

1.2. GENERAL INTRODUCTION TO THE SUBGROUPS OF SPACE GROUPS

- (1) The translations of phase **B** are translations of phase **A**. Thus, the space group \mathcal{H} of **B** is a subgroup of the space group \mathcal{G} of **A**, $\mathcal{H} < \mathcal{G}$. Without the PCA, the translations of **B** would not be translations of **A** and, therefore, **H** would not be a subgroup of \mathcal{G} .
- (2) Under the PCA, the more complicated ferroelastic phases¹¹ display the same simple behaviour as the non-ferroelastic ones. Disturbances which otherwise would be caused in ferroelastic phase transitions do not appear because there is no spontaneous strain.

The domain walls, *i.e.* the boundaries which separate different domains, will not be treated here because their symmetries are layer groups which are two-periodic groups in three-dimensional space and not space groups with three-dimensional periodicity. Layer groups are described in *International Tables for Crystallography*, Vol. E (2002).

Under these assumptions the domains formed may exhibit different chiralities and polarities of their structures and different spatial orientations of their symmetry elements, but 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} .

In the discussion of domain structures, the following basic concepts are established: domain, domain state, symmetry state, orientation state. These concepts are defined and then applied in different examples of phase transitions in which the group-theoretical procedures and their results are explained.

The second step, the physically realistic situation at a temperature $T_x < T_C$ with the removal of the PCA, is only partly considered in this section. The relaxation of the PCA does not change the relations in a non-ferroelastic phase because all crystal regions suffer the same affine deformation. On the other hand, in ferroelastic phases the different spontaneous strains complicate the relations.

1.2.7.2. Domains, domain states and symmetry states

In a (continuous) phase transition with the symmetry reduction of the space group \mathcal{G} to a subgroup $\mathcal{H} < \mathcal{G}$, a splitting of the parent phase **A** into many crystals of the type **B** is observed. The number of such crystals of **B** is not limited; they differ in their locations in space, in their orientations, in their shapes and in their space groups which, however, all belong to the same space-group type. In order to describe what happens in such a transition, a few notions are useful. If not explicitly stated, the validity of the PCA is assumed.

Definition 1.2.7.2.1. A connected homogeneous part of a domain structure or of a twinned crystal with structure type **B** is called a *domain*. Each domain is a single crystal. The part of the space that is occupied by a domain is the *region* of that domain. \square

If the domains of phase **B** have been formed from a single crystal of phase **A**, then relations between the domains exist which are determined by group theory. In particular, the domains belong to a finite (small) number of domain states which have well defined relations to the original crystal **A** and its space group \mathcal{G} . In order

to describe the relation of **B** to **A**, 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 which contains translations. Here, this (infinite) periodic object is called a *crystal pattern*, *cf.* Section 1.2.2.1.

Definition 1.2.7.2.2. Two domains belong to the same *domain state* if their crystal patterns are identical, *i.e.* if they occupy different regions of space that are part of the *same* crystal pattern. In other words: a domain state is a crystal pattern. \square

The number of domain states which are observed after a phase transition is limited and determined by the space groups \mathcal{G} and \mathcal{H} . The number of domains which 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.

A trivial domain structure is formed when phase **B** consists of one domain only, *i.e.* when it forms a *single-domain structure*. This is possible, in particular under an external electric field or under external stress. Such a procedure is known as ‘detwinning’. The corresponding domain state is a *single-domain state*. For a phase transition of the type considered, there are always several single-domain states which have the same *a priori* probability of appearing after a phase transition. In reality not all of them will be observed and/or their relative frequencies and sizes will be rather different.

Single-domain states are introduced in theoretical considerations in order to avoid the complications which may be caused by the coexistence of domains with different spontaneous strain in ferroelastic crystals of the structure **B** if the PCA cannot be assumed. In polydomain structures, the domains would distort or rotate each other a little and thus disturb the simple relations described now. These disturbances do not occur in non-ferroelastic transitions, so for them the simple relations also hold in polydomain structures without the PCA.

Lemma 1.2.7.2.3. The number Z of possible domain states after a phase transition under the PCA is equal to the index i of \mathcal{H} in \mathcal{G} , $Z = |\mathcal{G} : \mathcal{H}| = [i]$. Let $\mathcal{G} = \mathcal{H}_1 \cup \dots \cup g_j \mathcal{H}_1 \cup \dots \cup g_i \mathcal{H}_1$ be the coset decomposition of \mathcal{G} relative to \mathcal{H}_1 , where $g_1 = e, \dots, g_i$ are the coset representatives, and \mathcal{H}_1 is the space group of the domain state **B**₁. The other domain states are obtained from **B**₁ by **B**_{*k*} = $g_k \mathbf{B}_1$, $k = 2, \dots, i$. For the space group \mathcal{H}_k of the domain state **B**_{*k*} the following holds: \mathcal{H}_k is obtained by conjugation of the space group \mathcal{H}_1 of **B**₁ with the same element g_k : $\mathcal{H}_k = g_k \mathcal{H}_1 g_k^{-1}$. \square

If in a group–subgroup relation $\mathcal{G} > \mathcal{H}_q$ with index i_q the subgroups \mathcal{H}_q belong to more than one conjugacy class, then each conjugacy class corresponds to a separate phase transition **A** \rightarrow **B**_{*k*}⁽¹⁾, **A** \rightarrow **B**_{*k*}⁽²⁾ *etc.* These different phase transitions lead to different low-symmetry structures **B**^(*m*), have different transition temperatures and different probabilities of happening.

There are more elements of the group \mathcal{G} than just g_k that map the domain state **B**₁ onto the domain state **B**_{*k*}. The elements of the space group \mathcal{H}_1 map the domain state of **B**₁ onto itself: $h_m \mathbf{B}_1 = \mathbf{B}_1$, $h_m \in \mathcal{H}_1$. Therefore, not just the element g_k but all elements $g_k h_m$ of the coset $g_k \mathcal{H}_1$ map the domain state of **B**₁ onto the domain state **B**_{*k*}: **B**_{*k*} = $g_k \mathcal{H}_1 \mathbf{B}_1 = g_k \mathbf{B}_1$. This can be expressed in the form:

There is a one-to-one correspondence between the cosets of the decomposition $(\mathcal{G} : \mathcal{H}_1)$ and the possible domain states which may be observed after the transition.

¹¹ A phase transition is called non-ferroelastic if the space groups \mathcal{G} and \mathcal{H} belong to the same crystal family, of which there are six: triclinic, monoclinic, orthorhombic, tetragonal, trigonal–hexagonal and cubic. A phase transition is called ferroelastic if the strain tensor of the low-symmetry phase **B** has more independent components than the strain tensor of the high-symmetry phase **A**. This can only happen if the space groups \mathcal{G} of **A** and \mathcal{H} of **B** belong to different crystal families. In this case, the additional components of the strain tensor of **B** are called *spontaneous strain-tensor components* or *components of the spontaneous deformation*.

Similarly, all elements $g_k h_m$ map the space group \mathcal{H}_1 onto \mathcal{H}_k by conjugation: $\mathcal{H}_k = g_k h_m \mathcal{H}_1 h_m^{-1} g_k^{-1} = g_k \mathcal{H}_1 g_k^{-1}$.

Note that due to these formulae the i different domain states do not necessarily belong to i different space groups and that *different* domain states may belong to the *same* space group, cf. Lemma 1.2.7.2.6 and Example 1.2.7.2.4.

The terms just defined shall be explained in a few examples. By Example 1.2.7.2.4 a *translationengleiche* transition is displayed; i.e. \mathcal{H} is a *translationengleiche* subgroup of \mathcal{G} . Then the relation between \mathcal{G} and \mathcal{H} is essentially reflected by the relation between the point groups $\mathcal{P}_{\mathcal{G}}$ and $\mathcal{P}_{\mathcal{H}}$.

Example 1.2.7.2.4.

Perovskite BaTiO₃ exhibits a ferroelastic and ferroelectric phase transition from cubic to tetragonal, phase **A** with space group $\mathcal{G} = Pm\bar{3}m$, No. 221, and phase **B**₁ with a *translationengleiche* subgroup $\mathcal{H}_1 = P4mm$, No. 99. 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). These two domain states belong to the same space group of the type $P4mm$, i.e. the domains of each pair belong to the same symmetry state according to the following definition:

Definition 1.2.7.2.5. Two domains belong to the same *symmetry state* if their space groups are identical. \square

Note that here as in many other places of this section one has to distinguish strictly between ‘space group’ as a specimen, e.g. in ‘space group of a crystal’, and ‘space-group type’, which is one of the 230 classes frequently called simply but inexactly ‘the 230 space groups’, see the last paragraph of Section 1.2.5.3.

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 of symmetry states is limited and is smaller than or equal to the number of domain states. Moreover, the number of symmetry states is determined by the space groups \mathcal{G} and \mathcal{H} .

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 $\mathcal{G} \geq \mathcal{N}_{\mathcal{G}}(\mathcal{H}_1) \supseteq \mathcal{H}_1$ with the indices $|\mathcal{G} : \mathcal{H}_1| = [i]$ and $|\mathcal{G} : \mathcal{N}_{\mathcal{G}}(\mathcal{H}_1)| = [i_N]$ with $i_N \leq i$. By Lemma 1.2.7.2.3, the number $[i] = |\mathcal{G} : \mathcal{H}_1|$ of domain states is determined. For the number of symmetry states the following lemma holds:

Lemma 1.2.7.2.6. The number of symmetry states for the transition **A** \rightarrow **B** with space groups \mathcal{G} and \mathcal{H} is $|\mathcal{G} : \mathcal{N}_{\mathcal{G}}(\mathcal{H})| = i_N \leq i$. To each symmetry state there belong $d_i = i : i_N$ domain states, i.e. $d_i \cdot i_N = i$, cf. Janovec & Přívratská (2003). \square

For the perovskite transition of Example 1.2.7.2.4, the normalizer $\mathcal{N}_{\mathcal{G}}(\mathcal{H}_1)$ can be obtained from the Euclidean normalizer 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 $Pm\bar{3}m$. Because of the index 3 of $\mathcal{N}_{\mathcal{G}}(\mathcal{H}_1)$ in \mathcal{G} , there are three conjugate subgroups of the type $P4mm$ with their fourfold axes directed along the z , x and y directions of the cubic space group \mathcal{G} . The group \mathcal{H}_1 is a subgroup of index 2 of $\mathcal{N}_{\mathcal{G}}(\mathcal{H}_1)$. Therefore, two domain states (with opposite polar axes)

belong to each of the subgroups \mathcal{H}_j of the space-group type $P4mm$.

In reality, i.e. without the PCA, the additional degree of freedom c/a in tetragonal space groups leads to a metrical inequivalence of the directions of the fourfold axis and the axes perpendicular to it, due to the spontaneous strain. If this ‘true physical situation’ is considered, the 90° angles between the fourfold axes of the domains of different pairs will change slightly because of the ferroelastic tetragonal deformation with subsequent small rotations of the domains. The antiparallel nature of each of the three domain pairs, however, is preserved because they exhibit the same symmetry state, i.e. belong to the same space group.

The space groups \mathcal{G} and \mathcal{H} in the phase transition in perovskites, cf. Example 1.2.7.2.4, are *translationengleiche*. Therefore, $\mathcal{T}(\mathcal{G}) = \mathcal{T}(\mathcal{H})$, and the coset decomposition $(\mathcal{G} : \mathcal{H})$ of the space groups corresponds to the coset decomposition $(\mathcal{P}_{\mathcal{G}} : \mathcal{P}_{\mathcal{H}})$ of their point groups, cf. Section 1.2.6.2. Indeed, in the literature the perovskite transition is nearly always treated using point groups. Other than the *microscopic description* by space groups, the description by point groups is called the *macroscopic* or *continuum description*. Because there are no translations involved, the continuum approach does not require the PCA at all; the point group $4mm$ is for any translations of phase **B** a subgroup of the point group $m\bar{3}m$. However, the spontaneous strains will appear in this ferroelastic transition and will cause the complications mentioned at the end of Section 1.2.7.1 and in the paragraph preceding Lemma 1.2.7.2.3. For non-ferroelastic *translationengleiche* transitions, the application of point groups and of space groups yields equivalent results.

Example 1.2.7.2.4 presents an opportunity to mention another feature of this phase transition which, however, will not be discussed further. The group \mathcal{H}_1 is not a maximal subgroup of \mathcal{G} but $\mathcal{G} > \mathcal{Z}_1 > \mathcal{H}_1$ with $\mathcal{Z}_1 = P4/mmm$ of index 3 in $\mathcal{G} = m\bar{3}m$ and \mathcal{H}_1 of index 2 in \mathcal{Z}_1 . Such ‘intermediate’ domain states between **A** and **B**, like the domain state with the space group \mathcal{Z}_1 , are called *secondary domain states* for thermodynamic reasons. They do not appear in the transition but \mathcal{Z}_1 is the symmetry of the spontaneous strain in the domain state with space group \mathcal{H}_1 . Accidentally, in the present example $\mathcal{Z}_1 = \mathcal{N}_{\mathcal{G}}(\mathcal{H}_1)$ holds. Secondary domain states are treated by Janovec & Přívratská (2003).

1.2.7.3. Translational domain structures (translation twins)

In Example 1.2.7.2.4, a phase transition was discussed which involves only *translationengleiche* group–subgroup relations and, hence, only orientational relations between the domains. The following two examples treat *klassengleiche* transitions, i.e. \mathcal{H} is a *klassengleiche* subgroup of \mathcal{G} , and *translational domain structures*, also called *translation twins*, may appear.

Translational domain structures consist of domains which are parallel, i.e. have the same orientation of their structures (and thus of their lattices) but differ in their location because of the loss of translations of the parent phase in the phase transition. The origins of the larger unit cells of the phase **B** with subgroup \mathcal{H} may coincide with any of the origins of the smaller unit cells of the parent structure **A** with space group \mathcal{G} . Again the number of such domain states is equal to the index of \mathcal{H} in \mathcal{G} , $[i] = |\mathcal{G} : \mathcal{H}|$; the number of symmetry states is $[i_N] = |\mathcal{G} : \mathcal{N}_{\mathcal{G}}(\mathcal{H})|$.

Example 1.2.7.3.1.

Let $\mathcal{G} = Fm\bar{3}m$, No. 225, with lattice parameter a and $\mathcal{H} = Pm\bar{3}m$, No. 221, with the same lattice parameter a . The relation $\mathcal{H} < \mathcal{G}$ is of index 4 and is found between the disordered and ordered modifications of the alloy AuCu₃. In the disor-