International Tables for Crystallography (2011). Vol. A1, Section 1.5.3, pp. 42–43.

$Im\bar{3}m$, 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 *Imm*2, 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 *P*4*mm*, 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;

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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