 22, P4 ₁ 2 ₁ 2, P4 ₂ 22, P4 ₂ 2 ₁ 2, P4 ₃ 22, P4 ₃ 2 ₁ 2, I422, I4 ₁ 22
	4mm	P4mm, P4bm, P4 ₂ cm, P4 ₂ nm, P4cc, P4nc, P4 ₂ mc, P4 ₂ bc, I4mm, I4cm, I4 ₁ md, I4 ₁ cd
	$\bar{4}m$	P $\bar{4}$ 2m, P $\bar{4}$ 2c, P $\bar{4}$ 2 ₁ m, P $\bar{4}$ 2 ₁ c, P $\bar{4}$ 2m, P $\bar{4}$ 2c, P462, P4n2, I4m2, I4c2, I42m, I42d
	4/mmm	P4/mmm, P4/mcc, P4/nbm, P4nnc, P4/mbm, P4/mnc, P4nmm, P4/ncc, P4 ₂ /mmc, P4 ₂ /mcm, P4 ₂ /nbc, P4 ₂ /nrm, P4 ₂ /mbc, P4 ₂ /mmn, P4 ₂ /nmc, P4 ₂ /ncm, I4/mmm, I4mcm, I4 ₁ /amd, I4 ₁ /acd
Trigonal-hexagonal	3	P3, P3 ₁ , P3 ₁ , R3
	$\bar{3}$	P $\bar{3}$, R $\bar{3}$
	32	P312, P321, P3 ₁ 12, P3 ₁ 21, P3 ₂ 12, P3 ₂ 21, R32
	3m	P3m1, P31m, P3c1, P31c, R3m, R3c
	$\bar{3}m$	P $\bar{3}$ 2m, P $\bar{3}$ 2c, P $\bar{3}$ m1, P $\bar{3}$ c1, R $\bar{3}$ m, R $\bar{3}$ c
	6	P6, P6 ₁ , P6 ₅ , P6 ₃ , P6 ₂ , P6 ₄
	$\bar{6}$	P $\bar{6}$
	6/m	P6/m, P6 ₃ /m
	622	P622, P6 ₁ 22, P6 ₅ 22, P6 ₂ 22, P6 ₄ 22, P6 ₃ 22
	6mm	P6mm, P6cc, P6 ₃ cm, P6 ₃ mc
	$\bar{6}m$	P $\bar{6}$ m2, P $\bar{6}$ c2, P $\bar{6}$ 2m, P $\bar{6}$ 2c
	6/mmm	P6mmm, P6mcc, P6 ₃ /mcm, P6 ₃ /mmc
Cubic	23	P23, F23, I23, P2 ₁ 3, I2 ₁ 3
	m $\bar{3}$	Pm $\bar{3}$, Pn $\bar{3}$, Fm $\bar{3}$, Fd $\bar{3}$, Im $\bar{3}$, Pa $\bar{3}$, Ia $\bar{3}$
	432	P432, P4 ₂ 32, F432, F4 ₁ 32, I432, P4 ₃ 32, P4 ₁ 32, I4 ₁ 32
	$\bar{4}3m$	P $\bar{4}$ 3m, F $\bar{4}$ 3m, I $\bar{4}$ 3, P $\bar{4}$ 3n, F $\bar{4}$ 3c, I $\bar{4}$ 3d
	m $\bar{3}m$	Pm $\bar{3}$ m, Pn $\bar{3}$ m, Pm $\bar{3}$ n, Pn $\bar{3}$ m, Fm $\bar{3}$ m, Fd $\bar{3}$ m, Fd $\bar{3}$ c, Fm $\bar{3}$ c, Im $\bar{3}$ m, Ia $\bar{3}$ d

- For orthorhombic groups, the three dyads (proper and/or inversion) along x , y and z are given in sequential order. Thus Pca21 means: primitive cell, glide plane of type c (translational component along z) normal to the x -axis, glide plane of type a (translational component along x) normal to the y -axis with a two-fold screw axis along z .
- For tetragonal groups, first the tetrad (proper and/or inversion) axis along z is specified, then the dyad (proper and/or inversion) along x is given, and after that the dyad along $[110]$ is specified. For instance, P4₂/nbc denotes a space group with primitive cell, a 4₂ screw axis along z , to which a diagonal (n) glide plane is perpendicular, a glide plane of type b normal to x , and a c glide plane normal to $[110]$. Because of the tetragonal symmetry, the x and y axes are equivalent and there is no need to specify the symmetry along y .
- For trigonal and hexagonal groups, the triad or hexad (proper and/or inversion) along the z -axis is first given, then the dyad along x and after that the dyad along $[1\bar{1}0]$ is specified. For example, P6₃mc has a primitive cell, a six-fold screw axis 6₃ along z , a reflection plane normal to x and a c glide normal to $[1\bar{1}0]$.
- For cubic groups, the order is: dyads or tetrads (proper and/or inversion) along x , followed by triads along $[111]$ and dyads along $[110]$. Thus F4₁32 has a face centred cell, a 4₁ axis along x , a three-fold rotation axis along $[111]$ and a two-fold rotation axis along $[110]$.

For a given space group, lattice symmetry directions that carry no symmetry elements are represented by the symbol '1', as in P3m1 and P31m. In general, the '1' at the end of the space group symbol is omitted, as in P6 (instead of P611) or F23 (instead of F231). We note that:

- The 73 space groups obtained from combinations of the Bravais lattices with symmetry elements which have no translational components are called *symmorphic* space groups. Examples are: Pm, P222, Cmm2, F23, etc.
- Many compounds, such as biological molecules, are enantiomorphic and will then crystallize in space groups with no inversion centres or mirror planes; there are 65 groups of this type.
- Among the 230 space groups, there are 11 enantiomorphic pairs: P3₁-P3₂, P3₁12-P3₂12, P3₁21-P3₂21, P4₁-P4₃, P4₁22-P4₃22, P4₁2₁2-P4₃2₁2, P6₁-P6₅, P6₂-P6₄, P6₁22-P6₅22, P6₂22-P6₄22, P4₁32-P4₃32. If one chiral form of an optically active compound crystallizes in one of the two enantiomorphic space groups, the other form will crystallize in the other.
- The point group to which a given space group belongs may be obtained from its symbol by omitting the lattice indication and by replacing the screw axes and the glide planes with their corresponding symmorphic symmetry elements. For instance, the space groups P4₂/mmc, P4/nnc, I4₁/acd all belong to the point group 4/mmm.
- The frequency of the different space groups is not uniform. Organic compounds tend to crystallize in those space groups which permit close packing of objects of irregular shape. It may be understood intuitively that this close packing is better achieved when screw axes and glide planes are present. Indeed, these symmetry elements, through their translational components, facilitate the approach of concave and convex parts of an irregular molecule in crystal formation.

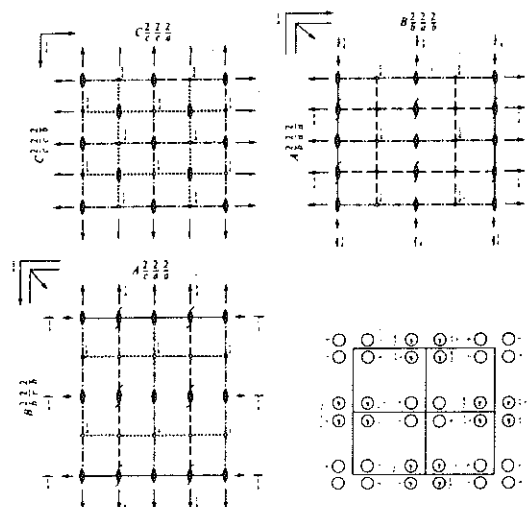
$Ccca$

No. 68

ORIGIN CHOICE 1

 D_{2h}^{22} $C2/c2/c2/a$ mmm

Orthorhombic

Patterson symmetry $Cmmm$ Origin at 222 at $2/n2/n2$, at $0, 1, 1$ from $\bar{1}$ Asymmetric unit $0 \leq x \leq 1; 0 \leq y \leq 1; 0 \leq z \leq 1$

Symmetry operations

For $(0,0,0)+$ set

- (1) $\bar{1}$ (2) 2 $4,1,z$ (3) 2 $0,y,0$ (4) $2(1,0,0)$ $x,1,0$
 (5) $\bar{1}$ $0,1,z$ (6) a $x,y,1$ (7) c $x,1,z$ (8) c $1,y,z$

For $(1,1,0)+$ set

- (1) $\bar{1}(1,1,0)$ (2) 2 $0,0,z$ (3) $2(0,1,0)$ $1,y,0$ (4) 2 $x,0,0$
 (5) $\bar{1}$ $1,0,z$ (6) b $x,y,1$ (7) $n(1,0,1)$ $x,0,z$ (8) $n(0,1,1)$ $0,y,z$

Generators selected (1); $\bar{1}(1,0,0)$; $\bar{1}(0,1,0)$; $\bar{1}(0,0,1)$; $\bar{1}(1,1,0)$; (2); (3); (5)

Positions

Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

 $(0,0,0)+$ $(1,1,0)+$

- 16 i 1 (1) x,y,z (2) $x+1,y+1,z$ (3) x,y,\bar{z} (4) $x+1,y+1,\bar{z}$
 (5) $x,y+1,\bar{z}+1$ (6) $x+1,y,\bar{z}+1$ (7) $x,y+1,z+1$ (8) $x+1,y,z+1$

Reflection conditions

General:

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

Special: as above, plus

 $hkl: l=2n$ $hkl: k+l=2n$ $hkl: k+l=2n$ $hkl: k+l=2n$ $hkl: k,l=2n$ $hkl: k,l=2n$ $hkl: k+l=2n$ $hkl: k+l=2n$

- 8 h $\bar{2}$ $1,1,z$ $1,1,\bar{z}$ $1,1,z+1$ $1,1,z+1$
 8 g $\bar{2}$ $0,0,z$ $0,0,\bar{z}$ $0,1,z+1$ $0,1,z+1$
 8 f $\bar{2}$ $0,y,0$ $1,y+1,0$ $0,y+1,1$ $1,y,1$
 8 e $\bar{2}$ $x,0,0$ $x+1,1,0$ $x,1,1$ $x+1,0,1$
 8 d $\bar{1}$ $0,1,1$ $1,1,1$ $0,1,1$ $1,1,1$
 8 c $\bar{1}$ $1,0,1$ $1,1,1$ $1,0,1$ $1,1,1$
 4 b 222 $0,1,1$ $0,1,1$
 4 a 222 $0,0,1$ $0,1,1$

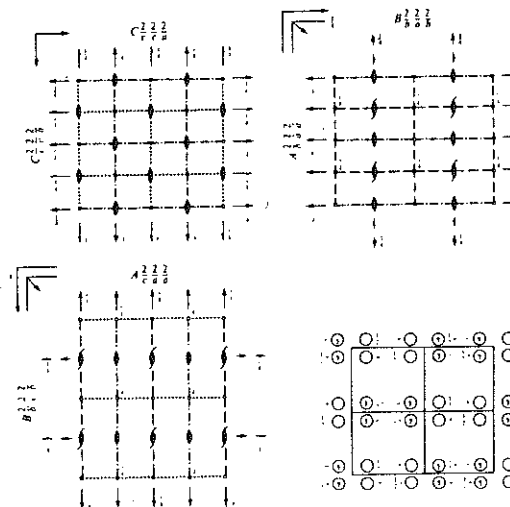
 $Ccca$

No. 68

ORIGIN CHOICE 2

 D_{2h}^{22} $C2/c2/c2/a$ mmm

Orthorhombic

Patterson symmetry $Cmmm$ Origin at $\bar{1}$ at nca , at $0, -1, -1$ from 222 Asymmetric unit $0 \leq x \leq 1; 0 \leq y \leq 1; 0 \leq z \leq 1$

Symmetry operations

For $(0,0,0)+$ set

- (1) $\bar{1}$ (2) 2 $1,0,z$ (3) 2 $0,y,1$ (4) $2(1,0,0)$ $x,0,1$
 (5) $\bar{1}$ $0,0,0$ (6) a $x,y,0$ (7) c $x,0,z$ (8) c $1,y,z$

For $(1,1,0)+$ set

- (1) $\bar{1}(1,1,0)$ (2) 2 $0,1,z$ (3) $2(0,1,0)$ $1,y,1$ (4) 2 $x,1,1$
 (5) $\bar{1}$ $1,1,0$ (6) b $x,y,0$ (7) $n(1,0,1)$ $x,1,z$ (8) $n(0,1,1)$ $0,y,z$

Generators selected (1); $\bar{1}(1,0,0)$; $\bar{1}(0,1,0)$; $\bar{1}(0,0,1)$; $\bar{1}(1,1,0)$; (2); (3); (5)

Positions

Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

 $(0,0,0)+$ $(1,1,0)+$

- 16 i 1 (1) x,y,z (2) $x+1,y,z$ (3) $x,y,\bar{z}+1$ (4) $x+1,y,\bar{z}+1$
 (5) x,y,\bar{z} (6) $x+1,y,\bar{z}$ (7) $x,y,z+1$ (8) $x+1,y,z+1$

Reflection conditions

General:

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

Special: as above, plus

 $hkl: l=2n$ $hkl: k+l=2n$ $hkl: k+l=2n$ $hkl: k+l=2n$ $hkl: k,l=2n$ $hkl: k,l=2n$ $hkl: k+l=2n$ $hkl: k+l=2n$

- 8 h $\bar{2}$ $1,0,z$ $1,0,\bar{z}+1$ $1,0,z$ $1,0,z+1$
 8 g $\bar{2}$ $0,1,z$ $0,1,\bar{z}+1$ $0,1,z$ $0,1,z+1$
 8 f $\bar{2}$ $0,y,1$ $1,y,1$ $0,y,1$ $1,y,1$
 8 e $\bar{2}$ $x,1,1$ $x+1,1,1$ $x,1,1$ $x+1,1,1$
 8 d $\bar{1}$ $0,0,0$ $1,0,0$ $0,0,1$ $1,0,1$
 8 c $\bar{1}$ $1,1,0$ $1,1,0$ $1,1,1$ $1,1,1$
 4 b 222 $0,1,1$ $0,1,1$
 4 a 222 $0,1,1$ $0,1,1$

Figure 12. (a): The space group $Ccca$, as described in Volume A of the *International Tables of Crystallography* [1]: Origin Choice 1.Figure 12. (b): The space group $Ccca$, as described in Volume A of the *International Tables of Crystallography* [1]: Origin Choice 2.

$P4_222$

D_4^5

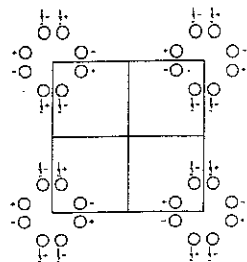
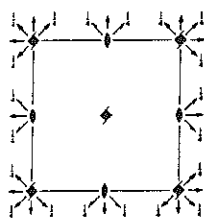
422

Tetragonal

No. 93

$P4_222$

Patterson symmetry $P4/mmm$



Origin at 222 at 4_221

Asymmetric unit $0 \leq x \leq 1; 0 \leq y \leq 1; 0 \leq z \leq 1$

Symmetry operations

(1) 1 (2) 2 $0,0,z$ (3) 4 $(0,0,1)$ $0,0,z$ (4) 4 $(0,0,1)$ $0,0,z$
(5) 2 $0,y,0$ (6) 2 $x,0,0$ (7) 2 $x,x,1$ (8) 2 $x,x,1$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5)

Positions

Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

Reflection conditions

General:

$00l: l = 2n$

Special: as above, plus

$Okf: l = 2n$

$Okf: l = 2n$

$hhl: l = 2n$

$hhl: l = 2n$

$hhl: l = 2n$

$hhl: l = 2n$

$hkl: h+k+l = 2n$

$hkl: l = 2n$

$hkl: l = 2n$

$hkl: l = 2n$

$hkl: l = 2n$

$hkl: h+k+l = 2n$

$hkl: h+k+l = 2n$

$hkl: l = 2n$

$hkl: l = 2n$

8 p 1 (1) x,y,z (2) x,y,z (3) $y,x,z+1$ (4) $y,x,z+1$
(5) x,y,z (6) x,y,z (7) $y,x,z+1$ (8) $y,x,z+1$

4 o 2 $x,x,1$ $x,x,1$ $x,x,1$ $x,x,1$

4 n 2 $x,x,1$ $x,x,1$ $x,x,1$ $x,x,1$

4 m 2 $x,1,0$ $x,1,0$ $1,x,1$ $1,x,1$

4 l 2 $x,0,1$ $x,0,1$ $0,x,0$ $0,x,0$

4 k 2 $x,1,1$ $x,1,1$ $1,x,0$ $1,x,0$

4 j 2 $x,0,0$ $x,0,0$ $0,x,1$ $0,x,1$

4 i 2 $1,1,z$ $1,1,z+1$ $1,1,z$ $1,1,z+1$

4 h 2 $1,1,z$ $1,1,z+1$ $1,1,z$ $1,1,z+1$

4 g 2 $0,0,z$ $0,0,z+1$ $0,0,z$ $0,0,z+1$

2 f 2 22 $1,1,1$ $1,1,1$

2 e 2 22 $0,0,1$ $0,0,1$

2 d 2 22 $0,1,1$ $1,0,0$

2 c 2 22 $0,1,0$ $1,0,1$

2 b 2 22 $1,1,0$ $1,1,1$

2 a 2 22 $0,0,0$ $0,0,1$

As we have already mentioned, the standard description of the crystallographic space groups is contained in Volume A of the *International Tables of Crystallography* [1]. For each space group the *Tables* include an extensive set of descriptors. In Figures 12 and 13, the space groups $Ccca$ and $P4_222$ are shown as examples. Here is an outline of the information most relevant to this course.

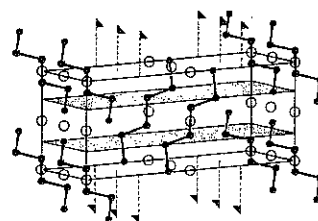
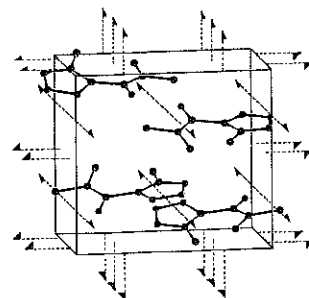


Figure 14. (a) A $P2_12_12_1$ crystal structure and its symmetry elements (G. Chiari, D. Viterbo, A. Gaetani Manfredotti and C. Guastini (1975), *Cryst. Struct. Commun.*, 4, 561) and (b) a $P2_1/c$ crystal structure and its symmetry elements. Glide planes are emphasised by the shading (M. Calleri, G. Ferraris and D. Viterbo (1966), *Acta Cryst.*, 20, 73). For clarity, hydrogen atoms are not shown in either figure.

1. The first line gives the abbreviated international Herman-Mauguin and Schoenflies symbols of the space group, the point group symbol and the crystal system.
2. The second line gives the sequential number of the space group, the full international Herman-Mauguin symbol and the so called Patterson symmetry (this corresponds to the point group symbol, preceded by the lattice symbol and we shall not consider it further). The short and full versions of the symbols differ only in some space groups. While in the short symbols symmetry axes are suppressed as much as possible, in the full symbols, axes and planes are listed for each direction.
3. When needed, the third line gives the chosen unique axis, settings, origin choices or reference axes.
4. Two types of space group diagrams (as orthogonal projections along a cell axis) are given: one shows the arrangement of the symmetry elements and the other, the position of a set of symmetry equivalent points. Close to the graphical symbols of a symmetry plane or axis parallel to the projection plane, the 'height' is printed as h , a fraction of the shortest lattice translation normal to the projection plane (unless $h = 0$). For some space groups, the diagrams illustrating the arrangement of the symmetry elements are shown in more

Figure 13. The space group $P4_222$, as described in Volume A of the *International Tables of Crystallography* [1].

than one projection. In the most recent edition of the *Tables*, for the cubic groups, the second type of diagram is shown as a stereo pair.

5. Information is next given concerning the chosen origin position (see later), the definition of the asymmetric unit, the list of symmetry operations with their positions and the symmetry generators (the minimum set of symmetry operations of the group from which all the others are derived).
6. The block *positions* (called also *Wyckoff positions*) contain: (a) the *general position*, a set of symmetry equivalent points, each of which is left invariant only by application of the identity operation and (b) a list of *special positions*. A set of symmetry equivalent points is in a special position if each point is left invariant by at least two symmetry operations of the space group; this usually happens when the points are on a symmetry element or at the intersection of more than one symmetry element. For instance, a point on a three-fold rotation axis is left invariant not only by the identity, but also by the rotation itself. The first three columns of the block give the *multiplicity* (number of equivalent points per unit cell), the *Wyckoff letter* (a code scheme starting with *a* at the bottom position and continuing upwards in alphabetical order) and the *site symmetry* (the group of symmetry operations which leave the site invariant). The symbol adopted for describing the site symmetry has the same sequence of symmetry directions as the space group symbol and a dot marks the directions which do not contribute any element to the site symmetry. In the next column, the fractional coordinates of the Wyckoff positions are given. We note that, by definition, the general position always has site symmetry 1. For this position, each fractional coordinate is preceded by a number between parentheses, which is the same number preceding the corresponding symmetry operation listed in a previous block. For structures, such as molecular crystals, in which a formula unit is well defined, crystallographic papers give the number of 'molecules' in the unit cell (usually denoted by the letter *Z*). If the molecules, as in the case of the structure illustrated in Figure 6 (a), are in a general position, *Z* is equal to the multiplicity of the general position (in $P2_12_12_1$, $Z = 4$). In the structure shown in Figure 6 (b), the centre of the molecule lies on an inversion centre and the asymmetric unit is formed by half a molecule; *Z* is then equal to the multiplicity of the special position at site $\bar{1}$ (in $P2_1/c$, $Z = 2$), which is half that of the general position. We shall not consider the final column which contains the *reflection conditions*, which are important for diffraction experiments, nor describe the information given in the remaining blocks, which have not been reproduced in Figures 12 and 13.

6.1. Choice of origin

The characterization and description of crystal structures are greatly simplified by the choice of a suitable *origin*. In the *International Tables*, the following conventions are used.

- For centrosymmetric space groups, the origin is normally chosen on an inversion centre. An alternative choice is given if the space group possesses

points of high site symmetry not coincident with the inversion centre. Thus for $Pn\bar{3}n$, two origin choices are considered: at $-\frac{1}{4}-\frac{1}{4}-\frac{1}{4}$ from the centre of $\bar{4}3m$ and at the centre of $\bar{3}m$.

- For non-centrosymmetric space groups, the origin is chosen at the point of highest site symmetry (e.g. the origin for $P4c$ is chosen to be at $\bar{4}1c$) or at a point conveniently placed with respect to the symmetry elements. For example, on the 2_1 axis in $P2_1$, on the glide plane in Pc , at $1a2_1$ in $Pca2_1$ or at a point symmetrically surrounded by the three screw axes in $P2_12_12_1$.

6.2. The plane groups

In two dimensions, 17 plane groups may be defined. They are listed in Table 7.

Table 7. The 17 plane groups.

Oblique cell	p1, p2
Rectangular cell	pm, pg, cm, p3mm, p3mg, p2gg, c2mm
Square cell	p4, p4mm, p4gm
Hexagonal cell	p3, p3m1, p32m, p6, p6mm

In the symbols, the lattice letter is lower case and *g* is a glide reflection line. The 17 plane group diagrams are shown in Figure 15 and the ways by which they repeat a given motif are shown in Figure 16. It should be noted that any periodic decoration of a plane surface, such as a floor, wall or fabric, will belong to one of these plane groups. Some very beautiful examples are given in reference [10], where many drawings and paintings of the Dutch painter M.C. Escher are reproduced.

6.3. Matrix representation of symmetry operators

A symmetry operation acts on the fractional coordinates (*x, y, z*) of a point *P* to obtain the coordinates (*x', y', z'*) of a symmetry equivalent point *P'*. In matrix notation, this transformation is written as

$$\mathbf{X}' = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} T_1 \\ T_2 \\ T_3 \end{pmatrix} = \mathbf{R}\mathbf{X} + \mathbf{T} \quad (22)$$

The matrix **R** is the *rotational component* (proper or improper) of the symmetry operation, while **T** is the matrix of the *translational component*. As an example, let us consider the space group *Ccca* (origin choice 1) shown in Figure 12. In the block 'positions', we can see that under the operation number (2) (a 2-axis)

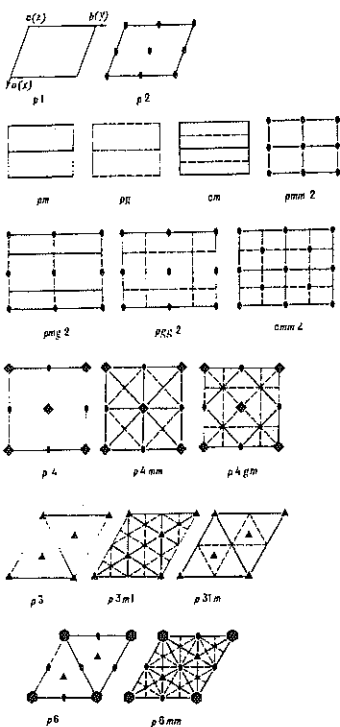


Figure 15. The 17 plane group diagrams.

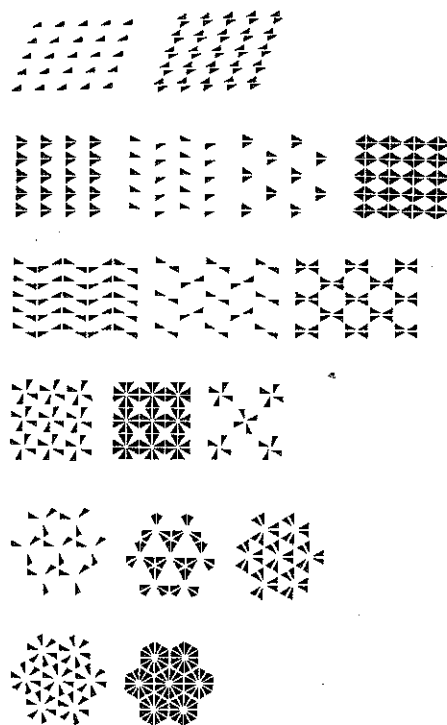


Figure 16. A simple motif repeated through the 17 plane groups.

a point at (x, y, z) is moved to $(-x + \frac{1}{2}, -y + \frac{1}{2}, z)$. Using matrix notation, this operation is represented as

$$\begin{pmatrix} -x + \frac{1}{2} \\ -y + \frac{1}{2} \\ z \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \\ 0 \end{pmatrix}$$

It may easily be seen that all rotation matrices have a determinant equal to ± 1 (the + sign corresponds to a proper rotation and the - sign to an improper rotation) and their elements have values 0, 1 and -1.

Acknowledgements

I would like to express my thanks to Prof. Piero Ugliengo for the helpful discussions and the critical reading of these notes.

References

1. *International Tables for Crystallography, Vol. A, Space group symmetry*, (T. Hahn, ed.), Kluwer, Dordrecht (1992).
2. C.J. Bradley and A.P. Cracknell, *The Mathematical Theory of Symmetry in Solids. Representation theory for Point and Space groups*, Clarendon Press, Oxford (1972).
3. E.H. Lockwood and R.H. MacMillan, *Geometric Symmetry*, Cambridge University Press (1978).
4. B.K. Vainshtein, *Modern Crystallography I: Symmetry of Crystals, Methods of Structural Crystallography*, Springer, Berlin (1981).
5. C. Giacovazzo, H.L. Monaco, D. Viterbo, F. Scordari, G. Gilli, G. Zanotti and M. Catti, *Fundamentals of Crystallography*, Oxford University Press (1992).
6. G. Rigault, *Introduzione alla Cristallografia*, Levrotto-Bella, Torino (1983).
7. E. Prince, *Mathematical Techniques in Crystallography and Materials Science*, Springer-Verlag, Berlin (1994).
8. D.E. Sands, *Vectors and Tensors in Crystallography*, Addison-Wesley, Reading MA (1982).
9. T. Hahn and H. Wondratschek, *Symmetry of Crystals*, Heron Press, Sofia (1994).
10. D. Schattschneider, *Visions of symmetry. Notebooks, periodic drawings, and related works of M.C. Escher*, W.H. Freeman, New York (1990).