

1. INTRODUCTION TO SPACE-GROUP SYMMETRY

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.

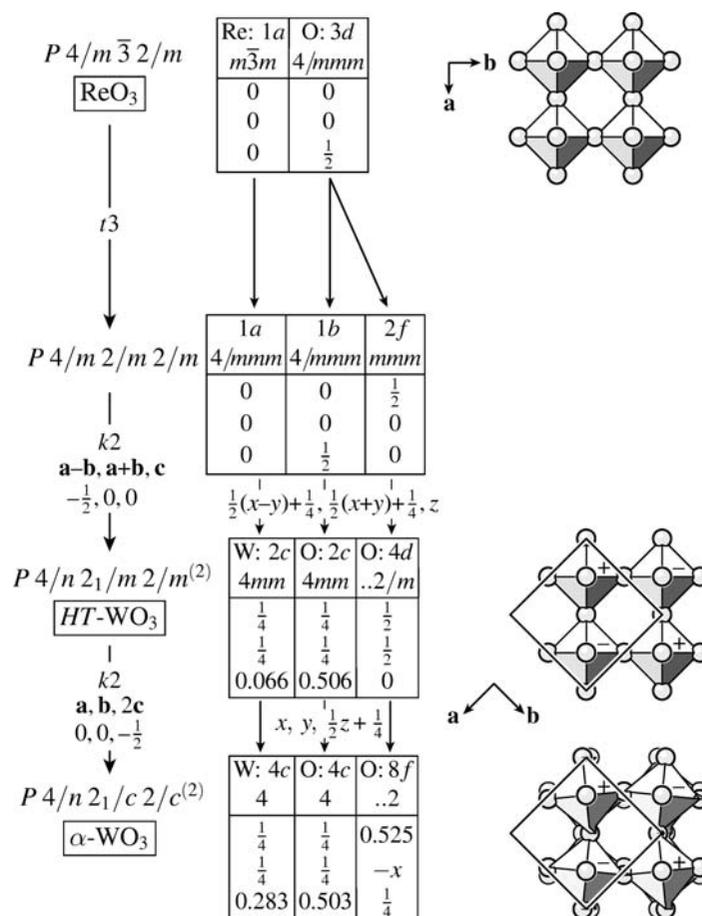


Figure 1.7.2.2

Group–subgroup relations (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)	a	b	c	$P\bar{3}m1$	$0d, \frac{1}{2}d$ [<i>sd</i> , - <i>sd</i>]	$p\bar{3}m1$	L72
						$p3m1$	L69

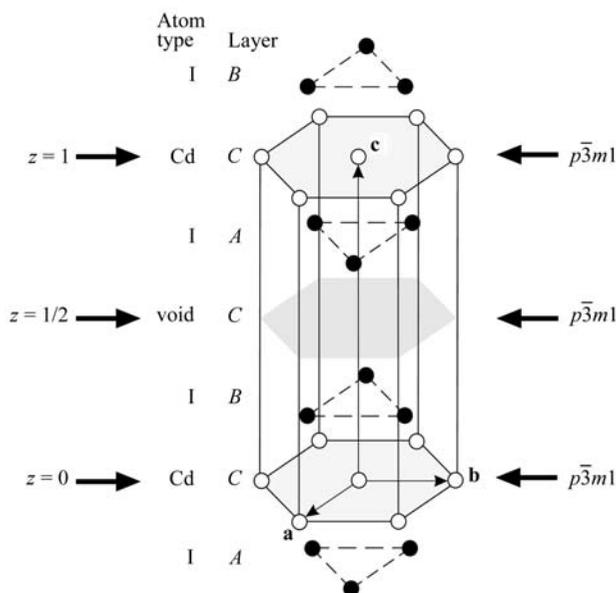


Figure 1.7.3.1

The scanning table for the space-group type $P\bar{3}m1$ (164) and orientation orbit (0001), and the structure of cadmium iodide, CdI_2 . 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

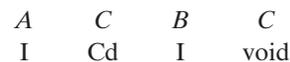
wall or twin boundary is not arbitrary, but has crystallographic restrictions. The group-theoretical basis for an analysis of domain pairs is given by Janovec (1972), and the structure of domain walls and twin boundaries is considered by Janovec (1981) and Zikmund (1984) [see also Janovec & Přívratká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

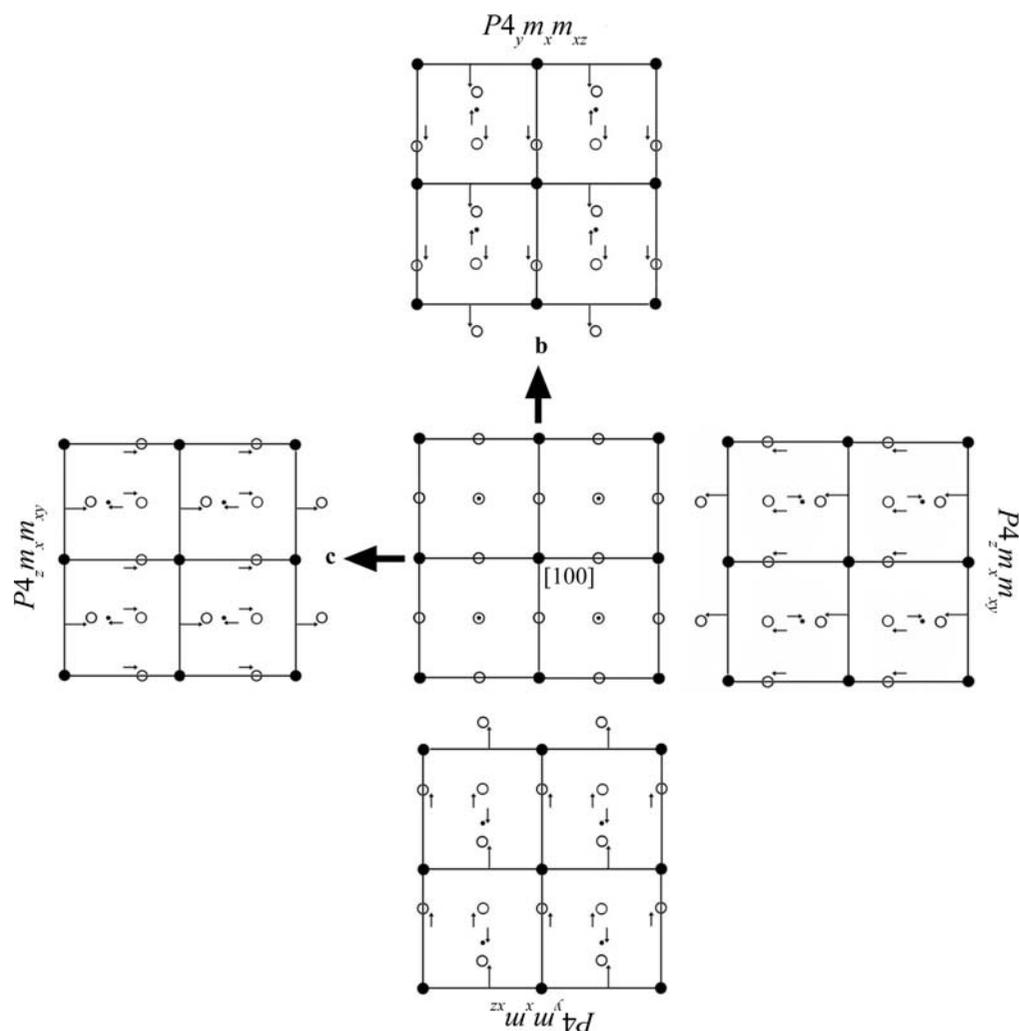
An example of the application of the scanning tables to determine the layer-group symmetry of planes in a crystal is given in Section 1.7.3.1. In Section 1.7.3.2 the derivation of the layer-group symmetry of a domain wall is described.

1.7.3.1. Layer symmetries in three-dimensional crystal structures

Fig. 1.7.3.1 shows the crystal structure of cadmium iodide, CdI_2 . 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_2 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_3 , 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.

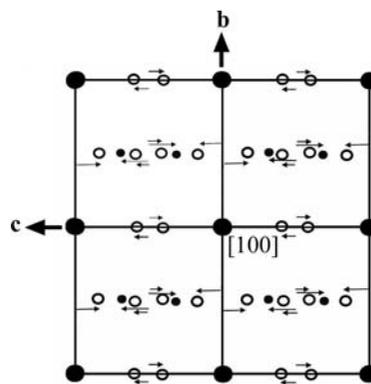
1.7.3.2. The symmetry of domain walls

The cubic phase of barium titanate BaTiO_3 , 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 $0\mathbf{d}$, 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.

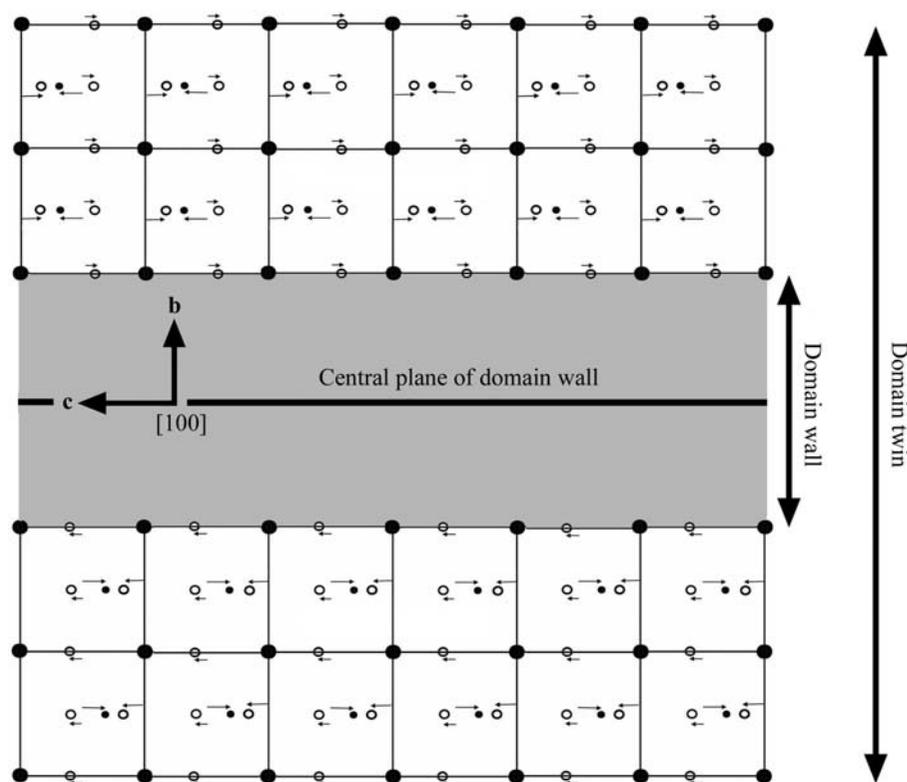


Figure 1.7.3.4

The domain twin consisting of the two domain states of tetragonal symmetry $P4_z m_x m_y$ 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 $pm_x m_z m_y$, 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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