

## 2. THE SPACE-GROUP TABLES

## 2.1.3.6.8. Diagrams of the general position (by K. Momma and M. I. Aroyo)

*Non-cubic space groups.* In these diagrams, the ‘heights’ of the points are  $z$  coordinates, except for monoclinic space groups with unique axis  $b$  where they are  $y$  coordinates. For rhombohedral space groups, the heights are always fractions of the hexagonal  $c$  axis. The symbols  $+$  and  $-$  stand for  $+z$  and  $-z$  (or  $+y$  and  $-y$ ) in which  $z$  or  $y$  can assume any value. For points with symbols  $+$  or  $-$  preceded by a fraction, e.g.  $\frac{1}{2}+$  or  $\frac{1}{3}-$ , the relative  $z$  or  $y$  coordinate is  $\frac{1}{2}$  etc. higher than that of the point with symbol  $+$  or  $-$ .

Where a mirror plane exists parallel to the plane of projection, the two positions superimposed in projection are indicated by the use of a ring divided through the centre. The information given on each side refers to one of the two positions related by the mirror plane, as in  $-\oplus+$ .

*Diagrams for cubic space groups (Fig. 2.1.3.10).* Following the approach of *IT* (1935), for each cubic space group a diagram showing the points of the general position as the vertices of polyhedra is given. In these diagrams, the polyhedra are transparent, but the spheres at the vertices are opaque. For most of the space groups, ‘starting points’ with the same coordinate values,  $x = 0.048$ ,  $y = 0.12$ ,  $z = 0.089$ , have been used. The origins of the polyhedra are chosen at special points of highest site symmetry, which for most space groups coincide with the origin (and its equivalent points in the unit cell). Polyhedra with origins at sites  $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$  have been chosen for the space groups  $P4_332$  (212) and  $I4_132$  (214), and  $(\frac{3}{8}, \frac{3}{8}, \frac{3}{8})$  for  $P4_132$  (213). The two diagrams shown for the space groups  $I43d$  (220) and  $Ia\bar{3}d$  (230) correspond to polyhedra with origins chosen at two different special sites with site-symmetry groups of equal (32 versus  $\bar{3}$  in  $Ia\bar{3}d$ ) or nearly equal order (3 versus  $\bar{4}$  in  $I43d$ ). The height  $h$  of the centre of each polyhedron is given on the diagram, if different from zero. For space-group Nos. 198, 199 and 220,  $h$  refers to the special point to which the polyhedron (triangle) is connected. Polyhedra with height 1 are omitted in all the diagrams. A grid of four squares is drawn to represent the four quarters of the basal plane of the cell. For space groups  $F\bar{4}3c$  (219),  $Fm\bar{3}c$  (226) and  $Fd\bar{3}c$  (228), where the number of points is too large for one diagram, two diagrams are provided, one for the upper half and one for the lower half of the cell.

*Notes:*

- (i) For space group  $P4_132$  (213), the coordinates  $\bar{x}, \bar{y}, \bar{z}$  have been chosen for the ‘starting point’ to show the enantiomorphism with  $P4_332$  (212).
- (ii) For the description of a space group with ‘origin choice 2’, the coordinates  $x, y, z$  of all points have been shifted with the origin to retain the same polyhedra for both origin choices.

An additional general-position diagram is shown on the fourth page for each of the ten space groups of the  $m\bar{3}m$  crystal class. To provide a clearer three-dimensional-style overview of the arrangements of the polyhedra, these general-position diagrams are shown in tilted projection (in contrast to the orthogonal-projection diagrams described above).

The general-position diagrams of the cubic groups in both orthogonal and tilted projections were generated using the program *VESTA* (Momma & Izumi, 2011).

Readers who wish to compare other approaches to space-group diagrams and their history are referred to *IT* (1935), *IT* (1952), the fifth edition of *IT A* (2002) (where general-position stereodiagrams of the cubic space groups are shown) and the following publications: Astbury & Yardley (1924), Belov *et al.*

(1980), Buerger (1956), Fedorov (1895; English translation, 1971), Friedel (1926), Hilton (1903), Niggli (1919) and Schiebold (1929).

## 2.1.3.7. Origin

The determination and description of crystal structures and particularly the application of direct methods are greatly facilitated by the choice of a suitable origin and its proper identification. This is even more important if related structures are to be compared or if ‘chains’ of group–subgroup relations are to be constructed. In this volume, as well as in *IT* (1952) and *IT A* (2002), the origin of the unit cell has been chosen according to the following conventions (*cf.* Sections 2.1.1 and 2.1.3.2):

- (i) All centrosymmetric space groups are described with an inversion centre as origin. A further description is given if a centrosymmetric space group contains points of high site symmetry that do not coincide with a centre of symmetry. As an example, study the origin choice 1 and origin choice 2 descriptions of  $I4_1/amd$  (141).
- (ii) For noncentrosymmetric space groups, the origin is at a point of highest site symmetry, as in  $P\bar{6}m2$  (187). If no site symmetry is higher than 1, except for the cases listed below under (iii), the origin is placed on a screw axis, or a glide plane, or at the intersection of several such symmetry elements, see for example space groups  $Pca2_1$  (29) and  $P\bar{6}_1$  (169).
- (iii) In space group  $P2_12_12_1$  (19), the origin is chosen in such a way that it is surrounded symmetrically by three pairs of  $2_1$  axes. This principle is maintained in the following noncentrosymmetric cubic space groups of classes 23 and 432, which contain  $P2_12_12_1$  as subgroup:  $P2_13$  (198),  $I2_13$  (199),  $F4_332$  (210). It has been extended to other noncentrosymmetric orthorhombic and cubic space groups with  $P2_12_12_1$  as subgroup, even though in these cases points of higher site symmetry are available:  $I2_12_12_1$  (24),  $P4_332$  (212),  $P4_132$  (213),  $I4_132$  (214).

There are several ways of determining the location and site symmetry of the origin. First, the origin can be inspected directly in the space-group diagrams (*cf.* Section 2.1.3.6). This method permits visualization of all symmetry elements that intersect the chosen origin.

Another procedure for finding the site symmetry at the origin is to look for a special position that contains the coordinate triplet 0, 0, 0 or that includes it for special values of the parameters, e.g. position  $1a$ : 0, 0,  $z$  in space group  $P4$  (75), or position  $3a$ :  $x, 0, \frac{1}{3}$ ;  $0, x, \frac{2}{3}$ ;  $\bar{x}, \bar{x}, 0$  in space group  $P3_121$  (152). If such a special position occurs, the symmetry at the origin is given by the oriented site-symmetry symbol (see Section 2.1.3.12) of that special position; if it does not occur, the site symmetry at the origin is 1. For most practical purposes, these two methods are sufficient for the identification of the site symmetry at the origin.

*Origin statement.* In the line *Origin* immediately below the diagrams, the site symmetry of the origin is stated, if different from the identity. A further symbol indicates all symmetry elements (including glide planes and screw axes) that pass through the origin, if any. For space groups with two *origin choices*, for each of the two origins the location relative to the other origin is also given. An example is space group  $Ccce$  (68).

In order to keep the notation as simple as possible, no rigid rules have been applied in formulating the origin statements. Their meaning is demonstrated by the examples in Table 2.1.3.5.

**Table 2.1.3.5**

Examples of origin statements

Example number	Space group (No.)	Origin statement	Meaning of last symbol in <i>E4–E11</i>
<i>E1</i>	$P\bar{1}$ (2)	at $\bar{1}$	
<i>E2</i>	$P2/m$ (10)	at centre ( $2/m$ )	
<i>E3</i>	$P222$ (16)	at 222	
<i>E4</i>	$Pcca$ (54)	at $\bar{1}$ on $1ca$	$c \perp [010]$ , $a \perp [001]$
<i>E5</i>	$Cmcm$ (63)	at centre ( $2/m$ ) at $2/mc2_1$	$2 \parallel [100]$ , $m \perp [100]$ , $c \perp [010]$ , $2_1 \parallel [001]$
<i>E6</i>	$Pcc2$ (27)	on $cc2$ ; short for: on 2 on $cc2$	$c \perp [100]$ , $c \perp [010]$ , $2 \parallel [001]$
<i>E7</i>	$P4bm$ (100)	on 41g; short for: on 4 on 41g	$4 \parallel [001]$ , $g \perp [110]$ and $g \perp [110]$
<i>E8</i>	$P4_2mc$ (105)	on $2mm$ on $4_2mc$	$4_2 \parallel [001]$ , $m \perp [100]$ and $m \perp [010]$ , $c \perp [1\bar{1}0]$ and $c \perp [110]$
<i>E9</i>	$P4_32_12$ (96)	on $2[110]$ at $2_11(1, 2)$	$2_1 \parallel [001]$ , 1 in $[1\bar{1}0]$ and $2 \parallel [110]$
<i>E10</i>	$P3_121$ (152)	on $2[110]$ at $3_1(1, 1, 2)1$	$3_1 \parallel [001]$ , $2 \parallel [110]$
<i>E11</i>	$P3_112$ (151)	on $2[210]$ at $3_11(1, 1, 2)$	$3_1 \parallel [001]$ , $2 \parallel [210]$

which should be studied together with the appropriate space-group diagrams.

These examples illustrate the following points:

- (i) The site symmetry at the origin corresponds to the point group of the space group (examples *E1–E3*) or to a subgroup of this point group (*E4–E11*).

The presence of a symmetry centre at the origin is always stated explicitly, either by giving the symbol  $\bar{1}$  (*E1* and *E4*) or by the words ‘at centre’, followed by the full site symmetry between parentheses (*E2* and *E5*). This completes the origin line if no further glide planes or screw axes are present at the origin.

- (ii) If glide planes or screw axes are present, as in examples *E4–E11*, they are given in the order of the symmetry directions listed in Table 2.1.3.1. Such a set of symmetry elements is described here in the form of a ‘point-group-like’ symbol (although it does not describe a group). With the help of the orthorhombic symmetry directions, the symbols in *E4–E6* can be interpreted easily. The shortened notation of *E6* and *E7* is used for space groups of crystal classes  $mm2$ ,  $4mm$ ,  $\bar{4}2m$ ,  $3m$ ,  $6mm$  and  $\bar{6}2m$  if the site symmetry at the origin can be easily recognized from the shortened symbol.

- (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 2.1.3.1). 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 *E7*: ‘on 41g’ instead of ‘on 41( $g, g$ )’]. An exception occurs for the site-symmetry group  $2mm$  (example *E8*), which is always written in full rather than as  $2m1$ .

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 2.1.3.1. Directions without symmetry are indicated by the symbol 1. With this rule, the last symbols in the examples *E9–E11* 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 2.1.3.9 and 1.4.2.1.

- (iv) To emphasize the orientation of the site-symmetry elements at the origin, examples *E9* and *E10* start with ‘on  $2[110]$ ’ and *E11* with ‘on  $2[210]$ ’. In *E8*, the site-symmetry group is  $2mm$ . 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.

### 2.1.3.8. 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  $\frac{1}{4}V(\text{cell})$ , 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, following *IT A* (2002), the asymmetric units