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those of *Pmmb*, which is a non-standard setting of *Pmma* (51). (A combination of the generators of *Pmma* with the *C*- or *I*-centring translation results in non-standard settings of *Cmme* and *Imma*.)

For the space groups with lattice symbol *P*, the generation procedure has given the same triplets (except for their sequence) as in *IT* (1952). In non-*P* space groups, the triplets listed sometimes differ from those of *IT* (1952) by a centring translation.

1.4.4. General and special Wyckoff positions

By B. Souvignier

One of the first tasks in the analysis of crystal patterns is to determine the actual positions of the atoms. Since the full crystal pattern can be reconstructed from a single unit cell or even an asymmetric unit, it is clearly sufficient to focus on the atoms inside such a restricted volume. What one observes is that the atoms typically do not occupy arbitrary positions in the unit cell, but that they often lie on geometric elements, *e.g.* reflection planes or lines along rotation axes. It is therefore very useful to analyse the symmetry properties of the points in a unit cell in order to predict likely positions of atoms.

We note that in this chapter all statements and definitions refer to the usual three-dimensional space $\mathbb{E}^3$, but also can be formulated, *mutatis mutandis*, for plane groups acting on $\mathbb{E}^2$ and for higher-dimensional groups acting on *n*-dimensional space $\mathbb{E}^n$.

1.4.4.1. Crystallographic orbits

Since the operations of a space group provide symmetries of a crystal pattern, two points X and Y that are mapped onto each other by a space-group operation are regarded as being *geometrically equivalent*. Starting from a point $X \in \mathbb{E}^3$, infinitely many points Y equivalent to X are obtained by applying all space-group operations $g = (\boldsymbol{W}, \boldsymbol{w})$ to X: $Y = g(X) = (\boldsymbol{W}, \boldsymbol{w})X = (\boldsymbol{W}X + \boldsymbol{w})$.

Definition

For a space group $\mathcal{G}$ acting on the three-dimensional space $\mathbb{E}^3$, the (infinite) set

$$\mathcal{O} = \mathcal{G}(X) := \{g(X) | g \in \mathcal{G}\}$$

is called the *orbit of X under* $\mathcal{G}$.

The orbit of X is the smallest subset of $\mathbb{E}^3$ that contains X and is closed under the action of $\mathcal{G}$. It is also called a *crystallographic orbit*.

Every point in direct space $\mathbb{E}^3$ belongs to precisely one orbit under $\mathcal{G}$ and thus the orbits of $\mathcal{G}$ partition the direct space into disjoint subsets. It is clear that an orbit is completely determined by its points in the unit cell, since translating the unit cell by the translation subgroup $\mathcal{T}$ of $\mathcal{G}$ entirely covers $\mathbb{E}^3$.

It may happen that two different symmetry operations g and h in $\mathcal{G}$ map X to the same point. Since $g(X) = h(X)$ implies that $h^{-1}g(X) = X$, the point X is fixed by the nontrivial operation $h^{-1}g$ in $\mathcal{G}$.

Definition

The subgroup $\mathcal{S}_X = \mathcal{S}_{\mathcal{G}}(X) := \{g \in \mathcal{G} | g(X) = X\}$ of symmetry operations from $\mathcal{G}$ that fix X is called the *site-symmetry group of X in* $\mathcal{G}$.

Since translations, glide reflections and screw rotations fix no point in $\mathbb{E}^3$, a site-symmetry group $\mathcal{S}_X$ never contains operations of these types and thus consists only of reflections, rotations, inversions and rotoinversions. Because of the absence of translations, $\mathcal{S}_X$ contains at most one operation from a coset $\mathcal{T}g$ relative to the translation subgroup $\mathcal{T}$ of $\mathcal{G}$, since otherwise the quotient of two such operations tg and $t'g$ would be the nontrivial translation $tgg^{-1}t'^{-1} = tt'^{-1}$ (see Chapter 1.3 for a discussion of coset decompositions). In particular, the operations in $\mathcal{S}_X$ all have different linear parts and because these linear parts form a subgroup of the point group $\mathcal{P}$ of $\mathcal{G}$, the order of the site-symmetry group $\mathcal{S}_X$ is a divisor of the order of the point group of $\mathcal{G}$.

The site-symmetry group of a point X is thus a finite subgroup of the space group $\mathcal{G}$, a subgroup which is isomorphic to a subgroup of the point group $\mathcal{P}$ of $\mathcal{G}$.

Example

For a space group $\mathcal{G}$ of type $P\bar{1}$, the site-symmetry group of the origin $X = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$ is clearly generated by the inversion in the origin: $\{\bar{1}|0\}(X) = X$. On the other hand, the point $Y = \begin{pmatrix} \frac{1}{2} \\ 0 \\ \frac{1}{2} \end{pmatrix}$ is fixed by the inversion in Y, *i.e.*

$$\{\bar{1}|1, 0, 1\}(Y) = \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} \begin{pmatrix} \frac{1}{2} \\ 0 \\ \frac{1}{2} \end{pmatrix} + \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} \\ 0 \\ \frac{1}{2} \end{pmatrix} = Y.$$

The symmetry operation $\{\bar{1}|1, 0, 1\}$ also belongs to $\mathcal{G}$ and generates the site-symmetry group of Y. The site-symmetry groups $\mathcal{S}_X = \{\{1|0\}, \{\bar{1}|0\}\}$ of X and $\mathcal{S}_Y = \{\{1|0\}, \{\bar{1}|1, 0, 1\}\}$ of Y are thus different subgroups of order 2 of $\mathcal{G}$ which are isomorphic to the point group of $\mathcal{G}$ (which is generated by $\bar{1}$).

The order $|\mathcal{S}_X|$ of the site-symmetry group $\mathcal{S}_X$ is closely related to the number of points in the orbit of X that lie in the unit cell. An application of the orbit–stabilizer theorem (see Section 1.1.7) yields the crucial observation that each point $Y = g(X)$ in the orbit of X under $\mathcal{G}$ is obtained precisely $|\mathcal{S}_X|$ times as an orbit point: for each $h \in \mathcal{S}_X$ one has $gh(X) = g(X) = Y$ and conversely $g'(X) = g(X)$ implies that $g^{-1}g' = h \in \mathcal{S}_X$ and thus $g' = gh$ for an operation h in $\mathcal{S}_X$.

Assuming first that we are dealing with a space group $\mathcal{G}$ described by a *primitive* lattice, each coset of $\mathcal{G}$ relative to the translation subgroup $\mathcal{T}$ contains precisely one operation g such that $g(X)$ lies in the primitive unit cell. Since the number of cosets equals the order $|\mathcal{P}|$ of the point group $\mathcal{P}$ of $\mathcal{G}$ and since each orbit point is obtained $|\mathcal{S}_X|$ times, it follows that the number of orbit points in the unit cell is $|\mathcal{P}|/|\mathcal{S}_X|$.

If we deal with a space group with a centred unit cell, the above result has to be modified slightly. If there are $k - 1$ centring vectors, the lattice spanned by the conventional basis is a sublattice of index k in the full translation lattice. The conventional cell therefore is built up from k primitive unit cells (spanned by a primitive lattice basis) and thus in particular contains k times as many points as the primitive cell (see Chapter 1.3 for a detailed discussion of conventional and primitive bases and cells).

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Proposition

Let $\mathcal{G}$ be a space group with point group $\mathcal{P}$ and let $\mathcal{S}_X$ be the site-symmetry group of a point X in $\mathbb{E}^3$. Then the number of orbit points of the orbit of X which lie in a conventional cell for $\mathcal{G}$ is equal to the product $k \times |\mathcal{P}|/|\mathcal{S}_X|$, where k is the volume of the conventional cell divided by the volume of a primitive unit cell.

1.4.4.2. Wyckoff positions

As already mentioned, one of the first issues in the analysis of crystal structures is the determination of the actual atom positions. Energetically favourable configurations in inorganic compounds are often achieved when the atoms occupy positions that have a nontrivial site-symmetry group. This suggests that one should classify the points in $\mathbb{E}^3$ into equivalence classes according to their site-symmetry groups.

Definition

A point $X \in \mathbb{E}^3$ is called a point in a *general position* for the space group $\mathcal{G}$ if its site-symmetry group contains only the identity element of $\mathcal{G}$. Otherwise, X is called a point in a *special position*.

The distinctive feature of a point in a general position is that the points in its orbit are in one-to-one correspondence with the symmetry operations of the group $\mathcal{G}$ by associating the orbit point $g(X)$ with the group operation g. For different group elements g and g', the orbit points $g(X)$ and $g'(X)$ must be different, since otherwise $g^{-1}g'$ would be a non-trivial operation in the site-symmetry group of X. Therefore, the entries listed in the space-group tables for the general positions can not only be interpreted as a shorthand notation for the symmetry operations in $\mathcal{G}$ (as seen in Section 1.4.2.3), but also as coordinates of the points in the orbit of a point X in a general position with coordinates x, y, z (up to translations).

Whereas points in general positions exist for every space group, not every space group has points in a special position. Such groups are called *fixed-point-free space groups* or *Bieberbach groups* and are precisely those groups that may contain glide reflections or screw rotations, but no proper reflections, rotations, inversions and rotoinversions.

Example

The group $\mathcal{G}$ of type $Pna2_1$ (33) has a point group of order 4 and representatives for the non-trivial cosets relative to the translation subgroup are the twofold screw rotation $\bar{x}, \bar{y}, z+\frac{1}{2}$, the a glide $x+\frac{1}{2}, \bar{y}+\frac{1}{2}, z$ and the n glide $\bar{x}+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2}$. No operation in the coset of the twofold screw rotation can have a fixed point, since such an operation maps the z component to $z+\frac{1}{2}+t_z$ for an integer t_z, and this is never equal to z. The same argument applies to the x component of the a glide and to the y component of the n glide, hence this group contains no operation with a fixed point (apart from the identity element) and is thus a fixed-point-free space group.

The distinction into general and special positions is of course very coarse. In a finer classification, it is certainly desirable that two points in the same orbit under the space group belong to the same class, since they are symmetry equivalent. Such points have *conjugate* site-symmetry groups (*cf.* the orbit–stabilizer theorem in Section 1.1.7).

Lemma

Let X and Y be points in the same orbit of a space group $\mathcal{G}$ and let $g \in \mathcal{G}$ such that $g(X) = Y$. Then the site-symmetry groups of X and Y are conjugate by the operation mapping X to Y, *i.e.* one has $\mathcal{S}_Y = g \cdot \mathcal{S}_X \cdot g^{-1}$.

The classification motivated by the conjugacy relation between the site-symmetry groups of points in the same orbit is the classification into *Wyckoff positions*.

Definition

Two points X and Y in $\mathbb{E}^3$ belong to the same *Wyckoff position* with respect to $\mathcal{G}$ if their site-symmetry groups $\mathcal{S}_X$ and $\mathcal{S}_Y$ are conjugate subgroups of $\mathcal{G}$.

In particular, the Wyckoff position containing a point X also contains the full orbit $\mathcal{G}(X)$ of X under $\mathcal{G}$.

Remark: It is built into the definition of Wyckoff positions that points that are related by a symmetry operation of $\mathcal{G}$ belong to the same Wyckoff position. However, a single site-symmetry group may have more than one fixed point, *e.g.* points on the same rotation axis or in the same reflection plane. These points are in general not symmetry related but, having identical site-symmetry groups, clearly belong to the same Wyckoff position. This situation can be analyzed more explicitly:

Let $\mathcal{S}_X$ be the site-symmetry group of the point X and assume that Y is another point with the same site-symmetry group $\mathcal{S}_Y = \mathcal{S}_X$. Choosing a coordinate system with origin X, the operations in $\mathcal{S}_X$ all have translational part equal to zero and are thus matrix–column pairs of the form $(\boldsymbol{W}, \boldsymbol{o})$. In particular, these operations are *linear* operations, and since both points X and Y are fixed by all operations in $\mathcal{S}_X$, the vector $\mathbf{v} = Y - X$ is also fixed by the linear operations $(\boldsymbol{W}, \boldsymbol{o})$ in $\mathcal{S}_X$. But with the vector $\mathbf{v}$ each scaling $c \cdot \mathbf{v}$ of $\mathbf{v}$ is fixed as well, and therefore all the points on the line through X and Y are fixed by the operations in $\mathcal{S}_X$. This shows that the Wyckoff position of X is a union of infinitely many orbits if $\mathcal{S}_X$ has more than one fixed point.

Lemma

Let $\mathcal{S}_X$ be the site-symmetry group of X in $\mathcal{G}$:

(i) The points belonging to the same Wyckoff position as X are precisely the points in the orbit of X under $\mathcal{G}$ if and only if X is the only point fixed by all operations in $\mathcal{S}_X$. In this case the coordinates of a point belonging to this Wyckoff position have fixed values not depending on a parameter.

(ii) If Y is a further point fixed by all operations in $\mathcal{S}_X$ but there is no fixed point of $\mathcal{S}_X$ outside the line through X and Y, then all the points on the line through X and Y are fixed by $\mathcal{S}_X$. The Wyckoff position of X is then the union of the orbits of points on this line (with the exception of a possibly empty discrete subset of points which have a larger site-symmetry group). In this case the coordinates of a point belonging to this Wyckoff position have values depending on a single variable parameter.

(iii) If Y and Z are points fixed by all operations in $\mathcal{S}_X$ such that X, Y, Z do not lie on a line, then all the points on the plane through X, Y and Z are fixed by $\mathcal{S}_X$. The Wyckoff position of X is then the union of the orbits of points in this plane with the exception of a (possibly empty) discrete subset of lines or points which have a larger site-symmetry group. In this case the coordinates of a point belonging to this Wyckoff position have values depending on two variable parameters.

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates			
8	d	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{y},x,z$	(4) $y,\bar{x},z$
			(5) $x+\frac{1}{2},\bar{y}+\frac{1}{2},z$	(6) $\bar{x}+\frac{1}{2},y+\frac{1}{2},z$	(7) $\bar{y}+\frac{1}{2},\bar{x}+\frac{1}{2},z$	(8) $y+\frac{1}{2},x+\frac{1}{2},z$

Figure 1.4.4.1
General-position block as given in the space-group tables for space group $P4bm$ (100).

(iv) Only the points belonging to the general position depend on three variable parameters.

The space-group tables of Chapter 2.3 contain the following information about the Wyckoff positions of a space group $\mathcal{G}$:

Multiplicity: The Wyckoff multiplicity is the number of points in an orbit for this Wyckoff position which lie in the conventional cell. For a group with a primitive unit cell, the multiplicity for the general position equals the order of the point group of $\mathcal{G}$, while for a centred cell this is multiplied by the quotient of the volumes of the conventional cell and a primitive unit cell.

The quotient of the multiplicity for the general position by that of a special position gives the order of the site-symmetry group of the special position.

Wyckoff letter: Each Wyckoff position is labelled by a letter in alphabetical order, starting with '*a*' for a position with site-symmetry group of maximal order and ending with the highest letter (corresponding to the number of different Wyckoff positions) for the general position.

It is common to specify a Wyckoff position by its multiplicity and Wyckoff letter, *e.g.* by 4*a* for a position with multiplicity 4 and letter *a*.

Site symmetry: The point group isomorphic to the site-symmetry group is indicated by an *oriented symbol*, which is a variation of the Hermann–Mauguin point-group symbol that provides information about the orientation of the symmetry elements. The constituents of the oriented symbol are ordered according to the symmetry directions of the corresponding crystal lattice (primary, secondary and tertiary). A symmetry operation in the site-symmetry group gives rise to a symbol in the position corresponding to the direction of its geometric element. Directions for which no symmetry operation contributes to the site-symmetry group are represented by a dot in the oriented symbol.

Coordinates: Under this heading, the coordinates of the points in an orbit belonging to the Wyckoff position are given, possibly depending on one or two variable parameters (three for the general position). The points given represent the orbit up to translations from the full translational subgroup. For a space group with a centred lattice, centring vectors which are coset representatives for the translation lattice relative to the lattice spanned by the conventional basis are given at the top of the table. To obtain representatives of the orbit up to translations from the lattice spanned by the conventional basis, these centring vectors have to be added to each of the given points.

As already mentioned, the coordinates given for the general position can also be interpreted as a compact notation for the symmetry operations, specified up to translations.

The entries in the last column, the *reflection conditions*, are discussed in detail in Chapter 1.6. This column lists the conditions for the reflection indices *hkl* for which the corresponding structure factor is not systematically zero.

Examples

(1) Let $\mathcal{G}$ be the space group of type $Pbca$ (61) generated by the twofold screw rotations $\{2_{001}|\frac{1}{2},0,\frac{1}{2}\}$: $\bar{x}+\frac{1}{2},\bar{y},z+\frac{1}{2}$ and $\{2_{010}|0,\frac{1}{2},\frac{1}{2}\}$: $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$, the inversion $\{\bar{1}|0\}$: $\bar{x},\bar{y},\bar{z}$ and the translations $t(1,0,0)$, $t(0,1,0)$, $t(0,0,1)$.
Applying the eight coset representatives of $\mathcal{G}$ with respect to the translation subgroup, the points in the orbit of the origin $X_1=\begin{pmatrix}0\\0\\0\end{pmatrix}$ that lie in the unit cell are found to be X_1, $X_2=\begin{pmatrix}\frac{1}{2}\\0\\\frac{1}{2}\end{pmatrix}$, $X_3=\begin{pmatrix}0\\\frac{1}{2}\\\frac{1}{2}\end{pmatrix}$ and $X_4=\begin{pmatrix}\frac{1}{2}\\\frac{1}{2}\\0\end{pmatrix}$, and the Wyckoff position to which X_1 belongs has multiplicity 4 and is labelled 4*a*.
Since the point group $\mathcal{P}$ of $\mathcal{G}$ has order 8, the site-symmetry group $\mathcal{S}_{X_1}$ has order 8/4 = 2. The inversion in the origin X_1 obviously fixes X_1, hence $\mathcal{S}_{X_1}=\{\{1|0\},\{\bar{1}|0\}\}$. The oriented symbol for the site symmetry is $\bar{1}$, indicating that the site-symmetry group is generated by an inversion.
The points X_2, X_3 and X_4 belong to the same Wyckoff position as X_1, since they lie in the orbit of X_1 and thus have conjugate site-symmetry groups.
The point $Y_1=\begin{pmatrix}0\\0\\\frac{1}{2}\end{pmatrix}$ also has an orbit with 4 points in the unit cell, namely Y_1, $Y_2=\begin{pmatrix}\frac{1}{2}\\0\\0\end{pmatrix}$, $Y_3=\begin{pmatrix}0\\\frac{1}{2}\\0\end{pmatrix}$ and $Y_4=\begin{pmatrix}\frac{1}{2}\\\frac{1}{2}\\\frac{1}{2}\end{pmatrix}$. These points therefore belong to a common Wyckoff position, namely position 4*b*. Moreover, the site-symmetry group of Y_1 is also generated by an inversion, namely the inversion $\{\bar{1}|0,0,1\}$: $\bar{x},\bar{y},\bar{z}+1$ located at Y_1 and is thus denoted by the oriented symbol $\bar{1}$.
The points X_1 and Y_1 do not belong to the same Wyckoff position, because an operation $(\boldsymbol{W},\boldsymbol{w})$ in $\mathcal{G}$ conjugates the inversion $\{\bar{1}|0,0,0\}$ in the origin to an inversion in $\boldsymbol{w}$. Since the translational parts of the operations in $\mathcal{G}$ are (up to integers) $(0,0,0)$, $(\frac{1}{2},\frac{1}{2},0)$, $(\frac{1}{2},0,\frac{1}{2})$ and $(0,\frac{1}{2},\frac{1}{2})$, an inversion in $Y_1=\begin{pmatrix}0\\0\\\frac{1}{2}\end{pmatrix}$ can not be obtained by conjugation with operations from $\mathcal{G}$.

(2) Let $\mathcal{G}$ be the space group of type $P4bm$ (100) generated by the fourfold rotation $\{4^+|0\}$: $\bar{y},x,z$, the glide reflection (of b type) $\{m_{100}|\frac{1}{2},\frac{1}{2},0\}$: $\bar{x}+\frac{1}{2},y+\frac{1}{2},z$ and the translations $t(1,0,0)$, $t(0,1,0)$, $t(0,0,1)$. The general-position coordinate triplets are shown in Fig. 1.4.4.1
From this information, the coordinates for the orbit of a specific point X in a special position can be derived by simply inserting the coordinates of X into the general-

position coordinates, normalizing to values between 0 and 1 (by adding ±1 if required) and eliminating duplicates.

For example, for the point $X = \begin{pmatrix} \frac{1}{2} \\ 0 \\ \frac{1}{4} \end{pmatrix}$ in Wyckoff position $2b$ one obtains X and $Y = \begin{pmatrix} 0 \\ \frac{1}{2} \\ \frac{1}{4} \end{pmatrix}$ as the points in the orbit of X that lie in the unit cell. Since the point group $\mathcal{P}$ of $\mathcal{G}$ has order 8, the site-symmetry group $\mathcal{S}_X$ is a group of order 8/2 = 4. Its four operations are

Coordinate triplet	Description
x, y, z	Identity operation
$\bar{x}+1, \bar{y}, z$	Twofold rotation with axis $\frac{1}{2}, 0, z$
$\bar{y}+\frac{1}{2}, \bar{x}+\frac{1}{2}, z$	Reflection with plane $x+\frac{1}{2}, -x, z$
$y+\frac{1}{2}, x-\frac{1}{2}, z$	Reflection with plane $x+\frac{1}{2}, x, z$

The corresponding oriented symbol for the site-symmetry is $2.mm$, indicating that the site-symmetry group contains a twofold rotation along a primary lattice direction, no symmetry operations along the secondary directions and two reflections along tertiary directions.

Since X and Y lie in the same orbit, they clearly belong to the same Wyckoff position. But every point $X' = \begin{pmatrix} \frac{1}{2} \\ 0 \\ z \end{pmatrix}$ with $0 \le z < 1$ has the same site-symmetry group as X and therefore also belongs to the same Wyckoff position as X. Inserting the coordinates of X' in the general-position coordinates, one obtains $Y' = \begin{pmatrix} 0 \\ \frac{1}{2} \\ z \end{pmatrix}$ as the only other point in the orbit of X' that lies in the unit cell. Clearly, Y' has the same site-symmetry group as Y. The Wyckoff position $2b$ to which X belongs therefore consists of the union of the orbits of the points $X' = \begin{pmatrix} \frac{1}{2} \\ 0 \\ z \end{pmatrix}$ with $0 \le z < 1$.

In the space-group diagram in Fig. 1.4.4.2, the points belonging to Wyckoff position $2b$ can be identified as the points on the intersection of a twofold rotation axis directed along [001] and two reflection planes normal to the square diagonals and crossing the centres of the sides bordering the unit cell. It is clear that for every value of z, the four intersection points in the unit cell lie in one orbit under the fourfold rotation located in the centre of the displayed cell.

Applying the same procedure to a point $X = \begin{pmatrix} 0 \\ 0 \\ z \end{pmatrix}$ in Wyckoff position $2a$, the points in the orbit that lie in the unit cell are seen to be X and $Y = \begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \\ z \end{pmatrix}$. The site-symmetry group $\mathcal{S}_X$ is again of order 4 and since the fourfold rotation $\{4^+|0\}$ fixes X, $\mathcal{S}_X$ is the cyclic group of order 4 generated by this fourfold rotation. The oriented symbol for this site-symmetry group is 4.. and the corresponding points can easily be identified in the space-group diagram in Fig. 1.4.4.2 by the symbol for a fourfold rotation.

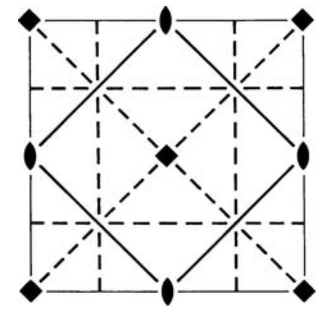

Figure 1.4.4.2
Symmetry-element diagram for the space group *P*4*bm* (100) for the orthogonal projection along [001].

Since a point in a special position has to lie on the geometric element of a reflection, rotation or inversion, the special positions can in principle be read off from the space-group diagrams. In the present example, we have dealt with the positions fixed by twofold or fourfold rotations, and from the diagram in Fig. 1.4.4.2 one sees that the only remaining case is that of points on reflection planes, indicated by the solid lines. A point on such a reflection plane is $X = \begin{pmatrix} x \\ x+\frac{1}{2} \\ z \end{pmatrix}$ and by inserting these coordinates into the general-position coordinates one obtains the points $\bar{x}, \bar{x}+\frac{1}{2}, z$, $\bar{x}+\frac{1}{2}, x, z$ and $x+\frac{1}{2}, \bar{x}, z$ as the other points in the orbit of X (up to translations). Here, the site-symmetry group $\mathcal{S}_X$ is of order 2, it is generated by the reflection $\{m_{1\bar{1}0}| -\frac{1}{2}, \frac{1}{2}, 0\}$: $y-\frac{1}{2}, x+\frac{1}{2}, z$ having the plane $x, x+\frac{1}{2}, z$ as geometric element. The oriented symbol of $\mathcal{S}_X$ is $..m$, since the reflection is along a tertiary direction.

1.4.4.3. Wyckoff sets

Points belonging to the same Wyckoff position have conjugate site-symmetry groups and thus in particular all those points are collected together that lie in one orbit under the space group $\mathcal{G}$. However, in addition, points that are not symmetry-related by a symmetry operation in $\mathcal{G}$ may still play geometrically equivalent roles, *e.g.* as intersections of rotation axes with certain reflection planes.

Example

In the conventional setting, the fourfold axes of a space group $\mathcal{G}$ of type $P4$ (75) intersect the ab plane in the points $u_1, u_2, 0$ and $u_1+\frac{1}{2}, u_2+\frac{1}{2}, 0$ for integers u_1, u_2, as can be seen from the space-group diagram in Fig. 1.4.4.3.

The points $u_1, u_2, 0$ lie in one orbit under the translation subgroup of $\mathcal{G}$, and thus belong to the same Wyckoff position, labelled $1a$. For the same reason, the points $u_1+\frac{1}{2}, u_2+\frac{1}{2}, 0$ belong to a single Wyckoff position, namely to position $1b$. The points $X = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$ and $Y = \begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \\ 0 \end{pmatrix}$ do not belong to the same Wyckoff position, because the site-symmetry group $\mathcal{S}_X$ is generated by the fourfold rotation 4_{001} and conjugating this by an operation $(\boldsymbol{W}, \boldsymbol{w}) \in \mathcal{G}$ results in a fourfold rotation with axis parallel to the c axis and running through $\boldsymbol{w}$. But since the translation parts of all operations in $\mathcal{G}$ are integral, such an axis

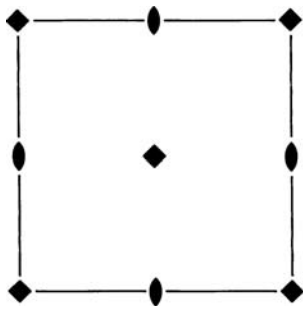

Figure 1.4.4.3
Symmetry-element diagram for the space group $P4$ (75) for the orthogonal projection along [001].

can not contain $Y = \begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \\ 0 \end{pmatrix}$ and thus $\mathcal{S}_X$ and $\mathcal{S}_Y$ are not conjugate in $\mathcal{G}$.
However, the translation by $(\frac{1}{2}, \frac{1}{2}, 0)$ conjugates $\mathcal{S}_X$ to $\mathcal{S}_Y$, while fixing the group $\mathcal{G}$ as a whole. This shows that there is an ambiguity in choosing the origin either at 0, 0, 0 or $\frac{1}{2}, \frac{1}{2}, 0$, since these points are geometrically indistinguishable (both being intersections of a fourfold axis with the *ab* plane).

The ambiguity in the origin choice in the above example can be explained by the *affine normalizer* of the space group $\mathcal{G}$ (see Section 1.1.8 for a general introduction to normalizers). The full group $\mathcal{A}$ of affine mappings acts *via* conjugation on the set of space groups and the space groups of the same affine type are obtained as the orbit of a single group of that type under $\mathcal{A}$.

Definition

The group $\mathcal{N}$ of affine mappings $n \in \mathcal{A}$ that fix a space group $\mathcal{G}$ under conjugation is called the *affine normalizer* of $\mathcal{G}$, *i.e.*

$$\mathcal{N} = \mathcal{N}_{\mathcal{A}}(\mathcal{G}) = \{n \in \mathcal{A} | n\mathcal{G}n^{-1} = \mathcal{G}\}.$$

The affine normalizer is the largest subgroup of $\mathcal{A}$ such that $\mathcal{G}$ is a normal subgroup of $\mathcal{N}$.

Conjugation by operations of the affine normalizer results in a permutation of the operations of $\mathcal{G}$, *i.e.* in a relabelling without changing their geometric properties. The additional translations contained in the affine normalizer can in fact be derived from the space-group diagrams, because shifting the origin by such a translation results in precisely the same diagram. More generally, an element of the affine normalizer can be interpreted as a change of the coordinate system that does not alter the space-group diagrams.

A more thorough description of the affine normalizers of space groups is given in Chapter 3.5, where tables with the affine normalizers are also provided.

Since the affine normalizer of a space group $\mathcal{G}$ is in general a group containing $\mathcal{G}$ as a proper subgroup, it is possible that subgroups of $\mathcal{G}$ that are not conjugate by any operation of $\mathcal{G}$ may be conjugate by an operation in the affine normalizer. As a consequence, the site-symmetry groups $\mathcal{S}_X$ and $\mathcal{S}_Y$ of two points X and Y belonging to different Wyckoff positions of $\mathcal{G}$ may be conjugate under the affine normalizer of $\mathcal{G}$. This reveals that the points X and Y are in fact geometrically equivalent, since they fall into the same orbit under the affine normalizer of $\mathcal{G}$. Joining the equivalence classes of these points into a single class results in a coarser classification with larger classes, which are called *Wyckoff sets*.

Definition

Two points X and Y belong to the same *Wyckoff set* if their site-symmetry groups $\mathcal{S}_X$ and $\mathcal{S}_Y$ are conjugate subgroups of the affine normalizer $\mathcal{N}_{\mathcal{A}}(\mathcal{G})$ of $\mathcal{G}$.
In particular, the Wyckoff set containing a point X also contains the full orbit of X under the affine normalizer of $\mathcal{G}$.

Example

Let $\mathcal{G}$ be the space group of type $P222_1$ (17) generated by the translations of an orthorhombic lattice, the twofold rotation $\{2_{100}|0\}$: $x, \bar{y}, \bar{z}$ and the twofold screw rotation $\{2_{001}|0, 0, \frac{1}{2}\}$: $\bar{x}, \bar{y}, z + \frac{1}{2}$. Note that the composition of these two elements is the twofold rotation with the line $0, y, \frac{1}{4}$ as its geometric element. The group $\mathcal{G}$ has four different Wyckoff positions with a site-symmetry group generated by a twofold rotation; representatives of these Wyckoff positions are the points $X_1 = \begin{pmatrix} x \\ 0 \\ 0 \end{pmatrix}$ (Wyckoff position 2*a*, site-symmetry symbol 2..), $X_2 = \begin{pmatrix} x \\ \frac{1}{2} \\ 0 \end{pmatrix}$ (position 2*b*, symbol 2..), $Y_1 = \begin{pmatrix} 0 \\ y \\ \frac{1}{4} \end{pmatrix}$ (position 2*c*, symbol .2.) and $Y_2 = \begin{pmatrix} \frac{1}{2} \\ y \\ \frac{1}{4} \end{pmatrix}$ (position 2*d*, symbol .2.).
From the tables of affine normalizers in Chapter 3.5, but also by a careful analysis of the space-group diagrams in Fig. 1.4.4.4, one deduces that the affine normalizer of $\mathcal{G}$ contains the additional translations $t(\frac{1}{2}, 0, 0)$, $t(0, \frac{1}{2}, 0)$ and $t(0, 0, \frac{1}{2})$, since all the diagrams are invariant by a shift of $\frac{1}{2}$ along any of the coordinate axes. Moreover, the symmetry operation $\{m_{1\bar{1}0}|0, 0, \frac{1}{4}\}$: $y, x, z + \frac{1}{4}$ which interchanges the *a* and *b* axes and shifts the origin by $\frac{1}{4}$ along the *c* axis belongs to the affine

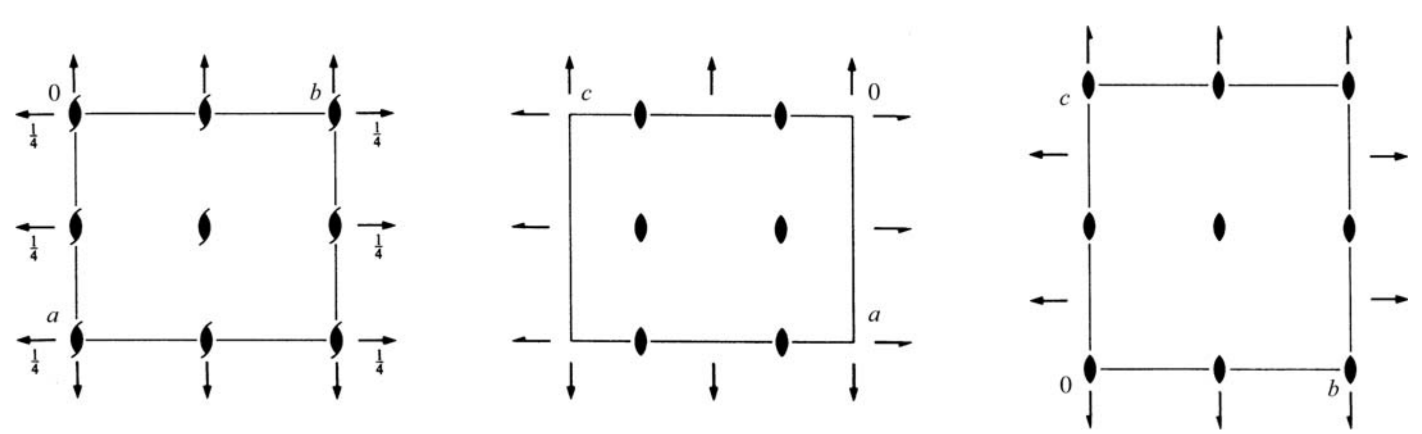

Figure 1.4.4.4
Symmetry-element diagrams for the space group $P222_1$ (17) for orthogonal projections along [001], [010], [100] (left to right).

normalizer, because it precisely interchanges the twofold rotations around axes parallel to the a and to the b axes. The translation $t(0, \frac{1}{2}, 0)$ maps X_1 to X_2, and hence X_1 and X_2 have site-symmetry groups which are conjugate under the affine normalizer of $\mathcal{G}$ and thus belong to the same Wyckoff set. Analogously, Y_1 and Y_2 belong to the same Wyckoff set, because $t(\frac{1}{2}, 0, 0)$ maps Y_1 to Y_2. Finally, the operation $\{m_{1\bar{1}0}|0, 0, \frac{1}{4}\}$ found in the affine normalizer maps X_1 to Y_1. This shows that the points of all four Wyckoff positions actually belong to the same Wyckoff set.

Geometrically, the positions in this Wyckoff set can be described as those points that lie on a twofold rotation axis.

The assignments of Wyckoff positions of plane and space groups to Wyckoff sets are discussed and tabulated in Chapter 3.4.

Remark: The previous example deserves some further discussion. The group $\mathcal{G}$ of type $P222_1$ belongs to the orthorhombic crystal family, and the conventional unit cell is spanned by three basis vectors **a**, **b**, **c** with lengths a, b, c and right angles between each pair of basis vectors. Unless the parameters a and b are equal because of some metric specialization, the operation $\{m_{1\bar{1}0}|0, 0, \frac{1}{4}\}$ of the affine normalizer is not an isometry but changes lengths. If it is desired that the metric properties are preserved, the full affine normalizer cannot be taken into account, but only the subgroup that consists of isometries. This subgroup is called the *Euclidean normalizer* of $\mathcal{G}$. (A detailed discussion of Euclidean normalizers of space groups and their tabulation are given in Chapter 3.5.)

Taking conjugacy of the site-symmetry groups under the Euclidean normalizer as a condition results in a notion of equivalence which lies between that of Wyckoff positions and Wyckoff sets. In the above example, the four Wyckoff positions would be merged into two classes represented by X_1 and Y_1, but X_1 and Y_1 would not be regarded as equivalent, since they are not related by an operation of the Euclidean normalizer.

It turns out, however, that in many cases this intermediate classification coincides with the Wyckoff sets, because points belonging to different Wyckoff positions are often related to each other by a translation contained in the affine normalizer. Since translations are always isometries, the translations contained in the affine normalizer always belong to the Euclidean normalizer as well.

1.4.4.4. Eigensymmetry groups and non-characteristic orbits

A crystallographic orbit $\mathcal{O}$ has been defined as the set of points $g(X)$ obtained by applying all operations of some space group $\mathcal{G}$ to a point $X \in \mathbb{E}^3$. From that it is clear that the set $\mathcal{O}$ is invariant as a whole under the action of operations in $\mathcal{G}$, since for some point $Y = g(X)$ in the orbit and $h \in \mathcal{G}$ one has $h(Y) = (hg)(X)$, which is again contained in $\mathcal{O}$ because hg belongs to $\mathcal{G}$. However, it is possible that the orbit $\mathcal{O}$ is also invariant under some isometries of $\mathbb{E}^3$ that are not contained in $\mathcal{G}$. Since the composition of two such isometries still keeps the orbit invariant, the set of all isometries leaving $\mathcal{O}$ invariant forms a group which contains $\mathcal{G}$ as a subgroup.

Definition

Let $\mathcal{O} = \{g(X) | g \in \mathcal{G}\}$ be the orbit of a point $X \in \mathbb{E}^3$ under a space group $\mathcal{G}$. Then the group $\mathcal{E}$ of isometries of $\mathbb{E}^3$ which leave $\mathcal{O}$ invariant as a whole is called the *eigensymmetry group* of $\mathcal{O}$.

Since the orbit is a discrete set, the eigensymmetry group has to be a space group itself. One distinguishes the following cases:

(i) The eigensymmetry group $\mathcal{E}$ equals the group $\mathcal{G}$ by which the orbit was generated. In this case the orbit is called a *characteristic orbit* of $\mathcal{G}$.

(ii) The eigensymmetry group $\mathcal{E}$ contains $\mathcal{G}$ as a proper subgroup. Then the orbit is called a *non-characteristic orbit*.

(iii) If the eigensymmetry group $\mathcal{E}$ contains translations that are not contained in $\mathcal{G}$, *i.e.* if $\mathcal{T}_{\mathcal{G}}$ is a proper subgroup of $\mathcal{T}_{\mathcal{E}}$, the orbit is called an *extraordinary orbit*. Of course, extraordinary orbits are a special kind of non-characteristic orbits.

Non-characteristic orbits are closely related to the concept of *lattice complexes*, which are discussed in Chapter 3.4. An extensive listing of non-characteristic orbits of space groups can be found in Engel *et al.* (1984).

The fact that an orbit of a space group has a larger eigensymmetry group is an important example of a pair of groups that are in a group–subgroup relation. Knowledge of subgroups and supergroups of a given space group play a crucial role in the analysis of phase transitions, for example, and are discussed in detail in Chapter 1.7.

The occurrence of non-characteristic orbits does not require the point X to be chosen at a special position. Even the general position of a space group $\mathcal{G}$ may give rise to a non-characteristic orbit. Moreover, special values of the coordinates of the general position may give rise to additional eigensymmetries without the position becoming a special position. Conversely, the orbit of a point at a special position need not be non-characteristic.

Example

We compare space groups of types $P4_1$ (76) and $P4_2$ (77). For a space group of type $P4_1$, the general position with generic coordinates x, y, z gives rise to a characteristic orbit, whereas the general-position orbit for a space group of type $P4_2$ consists of the points $X_1 = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$, $X_2 = \begin{pmatrix} \bar{x} \\ \bar{y} \\ z \end{pmatrix}$, $X_3 = \begin{pmatrix} \bar{y} \\ x \\ z + \frac{1}{2} \end{pmatrix}$ and $X_4 = \begin{pmatrix} y \\ \bar{x} \\ z + \frac{1}{2} \end{pmatrix}$. An inversion $\{\bar{1}|0, 0, 2z\}$ in $0, 0, z$ interchanges X_1 and X_2, and maps X_3 to $y, \bar{x}, z - \frac{1}{2}$, which is clearly equivalent to X_4 under a translation. This shows that the general-position orbit for a space group of type $P4_2$ is a non-characteristic orbit, and the eigensymmetry group of this orbit is of type $P4_2/m$ (84), where the origin has to be shifted to the inversion point $0, 0, z$ to obtain the conventional setting. Since the unit cell and the orbit are unchanged, but the point group of $P4_2$ is a subgroup of index 2 in the point group of $P4_2/m$, the orbit points must belong to a special position for $P4_2/m$, namely the position labelled $4j$. In the conventional setting of $P4_2/m$, a point belonging to this Wyckoff position is given by x, y, 0 and one finds that the orbit of this point in special position is characteristic, *i.e.* its eigensymmetry group is just $P4_2/m$.

If we assume that the metric of the space group is not special, the eigensymmetry group is restricted to the same crystal family (for the definition of 'specialized' metrics, *cf.* Section 1.3.4.3 and Chapter 3.5). Therefore, a space group $\mathcal{G}$ for which the point group is a holohedry can only have non-characteristic orbits by additional translations, *i.e.* extraordinary orbits. However, if we allow specialized metrics, the eigensymmetry group may belong to a higher crystal family. For example, if a space group belongs to the orthorhombic family, but the unit cell has equal parameters

$a = b$, then the eigensymmetry group of an orbit can belong to the tetragonal family.

Note: A space group $\mathcal{G}$ is equal to the intersection of the eigensymmetry groups of the orbits of all its positions. If none of the positions of a space group $\mathcal{G}$ gives rise to a characteristic orbit, this means that each single orbit under $\mathcal{G}$ does not have $\mathcal{G}$ as its symmetry group, but a larger group that contains $\mathcal{G}$ as a proper subgroup. It may thus be necessary to have the union of at least two orbits under $\mathcal{G}$ to obtain a structure that has precisely $\mathcal{G}$ as its group of symmetry operations.

Examples

(1) For the group $\mathcal{G}$ of type *Pmmm* (47) all Wyckoff positions with no further special values of the coordinates give rise to characteristic orbits, because the point group of $\mathcal{G}$ is a holohedry and the general coordinates allow no further translations. However, there are various 'specializations' of the positions that give rise to extraordinary orbits. For example, setting x to the special value $\frac{1}{4}$ for the general position introduces the additional translation $t(\frac{1}{2}, 0, 0)$. In fact, for all positions in which the first coordinate has no specified value (positions $2i$–$2l$, $4w$–$4z$, 8α), setting $x = \frac{1}{4}$ introduces the translation $t(\frac{1}{2}, 0, 0)$ and thus gives rise to an extraordinary orbit. In all these cases, the resulting eigensymmetry group is of type *Pmmm* with primitive lattice basis $\frac{1}{2}\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$.

(2) For the group $\mathcal{G}$ of type *Pmm*2 (25) no Wyckoff position gives rise to a characteristic orbit, because this is a polar group (with respect to the c axis). Any orbit of a point with third coordinate z allows an additional mirror plane normal to the c axis and located at $0, 0, z$. For example, the general position gives rise to a non-characteristic orbit with eigensymmetry group *Pmmm* (47). Since the general coordinates allow no additional translation, this is not an extraordinary orbit. However, setting $x = \frac{1}{4}$ for the general position introduces the translation $t(\frac{1}{2}, 0, 0)$ (as in the above example) and thus gives rise to an extraordinary orbit. The eigensymmetry group is *Pmmm* with primitive lattice basis $\frac{1}{2}\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$.

On the other hand, the special positions $x, 0, z$ (Wyckoff position $2e$) and $x, \frac{1}{2}, z$ (Wyckoff position $2f$) both have the same eigensymmetry group as the general position and setting $x = \frac{1}{4}$ for each, giving $\frac{1}{4}, 0, z$ and $\frac{1}{4}, \frac{1}{2}, z$, results in these positions having the same eigensymmetry group as the $\frac{1}{4}, y, z$ case of the general position.

(3) For a group $\mathcal{G}$ of type $P\bar{4}c2$ (116) the general-position coordinates are

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

A point x, y, z in a general position does not give rise to an extraordinary orbit because, owing to the general coordinates, there can not be any additional translation. Furthermore, the point group $\bar{4}m2$ of $\mathcal{G}$ has index 2 in the holohedry $4/mmm$. Thus, in order to have a non-characteristic orbit one would require an inversion in some point as an additional operation. But an inversion in p_1, p_2, p_3 would map x, y, z to $\bar{x} + 2p_1, \bar{y} + 2p_2, \bar{z} + 2p_3$ and no such point is contained in the orbit for generic x, y, z. The point x, y, z therefore gives rise to a characteristic orbit.

However, if the point in a general position is chosen with $x = y$, one indeed obtains an additional inversion at $0, 0, \frac{1}{4}$ which maps x, x, z to the orbit point $\bar{x}, \bar{x}, \bar{z} + \frac{1}{2}$ (general position point No. 8). This orbit thus is non-characteristic, but it is not extraordinary, since no additional translation is introduced. The eigensymmetry group obtained is $P4_2/mcm$ (132).

On the other hand, if the general position is chosen with $y = 0$, no additional inversion is obtained, but the translation by $\frac{1}{2}\mathbf{c}$ maps $x, 0, z$ to $x, 0, z + \frac{1}{2}$ (general-position point No. 5). The position $x, 0, z$ therefore gives rise to an extraordinary orbit with eigensymmetry group $P\bar{4}m2$ (115).

Knowledge of the eigensymmetry groups of the different positions for a group is of utmost importance for the analysis of diffraction patterns. Atoms in positions that give rise to non-characteristic orbits, in particular extraordinary orbits, may cause systematic absences that are not explained by the space-group operations. These absences are specified as *special reflection conditions* in the space-group tables of this volume, but only as long as no specialization of the coordinates is involved. For the latter case, the possible existence of systematic absences has to be deduced from the tables of noncharacteristic orbits. Reflection conditions are discussed in detail in Chapter 1.6.

Example

For the group $\mathcal{G}$ of type *Pccm* (49) the special position $\frac{1}{2}, 0, z$ (Wyckoff position $4p$) gives rise to an extraordinary orbit, since it allows the additional translation $\frac{1}{2}\mathbf{c}$. The special reflection condition corresponding to this additional translation is the integral reflection condition hkl: $l = 2n$. However, if the z coordinate in position $4p$ is set to $z = \frac{1}{8}$, the eigensymmetry group also contains the translation $\frac{1}{4}\mathbf{c}$. In this case, the special reflection condition becomes hkl: $l = 4n$.

1.4.5. Sections and projections of space groups

By B. Souvignier

In crystallography, two-dimensional sections and projections of crystal structures play an important role, *e.g.* in structure determination by Fourier and Patterson methods or in the treatment of twin boundaries and domain walls. Planar sections of three-dimensional scattering density functions are used for finding approximate locations of atoms in a crystal structure. They are indispensable for the location of Patterson peaks corresponding to vectors between equivalent atoms in different asymmetric units (the Harker vectors).

1.4.5.1. Introduction

A two-dimensional section of a crystal pattern takes out a slice of a crystal pattern. In the mathematical idealization, this slice is regarded as a two-dimensional plane, allowing one, however, to distinguish its upper and lower side. Depending on how the slice is oriented with respect to the crystal lattice, the slice will be invariant by translations of the crystal pattern along zero, one or two linearly independent directions. A section resulting in a slice with two-dimensional translational symmetry is called a *rational section* and is by far the most important case for crystallography.

Because the slice is regarded as a two-sided plane, the symmetries of the full crystal pattern that leave the slice invariant fall into two types:

references