

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.

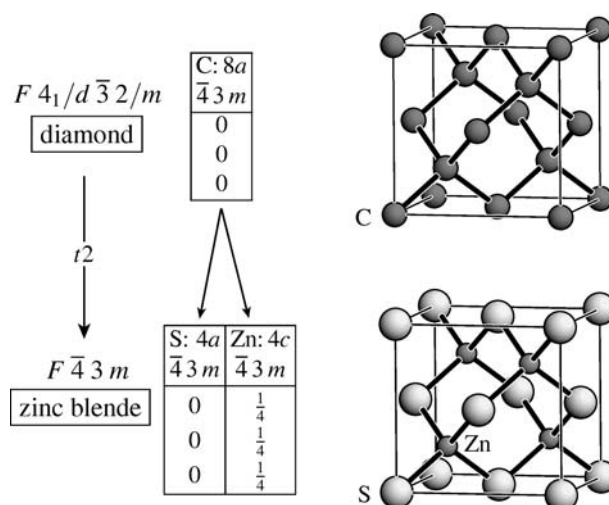


Figure 1.7.2.1

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 *k2* 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