

1. SPACE GROUPS AND THEIR SUBGROUPS

union $\mathcal{T}_g \cup (\mathcal{T}_g (t_a \bar{1}_0))$. There are thus two maximal isomorphic subgroups of index 2 which are obtained by doubling the a lattice parameter. There are altogether 14 isomorphic subgroups of index 2 for any space group of type $P\bar{1}$ which are obtained by seven different cell enlargements.

If \mathcal{G} belongs to a pair of enantiomorphic space-group types, then the isomorphic subgroups of \mathcal{G} may belong to different crystallographic space-group types with different HM symbols and different space-group numbers. In this case, an infinite number of subgroups belong to the crystallographic space-group type of \mathcal{G} and another infinite number belong to the enantiomorphic space-group type.

Example 1.2.6.2.7.

Space group $P4_1$, No. 76, has for any prime number $p > 2$ an isomorphic maximal subgroup of index p with the lattice parameters a, b, pc . This is an infinite number of subgroups because there is an infinite number of primes. The subgroups belong to the space-group type $P4_1$ if $p \equiv 1 \pmod{4}$; they belong to the type $P4_3$ if $p \equiv 3 \pmod{4}$.

Definition 1.2.6.2.8. A subgroup of a space group is called *general* or a *general subgroup* if it is neither a *translationengleiche* nor a *klassengleiche* subgroup. It has lost translations as well as linear parts, *i.e.* point-group symmetry. \square

Example 1.2.6.2.9.

The subgroup \mathcal{T}_g in Example 1.2.6.2.6 has lost all inversions of the original space group $P\bar{1}$ as well as all translations with odd u . It is a general subgroup $P1$ of the space group $P\bar{1}$ of index 4.

1.2.6.3. The role of normalizers for group–subgroup pairs of space groups

In Section 1.2.4.5, the normalizer $\mathcal{N}_{\mathcal{G}}(\mathcal{H})$ of a subgroup $\mathcal{H} < \mathcal{G}$ in the group \mathcal{G} was defined. The equation $\mathcal{H} \triangleleft \mathcal{N}_{\mathcal{G}}(\mathcal{H}) \leq \mathcal{G}$ holds, *i.e.* \mathcal{H} is a normal subgroup of $\mathcal{N}_{\mathcal{G}}(\mathcal{H})$. The normalizer $\mathcal{N}_{\mathcal{G}}(\mathcal{H})$, by its index in \mathcal{G} , determines the number $N_j = |\mathcal{G} : \mathcal{N}_{\mathcal{G}}(\mathcal{H})|$ of subgroups $\mathcal{H}_j < \mathcal{G}$ that are conjugate in the group \mathcal{G} , *cf.* Remarks (2) and (3) below Definition 1.2.4.5.1.

The group–subgroup relations between space groups become more transparent if one looks at them from a more general point of view. Space groups are part of the general theory of mappings. Particular groups are the *affine group* \mathcal{A} of all reversible affine mappings, the *Euclidean group* \mathcal{E} of all isometries, the *translation group* \mathcal{T} of all translations and the *orthogonal group* \mathcal{O} of all orthogonal mappings.

Connected with any particular space group \mathcal{G} are its group of translations $\mathcal{T}(\mathcal{G})$ and its point group $\mathcal{P}_{\mathcal{G}}$. In addition, the normalizers $\mathcal{N}_{\mathcal{A}}(\mathcal{G})$ of \mathcal{G} in the affine group \mathcal{A} and $\mathcal{N}_{\mathcal{E}}(\mathcal{G})$ in the Euclidean group \mathcal{E} are useful. They are listed in Section 15.2.1 of *IT A*. Although consisting of isometries only, $\mathcal{N}_{\mathcal{E}}(\mathcal{G})$ is not necessarily a space group, see the paragraph below Lemma 1.2.7.2.6.

For the group–subgroup pairs $\mathcal{H} < \mathcal{G}$ the following relations hold:

$$(1) \mathcal{T}(\mathcal{H}) \leq \mathcal{H} \leq \mathcal{N}_{\mathcal{G}}(\mathcal{H}) \leq \mathcal{G} \leq \mathcal{N}_{\mathcal{E}}(\mathcal{G}) < \mathcal{E};$$

$$(1a) \mathcal{H} \leq \mathcal{N}_{\mathcal{G}}(\mathcal{H}) \leq \mathcal{N}_{\mathcal{E}}(\mathcal{H}) < \mathcal{E};$$

$$(1b) \mathcal{N}_{\mathcal{E}}(\mathcal{H}) \leq \mathcal{N}_{\mathcal{A}}(\mathcal{H}) < \mathcal{A};$$

$$(2) \mathcal{T}(\mathcal{H}) \leq \mathcal{T}(\mathcal{G}) < \mathcal{T} < \mathcal{E};$$

$$(3) \mathcal{T}(\mathcal{G}) \leq \mathcal{G} \leq \mathcal{N}_{\mathcal{E}}(\mathcal{G}) \leq \mathcal{N}_{\mathcal{A}}(\mathcal{G}) < \mathcal{A}.$$

The subgroup \mathcal{H} may be a *translationengleiche* or a *klassengleiche* or a general subgroup of \mathcal{G} . In any case, the normalizer $\mathcal{N}_{\mathcal{G}}(\mathcal{H})$ 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 1.2.7.¹⁰

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* (2002), Section 15.2.1.

1.2.7. Application to domain structures

1.2.7.1. Introductory remarks

In this section, the group-theoretical aspects of domain (twin) formation (domain structure, transformation twin) from a homogeneous single crystal (phase **A**, parent phase) to a crystalline phase **B** (daughter phase, deformed phase) are discussed, where the space group \mathcal{H} of phase **B** is a subgroup of the space group \mathcal{G} of phase **A**, $\mathcal{H} < \mathcal{G}$. This happens, *e.g.*, in a displacive or order–disorder phase transition. In most cases phase **B**, the *domain structure*, is inhomogeneous, consisting of homogeneous regions which are called *domains*, defined below.

Only the basic group-theoretical relations are considered here. A deeper discussion of domain structures and their properties needs methods using representation theory, thermodynamic points of view (Landau theory), lattice dynamics and tensor properties of crystals. Such treatments are beyond the scope of this section. A detailed discussion of them is given by Tolédano *et al.* (2003) and by Janovec & Přívratská (2003).

In order to make the group-theoretical treatment possible, the *parent-clamping approximation*, abbreviated PCA, is introduced, by which the lattice parameters of phase **A** are not allowed to change at and after the transition to phase **B**, *cf.* Janovec & Přívratská (2003). Under the assumption of the PCA, two essential conditions hold:

¹⁰ 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 *Subgroupgraph*.

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- (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 **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*.

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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-

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dered state, one Au and three Cu atoms occupy the positions of a cubic F -lattice statistically; 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} is $\mathcal{N}_{\mathcal{E}}(\mathcal{H}) = Im\bar{3}m$ with lattice parameter a . The additional I centring translations of $\mathcal{N}_{\mathcal{E}}(\mathcal{H})$ are not translations of \mathcal{G} and thus $\mathcal{N}_{\mathcal{G}}(\mathcal{H}) = \mathcal{H}$. There are four domain states, each one with its own distinct space group and symmetry state \mathcal{H}_j , $j = 1, \dots, 4$, and consequently its own conventional origin relative to the origin of the disordered crystal \mathbf{A} with the space group \mathcal{G} . The origin shifts 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. Indeed, one is normally neither interested in those translations of \mathcal{G} which are lost in the transition to the subgroup \mathcal{H} , nor in the position of the conventional origin of \mathbf{B} relative to that of \mathbf{A} but only in the orientation of the domain states \mathbf{B}_k . If so, the observed relations are not governed by the space groups \mathcal{G} and \mathcal{H} but by \mathcal{G} and Hermann's group \mathcal{M} , $\mathcal{G} \geq \mathcal{M} \geq \mathcal{H}$, cf. Lemma 1.2.8.1.2. The group \mathcal{M} is uniquely determined as the space group with the translations of \mathcal{G} and the point-group operations of \mathcal{H} . The group \mathcal{M} can thus be characterized as that *translationengleiche* subgroup of \mathcal{G} which is at the same time a *klassengleiche* supergroup of \mathcal{H} . This group \mathcal{M} plays a role in the practical treatment of domains. It was applied to domain structures first by Janovec (1976).

In the current literature, the following considerations are mostly restricted to the point groups of the phases involved. In the following, the use of Hermann's group \mathcal{M} is discussed in parallel with the normal use of the point groups. The (admittedly rather abstract) discussion may thus be unfamiliar to the reader. Nevertheless, it is offered here because it opens up the possibility of treating phase transitions on a microscopic or atomistic level, whereas the point-group approach can only deal with the continuum or macroscopic aspect. The microscopic approach is necessary in particular when discussing domain boundaries, which will not be done here.

Definition 1.2.7.3.2. Two domain states \mathbf{B}_1 and \mathbf{B}_k with space groups \mathcal{H}_1 and \mathcal{H}_k and point groups $\mathcal{P}_{\mathcal{H}_1}$ and $\mathcal{P}_{\mathcal{H}_k}$ have the *same orientation state* if their orientation is identical, *i.e.* if the linear part of the operation $g_k \in \mathcal{G}$ of Lemma 1.2.7.2.3 is the identity operation. This means that $g_k \in \mathcal{G}$ is a translation $t \in \mathcal{T}$ and implies that the point groups of \mathbf{B}_1 and \mathbf{B}_k are the same: $\mathcal{P}_{\mathcal{H}_1} = \mathcal{P}_{\mathcal{H}_k}$. Thus the space groups \mathcal{H}_1 and \mathcal{H}_k are subgroups of the same space group \mathcal{M} . \square

Lemma 1.2.7.3.3. The number of orientation states in the transition $\mathbf{A} \rightarrow \mathbf{B}$ with space groups $\mathcal{G} \rightarrow \mathcal{H}_m$ is $|\mathcal{G} : \mathcal{M}_m|$, *i.e.* the index of \mathcal{M}_m in \mathcal{G} , where \mathcal{M}_m is Hermann's group in the sequence $\mathcal{G} \geq \mathcal{M}_m \geq \mathcal{H}_m$. These orientation states belong to $|\mathcal{G} : \mathcal{N}_{\mathcal{G}}(\mathcal{M}_m)|$ space groups. The number of domain states which belong to the same orientation state is $|\mathcal{M}_m : \mathcal{H}_m|$, *i.e.* the index of \mathcal{H}_m in \mathcal{M}_m . \square

In Example 1.2.7.3.1 of AuCu_3 , $\mathcal{G} = \mathcal{M}_1$ because \mathcal{H}_1 is a *klassengleiche* subgroup of \mathcal{G} . Therefore, $|\mathcal{G} : \mathcal{M}_1| = 1$ and all four domain states belong to the same orientation state. This is obvious visually, because, as stated above, all four domain states are parallel and only shifted against each other.

Lemma 1.2.7.3.4. Because of the isomorphism $(\mathcal{G} : \mathcal{M}) \cong (\mathcal{P}_{\mathcal{G}} : \mathcal{P}_{\mathcal{H}})$ between the factor groups $(\mathcal{G} : \mathcal{M})$ and $(\mathcal{P}_{\mathcal{G}} : \mathcal{P}_{\mathcal{H}})$, the

results of the application of the groups \mathcal{G} and \mathcal{M} are the same as the results of the application of the groups $\mathcal{P}_{\mathcal{G}}$ and $\mathcal{P}_{\mathcal{H}}$. The latter application is called the 'continuum approach to phase transitions' which is nearly always applied in practice. \square

Lemma 1.2.7.3.3 is the microscopic formulation of the (macroscopic) continuum treatment of phase transitions and forms the bridge from the (macroscopic) continuum to the (microscopic) atomistic approach to phase transitions.

Example 1.2.7.3.5.

There is an order-disorder transition of the alloy β -brass, CuZn . In the disordered state the Cu and Zn atoms occupy statistically 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, such that a space group $Pm\bar{3}m$, No. 221, is formed, see also Example 1.3.3.1. For the space groups the relation $\mathcal{G} = Im\bar{3}m > \mathcal{H} = Pm\bar{3}m$ of index 2 holds with the same cubic lattice parameter a . In this case, $\mathcal{G} = \mathcal{N}_{\mathcal{E}}(\mathcal{H})$, see *IT A*, Table 15.2.1.4. As the index $|\mathcal{G} : \mathcal{H}| = 2$, there are two domain states with their crystal structures shifted relative to each other by $\frac{1}{2}(\mathbf{a} + \mathbf{b} + \mathbf{c})$. Thus, both domain states belong to the same orientation state. This also follows from $\mathcal{G} = \mathcal{M}$. Because $\mathcal{G} = \mathcal{N}_{\mathcal{G}}(\mathcal{H})$ and thus $|\mathcal{G} : \mathcal{N}_{\mathcal{G}}(\mathcal{H})| = 1$, there is one symmetry state, and both domain states belong to the same space group.

1.2.7.4. Domain structures of a general phase transition

Up to now, the examples have been concerned either with *translationengleiche* or with *klassengleiche* transitions only. In this section, the domain structure of a *general* transition will be considered, *i.e.* a transition where \mathcal{H} is a general subgroup of \mathcal{G} . General subgroups are 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 1.2.7.4.2, the chain has two steps. The results obtained under the PCA and without it are different and, therefore, will be discussed in some detail. Example 1.2.7.4.2 further shows how the subgroup data of this volume can be used for the analysis of continuous or quasi-continuous phase transitions.

We start with a lemma for general subgroups which contains the results of Lemmata 1.2.7.3.3 and 1.2.7.3.4.

Lemma 1.2.7.4.1. For general subgroups, owing to the existence of the group \mathcal{M} of Hermann, it always holds that $|\mathcal{G} : \mathcal{H}| = |\mathcal{G} : \mathcal{M}| \cdot |\mathcal{M} : \mathcal{H}| = |\mathcal{P}_{\mathcal{G}} : \mathcal{P}_{\mathcal{H}}| \cdot |\mathcal{T}(\mathcal{G}) : \mathcal{T}(\mathcal{H})| = i_P \cdot i_T$. Here i_P is the index of the point groups of \mathcal{G} and \mathcal{H} and i_T is the index of the translation subgroups of \mathcal{G} and \mathcal{H} . \square

Example 1.2.7.4.2.

β -Gadolinium molybdate, $\text{Gd}_2(\text{MoO}_4)_3$, is ferroelectric and ferroelastic. 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} . At $T_C \sim 433$ K, 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 $\mathbf{c}' = \mathbf{c}$. The group \mathcal{M} , $\mathcal{G} > \mathcal{M} > \mathcal{H}$ is of the type $Cmm2$ with the lattice parameters of \mathcal{H} . The index of \mathcal{H} in \mathcal{G} is $i = |P\bar{4}2_1m : Pba2| = 4$. A factor of 2 stems from the reduction $i_P = |\mathcal{G} : \mathcal{M}| = 2$ and leads to two orientation states. The other factor of 2 is caused by the loss of half of the translations, because $i_T = |\mathcal{M} : \mathcal{H}| = 2$.

In the continuum description, we consider the point groups and $|\bar{4}2m : mm2| = 2$. There is only one subgroup of $\bar{4}2m$ of the type $mm2$. Thus, the two orientation states belong to the same

point group. The orientation state \mathbf{B}_2 is obtained from \mathbf{B}_1 by the (lost) $\bar{4}$ operation of $\bar{4}2m$.

This is the *macroscopic* or *continuum treatment*; it is the most common treatment of domains in phase transitions. In reality, *i.e.* lifting the PCA, due to the orthorhombic symmetry of phase \mathbf{B} the domains will be slightly distorted and rotated, and thus the symmetry planes of the two domain states are no longer parallel.

The full microscopic or atomistic treatment has to consider the crystal structures of phases \mathbf{A} and \mathbf{B} . Under the PCA, the length of a' and b' is $(2)^{1/2}a$, the content of the unit cell of \mathbf{B}_1 is twice that of \mathbf{A} . Because the index $[i] = 4$ there are four domain states \mathbf{B}_1 to \mathbf{B}_4 of $Pba2$. The domain state \mathbf{B}_2 is obtained from \mathbf{B}_1 by the (lost) $\bar{4}$ operation of $P\bar{4}2_1m$. The same holds for the pair \mathbf{B}_3 and \mathbf{B}_4 . Thus, \mathbf{B}_2 & \mathbf{B}_4 are rotated by 90° around a $\bar{4}$ centre in the $(a' b')$ plane with respect to the pair \mathbf{B}_1 & \mathbf{B}_3 , and the c' axes are antiparallel for \mathbf{B}_2 & \mathbf{B}_4 relative to those of \mathbf{B}_1 & \mathbf{B}_3 . The orientation state of the pair \mathbf{B}_1 & \mathbf{B}_3 is different from that of \mathbf{B}_2 & \mathbf{B}_4 . The two pairs \mathbf{B}_1 & \mathbf{B}_2 and \mathbf{B}_3 & \mathbf{B}_4 are shifted relative to each other by a (lost) translation of $P\bar{4}2_1m$, *e.g.* by $t(1, 0, 0)$ in the basis of $P\bar{4}2_1m$, corresponding to $t(\frac{1}{2}, \frac{1}{2}, 0)$ in the basis of $Pba2$.

To calculate the number of space groups $Pba2$, *i.e.* the number of symmetry states, one determines the normalizer of $Pba2$ in $P\bar{4}2_1m$. From IT A, Table 15.2.1.3, one finds $\mathcal{N}_{\mathcal{E}}(Pba2) = P^14/mmm$ for the Euclidean normalizer of $Pba2$ under the PCA, which includes the condition $a = b$. P^14/mmm is a supergroup of $P\bar{4}2_1m$. Thus, $\mathcal{N}_{\mathcal{G}}(Pba2) = (\mathcal{N}_{\mathcal{E}}(Pba2) \cap \mathcal{G}) = \mathcal{G}$ and $|\mathcal{G} : \mathcal{N}_{\mathcal{G}}(Pba2)| = |\mathcal{G} : \mathcal{G}| = 1$. Therefore, under the PCA all four domain states belong to one symmetry state, *i.e.* to one space group $Pba2$.

Analysing the group–subgroup relations between $P\bar{4}2_1m$ and $Pba2$ with the tables of this volume, one finds only one chain $P\bar{4}2_1m \rightarrow Cmm2 \rightarrow Pba2$. For $P\bar{4}2_1m$ only one maximal subgroup of type $Cmm2$ is listed, for which again only one maximal subgroup of type $Pba2$ is found, in agreement with the previous paragraph.

In reality, *i.e.* relaxing the PCA, the observations are made at temperatures $T_x < T_C$ where the lattice parameters deviate from those of phase \mathbf{A} and the basis no longer has tetragonal symmetry, but orthorhombic symmetry, $a' < b'$. The previous single space group now splits into *two* different space groups of type $Pba2$ with orthorhombic metrics at T_x , one belonging to the pair \mathbf{B}_1 & \mathbf{B}_3 , the other to \mathbf{B}_2 & \mathbf{B}_4 . The $(\mathbf{a}', \mathbf{b}')$ bases of these pairs are oriented perpendicular to each other and the c' axes of their domains are antiparallel. The loss of the centring translation of $Cmm2$ does not produce a new space group.

The number, two, of these space groups if the PCA is not valid can also be calculated in the usual way with the help of the normalizer. The Euclidean normalizer of $Pba2$ with $a' \neq b'$ is $\mathcal{N}_{\mathcal{E}}(Pba2) = P^1mmm$. This is an orthorhombic group with continuous translations along the c' direction. P^1mmm with $a' \neq b'$ is not really a subgroup of $P\bar{4}2_1m$ because the translations of $Pba2$ and thus of $Cmm2$ and P^1mmm are not strictly translations of $P\bar{4}2_1m$. The first three groups have orthorhombic lattices and the last a tetragonal one. However, by relaxing the PCA only gradually, the difference between the orthorhombic groups and the corresponding groups with tetragonal lattices is arbitrarily small. Therefore, one considers the sequence $\mathcal{G} > \mathcal{M} = \mathcal{N}_{\mathcal{G}}(\mathcal{H}) > \mathcal{H}$, *i.e.* $P\bar{4}2_1m > Cmm2 > Pba2$ as a group–subgroup chain, forms the intersection $(P^1mmm \cap P\bar{4}2_1m)$ as if the groups would have common translations, and finds $\mathcal{N}_{\mathcal{G}}(\mathcal{H}) = Cmm2$ with approxi-

mately the lattice parameters of $P\bar{4}2_1m$. The index $|P\bar{4}2_1m : Cmm2| = 2$, such that there are two space groups of type $Pba2$ which are approximately subgroups of $P\bar{4}2_1m$. To each of these space groups $Pba2$ belong two domain states of phase \mathbf{B} , see above.

This example shows that without the PCA, in order to cope with real observations, the terms ‘subgroup’, ‘intersection of groups’ *etc.* must not be used *sensu stricto* but have to be relaxed. The orthorhombic translations in this example are not group elements of \mathcal{G} but are slightly modified from the original translations of \mathcal{G} . All group–subgroup relations in crystal chemistry, *e.g.* diamond (C)–sphalerite (ZnS), as well as many phase transitions, as in this example, require such a ‘softened’ approach.

It turns out that the transition of $Gd_2(MoO_4)_3$ can be considered both under the PCA (allowing exact group-theoretical arguments) and under physically realistic arguments (which require certain relaxations of the group-theoretical methods). The results are different but the realistic approach can be developed by means of an increasing deviation from the PCA, starting from idealized but unrealistic considerations.

1.2.8. Lemmata on subgroups of space groups

There are several lemmata on subgroups $\mathcal{H} < \mathcal{G}$ of space groups \mathcal{G} which may help in getting an insight into the laws governing group–subgroup relations of plane and space groups. They were also used for the derivation and the checking of the tables of Part 2. These lemmata are proved or at least stated and explained in Chapter 1.5. They are repeated here as statements, separated from their mathematical background, and are formulated for the three-dimensional space groups. They are valid by analogy for the (two-dimensional) plane groups.

1.2.8.1. General lemmata

Lemma 1.2.8.1.1. A subgroup \mathcal{H} of a space group \mathcal{G} is a space group again, if and only if the index $i = |\mathcal{G} : \mathcal{H}|$ is finite. \square

In this volume, only subgroups of finite index i are listed. However, the index i is not restricted, *i.e.* there is no number I with the property $i < I$ for any i . Subgroups $\mathcal{H} < \mathcal{G}$ with infinite index are considered in *International Tables for Crystallography*, Vol. E (2002).

Lemma 1.2.8.1.2. Hermann’s theorem. For any group–subgroup chain $\mathcal{G} > \mathcal{H}$ between space groups there exists a uniquely defined space group \mathcal{M} with $\mathcal{G} \geq \mathcal{M} \geq \mathcal{H}$, where \mathcal{M} is a *translationengleiche* subgroup of \mathcal{G} and \mathcal{H} is a *klassengleiche* subgroup of \mathcal{M} . \square

The decisive point is that any group–subgroup chain between space groups can be split into a *translationengleiche* subgroup chain between the space groups \mathcal{G} and \mathcal{M} and a *klassengleiche* subgroup chain between the space groups \mathcal{M} and \mathcal{H} .

It may happen that either $\mathcal{G} = \mathcal{M}$ or $\mathcal{H} = \mathcal{M}$ holds. In particular, one of these equations must hold if $\mathcal{H} < \mathcal{G}$ is a maximal subgroup of \mathcal{G} .

Lemma 1.2.8.1.3. (Corollary to Hermann’s theorem.) A maximal subgroup of a space group is either a *translationengleiche* subgroup or a *klassengleiche* subgroup, never a general subgroup. \square

The following lemma holds for space groups but not for arbitrary groups of infinite order.

Lemma 1.2.8.1.4. For any space group, the number of subgroups with a given finite index i is *finite*. \square