Table 2.2.7.1. *Examples of origin statements*

Example number	Space group (No.)	Origin statement	Meaning of last symbol in *E*4–*E*11
*E*1	$P\bar{1}$ (2)	at $\bar{1}$	
*E*2	$P2/m$ (10)	at centre $(2/m)$	
*E*3	*P*222 (16)	at 222	
*E*4	*Pcca* (54)	at $\bar{1}$ on 1*ca*	$c \perp [010]$, $a \perp [001]$
*E*5	*Cmcm* (63)	at centre $(2/m)$ at $2/mc2_1$	$2 \parallel [100]$, $m \perp [100]$, $c \perp [010]$, $2_1 \parallel [001]$
*E*6	*Pcc*2 (27)	on *cc*2; short for: on 2 on *cc*2	$c \perp [100]$, $c \perp [010]$, $2 \parallel [001]$
*E*7	*P*4*bm* (100)	on 41*g*; short for: on 4 on 41*g*	$4 \parallel [001]$, $g \perp [1\bar{1}0]$ and $g \perp [110]$
*E*8	$P4_2mc$ (105)	on 2*mm* on 4_2mc	$4_2 \parallel [001]$, $m \perp [100]$ and $m \perp [010]$, $c \perp [1\bar{1}0]$ and $c \perp [110]$
*E*9	$P4_32_12$ (96)	on 2[110] at $2_11(1,2)$	$2_1 \parallel [001]$, 1 in $[1\bar{1}0]$ and $2 \parallel [110]$
*E*10	$P3_121$ (152)	on 2[110] at $3_1(1,1,2)1$	$3_1 \parallel [001]$, $2 \parallel [110]$
*E*11	$P3_112$ (151)	on 2[210] at $3_11(1,1,2)$	$3_1 \parallel [001]$, $2 \parallel [210]$

(iii) For the tetragonal, trigonal and hexagonal space groups, the situation is more complicated than for the orthorhombic groups. The tetragonal space groups have one primary, two secondary and two tertiary symmetry directions. For hexagonal groups, these numbers are one, three and three (Table 2.2.4.1). If the symmetry elements passing through the origin are the same for the two (three) secondary or the two (three) tertiary directions, only one entry is given at the relevant position of the origin statement [example *E*7: 'on 41*g*' instead of 'on 41(*g*, *g*)']. An exception occurs for the site-symmetry group 2*mm* (example *E*8), which is always written in full rather than as 2*m*1.

If the symmetry elements are different, two (three) symbols are placed between parentheses, which stand for the two (three) secondary or tertiary directions. The order of these symbols corresponds to the order of the symmetry directions within the secondary or tertiary set, as listed in Table 2.2.4.1. Directions without symmetry are indicated by the symbol 1. With this rule, the last symbols in the examples *E*9–*E*11 can be interpreted.

Note that for some tetragonal space groups (Nos. 100, 113, 125, 127, 129, 134, 138, 141, 142) the glide-plane symbol *g* is used in the origin statement. This symbol occurs also in the block *Symmetry operations* of these space groups; it is explained in Sections 2.2.9 and 11.1.2.

(iv) To emphasize the orientation of the site-symmetry elements at the origin, examples *E*9 and *E*10 start with 'on 2[110]' and *E*11 with 'on 2[210]'. In *E*8, the site-symmetry group is 2*mm*. Together with the space-group symbol this indicates that 2 is along the primary tetragonal direction, that the two symbols *m* refer to the two secondary symmetry directions [100] and [010], and that the tertiary set of directions does not contribute to the site symmetry.

For monoclinic space groups, an indication of the orientation of the symmetry elements is not necessary; hence, the site symmetry at the origin is given by non-oriented symbols. For orthorhombic space groups, the orientation is obvious from the symbol of the space group.

(v) The extensive description of the symmetry elements passing through the origin is not retained for the cubic space groups, as this would have led to very complicated notations for some of the groups.

2.2.8. Asymmetric unit

An asymmetric unit of a space group is a (simply connected) smallest closed part of space from which, by application of all symmetry operations of the space group, the whole of space is filled. This implies that mirror planes and rotation axes must form boundary planes and boundary edges of the asymmetric unit. A twofold rotation axis may bisect a boundary plane. Centres of inversion must either form vertices of the asymmetric unit or be located at the midpoints of boundary planes or boundary edges. For glide planes and screw axes, these simple restrictions do not hold. An asymmetric unit contains all the information necessary for the complete description of the crystal structure. In mathematics, an asymmetric unit is called 'fundamental region' or 'fundamental domain'.

Example

The boundary planes of the asymmetric unit in space group *Pmmm* (47) are fixed by the six mirror planes x, y, 0; $x, y, \frac{1}{2}$; x, 0, z; $x, \frac{1}{2}, z$; 0, y, z; and $\frac{1}{2}, y, z$. For space group $P2_12_12_1$ (19), on the other hand, a large number of connected regions, each with a volume of $\frac{1}{4}V$(cell), may be chosen as asymmetric unit.

In cases where the asymmetric unit is not uniquely determined by symmetry, its choice may depend on the purpose of its application. For the description of the structures of molecular crystals, for instance, it is advantageous to select asymmetric units that contain one or more complete molecules. In the space-group tables of this volume, the asymmetric units are chosen in such a way that Fourier summations can be performed conveniently.

For all triclinic, monoclinic and orthorhombic space groups, the asymmetric unit is chosen as a parallelepiped with one vertex at the origin of the cell and with boundary planes parallel to the faces of the cell. It is given by the notation

$$0 \le x_i \le \text{upper limit of } x_i,$$

where x_i stands for x, y or z.

For space groups with higher symmetry, cases occur where the origin does not coincide with a vertex of the asymmetric unit or where not all boundary planes of the asymmetric unit are parallel to those of the cell. In all these cases, parallelepipeds

$$\text{lower limit of } x_i \le x_i \le \text{upper limit of } x_i$$

are given that are equal to or larger than the asymmetric unit. Where necessary, the boundary planes lying within these parallelepipeds are given by additional inequalities, such as $x \le y$, $y \le \frac{1}{2} - x$ *etc.*

In the trigonal, hexagonal and especially the cubic crystal systems, the asymmetric units have complicated shapes. For this reason, they are also specified by the coordinates of their vertices. Drawings of asymmetric units for cubic space groups have been published by Koch & Fischer (1974). Fig. 2.2.8.1 shows the boundary planes occurring in the tetragonal, trigonal and hexagonal systems, together with their algebraic equations.

Examples

(1) In space group *P*4*mm* (99), the boundary plane $y = x$ occurs in addition to planes parallel to the unit-cell faces; the asymmetric unit is given by

$$0 \le x \le \tfrac{1}{2}; \quad 0 \le y \le \tfrac{1}{2}; \quad 0 \le z \le 1; \quad x \le y.$$

(2) In *P*4*bm* (100), one of the boundary planes is $y = \frac{1}{2} - x$. The asymmetric unit is given by

$$0 \le x \le \tfrac{1}{2}; \quad 0 \le y \le \tfrac{1}{2}; \quad 0 \le z \le 1; \quad y \le \tfrac{1}{2} - x.$$

(3) In space group *R*32 (155; hexagonal axes), the boundary planes are, among others, $x = (1 + y)/2$, $y = 1 - x$, $y = (1 + x)/2$.

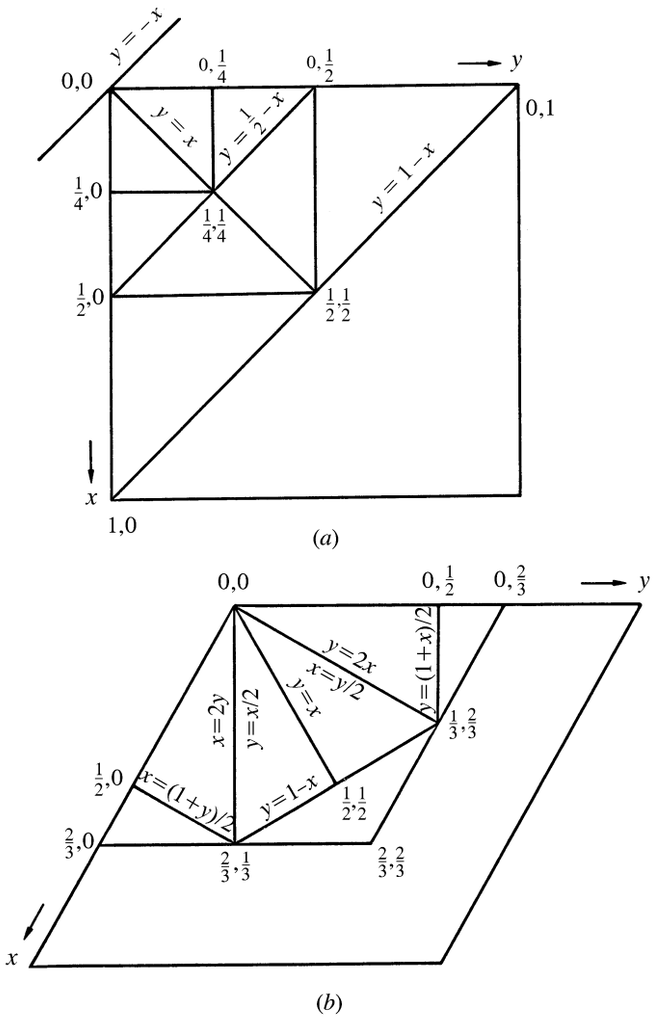

Fig. 2.2.8.1. Boundary planes of asymmetric units occurring in the space-group tables. (*a*) Tetragonal system. (*b*) Trigonal and hexagonal systems. The point coordinates refer to the vertices in the plane $z = 0$.

The asymmetric unit is defined by

$$0 \le x \le \tfrac{2}{3}; \quad 0 \le y \le \tfrac{2}{3}; \quad 0 \le z \le \tfrac{1}{6};$$
$$x \le (1+y)/2; \quad y \le \min(1-x, (1+x)/2)$$
Vertices: $0,0,0 \quad \tfrac{1}{2},0,0 \quad \tfrac{2}{3},\tfrac{1}{3},0 \quad \tfrac{1}{3},\tfrac{2}{3},0 \quad 0,\tfrac{1}{2},0$
$0,0,\tfrac{1}{6} \quad \tfrac{1}{2},0,\tfrac{1}{6} \quad \tfrac{2}{3},\tfrac{1}{3},\tfrac{1}{6} \quad \tfrac{1}{3},\tfrac{2}{3},\tfrac{1}{6} \quad 0,\tfrac{1}{2},\tfrac{1}{6}.$

It is obvious that the indication of the vertices is of great help in drawing the asymmetric unit.

Fourier syntheses

For complicated space groups, the easiest way to calculate Fourier syntheses is to consider the parallelepiped listed, without taking into account the additional boundary planes of the asymmetric unit. These planes should be drawn afterwards in the Fourier synthesis. For the computation of integrated properties from Fourier syntheses, such as the number of electrons for parts of the structure, the values at the boundaries of the asymmetric unit must be applied with a reduced weight if the property is to be obtained as the product of the content of the asymmetric unit and the multiplicity.

Example

In the parallelepiped of space group *Pmmm* (47), the weights for boundary planes, edges and vertices are $\frac{1}{2}$, $\frac{1}{4}$ and $\frac{1}{8}$, respectively.

Asymmetric units of the plane groups have been discussed by Buerger (1949, 1960) in connection with Fourier summations.

2.2.9. Symmetry operations

As explained in Sections 8.1.6 and 11.1.1, the coordinate triplets of the *General position* of a space group may be interpreted as a shorthand description of the symmetry operations in matrix notation. The geometric description of the symmetry operations is found in the space-group tables under the heading *Symmetry operations*.

2.2.9.1. *Numbering scheme*

The numbering $(1)\ldots(p)\ldots$ of the entries in the blocks *Symmetry operations* and *General position* (first block below *Positions*) is the same. Each listed coordinate triplet of the general position is preceded by a number between parentheses (p). The same number (p) precedes the corresponding symmetry operation. For space groups with *primitive* cells, both lists contain the same number of entries.

For space groups with *centred* cells, to the one block *General position* several (2, 3 or 4) blocks *Symmetry operations* correspond. The numbering scheme of the general position is applied to each one of these blocks. The number of blocks equals the multiplicity of the centred cell, *i.e.* the number of centring translations below the subheading *Coordinates*, such as $(0,0,0)+$, $(\frac{2}{3},\frac{1}{3},\frac{1}{3})+$, $(\frac{1}{3},\frac{2}{3},\frac{2}{3})+$.

Whereas for the *Positions* the reader is expected to add these centring translations to each printed coordinate triplet himself (in order to obtain the complete general position), for the *Symmetry operations* the corresponding data are listed explicitly. The different blocks have the subheadings 'For (0,0,0)+ set', 'For $(\frac{1}{2},\frac{1}{2},\frac{1}{2})+$ set', *etc.* Thus, an obvious one-to-one correspondence exists between the analytical description of a symmetry operation in the form of its general-position coordinate triplet and the geometrical description under *Symmetry operations*. Note that the coordinates are reduced modulo 1, where applicable, as shown in the example below.

Example: Ibca (73)

The centring translation is $t(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Accordingly, above the general position one finds $(0,0,0)+$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})+$. In the block *Symmetry operations*, under the subheading 'For $(0,0,0)+$ set', entry (2) refers to the coordinate triplet $\bar{x}+\frac{1}{2}$, $\bar{y}$, $z+\frac{1}{2}$. Under the subheading 'For $(\frac{1}{2},\frac{1}{2},\frac{1}{2})+$ set', however, entry (2) refers to $\bar{x}$, $\bar{y}+\frac{1}{2}$, z. The triplet $\bar{x}$, $\bar{y}+\frac{1}{2}$, z is selected rather than $\bar{x}+1$, $\bar{y}+\frac{1}{2}$, $z+1$, because the coordinates are reduced modulo 1.

In space groups with two origins where a 'symmetry element' and an 'additional symmetry element' are of different type (*e.g.* mirror *versus* glide plane, rotation *versus* screw axis, Tables 4.1.2.2 and 4.1.2.3), the origin shift may interchange the two *different* types in the *same* location (referred to the appropriate origin) under the same number (p). Thus, in $P4/nmm$ (129), $(p) = (7)$ represents a $\bar{2}$ and a 2_1 axis, both in $x,x,0$, whereas $(p) = (16)$ represents a *g* and an *m* plane, both in x,x,z.

2.2.9.2. *Designation of symmetry operations*

An entry in the block *Symmetry operations* is characterized as follows.