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*, ..., 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 4*c* 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 *I*222, No. 23, there are six Wyckoff positions with the site symmetry 2:

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

They are mapped onto one another by the affine normalizer of *I*222, 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 4*e*, 4*f* *vs.* 4*g*, 4*h* *vs.* 4*i*, 4*j*, 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 *I*222.

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 *I*222), the positions 4*e* and 4*f* are equivalent under the Euclidean normalizer (and so are 4*g*, 4*h* and also 4*i*, 4*j*). The Euclidean normalizer of the space group *I*222 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 4*e* and 4*f* as well as 4*g* and 4*h* of *I*222.

Example 1.5.1.2

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

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 8*a* 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 8*a* splits into the positions 4*a* and 4*c* 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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