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 $\overline{4}3m$ and each Wyckoff position comprises only one orbit.

1.3.3. 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 *basis 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 basis structure the term *aristotype* has also been coined, while its derivative structures are called *hettotypes* (Megaw, 1973). 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. 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 1.3.3.1.

The disorder–order transition of β-brass (CuZn) taking place at 741 K involves a space-group change from the space group $Im\overline{3}m$, No. 229, to its subgroup $Pm\overline{3}m$, No. 221. In the high-temperature form, Cu and Zn atoms randomly take the orbit of the Wyckoff position 2*a* of $Im\overline{3}m$. Upon transition to the ordered form, this position splits into the independent positions 1*a* and 1*b* of the subgroup $Pm\overline{3}m$. These positions are occupied by the Cu and Zn atoms, respectively. See also Example 1.2.7.3.5.

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 1.3.3.2.

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 4*i* 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 4*i* (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 4*i* orbits splits into two 2*a* orbits, but for every ion only one of the resulting orbits is now fully occupied: Na^+ at 2*a* (0, 0, 0.540) and N at 2*a* (0, 0, 0.074).

Example 1.3.3.3.

Paraelectric $BaTiO_3$ crystallizes in the space group $Pm\overline{3}m$, No. 221, and the position 1*a* of a Ti atom (0, 0, 0 with site symmetry $m\overline{3}m$) 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 $Pm\overline{3}m$; the Ti atom is now at 0, 0, *z* (1*a*, site symmetry 4*mm*) and is displaced from the octahedron centre. The orbit does not split, but the site symmetry is reduced.

1.3.4. 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 under the space groups $\mathcal{G}$ and $\mathcal{H}$ be $\mathcal{S}_\mathcal{G}(X)$ and $\mathcal{S}_\mathcal{H}(X)$, respectively. The reduction factor of the site symmetries is then

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

When the space-group symmetry is reduced from $\mathcal{G}$ to $\mathcal{H}$ and the orbit of the point X splits into n orbits, the following relation holds (Wondratschek, 2002):

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

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

Example 1.3.4.1.

The orbit of the Wyckoff position 24*d* of space group $Fm\overline{3}m$, 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 4*c* and 8*f* 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 $Fm\overline{3}m$.

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