

## 1.7. Topics on space groups treated in Volumes A1 and E of *International Tables for Crystallography*

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### 1.7.1. Subgroups and supergroups of space groups

BY H. WONDRATSCHEK

Relations between crystal structures play an important role for the comparison and classification of crystal structures, the analysis of phase transitions in the solid state, the understanding of topotactic reactions, and other applications. The relations can often be expressed by group–subgroup relations between the corresponding space groups. Such relations may be recognized from relations between the lattices and between the point groups<sup>1</sup> of the crystal structures.

In the first five editions of this Volume A of *International Tables for Crystallography*, subgroups and those supergroups of space groups that are space groups were listed for every space group. However, the listing was incomplete and it lacked additional information, such as, for example, possible unit-cell transformations and/or origin shifts involved. It became apparent that complete lists and more detailed data were necessary. Therefore, a supplementary volume of *International Tables for Crystallography* to this Volume A has been published: Volume A1, *Symmetry Relations between Space Groups* (2004; second edition 2010), abbreviated as *IT A1* in this chapter. The listing of the subgroups and supergroups has thus been discontinued in this sixth edition of Volume A.

This chapter gives a short outline of the contents and applications of the relations listed in Volume A1. In addition, information on Volume E of *International Tables for Crystallography* is presented. Volume E lists the subperiodic groups, which are other kinds of subgroups of the space groups.

Volume A1 consists of three parts. Part 1 covers the theory of space groups and their subgroups, space-group relations between crystal structures and the corresponding Wyckoff positions, and the Bilbao Crystallographic Server (<http://www.cryst.ehu.es/>). This server is freely accessible and offers access to computer programs that display the subgroups and supergroups of the space groups and other relevant data. Part 2 of Volume A1 contains complete lists of the maximal subgroups of the plane groups and space groups, including unit-cell transformations and origin shifts, if applicable. An overview of the group–subgroup relations is also displayed in diagrams. Part 3 contains tables of relations between the Wyckoff positions of group–subgroup-related space groups and a guide to their use.

#### Example

The crystal structures of silicon, Si, and sphalerite, ZnS, belong to space-group types  $Fd\bar{3}m$  ( $O_h^5$ ; No. 227) and  $F\bar{4}3m$  ( $T_d^2$ ; No. 216) with lattice parameters  $a_{\text{Si}} = 5.43 \text{ \AA}$  and  $a_{\text{ZnS}} = 5.41 \text{ \AA}$ . The structure of sphalerite (zinc blende) is obtained from that of silicon by replacing alternately half of the Si atoms by Zn and half by S, and by adjusting the lattice parameter. This proce-

sure is described in detail in Fig. 1.7.2.1. The strong connection between the two crystal structures is reflected in the relation between their space groups: the point group (crystal class) and the space group of sphalerite is a subgroup (of index 2) of that of silicon (ignoring the small difference in lattice parameters).

Data on subgroups and supergroups of the space groups are useful for the discussion of structural relations and phase transitions. It must be kept in mind, however, that group–subgroup relations only constitute symmetry relations. It is important, therefore, to ascertain that the consequential relations between the lattice parameters and between the atomic coordinates of the particles of the crystal structures also hold before a structural relation can be deduced from a symmetry relation.

#### Examples

NaCl and  $\text{CaF}_2$  belong to the same space-group type,  $Fm\bar{3}m$  ( $O_h^5$ ; No. 225), and have lattice parameters  $a_{\text{NaCl}} = 5.64 \text{ \AA}$  and  $a_{\text{CaF}_2} = 5.46 \text{ \AA}$ . The ions, however, occupy unrelated positions and so the symmetry relation does not express a structural relation.

Pyrite,  $\text{FeS}_2$ , and solid carbon dioxide,  $\text{CO}_2$ , belong to the same space-group type,  $Pa\bar{3}$  ( $T_h^6$ ; No. 205). They have lattice parameters  $a_{\text{FeS}_2} = 5.42 \text{ \AA}$  and  $a_{\text{CO}_2} = 5.55 \text{ \AA}$ , and the particles occupy analogous Wyckoff positions. Nevertheless, the structures of these compounds are not related, because the positional parameters  $x = 0.386$  of S in  $\text{FeS}_2$  and  $x = 0.118$  of O in  $\text{CO}_2$  differ so much that the coordinations of the corresponding atoms are dissimilar.

To formulate group–subgroup relations some definitions are necessary. Subgroups and their distribution into conjugacy classes, normal subgroups, supergroups, maximal subgroups, minimal supergroups, proper subgroups, proper supergroups and index are defined for groups in general in Chapter 1.1. These definitions are used also for crystallographic groups like space groups. In the present chapter, the data of *IT A1* are explained through many examples in order to enable the reader to use *IT A1*.

#### Examples

Maximal subgroups  $\mathcal{H}$  of a space group  $P1$  with basis vectors  $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$  are, among others, subgroups  $P1$  for which  $\mathbf{a}'' = p\mathbf{a}$ ,  $\mathbf{b}'' = \mathbf{b}$ ,  $\mathbf{c}'' = \mathbf{c}$ ,  $p$  prime. If  $p$  is not a prime number but a product of two integers  $p = q \times r$ , the subgroup  $\mathcal{H}$  is not maximal because a proper subgroup  $\mathcal{Z}$  of index  $q$  exists such that  $\mathbf{a}' = qa$ ,  $\mathbf{b}' = \mathbf{b}$ ,  $\mathbf{c}' = \mathbf{c}$ .  $\mathcal{Z}$  again has  $\mathcal{H}$  as a proper subgroup of index  $r$  with  $\mathcal{G} > \mathcal{Z} > \mathcal{H}$ .

$P12_1/c1$  has maximal subgroups  $P12_11$ ,  $P1c1$  and  $P\bar{1}$  with the same unit cell, whereas  $P1$  is not a maximal subgroup of  $P12_1/c1$ :  $P12_1/c1 > P12_11 > P1$ ;  $P12_1/c1 > P1c1 > P1$ ;  $P12_1/c1 > P\bar{1} > P1$ . These are all possible chains of maximal subgroups for  $P12_1/c1$  if the original translations are retained

<sup>1</sup> The point group determines both the symmetry of the physical properties of the macroscopic crystal and the symmetry of its ideal shape. Each space group belongs to a point group.

completely. Correspondingly, the seven subgroups of index 4 with the same translations as the original space group  $P6_3/mcm$  are obtained *via* the 21 different chains of Fig. 1.7.1.1.

While all group–subgroup relations considered here are relations between individual space groups, they are valid for all space groups of a space-group type, as the following example shows.

#### Example

A particular space group  $P121$  has a subgroup  $P1$  which is obtained from  $P121$  by retaining all translations but eliminating all rotations and combinations of rotations with translations. For every space group of space-group type  $P121$  such a subgroup  $P1$  exists.

From this example it follows that the relationship exists, in an extended sense, for the two space-group types involved. One can, therefore, list these relationships by means of the symbols of the space-group types.

A three-dimensional space group may have subgroups with no translations (*i.e.* site-symmetry groups; *cf.* Section 1.4.5), or with one- or two-dimensional lattices of translations (*i.e.* line groups, frieze groups, rod groups, plane groups and layer groups), *cf.* Volume E of *International Tables for Crystallography*, or with a three-dimensional lattice of translations (space groups).

The number of subgroups of a space group is always infinite. Not only the number of all subgroups but even the number of all maximal subgroups of a given space group is infinite.

In this section, only those subgroups of a space group that are also space groups will be considered. All *maximal* subgroups of space groups are themselves space groups. To simplify the discussion, let us suppose that we know all maximal subgroups of a space group  $\mathcal{G}$ . In this case, *any* subgroup  $\mathcal{H}$  of  $\mathcal{G}$  may be obtained *via* a chain of maximal subgroups  $\mathcal{H}_1, \mathcal{H}_2, \dots, \mathcal{H}_{r-1}, \mathcal{H}_r$  such that  $\mathcal{G} (= \mathcal{H}_0) > \mathcal{H}_1 > \mathcal{H}_2 > \dots > \mathcal{H}_{r-1} > \mathcal{H}_r (= \mathcal{H})$ , where  $\mathcal{H}_j$  is a maximal subgroup of  $\mathcal{H}_{j-1}$  of index  $[i_j]$ , with  $j = 1, \dots, r$ . There may be many such chains between  $\mathcal{G}$  and  $\mathcal{H}$ . On the other hand, all subgroups of  $\mathcal{G}$  of a given index  $[i]$  are obtained if all chains are constructed for which  $[i_1] \times [i_2] \times \dots \times [i_r] = [i]$  holds.

The index  $[i]$  of a subgroup has a geometric significance. It determines the ‘dilution’ of symmetry operations of  $\mathcal{H}$  compared with those of  $\mathcal{G}$ . The number of symmetry operations of  $\mathcal{H}$  is  $1/i$  times the number of symmetry operations of  $\mathcal{G}$ ; since space groups are infinite groups, this is to be understood in the same

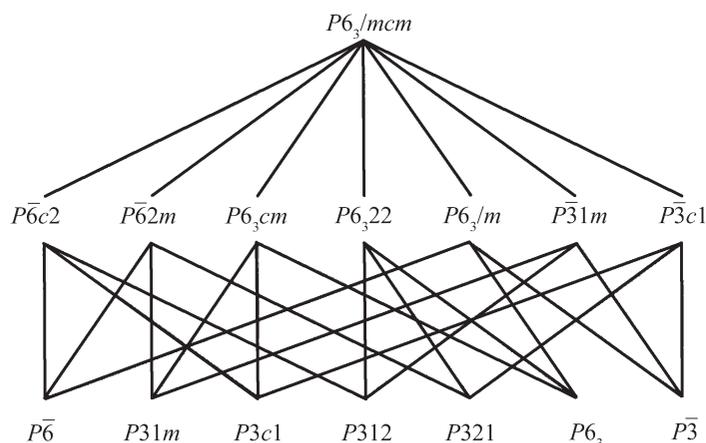
way as ‘the number of even numbers is one half of the number of all integer numbers’.

The infinite number of subgroups only occurs for a certain kind of subgroup and can be reduced as described below. It is thus useful to consider the different kinds of subgroups of a space group in the way introduced by Hermann (1929):

- (1) By reducing the order of the point group, *i.e.* by eliminating all symmetry operations of some kind. The example  $P12_11 \rightarrow P1$  mentioned above is of this type;
- (2) By loss of translations, *i.e.* by ‘thinning out’ the lattice of translations. For the space group  $P121$  mentioned above this may happen in different ways:
  - (a) by suppressing all translations of the kind  $(2u + 1)\mathbf{a} + v\mathbf{b} + w\mathbf{c}$ , where  $u, v$  and  $w$  are integers. The new basis is normally written  $\mathbf{a}' = 2\mathbf{a}$ ,  $\mathbf{b}' = \mathbf{b}$ ,  $\mathbf{c}' = \mathbf{c}$  and, hence, half of the twofold axes have been eliminated; or
  - (b) by  $\mathbf{a}' = \mathbf{a}$ ,  $\mathbf{b}' = 2\mathbf{b}$ ,  $\mathbf{c}' = \mathbf{c}$ , *i.e.* by thinning out the translations parallel to the twofold axes; or
  - (c) again by  $\mathbf{b}' = 2\mathbf{b}$  but replacing the twofold rotation axes by twofold screw axes.
- (3) By combination of (1) and (2), *e.g.* by reducing the order of the point group and by thinning out the lattice of translations.

Subgroups of the first kind, (1), are called *translationengleiche* (or *t*-) subgroups because the set  $\mathcal{T}$  of all (pure) translations is retained. In case (2), the point group  $\mathcal{P}$  and thus the crystal class of the space group is unchanged. These subgroups are called *klassengleiche* or *k*-subgroups. In the general case (3), both the translation subgroup  $\mathcal{T}$  of  $\mathcal{G}$  and the point group  $\mathcal{P}$  are reduced; the subgroup has lost translations *and* belongs to a crystal class of lower order: these are *general* subgroups.

Obviously, the general subgroups are more difficult to survey than kinds (1) and (2). Fortunately, a theorem of Hermann (1929) states that if  $\mathcal{H}$  is a proper subgroup of  $\mathcal{G}$ , then there always exists an intermediate group  $\mathcal{M}$  such that  $\mathcal{G} > \mathcal{M} > \mathcal{H}$ , where  $\mathcal{M}$  is a *t*-subgroup of  $\mathcal{G}$  and  $\mathcal{H}$  is a *k*-subgroup of  $\mathcal{M}$ . If  $\mathcal{H} < \mathcal{G}$  is maximal, then either  $\mathcal{M} = \mathcal{G}$  and  $\mathcal{H}$  is a *k*-subgroup of  $\mathcal{G}$  or  $\mathcal{M} = \mathcal{H}$  and  $\mathcal{H}$  is a *t*-subgroup of  $\mathcal{G}$ . It follows that a maximal subgroup of a space group  $\mathcal{G}$  is either a *t*-subgroup or a *k*-subgroup of  $\mathcal{G}$ . According to this theorem, general subgroups can never occur among the maximal subgroups. They can, however, be derived by a stepwise process of linking maximal *t*-subgroups and maximal *k*-subgroups by the chains discussed above.



**Figure 1.7.1.1**

Space group  $P6_3/mcm$  with *t*-subgroups of index 2 and 4. All 21 possible subgroup chains are displayed by lines.

#### 1.7.1.1. Translationengleiche (or *t*-) subgroups of space groups

The ‘point group’  $\mathcal{P}$  of a given space group  $\mathcal{G}$  is a finite group, *cf.* Chapter 1.3. Hence, the number of subgroups and consequently the number of maximal subgroups of  $\mathcal{P}$  is finite. There exist, therefore, only a finite number of maximal *t*-subgroups of  $\mathcal{G}$ . The possible *t*-subgroups were first listed in *Internationale Tabellen zur Bestimmung von Kristallstrukturen*, Band 1 (1935); corrections have been reported by Ascher *et al.* (1969). All maximal *t*-subgroups are listed individually for each space group  $\mathcal{G}$  in *IT A1* with the index, the (unconventional) Hermann–Mauguin symbol referred to the coordinate system of  $\mathcal{G}$ , the space-group number and conventional Hermann–Mauguin symbol, their general position and the transformation to the conventional coordinate system of  $\mathcal{H}$ . This may involve a change of basis and an origin shift from the coordinate system of  $\mathcal{G}$ .

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## 1.7.1.2. *Klassengleiche* (or *k*-) subgroups of space groups

Every space group  $\mathcal{G}$  has an infinite number of maximal  $k$ -subgroups. For dimensions 1, 2 and 3, however, it can be shown that the number of maximal  $k$ -subgroups is finite if subgroups belonging to the same affine space-group type as  $\mathcal{G}$  are excluded. The number of maximal subgroups of  $\mathcal{G}$  belonging to the same affine space-group type as  $\mathcal{G}$  is always infinite; these subgroups are called maximal *isomorphic* subgroups. Maximal *non-isomorphic klassengleiche* subgroups of plane groups and space groups always have index 2, 3 or 4. They are listed individually in *IT A1* together with the isomorphic subgroups of the same index. For practical reasons, the  $k$ -subgroups are distributed into two lists headed ‘Loss of centring translations’ and ‘Enlarged (conventional) unit cell’. The data consist of the index of the subgroup  $\mathcal{H}$ , the lattice relation between the lattices of  $\mathcal{H}$  and  $\mathcal{G}$ , the characterization of the space group  $\mathcal{H}$ , the general position of  $\mathcal{H}$  and the transformation from the coordinate system of  $\mathcal{G}$  to that of  $\mathcal{H}$ .

## 1.7.1.3. Isomorphic subgroups of space groups

The existence of isomorphic subgroups is of special interest. There can be no proper isomorphic subgroups  $\mathcal{H} < \mathcal{G}$  of finite groups  $\mathcal{G}$  because the difference of the orders  $|\mathcal{H}| < |\mathcal{G}|$  does not allow isomorphism. The point group  $\mathcal{P}$  of a space group  $\mathcal{G}$  is finite and its order cannot be reduced if  $\mathcal{H}$  is to be isomorphic to  $\mathcal{G}$ . Therefore, isomorphic subgroups are necessarily  $k$ -subgroups.

The number of isomorphic maximal subgroups and thus the number of all isomorphic subgroups of any space group is infinite. It can be shown that maximal subgroups of space groups of index  $i > 4$  are necessarily isomorphic. Depending on the crystallographic equivalence of the coordinate axes, the index of the subgroup is  $p$ ,  $p^2$  or  $p^3$ , where  $p$  is a prime. The isomorphic subgroups cannot be listed individually because of their number, but they can be listed as members of a few series. The series are mostly determined by the index  $p$ ; the members may be normal subgroups of  $\mathcal{G}$  or they form conjugacy classes the size of which is either  $p$ ,  $p^2$  or  $p^3$ . The individual members of a conjugacy class are determined by the locations of their origins. The size of the conjugacy class, a basis for the lattice of the subgroup, the generators of the individual isomorphic subgroups and the coordinate transformation from the coordinate system of  $\mathcal{G}$  to that of  $\mathcal{H}$  are listed in *IT A1* for all space-group types.

### Examples

Isomorphic subgroups of  $P1$ : the space group  $P1$  is an abelian space group, all of its subgroups are isomorphic and are normal subgroups. The index may be any prime  $p$ .

Isomorphic subgroups of  $P\bar{1}$ : the space group  $P\bar{1}$  is not abelian and subgroups exist of types  $P1$  and  $P\bar{1}$ . The latter are isomorphic. Those of index 2 are normal subgroups; for higher index  $p > 2$  they form conjugacy classes of prime size  $p$ .

Enantiomorphic space groups have an infinite number of maximal isomorphic subgroups of the same type and an infinite number of maximal isomorphic subgroups of the enantiomorphic type.

### Example

All  $k$ -subgroups  $\mathcal{H}$  of a given space group  $\mathcal{G} = P3_1$  with basis vectors  $\mathbf{a}' = \mathbf{a}$ ,  $\mathbf{b}' = \mathbf{b}$ ,  $\mathbf{c}' = p\mathbf{c}$ , where  $p$  is any prime number other than 3, are maximal isomorphic subgroups. They belong

to space-group type  $P3_1$  if  $p = 1 \pmod{3}$ . They belong to the enantiomorphic space-group type  $P3_2$  if  $p = 2 \pmod{3}$ .

In principle there is no difference in importance between  $t$ -, non-isomorphic  $k$ - and isomorphic  $k$ -subgroups. Roughly speaking, a group–subgroup relation is ‘strong’ if the index  $[i]$  of the subgroup is low. All maximal  $t$ - and maximal non-isomorphic  $k$ -subgroups have indices less than four in  $\mathbb{E}^2$  and less than five in  $\mathbb{E}^3$ , index four already being rather exceptional. Maximal isomorphic  $k$ -subgroups of arbitrarily high index exist for every space group.

## 1.7.1.4. Supergroups

Sometimes a space group  $\mathcal{H}$  is known and the possible space groups  $\mathcal{G}$ , of which  $\mathcal{H}$  is a subgroup, are of interest. A space group  $\mathcal{R}$  is called a *minimal supergroup* of a space group  $\mathcal{G}$  if  $\mathcal{G}$  is a maximal subgroup of  $\mathcal{R}$ .

### Examples of minimal supergroups

In Fig. 1.7.1.1, the space group  $P6_3/mcm$  is a minimal supergroup of  $P\bar{6}c2$ ,  $\dots$ ,  $P\bar{3}c1$ ;  $P\bar{6}c2$  is a minimal supergroup of  $P\bar{6}$ ,  $P3c1$  and  $P312$ ; etc.

If  $\mathcal{G}$  is a maximal  $t$ -subgroup of  $\mathcal{R}$ , then  $\mathcal{R}$  is a minimal  $t$ -supergroup of  $\mathcal{G}$ . If  $\mathcal{G}$  is a maximal  $k$ -subgroup of  $\mathcal{R}$ , then  $\mathcal{R}$  is a minimal  $k$ -supergroup of  $\mathcal{G}$ . Finally, if  $\mathcal{G}$  is a maximal isomorphic subgroup of  $\mathcal{R}$ , then  $\mathcal{R}$  is a minimal isomorphic supergroup of  $\mathcal{G}$ . Data for minimal  $t$ - and minimal non-isomorphic  $k$ -supergroups are listed in *IT A1*, although in a less explicit way than that in which the subgroups are listed. The data essentially make the detailed subgroup data usable for the search for supergroups of space groups. Data on minimal isomorphic supergroups are not listed because they can be derived from the corresponding subgroup relations.

The search for supergroups  $\mathcal{R} > \mathcal{G}$  of a space group  $\mathcal{G}$  differs from the search for subgroups  $\mathcal{H} < \mathcal{G}$  in one essential point: when looking for subgroups one knows the available group elements, namely the elements  $g \in \mathcal{G}$ ; when looking for supergroups, any isometry  $f \in \mathcal{E}$  may be a possible element of  $\mathcal{R}$ ,  $f \in \mathcal{R}$ , where  $\mathcal{E}$  is the Euclidean group of all isometries.

As we are mainly interested in the symmetries of crystal structures, it is reasonable only to look for groups  $\mathcal{R}$  that are themselves space groups. In this way the search for supergroups of space groups is a reversal of the search for subgroups. Nevertheless, even then there are new phenomena; only two of these shall be mentioned here.

### Example

For a given space group  $P\bar{1}$ , there is only one  $t$ -subgroup  $P1$ . However, for a space group  $P1$ , there is a continuously infinite number of  $t$ -supergroups  $P\bar{1}$ . Referred to the unit cell of  $P1$ , an additional centre of inversion can be placed in the range  $0 \leq x < \frac{1}{2}$ ,  $0 \leq y < \frac{1}{2}$ ,  $0 \leq z < \frac{1}{2}$ . The centre in each of these locations leads to a new supergroup resulting in a continuous set of  $t$ -supergroups.

If  $\mathcal{R}$  is a  $t$ -supergroup of  $\mathcal{G}$  belonging to a crystal system with higher symmetry than that of  $\mathcal{G}$ , then the metric of  $\mathcal{G}$  has to fulfil the conditions of the metric of  $\mathcal{R}$ . For example, if a tetragonal space group  $\mathcal{G}$  has a cubic  $t$ -supergroup  $\mathcal{R}$ , then the lattice of  $\mathcal{G}$  also has to have cubic symmetry.

In practice, small differences in the lattice parameters of  $\mathcal{G}$  and  $\mathcal{R}$  will occur, because lattice deviations can accompany a structural relationship.

### 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).<sup>2</sup>

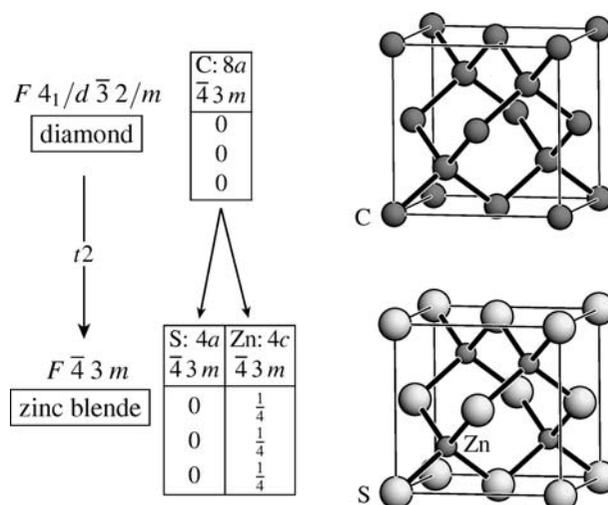
Group–subgroup relations between the space groups of homeotypic crystal structures are particularly suited to disclosing the relationship. A standardized procedure to set forth such relations was developed by Bärnighausen (1980). The concept is to start from a simple, highly symmetrical crystal structure 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

<sup>2</sup> 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  $F4_1/d\bar{3}2/m$ . Upon transition to zinc blende, this position splits into two independent Wyckoff positions, *4a* and *4c*, of the subgroup  $F\bar{4}3m$ , rendering possible occupation by atoms of the two different species zinc and sulfur. The site symmetry  $\bar{4}3m$  remains unchanged for all atoms.

Further substitutions of atoms require additional symmetry reductions. For example, in chalcopyrite,  $\text{CuFeS}_2$ , the zinc atoms of zinc blende have been substituted by copper and iron atoms. This implies a symmetry reduction from  $F\bar{4}3m$  to its subgroup  $I\bar{4}2d$ ; 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  $\text{ReO}_3$  structure type that result from distortions of this high-symmetry structure.  $\text{WO}_3$  itself does not adopt this structure, only several distorted variants. The first step of symmetry reduction involves a tetragonal distortion of the cubic  $\text{ReO}_3$  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  $\text{WO}_3$ , which is the most symmetrical known modification of  $\text{WO}_3$ . *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 reactions<sup>3</sup> 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.

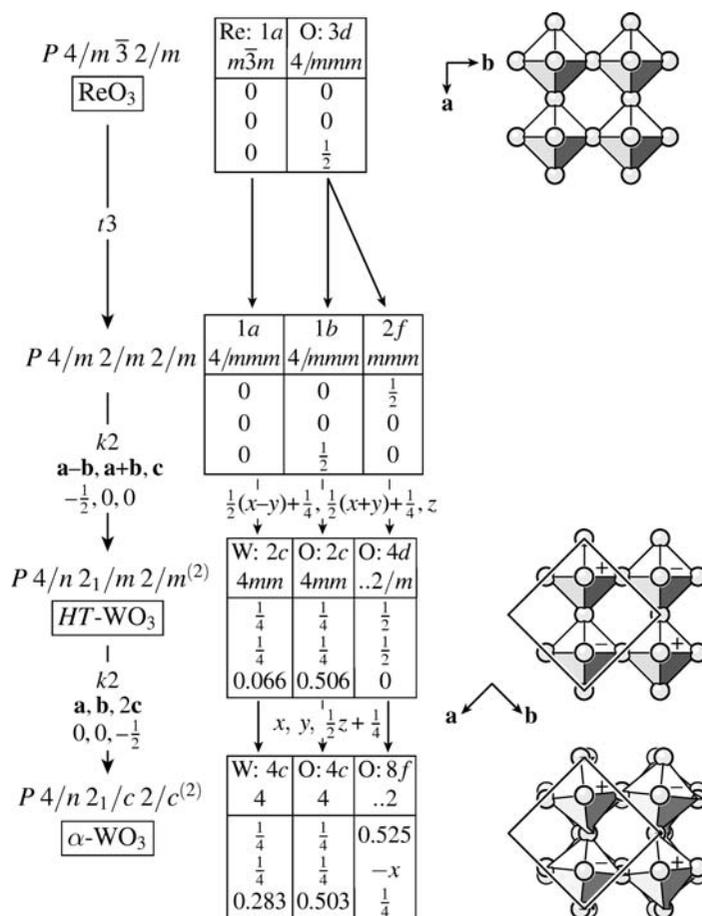
## 1.7.2.5. Presentation of the relations between the Wyckoff positions among group-subgroup-related space groups

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

<sup>3</sup> 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 (Bärnighausen 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).

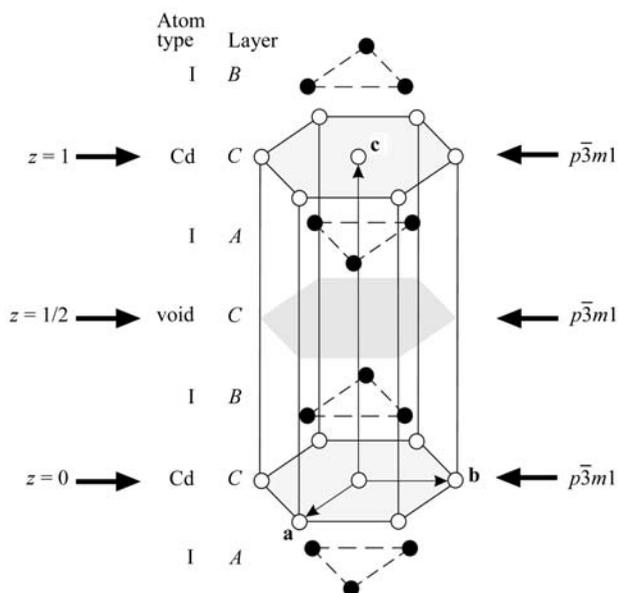
belong to the same or the enantiomorphic space-group type, *i.e.* group and subgroup have the same or the enantiomorphic space-group symbol; the unit cell of the subgroup is increased by some integral factor, which is  $p$ ,  $p^2$  or  $p^3$  ( $p$  = prime number) in the case of maximal isomorphic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

## 1.7.3. Relationships between space groups and subperiodic groups

BY D. B. LITVIN AND V. KOPSKÝ

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.

Orientation orbit ( <i>hkil</i> )	Conventional basis of the scanning group			Scanning group $\mathcal{H}$	Linear orbit <i>sd</i>	Sectional layer group	
	<i>a'</i>	<i>b'</i>	<i>d</i>			$\mathcal{L}(sd)$	
(0001)	<b>a</b>	<b>b</b>	<b>c</b>	$P\bar{3}m1$	$0d, \frac{1}{2}d$ [ <i>sd</i> , - <i>sd</i> ]	$p\bar{3}m1$	L72
						$p3m1$	L69

**Figure 1.7.3.1**

The scanning table for the space-group type  $P\bar{3}m1$  (164) and orientation orbit (0001), and the structure of cadmium iodide, CdI<sub>2</sub>. Cadmium and iodine ions are denoted by open and filled circles, respectively.

In Volume A, the relationship between the space group of a crystal and the point-group symmetry of individual points in the crystal is given by site symmetries, the point-group subgroups of the space group that leave the points invariant. In Volume E, an analogous relationship is given between the space group of a crystal and the subperiodic-group symmetry of planes that transect the crystal. Volume E contains *scanning tables* (with supplementary tables in Kopský & Litvin, 2004) from which the layer-group subgroups of the space group (called *sectional layer groups*) that leave the transecting planes invariant can be determined. The first attempts to derive sectional layer groups were made by Wondratschek (1971) and by using software written by Guigas (1971). Davies & Dirl (1993a,b) developed software for finding subgroups of space groups which was modified to find sectional layer groups. The use and determination of sectional layer groups have also been discussed by Janovec *et al.* (1988), Kopský & Litvin (1989) and Fuksa *et al.* (1993).

In Fig. 1.7.3.1, part of the scanning table for the space group  $P\bar{3}m1$  (164) is given. From this one can determine the layer-group subgroups of  $P\bar{3}m1$  that are symmetries of planes of orientation (*hkil*) = (0001). Vectors *a'* and *b'* are basic vectors of the translational subgroup of the layer-group symmetry of planes of this orientation. The vector *d* defines the *scanning direction* and is used to define the position of the plane within the crystal. The *linear orbit* is the set of all parallel planes obtained by applying all elements of the space group to any one plane. The *sectional layer group* is the layer subgroup of the space group that leaves the plane invariant.

Sectional layer groups were introduced by Holser (1958a,b) in connection with the consideration of domain walls and twin boundaries as symmetry groups of planes bisecting a crystal. The mutual orientation of the two domains separated by a domain

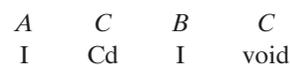
wall or twin boundary is not arbitrary, but has crystallographic restrictions. The group-theoretical basis for an analysis of domain pairs is given by Janovec (1972), and the structure of domain walls and twin boundaries is considered by Janovec (1981) and Zikmund (1984) [see also Janovec & Přívratká (2014)].

Layer symmetries have been used in *bicrystallography*. The term *bicrystal* was introduced by Pond & Bollmann (1979) in the study of grain boundaries [see also Pond & Vlachavas (1983) and Vlachavas (1985)]. A bicrystal is in general an edifice where two crystals, usually of the same structure but of different, possibly arbitrary, orientations, meet at a common boundary. The sectional layer groups describe the symmetries of such a boundary [see Volume E (2010), Section 5.2.5.2].

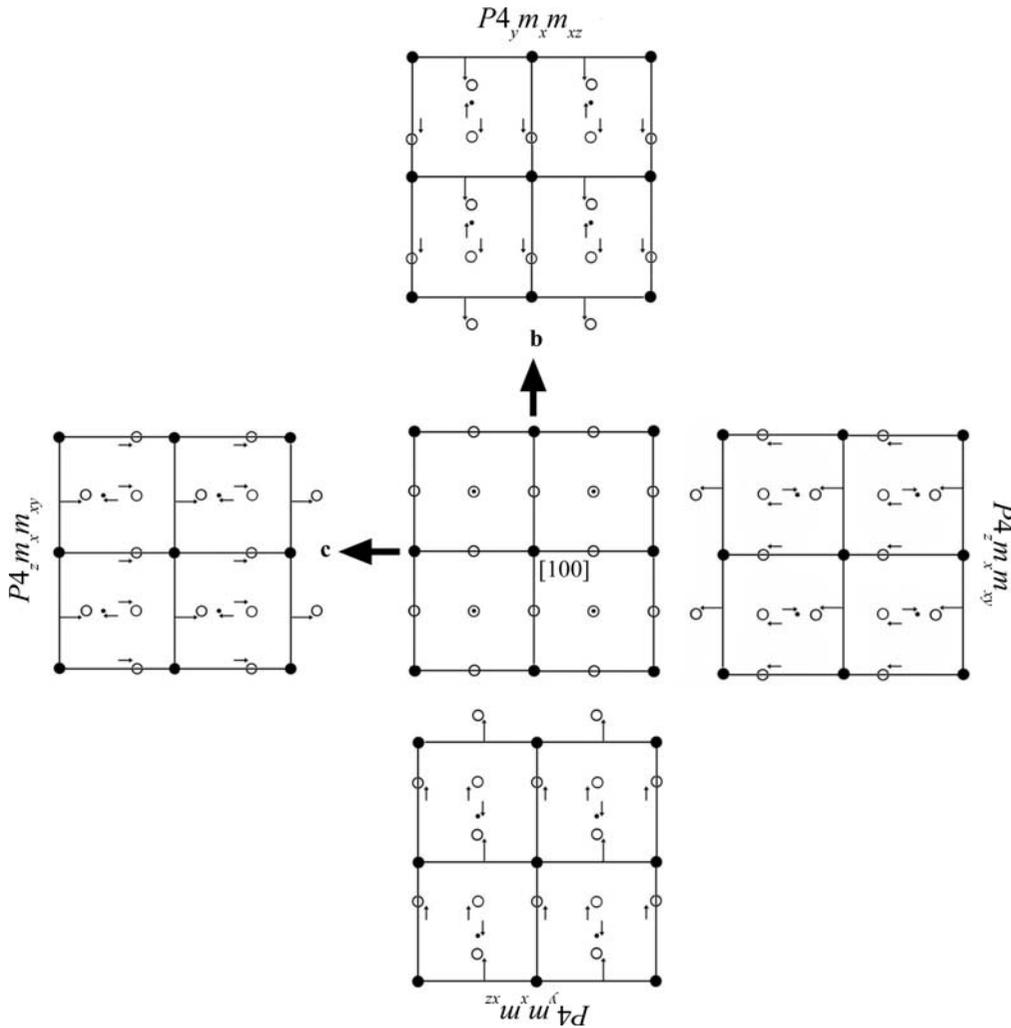
An example of the application of the scanning tables to determine the layer-group symmetry of planes in a crystal is given in Section 1.7.3.1. In Section 1.7.3.2 the derivation of the layer-group symmetry of a domain wall is described.

### 1.7.3.1. Layer symmetries in three-dimensional crystal structures

Fig. 1.7.3.1 shows the crystal structure of cadmium iodide, CdI<sub>2</sub>. The space group of this crystal is of type  $P\bar{3}m1$  (164). The anions form a hexagonal close packing of spheres and the cations occupy half of the octahedral holes, filling one of the alternate layers. In close-packing notation, the CdI<sub>2</sub> structure is



From the scanning tables, we obtain for planes with the (0001) orientation and at heights  $z = 0$  or  $z = \frac{1}{2}$  a sectional layer-group symmetry type  $p\bar{3}m1$  (layer group No. 72, or L72 for short), and for planes of this orientation at any other height a sectional layer-group symmetry type  $p3m1$  (L69).



**Figure 1.7.3.2**  
 At the centre is the structure of the cubic phase of barium titanate, BaTiO<sub>3</sub>, of symmetry type  $Pm\bar{3}m$ , surrounded by the structures of four of the six single-domain states of the tetragonal phase of symmetry type  $P4mm$ . All the diagrams are projections along the [100] direction. Arrows depict the atomic displacement amplitudes from their cubic-phase positions.

The  $x, y, 0$  plane contains cadmium ions. This plane is a constituent of the orbit of planes of orientation (0001) passing through the points with coordinates  $0, 0, u$ , where  $u$  is an integer. All these planes contain cadmium ions in the same arrangement ( $C$  layer filled with Cd).

The plane at height  $z = \frac{1}{2}$  is a constituent of the orbit of planes of orientation (0001) passing through the points with coordinates  $0, 0, u + \frac{1}{2}$ . All these planes contain only voids and lie midway between  $A$  and  $B$  layers of iodine ions with the  $B$  layer below and the  $A$  layer above the plane.

The planes at levels  $z = \frac{1}{4}$  and  $z = \frac{3}{4}$  contain  $B$  and  $A$  layers of iodine ions, respectively. These planes and all planes related to them by translations  $t(0, 0, u)$  belong to the same orbit because the operations  $\bar{3}$  exchange the  $A$  and  $B$  layers.

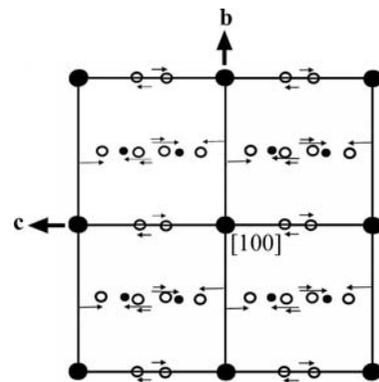
**1.7.3.2. The symmetry of domain walls**

The cubic phase of barium titanate BaTiO<sub>3</sub>, of symmetry type  $Pm\bar{3}m$ , undergoes a phase transition to a tetragonal phase of symmetry type  $P4mm$  which can give rise to six distinct single-domain states (Janovec *et al.*, 2004). This is represented in Fig. 1.7.3.2, where at the centre are four unit cells of the cubic phase with barium and titanium atoms represented by large and small filled circles, respectively, and oxygen atoms, which are located at the centre of each unit-cell face, as open circles. A cubic-to-

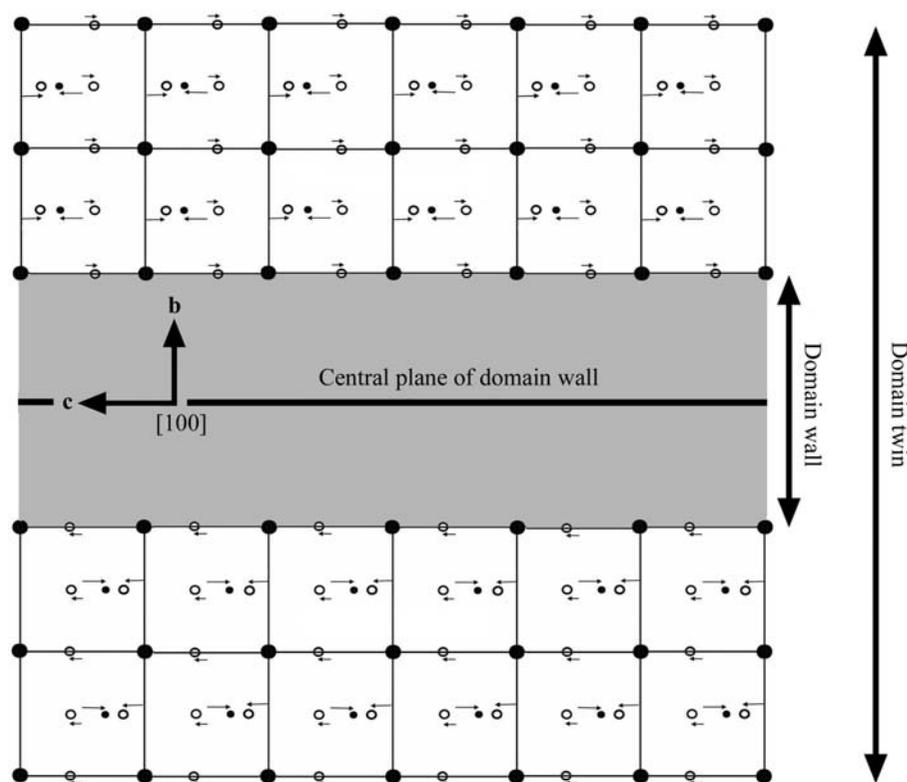
tetragonal phase transition gives rise to atomic displacements represented by arrows, and to six single-domain states, four of which are depicted in the figure. The polar tetragonal symmetry of each of these tetragonal domain states is also shown.

In determining the symmetry of a domain wall, we first construct a *domain twin* (Janovec & Přívratská, 2014): we choose two single-domain states, for this example the two in Fig. 1.7.3.2 with symmetry  $P4_z m_x m_{xy}$ , and construct a *domain pair* consisting of the superposition of these two single-domain states, see Fig. 1.7.3.3. The domain twin we choose to construct is obtained by passing a plane of orientation (010) through this domain pair at the origin and deleting from one side of the plane the atoms of one of the single-domain states, and the atoms of the second single-domain state from the other side of the plane, see Fig. 1.7.3.4. The plane is referred to as the *central plane of the domain wall*, and the atoms in and near this plane as the *domain wall*.

The symmetry of the central plane of the domain wall is determined from the symmetry of the domain pair and the scanning tables: The symmetry of the domain pair is the group of operations that either leaves both single-domain states invariant or simultaneously switches the two domain states.  $P4_z m_x m_{xy}$  leaves both single-domain states invariant and the symmetry operation of spatial inversion switches the two single-domain states, see Fig. 1.7.3.3. Consequently, the domain-pair symmetry is  $P4_z/m_z m_x m_{xy} = P4_z m_x m_{xy} \cup \{\bar{1}|0\}P4_z m_x m_{xy}$ . The symmetry of the central plane is determined from the scanning table for the space group  $P4_z/m_z m_x m_{xy}$ , the orientation orbit (010), the orientation of the domain wall and the linear orbit  $0d$ , since the central plane of the



**Figure 1.7.3.3**  
 The *domain pair* of symmetry  $P4_z/m_z m_x m_{xy}$  consisting of the superposition of those two single-domain states of tetragonal symmetry  $P4_z m_x m_{xy}$  shown in Fig. 1.7.3.2. The diagram is a projection along the [100] direction.



**Figure 1.7.3.4**

The domain twin consisting of the two domain states of tetragonal symmetry  $P4_zm_xm_y$  and a domain wall of orientation (010) passing through the origin of the domain twin.

wall passes through the origin (Volume E, 2010). The symmetry of the central plane is the sectional layer group  $pm_xm_zm_y$ , where  $p$  denotes the lattice of translations in the  $x, 0, z$  plane.

Let  $\mathbf{n}$  denote a unit vector perpendicular to the central plane of the domain wall; in this example  $\mathbf{n}$  is in the [010] direction. The symmetry of the domain wall consists of:

- (1) all elements of the symmetry group of the central plane that leave  $\mathbf{n}$  and both domain states invariant, *i.e.* in this example, all translations of  $p$ , 1 and  $m_x$ ; and
- (2) all elements of the symmetry group of the central plane that invert  $\mathbf{n}$  and switch the domain states, *i.e.* in this example,  $2_x$  and  $\bar{1}$ .

The symmetry of the domain wall is then  $p2_x/m_x$ .

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