

1. SPACE GROUPS AND THEIR SUBGROUPS

$\mathcal{N}_{\mathcal{G}}(\mathcal{H})$ determines the length of the conjugacy class of $\mathcal{H} < \mathcal{G}$, but it is not feasible to list for each group–subgroup pair $\mathcal{H} < \mathcal{G}$ its normalizer $\mathcal{N}_{\mathcal{G}}(\mathcal{H})$. Indeed, it is only necessary to list for any space group \mathcal{H} its normalizer $\mathcal{N}_{\mathcal{E}}(\mathcal{H})$ in the Euclidean group \mathcal{E} of all isometries, as is done in *IT A*, Section 15.2.1. From such a list the normalizers for the group–subgroup pairs can be obtained easily, because for any chain of space groups $\mathcal{H} < \mathcal{G} < \mathcal{E}$, the relations $\mathcal{H} \leq \mathcal{N}_{\mathcal{G}}(\mathcal{H}) \leq \mathcal{G}$ and $\mathcal{H} \leq \mathcal{N}_{\mathcal{G}}(\mathcal{H}) \leq \mathcal{N}_{\mathcal{E}}(\mathcal{H})$ hold. The normalizer $\mathcal{N}_{\mathcal{G}}(\mathcal{H})$ consists consequently of all those isometries of $\mathcal{N}_{\mathcal{E}}(\mathcal{H})$ that are also elements of \mathcal{G} , *i.e.* that belong to the intersection $\mathcal{N}_{\mathcal{E}}(\mathcal{H}) \cap \mathcal{G}$, *cf.* the examples of Section 1.2.7.¹¹

The isomorphism type of the Euclidean normalizer $\mathcal{N}_{\mathcal{E}}(\mathcal{H})$ may depend on the lattice parameters of the space group (*specialized* Euclidean normalizer). For example, if the lattice of the space group $P\bar{1}$ of a triclinic crystal is accidentally monoclinic at a certain temperature and pressure or for a certain composition in a continuous solid-solution series, then the Euclidean normalizer of this space group belongs to the space-group types $P2/m$ or $C2/m$, otherwise it belongs to $P\bar{1}$. Such a *specialized Euclidean normalizer* (here $P2/m$ or $C2/m$) may be distinguished from the *typical Euclidean normalizer* (here $P\bar{1}$), for which the lattice of \mathcal{H} is not more symmetric than is required by the symmetry of \mathcal{H} . The specialized Euclidean normalizers were first listed in the 5th edition of *IT A* (2005), Section 15.2.1.

1.2.7. Application to domain structures

1.2.7.1. Introductory remarks

In this section, the basic group-theoretical aspects of this chapter are exemplified using the topic of domain structures (transformation twins). Domain structures result from a displacive or order–disorder phase transition. A homogeneous single crystal phase **A** (parent or prototypic phase) is transformed to a crystalline phase **B** (daughter phase, distorted phase). In most cases phase **B** is inhomogeneous, consisting of homogeneous regions which are called *domains*.

Definition 1.2.7.1.1. A connected homogeneous part of a domain structure or of a twinned crystal of phase **B** is called a *domain*. Each domain is a single crystal. The part of space that is occupied by a domain is the *region* of that domain. □

The space groups \mathcal{H}_j of phase **B** are conjugate subgroups of the space group \mathcal{G} of phase **A**, $\mathcal{H}_j < \mathcal{G}$. The number of domains is not limited; they differ in their locations in space, in their orientations, in their sizes, in their shapes and in their space groups $\mathcal{H}_j < \mathcal{G}$ which, however, all belong to the same space-group type \mathcal{H} . The boundaries between the domains, called the domain walls, are assumed to be (infinitely) thin.

A deeper discussion of domain structures or transformation twins and their properties needs a much more detailed treatment, as is given in Volume D of *International Tables for Crystallography* (2003) (abbreviated as *IT D*) Part 3, by Janovec, Hahn & Klapper (Chapter 3.2), by Hahn & Klapper (Chapter 3.3) and by Janovec & Přívratská (Chapter 3.4) with more than 400

references. Domains are also considered in Section 1.6.6 of this volume.

In this section, non-ferroelastic phase transitions are treated without any special assumption as well as ferroelastic phase transitions under the simplifying *parent clamping approximation*, abbreviated PCA, introduced by Janovec *et al.* (1989), see also *IT D*, Section 3.4.2.5. A transition is *non-ferroelastic* if the strain tensors (metric tensors) of the low-symmetry phase **B** have the same independent components as the strain tensor of the phase **A**.¹² There are thus *no spontaneous strain components* which distort the lattices of the domains. In a *ferroelastic* phase transition the strain tensors of phase **B** have more independent components than the strain tensor of phase **A**. The additional strain components cause lattice strain. By the PCA the lattice parameters of phase **B** at the transition are adapted to those of phase **A**, *i.e.* to the lattice symmetry of phase **A**. Therefore, under the PCA the ferroelastic phases display the same behaviour as the non-ferroelastic phases.

If in this section ferroelastic phase transitions are considered, the PCA is assumed to be applied.

Under a non-ferroelastic phase transition or under the assumption of the PCA, the translations of the constituents of the phase **B** are translations of phase **A** and the space groups \mathcal{H}_j of **B** are subgroups of the space group \mathcal{G} of **A**, $\mathcal{H}_j < \mathcal{G}$.

Under this supposition the domain structure formed may exhibit different chiralities and/or polarities of its domains with different spatial orientations of their symmetry elements. Nevertheless, each domain has the same specific energy and the lattice of each domain is part of the lattice of the parent structure **A** with space group \mathcal{G} .

The description of domain structures by their crystal structures is called the *microscopic description*, *IT D*, Section 3.4.2.1. In the *continuum description*, the crystals are treated as anisotropic continua, *IT D*, Section 3.4.2.1. The role of the space groups is then taken over by the point groups of the domains. The continuum description is used when one is essentially interested in the macroscopic physical properties of the domain structure.

Different kinds of nomenclature are used in the discussion of domain structures. The basic concepts of *domain* and *domain state* are established in *IT D*, Section 3.4.2.1; the terms *symmetry state* and *directional state* are newly introduced here in the context of domain structures. All these concepts classify the domains and will be defined in the next section and applied in different examples of phase transitions in Section 1.2.7.3.

1.2.7.2. Domain states, symmetry states and directional states

In order to describe what happens in a phase transition of the kind considered, a few notions are useful.

If the domains of phase **B** have been formed from a single crystal of phase **A**, then they belong to a finite (small) number of domain states **B_j** with space groups \mathcal{H}_j . The domain states have well defined relations to the original crystal of phase **A** and its space group \mathcal{G} . In order to describe these relations, the notion of crystal pattern is used. Any perfect (ideal) crystal is a finite block of the corresponding infinite arrangement, the symmetry of which is a space group and thus contains translations. Here, this

¹¹ For *maximal* subgroups, a calculation of the conjugacy classes is not necessary because these are indicated in the subgroup tables of Part 2 of this volume by braces to the left of the data sets for the low-index subgroups and by text for the series of isomorphic subgroups. For non-maximal subgroups, the conjugacy relations are not indicated but can be calculated in the way described here. They are also available online on the Bilbao Crystallographic Server, <http://www.cryst.ehu.es/>, under the program *Subgroupaph*.

¹² A phase transition is non-ferroelastic if the space groups \mathcal{G} of the high-symmetry phase **A** and \mathcal{H}_j of the low-symmetry phase **B** belong to the *same crystal family*, of which there are six: triclinic, monoclinic, orthorhombic, tetragonal, trigonal–hexagonal and cubic. In ferroelastic phase transitions the space groups \mathcal{G} of **A** and \mathcal{H}_j of **B** belong to different crystal families. Only then can spontaneous strain components occur. They are avoided by the assumption of the PCA.

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(infinite) periodic object is called a *crystal pattern*, cf. Section 1.2.2.1. Each domain belongs to a crystal pattern.

Definition 1.2.7.2.1. The set of all domains which belong to the same crystal pattern forms a *domain state* \mathbf{B}_j . The domains of one domain state occupy different regions of space and are part of the *same* crystal pattern: to each domain state \mathbf{B}_j belongs a crystal pattern. \square

From the viewpoint of symmetry, different domains of the same domain state cannot be distinguished. The following considerations concern domain states and thus indirectly their constituents, the domains.

The number of domain states that may be observed in the distorted phase \mathbf{B} is limited and determined by the space groups \mathcal{G} and \mathcal{H}_j . The number of domains that belong to the same domain state is not limited. The diversity of the domains and their shapes is due to mechanical stresses, defects, electrical charges and nucleation phenomena, which strongly influence the kinetics of the phase transition; see, for example, Fig. 3.4.1.1 in *IT D*.

A trivial domain structure is formed when phase \mathbf{B} consists of one domain only, i.e. when it forms a *single-domain structure*. This is possible, for example, in nanocrystals (Chen *et al.*, 1997) and in particular under an external electric field or under external stress, and is stable under zero field and zero stress (detwinning). For a phase transition of the type considered, the different domain states have the same *a priori* probability of appearing in the distorted phase. In reality not all of them may be observed and/or their relative frequencies and sizes may be rather different.

In order to calculate the number of possible domain states, the space group \mathcal{G} will be decomposed into cosets relative to its subgroup \mathcal{H}_1 , which is the space group of the domain state \mathbf{B}_1 ,

$$\mathcal{G} = \mathcal{H}_1 \cup \dots \cup g_j \mathcal{H}_1 \cup \dots \cup g_i \mathcal{H}_1.$$

The elements $g_1 = e, \dots, g_j, \dots, g_i$ of \mathcal{G} are the coset representatives. The elements h_r of \mathcal{H}_1 map the domain state \mathbf{B}_1 onto itself, $h_r \mathbf{B}_1 = \mathbf{B}_1$, $h_r \in \mathcal{H}_1$. The elements of the other cosets map \mathbf{B}_1 onto the other domain states, for example, $g_j \mathbf{B}_1 = \mathbf{B}_j$.¹³

It follows:

Lemma 1.2.7.2.2. The number N of possible domain states of phase \mathbf{B} is equal to the index i of \mathcal{H}_1 in \mathcal{G} , $N = |\mathcal{G} : \mathcal{H}_1| = [i]$. \square

Having determined the number of domain states, we turn to their space groups, i.e. to the space groups of their crystal patterns.

From $\mathbf{B}_1 = h_r \mathbf{B}_1$ for any $h_r \in \mathcal{H}_1$, written as $\mathcal{H}_1 \mathbf{B}_1 = \mathbf{B}_1$, and $\mathbf{B}_j = g_j \mathbf{B}_1$ or $\mathbf{B}_1 = g_j^{-1} \mathbf{B}_j$, we conclude that $g_j^{-1} \mathbf{B}_j = \mathcal{H}_1 \mathbf{B}_1 = \mathcal{H}_1 g_j^{-1} \mathbf{B}_j$ or $\mathbf{B}_j = g_j \mathcal{H}_1 g_j^{-1} \mathbf{B}_j$.

This means: the space group $g_j \mathcal{H}_1 g_j^{-1}$ leaves the domain state \mathbf{B}_j invariant and is a subgroup of \mathcal{G} which is conjugate to \mathcal{H}_1 for any value of j .

For the classification of the domain states according to their space groups we now introduce the term *symmetry state*.

Definition 1.2.7.2.3. A *symmetry state* is a set of all domain states (crystal patterns) the space groups of which are identical. \square

¹³ The multiplication $h_r \mathbf{B}_1$ etc. is the performance of a symmetry operation h_r on the crystal pattern of the domain state \mathbf{B}_1 . Usually, the matrix of h_r is applied to the coordinates of the atoms of the crystal pattern of \mathbf{B}_1 . A symmetry operation of \mathbf{B}_1 maps the crystal pattern onto itself; another motion maps it onto another crystal pattern.

Domains of the same domain state always belong to the same symmetry state. Domains of different domain states may or may not belong to the same symmetry state. The number N_S of symmetry states is determined by the normalizer $\mathcal{N}_{\mathcal{G}}(\mathcal{H}_1)$ of \mathcal{H}_1 in \mathcal{G} .

Let $\mathcal{N}_{\mathcal{G}}(\mathcal{H}_1)$ be the normalizer of the space group \mathcal{H}_1 in the space group \mathcal{G} . Then $\mathcal{G} \supseteq \mathcal{N}_{\mathcal{G}}(\mathcal{H}_1) \supseteq \mathcal{H}_1$ with the indices $|\mathcal{G} : \mathcal{H}_1| = [i]$ and $|\mathcal{G} : \mathcal{N}_{\mathcal{G}}(\mathcal{H}_1)| = [i_S]$ with $i_S \leq i$. By Lemma 1.2.7.2.2 the number $N = |\mathcal{G} : \mathcal{H}_1|$ of domain states is determined. For the number N_S of symmetry states the following lemma holds:

Lemma 1.2.7.2.4. The number N_S of *symmetry states* for the transition $\mathbf{A} \rightarrow \mathbf{B}$ with space groups \mathcal{G} and \mathcal{H}_j is $|\mathcal{G} : \mathcal{N}_{\mathcal{G}}(\mathcal{H}_1)| = [i_S] = N_S \leq N$. To each symmetry state there belong $d_s = N : N_S$ domain states, i.e. $d_s \cdot N_S = N$, cf. *IT D*, Section 3.4.2.4.1. \square

In a group-subgroup relation such as that between \mathcal{G} and \mathcal{H}_j , \mathcal{H}_j has in general lost translations as well as non-translational symmetry operations. Thus, for the translation subgroups (the lattices) $\mathcal{T}_{\mathcal{G}} \geq \mathcal{T}_{\mathcal{H}_j}$ holds, and for the point groups $\mathcal{P}_{\mathcal{G}} \geq \mathcal{P}_{\mathcal{H}_j}$ holds. Then a uniquely determined space group \mathcal{M}_j exists, called *Hermann's group*, such that \mathcal{M}_j has the translations of \mathcal{G} and the point group of \mathcal{H}_j , *IT D*, Example 3.2.3.32. The group \mathcal{M}_j can thus be characterized as that *translationengleiche* subgroup of \mathcal{G} which is simultaneously a *klassengleiche* supergroup of \mathcal{H}_j . For general subgroups $\mathcal{G} > \mathcal{M}_j > \mathcal{H}_j$, for *translationengleiche* subgroups $\mathcal{H}_j = \mathcal{M}_j < \mathcal{G}$ and for *klassengleiche* subgroups $\mathcal{H}_j < \mathcal{M}_j = \mathcal{G}$ holds.

For the corresponding indices one finds by coset decomposition the following lemma, see *IT D*, equation (3.2.3.91).

Lemma 1.2.7.2.5. The index i of \mathcal{H}_j in \mathcal{G} can be factorized into the point-group part i_p and the lattice part i_L : $|\mathcal{G} : \mathcal{H}_j| = i = |\mathcal{G} : \mathcal{M}_j| \cdot |\mathcal{M}_j : \mathcal{H}_j| = i_p \cdot i_L$. \square

In the continuum description the lattices are ignored and only the relation between the point groups is considered. Because \mathcal{M}_j is a *translationengleiche* subgroup of \mathcal{G} , the index of \mathcal{M}_j in \mathcal{G} is the same as the index i_p of the point group of \mathcal{H}_j in the point group of \mathcal{G} .

In many cases one is only interested in the orientation of the domain states of a domain structure in the space. These orientations are determined by the crystal patterns and may be taken also from the values of the components of the property tensors of the domain states. A classification of the domain states according to their orientations into classes which shall be called *directional states* may be achieved in the following way.

Definition 1.2.7.2.6. A *directional state* is a set of all domain states that are parallel to each other. \square

Parallel domain states (crystal patterns) have space groups with the same point group and the same lattice; they are distinguished only by the locations of the conventional origins. If \mathbf{B}_1 and $\mathbf{B}_j = g_j \mathbf{B}_1$ are parallel, then the coset representative g_j is a translation and \mathcal{H}_j and \mathcal{H}_1 are *klassengleiche* subgroups of \mathcal{M}_1 . Both subgroups have also the same translations because a translation g_j commutes with all translations and thus leaves $\mathcal{T}(\mathcal{H}_1)$ invariant, see Examples 1.2.7.3.2 and 1.2.7.3.3.

To determine the number of directional states, we consider the coset decomposition of \mathcal{G} relative to Hermann's group \mathcal{M}_1 . Each coset of the decomposition $\mathcal{G} : \mathcal{M}_1$ maps the domain state \mathbf{B}_1

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onto a domain state \mathbf{B}_j with another directional state which results in the following lemma:

Lemma 1.2.7.2.7. The number of directional states in the transition $\mathbf{A} \rightarrow \mathbf{B}$ with space groups \mathcal{G} and \mathcal{H}_1 is $|\mathcal{G} : \mathcal{M}_1|$, i.e. the index $[i_p]$ of \mathcal{M}_1 in \mathcal{G} . \square

The number of directional states does not depend on the type of description, whether microscopic or continuum, and is thus the same for both. Therefore, the microscopic description of the directional state may form a bridge between both kinds of description.

1.2.7.3. Examples

The terms just defined shall be explained in a few examples. In Example 1.2.7.3.1 a *translationengleiche* transition is considered; i.e. \mathcal{H} is a *translationengleiche* subgroup of \mathcal{G} . Because $\mathcal{M}_j = \mathcal{H}_j$, the relation between \mathcal{G} and \mathcal{H}_j is reflected by the relation between the space groups \mathcal{G} and \mathcal{M}_j and the results of the microscopic and continuum description correspond to each other.

Example 1.2.7.3.1

Perovskite BaTiO_3 exhibits a ferroelastic and ferroelectric phase transition from phase \mathbf{A} with the cubic space group $\mathcal{G} = Pm\bar{3}m$, No. 221, to phase \mathbf{B} with tetragonal space groups of type $\mathcal{H} = P4mm$, No. 99. Several aspects of this transition are discussed in IT D. Let \mathbf{B}_1 be one of the domain states of phase \mathbf{B} . Because the index $|\mathcal{G} : \mathcal{H}_1| = 6$, there are six domain states, forming three pairs of domain states which point with their tetragonal c axes along the cubic x , y and z axes of \mathcal{G} . Each pair consists of two antiparallel domain states of opposite polarization (ferroelectric domains), related by, for example, the symmetry plane perpendicular to the symmetry axes 4.

The six domain states also form six directional states because $\mathcal{H}_j = \mathcal{M}_j$ (antiparallel domain states belong to different directional states).

To find the space groups of the domain states, the normalizers have to be determined. For the perovskite transition, the normalizer $\mathcal{N}_{\mathcal{G}}(\mathcal{H}_1)$ can be obtained from the Euclidean normalizer $\mathcal{N}_{\mathcal{E}}$ of $P4mm$ in Table 15.2.1.4 of IT A, which is listed as P^14/mmm . This Euclidean normalizer has continuous translations along the z direction (indicated by the P^1 lattice part of the HM symbol) and is thus not a space group. However, all additional translations of P^14/mmm are not elements of the space group \mathcal{G} , and $\mathcal{N}_{\mathcal{G}}(\mathcal{H}_1) = (\mathcal{N}_{\mathcal{E}}(\mathcal{H}_1) \cap \mathcal{G}) = (P^14/mmm \cap Pm\bar{3}m) = P4/mmm$ is a subgroup of $Pm\bar{3}m$ with index 3 and with the lattice of $Pm\bar{3}m$ due to the PCA. There are thus three symmetry states, i.e. three subgroups of the type $P4mm$ with their fourfold axes directed along the z , x and y directions of the cubic space group \mathcal{G} . Two domain states (with opposite polar axes) belong to each of the three subgroups \mathcal{H}_j of type $P4mm$.

In Example 1.2.7.3.1, a phase transition was discussed which involves only *translationengleiche* group–subgroup relations and, hence, only directional relations between the domain states occur. Each domain state forms its own directional state. The following two examples treat *klassengleiche* transitions, i.e. \mathcal{H} is a *klassengleiche* subgroup of \mathcal{G} . Then $\mathcal{M}_j = \mathcal{G}$ and there is only one directional state: a *translational domain structure*, also called *translation twin*, is formed.

The domain states of a translational domain structure differ in the origins of their space groups because of the loss of translations of the parent phase in the phase transition.

Example 1.2.7.3.2

Let $\mathcal{G} = Fm\bar{3}m$, No. 225, with lattice parameter a and $\mathcal{H}_1 = Pm\bar{3}m$, No. 221, with the same lattice parameter a . The relation $\mathcal{H}_1 < \mathcal{G}$ is *klassengleiche* of index 4 and is found between the disordered and ordered modifications of the alloy AuCu_3 . In the disordered state, one Au and three Cu atoms occupy the positions of a cubic F lattice at random; in the ordered compound the Au atoms occupy the positions of a cubic P lattice whereas the Cu atoms occupy the centres of all faces of this cube. According to IT A, Table 15.2.1.4, the Euclidean normalizer of \mathcal{H}_1 is $\mathcal{N}_{\mathcal{E}}(\mathcal{H}_1) = Im\bar{3}m$ with lattice parameter a . The additional I -centring translations of $\mathcal{N}_{\mathcal{E}}(\mathcal{H}_1)$ are not translations of \mathcal{G} and thus $\mathcal{N}_{\mathcal{G}}(\mathcal{H}_1) = \mathcal{H}_1$. There are four domain states, each one with its own distinct space group \mathcal{H}_j , $j = 1, \dots, 4$, and symmetry state. The shifts of the conventional origins of \mathbf{B}_j relative to the origin of \mathbf{A} are $0, 0, 0$; $\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2}, 0, \frac{1}{2}$; and $0, \frac{1}{2}, \frac{1}{2}$. These shifts do not show up in the macroscopic properties of the domains but in the mismatch at the boundaries (antiphase boundaries) where different domains (antiphase domains) meet. This may be observed, for example, by high-resolution transmission electron microscopy (HRTEM), IT D, Section 3.3.10.6.

In the next example there are two domain states and both belong to the same space group, i.e. to the same symmetry state.

Example 1.2.7.3.3

There is an order–disorder transition of the alloy β -brass, CuZn . In the disordered state the Cu and Zn atoms occupy at random the positions of a cubic I lattice with space group $\mathcal{G} = Im\bar{3}m$, No. 229. In the ordered state, both kinds of atoms form a cubic primitive lattice P each, and one kind of atom occupies the centres of the cubes of the other, as in the CsCl crystal structure. Its space group is $\mathcal{H} = Pm\bar{3}m$, No. 221, which is a subgroup of index [2] of \mathcal{G} with the same cubic lattice parameter a . There are two domain states with their crystal structures shifted relative to each other by $\frac{1}{2}(\mathbf{a} + \mathbf{b} + \mathbf{c})$. The space group \mathcal{H} is a normal subgroup of \mathcal{G} and both domain states belong to the same symmetry state.

Up to now, only examples with *translationengleiche* or *klassengleiche* transitions have been considered. Now we turn to the domain structure of a *general* transition, where \mathcal{H} is a general subgroup of \mathcal{G} . General subgroups are never maximal subgroups and are thus not listed in this volume, but have to be derived from the maximal subgroups of each single step of the group–subgroup chain between \mathcal{G} and \mathcal{H} . In the following Example 1.2.7.3.4, the chain has two steps.

Example 1.2.7.3.4

β -Gadolinium molybdate, $\text{Gd}_2(\text{MoO}_4)_3$, is ferroelectric and ferroelastic. It was treated as an example from different points of view in IT D by Tolédano (Section 3.1.2.5.2) and by Janovec & Přívratská (Example 3.4.2.6). The high-temperature phase \mathbf{A} has space group $\mathcal{G} = P\bar{4}2_1m$, No. 113, and basis vectors \mathbf{a} , \mathbf{b} and \mathbf{c} . A phase transition to a low-temperature phase \mathbf{B} occurs with space-group type $\mathcal{H} = Pba2$, No. 32, basis vectors $\mathbf{a}' = \mathbf{a} - \mathbf{b}$, $\mathbf{b}' = \mathbf{a} + \mathbf{b}$ and $\mathbf{c}' = \mathbf{c}$. In addition to the reduction of the point-group symmetry the primitive unit cell is doubled. The PCA will be applied because the transition from the tetragonal to the orthorhombic crystal family would without the PCA allow $a' \neq b'$ for the lattice parameters. The index of \mathcal{H} in \mathcal{G} is $[i] = |P\bar{4}2_1m : Pba2| = 4$ such that there are four domain states. These relations are displayed in Fig. 1.2.7.1.