

1.7. TOPICS ON SPACE GROUPS TREATED IN VOLUMES A1 AND E

1.7.2. Relations between Wyckoff positions for group–subgroup-related space groups

BY U. MÜLLER

1.7.2.1. Symmetry relations between crystal structures

The crystal structures of two compounds are *isotypic* if their atoms are arranged in the same way and if they have the same or the enantiomorphic space group. The absolute values of the lattice parameters and interatomic distances may differ and small deviations are permitted for non-fixed coordinates of corresponding atoms. The axial ratios and interaxial angles must be similar. Two structures are *homeotypic* if the conditions for isotypism are relaxed because (Lima-de-Faria *et al.*, 1990): (1) their space groups differ, allowing for a group–subgroup relation; (2) the geometric conditions differ (axial ratios, interaxial angles, atomic coordinates); or (3) an atomic position in one structure is occupied in an ordered way by various atomic species in the other structure (substitution derivatives or after a disorder–order phase transition).²

Group–subgroup relations between the space groups of homeotypic crystal structures are particularly suited to disclosing the relationship. A standardized procedure to set forth such relations was developed by Bärnighausen (1980). The concept is to start from a simple, highly symmetrical crystal structure and to derive more complicated structures by distortions and/or substitutions of atoms. A tree of group–subgroup relations between the space groups involved, now called a *Bärnighausen tree*, serves as the main guideline. The highly symmetrical starting structure is called the *aristotype* after Megaw (1973) or *basic structure* after Buerger (1947, 1951) or, in the literature on phase transitions in physics, *prototype* or *parent structure*. The derived structures are the *hettotypes* or *derivative structures* or, in phase-transition physics, *distorted structures* or *daughter phases*. In Megaw's terminology, the structures mentioned in the tree form a *family of structures*.

Detailed instructions on how to form a Bärnighausen tree, the information that can be drawn from it and some possible pitfalls are given in the second edition of *IT A1*, Chapter 1.6 and in the book by Müller (2013). In any case, setting up group–subgroup relations requires a thorough monitoring of how the Wyckoff positions develop from a group to a subgroup for every position occupied. The following examples give a concise impression of such relations.

1.7.2.2. Substitution derivatives

As an example, Fig. 1.7.2.1 shows the simple relation between diamond and zinc blende. This is an example of a substitution derivative. The reduction of the space-group symmetry from diamond to zinc blende is depicted by an arrow which points from the higher-symmetry space group of diamond to the lower-symmetry space group of zinc blende. The subgroup is *translationengleiche* of index 2, marked by *t2* in the middle of the arrow. *Translationengleiche* means that the subgroup has the

² In the strict sense, two isotypic compounds do not have the same space group if their translation lattices (lattice dimensions) differ. However, such a strict treatment would render it impossible to apply group-theoretical methods in crystal chemistry and crystal physics. Therefore, we treat isotypic and homeotypic structures as if their translation lattices were the same or related by an integral enlargement factor. For more details see the second edition of *IT A1* (2010), Sections 1.2.7 and 1.6.4.1. We prefer the term 'misorder' instead of the usual 'disorder' because there still is order in the 'disordered' structure, although it is a reduced order.

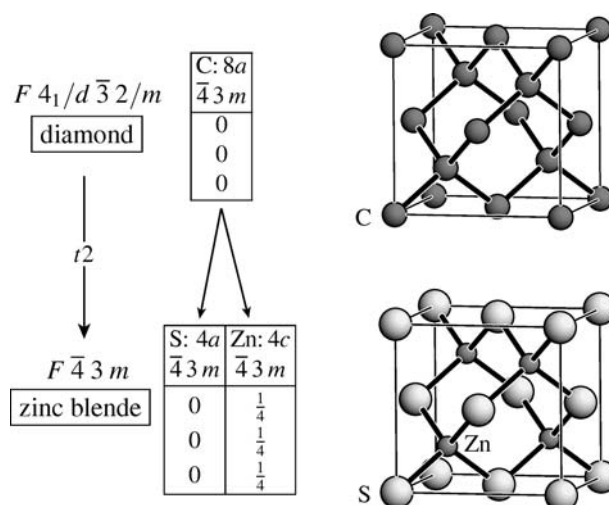


Figure 1.7.2.1

Group–subgroup relation from the aristotype diamond to its hettotype zinc blende. The numerical values in the boxes are atomic coordinates.

same translational lattice (the same size and dimensions of the primitive unit cell) but its crystal class is of reduced symmetry. The index [*i*] is the factor by which the total number of symmetry operations has been reduced, *i.e.* the subgroup has $1/i$ as many symmetry operations; as mentioned in Section 1.7.1, this is to be understood in the same way as 'the number of even numbers is half as many as the number of all integer numbers'.

The consequences of the symmetry reduction on the positions occupied by the atoms are important. As shown in the boxes next to the space-group symbols in Fig. 1.7.2.1, the carbon atoms in diamond occupy the Wyckoff position $8a$ of the space group $F 4_1/d \bar{3} 2/m$. Upon transition to zinc blende, this position splits into two independent Wyckoff positions, $4a$ and $4c$, of the subgroup $F \bar{4} 3 m$, rendering possible occupation by atoms of the two different species zinc and sulfur. The site symmetry $\bar{4} 3 m$ remains unchanged for all atoms.

Further substitutions of atoms require additional symmetry reductions. For example, in chalcopyrite, CuFeS_2 , the zinc atoms of zinc blende have been substituted by copper and iron atoms. This implies a symmetry reduction from $F \bar{4} 3 m$ to its subgroup $I \bar{4} 2 d$; this requires one *translationengleiche* and two steps of *klassengleiche* group–subgroup relations, including a doubling of the unit cell.

1.7.2.3. Phase transitions

Fig. 1.7.2.2 shows derivatives of the cubic ReO_3 structure type that result from distortions of this high-symmetry structure. WO_3 itself does not adopt this structure, only several distorted variants. The first step of symmetry reduction involves a tetragonal distortion of the cubic ReO_3 structure resulting in the space group $P4/mmm$; no example with this symmetry is yet known. The second step leads to a *klassengleiche* subgroup of index 2 (marked k_2 in the arrow), resulting in the structure of high-temperature WO_3 , which is the most symmetrical known modification of WO_3 . *Klassengleiche* means that the subgroup belongs to the same crystal class, but it has lost translational symmetry (its primitive unit cell has been enlarged). In this case this is a doubling of the size of the unit cell ($\mathbf{a} - \mathbf{b}, \mathbf{a} + \mathbf{b}, \mathbf{c}$) combined with an origin shift of $-\frac{1}{2}, 0, 0$ (in the coordinate system of $P4/mmm$). This cell transformation and origin shift cause a change of the atomic coordinates of the metal atom from $0, 0, 0$ to $\frac{1}{4}, \frac{1}{4}, \sim 0.0$ (the

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decimal value indicates that the coordinate is not fixed by symmetry). Simultaneously, the site symmetry of the metal atom is reduced from $4/m\bar{m}m$ to $4mm$ and the z coordinate becomes independent. In fact, the W atom is shifted from $z = 0$ to $z = 0.066$, *i.e.* it is not situated in the centre of the octahedron of the surrounding O atoms. This shift is the cause of the symmetry reduction. There is no splitting of the Wyckoff positions in this step of symmetry reduction, but a decrease of the site symmetries of all atoms.

When cooled, at 1170 K $HT\text{-}WO_3$ is transformed to $\alpha\text{-}WO_3$. This involves mutual rotations of the coordination octahedra along c and requires another step of symmetry reduction. Again, the Wyckoff positions do not split in this step of symmetry reduction, but the site symmetries of all atoms are further decreased.

Upon further cooling, WO_3 undergoes several other phase transitions that involve additional distortions and, in each case, an additional symmetry reduction to another subgroup (not shown in Fig. 1.7.2.2). For more details see Müller (2013), Section 11.6, and references therein.

1.7.2.4. Domain structures

In the case of phase transitions and of topotactic reactions³ that involve a symmetry reduction, the kind of group–subgroup relation determines how many kinds of domains and what domain states can be formed. If the lower-symmetry product results from a *translationengleiche* group–subgroup relation, twinned crystals are to be expected. A *klassengleiche* group–subgroup relation will cause antiphase domains. The number of different kinds of twin or antiphase domains corresponds to the index of the symmetry reduction. For example, the phase transition from $HT\text{-}WO_3$ to $\alpha\text{-}WO_3$ involves a *klassengleiche* group–subgroup relation of index 2 (k_2 in Fig. 1.7.2.2); no twins will be formed, but two kinds of antiphase domains can be expected.

1.7.2.5. Presentation of the relations between the Wyckoff positions among group–subgroup-related space groups

Group–subgroup relations as outlined in the preceding sections can only be correct if all atomic positions of the hettotypes result directly from those of the aristotype.

Every group–subgroup relation between space groups entails specific relations between their Wyckoff positions. If the index of symmetry reduction is 2, a Wyckoff position either splits into two symmetry-independent positions that keep the site symmetry, or there is no splitting and the site symmetry is reduced. If the index is 3 or higher, a Wyckoff position either splits, or its site symmetry is reduced, or both happen. Given the relative settings and origin choices of a space group and its subgroup, there exist unique relations between their Wyckoff positions. Laws governing these relations are considered in Chapter 1.5 of the second edition of *IT A1*.

Volume A1, Part 3, *Relations between the Wyckoff positions*, contains tables for all space groups. For every one of them, all maximal subgroups are listed, including the corresponding coordinate transformations. For all Wyckoff positions of a space group the relations to the Wyckoff positions of the subgroups are given. This includes the infinitely many maximal isomorphic subgroups, for which general formulae are given. Isomorphic subgroups are a special kind of *klassengleiche* subgroup that

³ A topotactic reaction is a chemical reaction in the solid state where the orientation of the product crystal is determined by the orientation of the educt crystal.

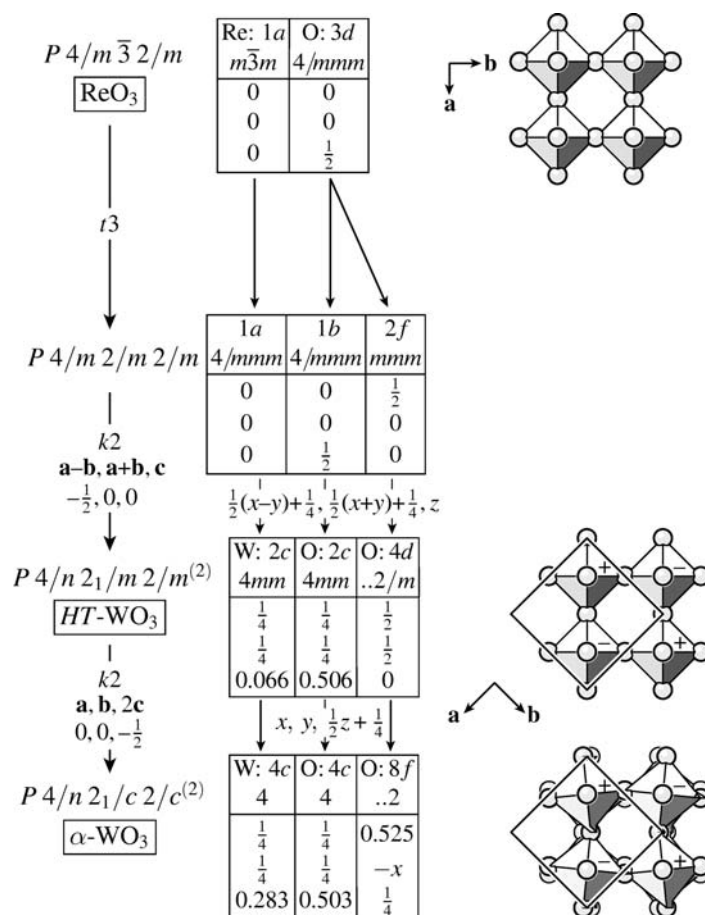


Figure 1.7.2.2 Group–subgroup relations (Barnighausen tree) from the ReO_3 type to two polymorphic forms of WO_3 . The superscript (2) after the space-group symbols states the origin choice. + and – in the images of high-temperature WO_3 and $\alpha\text{-}WO_3$ indicate the direction of the z shifts of the W atoms from the octahedron centres. Structural data for WO_3 are taken from Locherer *et al.* (1999).

belong to the same or the enantiomorphic space-group type, *i.e.* group and subgroup have the same or the enantiomorphic space-group symbol; the unit cell of the subgroup is increased by some integral factor, which is p , p^2 or p^3 (p = prime number) in the case of maximal isomorphic subgroups.

1.7.3. Relationships between space groups and subperiodic groups

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The present volume in the series *International Tables for Crystallography* (Volume A: *Space-Group Symmetry*) treats one-, two- and three-dimensional space groups. Volume E in the series, *Subperiodic Groups* (2010), treats two- and three-dimensional subperiodic groups: frieze groups (groups in two-dimensional space with translations in a one-dimensional subspace), rod groups (groups in three-dimensional space with translations in a one-dimensional subspace) and layer groups (groups in three-dimensional space with translations in a two-dimensional subspace). In the same way in which three-dimensional space groups are used to classify the atomic structure of three-dimensional crystals, the subperiodic groups are used to classify the atomic structure of other crystalline structures, such as liquid crystals, domain interfaces, twins and thin films.