

1.5. Remarks on Wyckoff positions

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1.5.1. Crystallographic orbits and Wyckoff positions

The set of symmetry-equivalent sites in a space group is referred to as a (*crystallographic point*) *orbit* (Koch & Fischer, 1985; Wondratschek, 1976, 1980, 2005; also called *point configuration*). If the coordinates of a site are completely fixed by symmetry (e.g. $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$), then the orbit is identical with the corresponding *Wyckoff position* of that space group (in German *Punktlage*). However, if there are one or more freely variable coordinates (e.g. z in $0, \frac{1}{2}, z$), the Wyckoff position comprises an infinity of possible orbits; they differ in the values of the variable coordinate(s). The set of sites that are symmetry equivalent to, say, $0, \frac{1}{2}, 0.391$ makes up one orbit. The set corresponding to $0, \frac{1}{2}, 0.468$ belongs to the same Wyckoff position, but to another orbit (its variable coordinate z is different).

The Wyckoff positions of the space groups are listed in Volume A of *International Tables for Crystallography* (2005). They are labelled with letters a, b, \dots , beginning from the position having the highest site symmetry. A Wyckoff position is usually given together with the number of points belonging to one of its orbits within a unit cell. This number is the *multiplicity* listed in Volume A, and commonly is set in front of the Wyckoff letter. For example, the denomination $4c$ designates the four symmetry-equivalent points belonging to an orbit c within the unit cell.

In many space groups, for some Wyckoff positions there exist several Wyckoff positions of the same kind that can be combined to form a *Wyckoff set* [called a *Konfigurationslage* by Koch & Fischer (1975)]. They have the same site symmetries and they are mapped onto one another by the affine normalizer of the space group (Koch & Fischer, 1975; Wondratschek, 2005).

Example 1.5.1.1

In space group $I222$, No. 23, there are six Wyckoff positions with the site symmetry 2:

$4e$ ($x, 0, 0$), $4f$ ($x, 0, \frac{1}{2}$) on twofold rotation axes parallel to \mathbf{a} ,
 $4g$ ($0, y, 0$), $4h$ ($\frac{1}{2}, y, 0$) on twofold rotation axes parallel to \mathbf{b} ,
 $4i$ ($0, 0, z$), $4j$ ($0, \frac{1}{2}, z$) on twofold rotation axes parallel to \mathbf{c} .

They are mapped onto one another by the affine normalizer of $I222$, which is isomorphic to $Pm\bar{3}m$, No. 221. These six Wyckoff positions make up one Wyckoff set.

However, in this example the positions $4e, 4f$ vs. $4g, 4h$ vs. $4i, 4j$, being on differently oriented axes, cannot be considered to be equivalent if the lattice parameters are $a \neq b \neq c$. The subdivision of the positions of the Wyckoff set into these three sets is accomplished with the aid of the *Euclidean normalizer* of the space group $I222$.

The Euclidean normalizer is that supergroup of a space group that maps all equivalent symmetry elements onto one another without distortions of the lattice. It is a subgroup of the affine normalizer (Fischer & Koch, 1983; Koch *et al.*, 2005). In Example 1.5.1.1 (space group $I222$), the positions $4e$ and $4f$ are equivalent under the Euclidean normalizer (and so are $4g, 4h$ and also $4i, 4j$). The Euclidean normalizer of the space group $I222$ is $Pmmm$, No. 47, with the lattice parameters $\frac{1}{2}\mathbf{a}, \frac{1}{2}\mathbf{b}, \frac{1}{2}\mathbf{c}$ (if $a \neq b \neq c$). If the origin of a space group is shifted, Wyckoff positions that are

equivalent under the Euclidean normalizer may have to be interchanged. The permutations they undergo when the origin is shifted have been listed by Boyle & Lawrenson (1973). An origin shift of $0, 0, \frac{1}{2}$ will interchange the Wyckoff positions $4e$ and $4f$ as well as $4g$ and $4h$ of $I222$.

Example 1.5.1.2

In the space group $Fm\bar{3}m$, No. 225, the orbits of the Wyckoff positions $4a$ ($0, 0, 0$) and $4b$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) are equivalent under the Euclidean normalizer. The copper structure can be described equivalently either by having the Cu atoms occupy the position $4a$ or the position $4b$. If we take Cu atoms in the position $4a$ and shift the origin from $(0, 0, 0)$ to $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, then they result in the position $4b$.

Unique relations exist between the Wyckoff positions of a space group and the Wyckoff positions of any of its subgroups (Billiet *et al.*, 1978; Wondratschek, 1993; Wondratschek *et al.*, 1995). Given the relative positions of their unit cells (axes transformations and relative origin positions), the labels of these Wyckoff positions are unique.

Example 1.5.1.3

In diamond, the carbon atoms occupy the orbit belonging to the Wyckoff position $8a$ of the space group $Fd\bar{3}m$, No. 227. Zinc blende (sphalerite) crystallizes in the maximal subgroup $F\bar{4}3m$, No. 216, of $Fd\bar{3}m$. With the transition $Fd\bar{3}m \rightarrow F\bar{4}3m$ the Wyckoff position $8a$ splits into the positions $4a$ and $4c$ of $F\bar{4}3m$. These are two symmetry-independent positions that allow an occupation by atoms of two different elements (zinc and sulfur). In this example, all of the positions retain the site symmetry $\bar{4}3m$ and each Wyckoff position comprises only one orbit.

1.5.2. Derivative structures and phase transitions

In crystal chemistry, structural relations such as the relation diamond–sphalerite are of fundamental interest. Structures that result from a *basic structure* by the substitution of atoms of one kind for atoms of different elements, the topology being retained, are called *derivative structures* after Buerger (1947, 1951). For the basic structure the term *aristotype* has also been coined, while its derivative structures are called *hettotypes* (Megaw, 1973). For more details, see Chapter 1.6. When searching for derivative structures, one must look for space groups that are subgroups of the space group of the aristotype and in which the orbit of the atom(s) to be substituted splits into different orbits.

Similar relations also apply to many phase transitions (*cf.* Section 1.6.6). Very often the space group of one of the phases is a subgroup of the space group of the other. For second-order phase transitions this is even mandatory (*cf.* Section 1.2.7). The positions of the atoms in one phase are related to those in the other one.

Example 1.5.2.1

The disorder–order transition of β -brass (CuZn) taking place at 741 K involves a space-group change from the space group

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$Im\bar{3}m$, No. 229, to its subgroup $Pm\bar{3}m$, No. 221. In the high-temperature form, Cu and Zn atoms randomly take the orbit of the Wyckoff position $2a$ of $Im\bar{3}m$. Upon transition to the ordered form, this position splits into the independent positions $1a$ and $1b$ of the subgroup $Pm\bar{3}m$. These positions are occupied by the Cu and Zn atoms, respectively. See also Example 1.2.7.3.3.

Phase transitions in which a paraelectric crystal becomes ferroelectric occur when atoms that randomly occupy several symmetry-equivalent positions become ordered in a space group with lower symmetry, or when a key atom is displaced to a position with reduced site symmetry, thus allowing a distortion of the structure. In both cases, the space group of the ferroelectric phase is a subgroup of the space group of the paraelectric phase. In the case of ordering, the orbits of the atoms concerned split; in the case of displacement this is not necessary.

Example 1.5.2.2

In paraelectric NaNO_2 , space group $Immm$, No. 71, Na^+ ions randomly occupy two sites close to each other around an inversion centre $(0, 0, \frac{1}{2})$ with half occupation (position $4i$ at $0, 0, \pm 0.540$). The same applies to the nitrite ions, which are disordered in two opposite orientations around the inversion centre at $0, 0, 0$, with the N atoms at $4i$ ($0, 0, \pm 0.072$). At the transition to the ferroelectric phase at 438 K, the space-group symmetry decreases to the subgroup $Imm2$, No. 44, and the ions become ordered in one orientation. Each of the $4i$ orbits splits into two $2a$ orbits, but for every ion only one of the resulting orbits is now fully occupied: Na^+ at $2a$ ($0, 0, 0.540$) and N at $2a$ ($0, 0, 0.074$).

Example 1.5.2.3

Paraelectric BaTiO_3 crystallizes in the space group $Pm\bar{3}m$, No. 221, and the position $1a$ of a Ti atom ($0, 0, 0$ with site symmetry $m\bar{3}m$) is in the centre of an octahedron of oxygen atoms. At 393 K, a phase transition to a ferroelectric phase takes place. It has space group $P4mm$, No. 99, which is a subgroup of $Pm\bar{3}m$; the Ti atom is now at $0, 0, z$ ($1a$, site symmetry $4mm$) and is displaced from the octahedron centre. The orbit does not split, but the site symmetry is reduced.

1.5.3. Relations between the positions in group–subgroup relations

The following statements are universally valid:

- (1) Between the points of an orbit and the corresponding points in a subgroup there exists a one-to-one relation; both sets of points have the same magnitude.
- (2) Between the Wyckoff positions of a space group and those of its subgroups there exist unique relations. These may involve different Wyckoff labels for different relative positions of the origins.
- (3) With the symmetry reduction from a group to a subgroup, an orbit either splits into different orbits, or its site symmetry is reduced, or both happen. In addition, coordinates fixed or coupled by symmetry may become independent.

Let \mathcal{G} be a space group and \mathcal{H} a subgroup of \mathcal{G} . Let the site-symmetry groups of a point X_j under the space groups \mathcal{G} and \mathcal{H} be $\mathcal{S}_{\mathcal{G}}(X_j)$ and $\mathcal{S}_{\mathcal{H}}(X_j)$, respectively. The reduction factor of the site symmetries is then

$$R_j = |\mathcal{S}_{\mathcal{G}}(X_j)|/|\mathcal{S}_{\mathcal{H}}(X_j)|.$$

When the space-group symmetry is reduced from \mathcal{G} to \mathcal{H} and the orbit of the point X_j splits into n orbits, the following relation holds (Wondratschek, 1993):

$$i = \sum_{j=1}^n R_j.$$

$i = |\mathcal{G} : \mathcal{H}|$ is the index of \mathcal{H} in \mathcal{G} (cf. Section 1.2.4.2).

Example 1.5.3.1

The orbit of the Wyckoff position $24d$ of space group $Fm\bar{3}m$, No. 225, has the site symmetry mmm with the order $|mmm| = 8$. Upon symmetry reduction to the space group $I4/mmm$, No. 139, this orbit splits into the two orbits $4c$ and $8f$ of $I4/mmm$ with the site symmetries mmm and $2/m$, respectively. $|2/m| = 4$. The reduction factors of the site symmetries are

$$|mmm|/|mmm| = 8/8 = 1 \quad \text{and} \quad |mmm|/|2/m| = 8/4 = 2.$$

They add up to $1 + 2 = 3$, which is the index of $I4/mmm$ in $Fm\bar{3}m$.

The multiplicities commonly used together with the Wyckoff labels depend on the size of the chosen unit cell. As a consequence, a change of the size of the unit cell also changes the multiplicities. For example, the multiplicities of the Wyckoff positions listed in Volume A are larger by a factor of three for rhombohedral space groups when the unit cell is referred not to rhombohedral, but to hexagonal axes.

The multiplicity of a Wyckoff position shows up in the sum of the multiplicities of the corresponding positions of the subgroup. If the unit cell selected to describe the subgroup does not change in size, then the sum of the multiplicities of the positions of the subgroup must be equal to the multiplicity of the position of the starting group. For example, from a position with a multiplicity of 6, a position with multiplicity of 6 can result, or it can split into two positions of multiplicity of 3, or into two with multiplicities of 2 and 4, or into three with multiplicity of 2 *etc.* If the unit cell of the subgroup is enlarged or reduced by a factor f , then the sum of the multiplicities must also be multiplied or divided by this factor f .

Relations between the Wyckoff positions of space groups and the Wyckoff positions of their maximal subgroups were listed by Lawrenson (1972). However, his tables are not complete, and they were never published. In addition, they lack information about the transformations of axes and coordinates when these differ in the subgroup.

More recently, a computer program to calculate these relations has been developed (Kroumova *et al.*, 1998; cf. Section 1.7.4). To be used, the program requires knowledge of the subgroups (maximal or non-maximal) and of the necessary axes transformations and origin shifts. The Wyckoff position(s) to be considered can be marked or specific coordinates of a position must be given. The output is a listing of the Wyckoff position(s) of the specified subgroup and optionally all corresponding site coordinates. Depending on the relations and positions considered, the listings of coordinates can be rather long. The program has not been designed to give a fast overview of the relations. If one is looking for those subgroups that will exhibit a splitting of a certain position, all subgroups have to be tried one by one. For these reasons, the program cannot substitute the present tables;

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for practical work, the program and the tables listed in Part 3 complement each other.

The tables in Part 3 are a complete compilation for all space groups and all of their maximal subgroups. For all Wyckoff positions of a space group, all relations to the Wyckoff positions of its subgroups are listed. This also applies to the infinite number of maximal isomorphic subgroups; for these, a parameterized form has been developed that allows the listing of all maximal subgroups and all of their resulting Wyckoff positions completely for every allowed index of symmetry reduction.

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