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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).

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.