1.6. Relating crystal structures by group–subgroup relations

By Ulrich Müller

1.6.1. Introduction

Symmetry relations using crystallographic group–subgroup relations have proved to be a valuable tool in crystal chemistry and crystal physics. Some important applications include:

(1) Structural relations between crystal-structure types can be worked out in a clear and concise manner by setting up family trees of group–subgroup relations (see following sections).
(2) Elucidation of problems concerning twinned crystals and antiphase domains (see Section 1.6.6).
(3) Changes of structures and physical properties taking place during phase transitions; applications of Landau theory (Aizu, 1970; Aroyo & Perez-Mato, 1998; Birman, 1966*a,b*, 1978; Cracknell, 1975; Howard & Stokes, 2005; Igartua *et al.*, 1996; Izyumov & Syromyatnikov, 1990; Landau & Lifshitz, 1980; Lyubarskii, 1960; Salje, 1990; Stokes & Hatch, 1988; Tolédano & Tolédano, 1987).
(4) Prediction of crystal-structure types and calculation of the numbers of possible structure types (see Section 1.6.4.7).
(5) Solution of the phase problem in the crystal structure analysis of proteins (Di Costanzo *et al.*, 2003).

Bärnighausen (1975, 1980) presented a standardized procedure to set forth structural relations between crystal structures with the aid of symmetry relations between their space groups. For a review on this subject see Müller (2004). Short descriptions are given by Chapuis (1992) and Müller (2006). The main concept is to start from a simple, highly symmetrical crystal structure and to derive more and more complicated structures by distortions and/or substitutions of atoms. Similar to the 'diagrams of lattices of subgroups' used in mathematics, a tree of group–subgroup relations between the space groups involved, now called a *Bärnighausen tree*, serves as the main guideline. The highly symmetrical starting structure is called the *aristotype* after Megaw (1973) or *basic structure* after Buerger (1947, 1951); other terms used in the literature on phase transitions in physics are *prototype* or *parent structure*. The derived structures are the *hettotypes* or *derivative structures*. In Megaw's (1973) terminology, the structures mentioned in the tree form a *family of structures*.

The structure type to be chosen as the aristotype depends on the specific problem and, therefore, the term aristotype cannot be defined in a strict manner. For example, a body-centred packing of spheres (space group $Im\bar{3}m$) can be chosen as the aristotype for certain intermetallic structures. By symmetry reduction due to a loss of the centring, the CsCl type (space group $Pm\bar{3}m$) can be derived. However, if all the structures considered are ionic, there is no point in starting from the body-centred packing of spheres and one can choose the CsCl type as the aristotype.

1.6.2. The symmetry principle in crystal chemistry

The usefulness of symmetry relations is intimately related to the symmetry principle in crystal chemistry. This is an old principle based on experience which has been worded during its long history in rather different ways. Bärnighausen (1980) summarized it in the following way:

(1) In crystal structures the arrangement of atoms reveals a pronounced tendency towards the highest possible symmetry.
(2) Counteracting factors due to special properties of the atoms or atom aggregates may prevent the attainment of the highest possible symmetry. However, in most cases the deviations from the ideal symmetry are only small (key word: pseudo-symmetry).
(3) During phase transitions and solid-state reactions which result in products of lower symmetry, the higher symmetry of the starting material is often indirectly preserved by the formation of oriented domains.

Aspect (1) is due to the tendency of atoms of the same kind to occupy equivalent positions, as stated by Brunner (1971). This has physical reasons: depending on chemical composition, the kind of chemical bonding, electron configuration of the atoms, relative sizes of the atoms, pressure, temperature *etc.*, there exists *one* energetically most favourable surrounding for atoms of a given species which all of these atoms strive to attain.
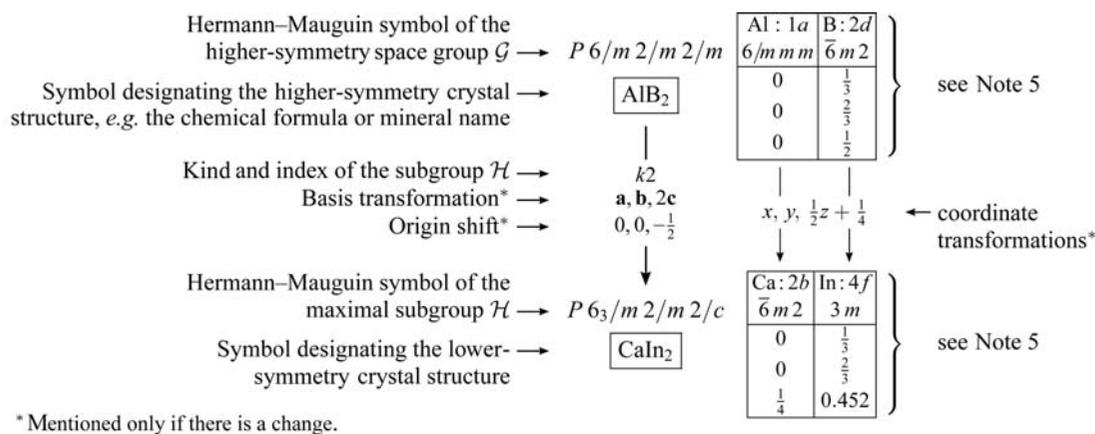
Aspect (2) of the symmetry principle is exploited in the following sections. Factors that counteract the attainment of the highest symmetry include: (1) stereochemically active lone electron pairs; (2) Jahn–Teller distortions; (3) covalent bonds; (4) Peierls distortions; (5) ordered occupation of originally equivalent sites by different atomic species (substitution derivatives); (6) partial occupation of voids in a packing of atoms; (7) partial vacation of atomic positions; (8) freezing (condensation) of lattice vibrations (soft modes) giving rise to phase transitions; and (9) ordering of atoms in a disordered structure.

Aspect (3) of the symmetry principle has its origin in an observation by Bernal (1938). He noted that in the solid state reaction $Mn(OH)_2 \rightarrow MnOOH \rightarrow MnO_2$ the starting and the product crystal had the same orientation. Such reactions are called *topotactic reactions* after Lotgering (1959) (for a more exact definition see Giovanoli & Leuenberger, 1969). In a paper by Bernal & Mackay (1965) we find the sentence: 'One of the controlling factors of topotactic reactions is, of course, symmetry. This can be treated at various levels of sophistication, ranging from Lyubarskii's to ours, where we find that the simple concept of Buridan's ass illumines most cases.' According to the metaphor of Buridan (French philosopher, died *circa* 1358), the ass starves to death between two equal and equidistant bundles of hay because it cannot decide between them. Referred to crystals, such an asinine behaviour would correspond to an absence of phase transitions or solid-state reactions if there are two or more energetically equivalent orientations of the domains of the product. Crystals, of course, do not behave like the ass; they take both.

1.6.3. Bärnighausen trees

To represent symmetry relations between different crystal structures in a concise manner, we construct a tree of group–subgroup relations in a modular design, beginning with the space group of the aristotype at its top. Each module represents one

	Al : 1a	B : 2d
Hermann–Mauguin symbol of the higher-symmetry space group $\mathcal{G}$ → $P\,6/m\,2/m\,2/m$	$6/m\,m\,m$	$\bar{6}\,m\,2$
Symbol designating the higher-symmetry crystal → structure, *e.g.* the chemical formula or mineral name $\boxed{AlB_2}$	0 0 0	$\frac{1}{3}$ $\frac{2}{3}$ $\frac{1}{2}$

see Note 5

Kind and index of the subgroup $\mathcal{H}$ → $k2$
Basis transformation* → $\mathbf{a}, \mathbf{b}, 2\mathbf{c}$ $x, y, \frac{1}{2}z + \frac{1}{4}$ ← coordinate
Origin shift* → $0, 0, -\frac{1}{2}$ transformations*

	Ca : 2b	In : 4f
Hermann–Mauguin symbol of the maximal subgroup $\mathcal{H}$ → $P\,6_3/m\,2/m\,2/c$	$\bar{6}\,m\,2$	$3\,m$
Symbol designating the lower- → symmetry crystal structure $\boxed{CaIn_2}$	0 0 $\frac{1}{4}$	$\frac{1}{3}$ $\frac{2}{3}$ 0.452

see Note 5

* Mentioned only if there is a change.

Explanatory Notes

(1) Possible kinds of maximal subgroups $\mathcal{H}$ of a given space group $\mathcal{G}$:

Symbol	Term	Meaning
t	*translationengleiche*	$\mathcal{G}$ and $\mathcal{H}$ have the same translations; the crystal class of $\mathcal{H}$ is of lower symmetry than that of $\mathcal{G}$
k	*klassengleiche*	$\mathcal{G}$ and $\mathcal{H}$ belong the same crystal class; $\mathcal{H}$ has lost translational symmetry, its primitive unit cell is larger than that of $\mathcal{G}$
i	isomorphic	$\mathcal{G}$ and $\mathcal{H}$ belong to the same or the enantiomorphic space-group type; $\mathcal{H}$ has lost translational symmetry, its unit cell is larger than that of $\mathcal{G}$

(2) The index i of a subgroup is the number of cosets of $\mathcal{H}$ in $\mathcal{G}$. The number of symmetry operations of $\mathcal{H}$ is $1/i$ of those of $\mathcal{G}$ (in the same way as the amount of even numbers is half the amount of all integer numbers).

(3) Basis transformation: The three basis vectors of $\mathcal{H}$ are expressed as linear combinations of the basis vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}$ of $\mathcal{G}$. Never omit this information if there is a change of the basis vectors.

(4) Origin shift: The coordinate triplet of the origin of $\mathcal{H}$ is given in the coordinate system of $\mathcal{G}$. Never omit this information if there is an origin shift.

(5) Additional information (only if there is enough space; otherwise this information must be listed in a separate table): The atomic positions are given in a box next to the space-group symbol in the following way:

element symbol: Wyckoff label site symmetry	The coordinates are given for one atom in the asymmetric unit. If a numeric
x	value is fixed by symmetry, it is stated as 0 or as a fraction, *e.g.* 0, $\frac{1}{4}$, $\frac{1}{2}$. Free
y	parameters are stated as decimal numbers, *e.g.* 0.0, 0.25, 0.53. If possible,
z	align the site-symmetry symbols in one line with the space-group symbol.

Fig. 1.6.3.1. Scheme of the formulation of the smallest step of symmetry reduction connecting two related crystal structures.

step of symmetry reduction to a *maximal* subgroup. Therefore, we have to discuss only one of these modules in detail.

For two structures we want to interrelate, we place their space-group symbols one below the other and indicate the direction of the symmetry reduction by an arrow pointing downwards (Fig. 1.6.3.1). Since they are more informative, it is advisable to use only the full Hermann–Mauguin symbols. In the middle of the arrow we insert the kind of maximal subgroup and the index of symmetry reduction, using the abbreviations t for *translationengleiche*, k for *klassengleiche* and i for isomorphic. If the unit cell changes, we also insert the new basis vectors expressed as vector sums of the basis vectors of the higher-symmetry cell. If there is an origin shift, we enter this as a triplet of numbers which express the coordinates of the new origin referred to the coordinate system of the higher-symmetry cell. This is a shorthand notation for the transformation matrices. *Any change of the basis vectors and the origin is essential information that should never be omitted.*

If the atomic coordinates of two related crystal structures differ because of different settings of their unit cells, the similarities of the structures become less clear and may even be obscured. Therefore, it is recommended to *avoid cell transformations whenever possible*. If necessary, it is much better to fully

exploit the possibilities offered by the Hermann–Mauguin symbolism and to choose nonconventional space-group settings [see Chapter 4.3 of *International Tables for Crystallography* Volume A (2005) and Section 3.1.4 of this volume].

Origin shifts also tend to obscure relations. However, they often cannot be avoided. There is no point in deviating from the standard origin settings, because otherwise much additional information would be required for an unequivocal description. *Note:* The coordinate triplet specifying the origin shift in the group–subgroup arrow refers to the *coordinate system of the higher-symmetry space group*, whilst the corresponding changes of the atomic coordinates refer to the coordinate system of the subgroup and therefore are different. Details are given in Section 3.1.3. Also note that in the tables of Parts 2 and 3 of this volume the origin shifts are given in different ways. In Part 2 they refer to the higher-symmetry space group. In Part 3 (relations of the Wyckoff positions) they are given only as parts of the coordinate transformations, *i.e.* in the coordinate systems of the subgroups. As explained in the Appendix, the chosen origin shifts themselves also differ in Parts 2 and 3; an origin transformation taken from Part 3 may be different from the one given in Part 2 for the same group–subgroup relation. If needed, one has to calculate the corresponding values with the formulae given in Section 3.1.3.

The calculation of coordinate changes due to cell transformations and origin shifts is prone to errors. Some useful hints are given in Section 1.6.5.

For space groups with two possible choices of origin ('origin choice 1' and 'origin choice 2'), the choice is specified by a superscript (1) or (2) after the space-group symbol, for example $P4/n^{(2)}$. The setting of rhombohedral space groups is specified, if necessary, by superscript (rh) or (hex). Occasionally it may be useful to use a nonconventional rhombohedral 'reverse' setting, *i.e.* with the centring vectors $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{3})$ instead of 'obverse' with $\pm(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$; this is specified by superscript (rev), for example $R\overline{3}^{(rev)}$.

In a Bärnighausen tree containing several group–subgroup relations, it is recommended that the vertical distances between the space-group symbols are kept proportional to the logarithms of the corresponding indices. This way all subgroups that are at the same hierarchical distance, *i.e.* at the same index, from the aristotype appear on the same line.

If several paths can be constructed from one space group to a general subgroup, *via* different intermediate groups, usually there is no point in depicting all of them. There is no general recipe indicating which of several possible paths should be preferred. However, crystal-chemical and physical aspects should be used as a guide. First of all, the chosen intermediate groups should be:

(1) Space groups having actually known representatives.
(2) Space groups that disclose a physically realizable path for the symmetry reduction. Observed phase transitions should be given high priority. For phase transitions that are driven by certain lattice vibrations, those intermediate space groups should be considered that are compatible with these lattice modes (*i.e.* irreducible representations; Stokes & Hatch, 1988).
(3) In the case of substitution derivatives: Space groups showing a splitting of the relevant Wyckoff position(s). These intermediate groups allow for substitution derivatives, even if no representative is yet known.

Bärnighausen trees sometimes contain intermediate space groups which, in Howard & Stokes' (2005) opinion, 'have no physical significance'. As an example, they cite the phase transition induced by the displacement of the octahedrally coordinated cations in a cubic perovskite along the $+z$ axis. This lowers the symmetry directly from $Pm\overline{3}m$ to the non-maximal subgroup $P4mm$, skipping the intermediate space group $P4/mmm$. In this particular case, $P4/mmm$ 'has no physical significance' in the sense that it cannot actually occur in this kind of phase transition. However, the intermediate space group $P4/mmm$ can occur in other instances (*e.g.* in order–disorder transitions) and it has been found among several perovskites. In addition, we are not dealing merely with phase transitions. Intermediate space groups do have significance for several reasons: (1) Any step of symmetry reduction reduces the restrictions for every Wyckoff position (either the site symmetry is reduced or the position splits into independent positions, or both happen); every intermediate space group offers new scope for effects with physical significance, even if none have yet been observed. (2) Skipping intermediate space groups in the tree of group–subgroup relations reduces the informative value of the symmetry relations. For example, it is no longer directly evident how many *translationengleiche* and *klassengleiche* steps are involved; this is useful to decide how many and what kind of twin domains may appear in a phase transition or topotactic reaction (see Sections 1.2.7 and 1.6.6).

Group–subgroup relations are of little value if the usual crystallographic data are not given for every structure. The mere mention of the space groups is insufficient. The atomic coordinates are of special importance. It is also important to present all structures in such a way that their relations become clearly visible. In particular, all atoms of the asymmetric units should exhibit strict correspondence, so that their positional parameters can immediately be compared.

For all structures, the same coordinate setting and among several symmetry-equivalent positions for an atom the same location in the unit cell should be chosen, if possible. For all space groups, except $Im\overline{3}m$ and $Ia\overline{3}d$, one can choose several different equivalent sets of coordinates describing one and the same structure in the same space-group setting. It is by no means a simple matter to recognize whether two differently documented structures are alike or not (the literature abounds with examples of 'new' structures that really had been well known). One is often forced to transform coordinates from one set to another to attain the necessary correspondence. In Section 15.3 of Volume A (editions 1987–2005) and in a paper by Koch & Fischer (2006) one can find a procedure for and examples of how to interconvert equivalent coordinate sets with the aid of the Euclidean normalizers of the space groups. *Note*: For enantiomorphic (chiral) space groups like $P3_1$ this procedure will yield equivalent sets of coordinates without a change of chirality; for chiral structures in non-enantiomorphic (non-chiral) space groups like $P2_12_12_1$ the sets of coordinates include the enantiomorphic pairs [for the distinction between chiral and non-chiral space groups see Flack (2003)].

If space permits, it is useful to list the site symmetries and the coordinates of the atoms next to the space-group symbols in the Bärnighausen tree, as shown in Fig. 1.6.3.1 and in the following examples. If there is not enough space, this information must be provided in a separate table.

1.6.4. The different kinds of symmetry relations among related crystal structures

In this section, using a few simple examples, we point out the different kinds of group–subgroup relations that are important among related (homeotypic) crystal structures.

The crystal structures of two compounds are *isotypic* if their atoms are arranged in the same way and if they have the same or the enantiomorphic space group. The absolute values of the lattice dimensions and interatomic distances may differ, and small deviations are permitted for non-fixed coordinates of corresponding atoms. The axial ratios and interaxial angles must be similar. Two structures are *homeotypic* if the conditions for isotypism are relaxed because: (1) their space groups differ, allowing for a group–subgroup relation; (2) the geometric conditions differ (axial ratios, interaxial angles, atomic coordinates); or (3) corresponding atomic positions are occupied by various atomic species (substitution derivatives). (Lima-de-Faria *et al.*, 1990.)

1.6.4.1. Translationengleiche maximal subgroups

The space group *Pbca* of PdS_2 is a *translationengleiche* maximal subgroup of $Pa\overline{3}$, the space group of pyrite (FeS_2; Bärnighausen, 1980). The threefold axes of the cubic space group have been lost, the index of the symmetry reduction is 3. As shown in Fig. 1.6.4.1, the atomic coordinates have not changed

much. However, the two structures differ widely, the c axis of PdS_2 being strongly stretched. This is due to the tendency of bivalent palladium towards square-planar coordination (electron configuration d^8), whereas the iron atoms in pyrite have octahedral coordination.

Strictly speaking, the space groups of FeS_2 and PdS_2 are not really *translationengleiche* because of the different lattice parameters. In the strict sense, however, FeS_2 at 293.0 and at 293.1 K would not have the same space group either, due to thermal expansion. Such a strict treatment would render it impossible to apply group-theoretical methods in crystal chemistry and physics. Instead, we use the concept of the *parent-clamping approximation*, *i.e.* we act as if the translations of the two homeotypic structures were the same (see Section 1.2.7). With the parent-clamping approximation we also treat isotypic structures with different lattice parameters (like NaCl and MgO) as if they had the same space group with the same translational lattice.

Upon transition from $Pa\overline{3}$ to $Pbca$ none of the occupied Wyckoff positions split, but their site symmetries are reduced. Without the symmetry reduction from $\overline{3}$ to $\overline{1}$ the square coordination of the Pd atoms would not be possible.

If the positions of the sulfur atoms of pyrite and PdS_2 are substituted by two different kinds of atoms in an ordered 1:1 ratio, this enforces further symmetry reductions. The corresponding subgroups may only be subgroups in which the sulfur positions split into symmetry-independent positions. In the chosen examples NiAsS and PtGeSe the symmetry reductions consist of the loss of the inversion centres of $Pa\overline{3}$ and $Pbca$ (Fig. 1.6.4.1). Coordinate changes are not necessary, but may occur depending on the site symmetries. In our examples there are minor coordinate changes.

To avoid a basis transformation, the nonconventional space-group setting $Pbc2_1$ has been chosen for PtGeSe; it corresponds to $Pca2_1$ after interchange of the axes a and b. Mind the origin shift from PdS_2 to PtGeSe; in the conventional description of $Pca2_1$, and therefore also of $Pbc2_1$, the origin is situated on one of the 2_1 axes and thus differs from that of $Pbca$. The origin shift of $-\frac{1}{4}$, 0, 0 in the coordinate system of $Pbca$ involves a change of the atomic coordinates by $+\frac{1}{4}$, 0, 0, *i.e.* with opposite sign.

The substitution derivatives NiAsS and PtGeSe can only be connected by the common supergroup $P2_1/a\overline{3}$. A direct group–subgroup relation from $P2_13$ to $Pbc2_1$ does not exist.

1.6.4.2. Klassengleiche maximal subgroups

Consider two derivatives of the AlB_2 type as an example of *klassengleiche* subgroups (Pöttgen & Hoffmann, 2001). AlB_2 has a simple hexagonal structure in the space group $P6/mmm$. In the $\mathbf{c}$ direction, aluminium atoms and sheets of boron atoms alternate; the boron-atom sheets are planar, like in graphite (Fig. 1.6.4.2; Hoffmann & Jäniche, 1935). The ZrBeSi type has a similar structure (Nielsen & Baenziger, 1953, 1954), but the sheets consist of Be and Si atoms. As a consequence, the inversion centres in the middles of the six-membered rings cannot be retained. This enforces a symmetry reduction to the *klassengleiche* subgroup $P6_3/mmc$ with doubled $\mathbf{c}$ vector.

The doubling of $\mathbf{c}$ is the essential aspect in the symmetry reduction from the AlB_2 to the ZrBeSi type. The index is 2: half of all translations are lost, together with half of the inversion centres, half of the symmetry axes perpendicular to $\mathbf{c}$ and half of the mirror planes perpendicular to $\mathbf{c}$. The Wyckoff position $2d$ of the boron atoms of AlB_2 splits into the two symmetry-independent positions $2c$ and $2d$ of the subgroup (Fig. 1.6.4.3,

Fe:4a	S: 8c
$\overline{3}$	3
0	0.386 [0.614]
0	0.386 [0.614]
0	0.386 [0.614]

Ni: 4a	S: 4a	As: 4a
3	3	3
−0.006	0.385	0.618
−0.006	0.385	0.618
−0.006	0.385	0.618

Pd:4a	S: 8c
$\overline{1}$	1
0	0.383 [0.607]
0	0.388 [0.612]
0	0.425 [0.575]

Pt:4a	Ge:4a	Se:4a
1	1	1
0.242	0.636	0.876
0.009	0.383	0.620
0	0.383	0.618

lattice parameters:

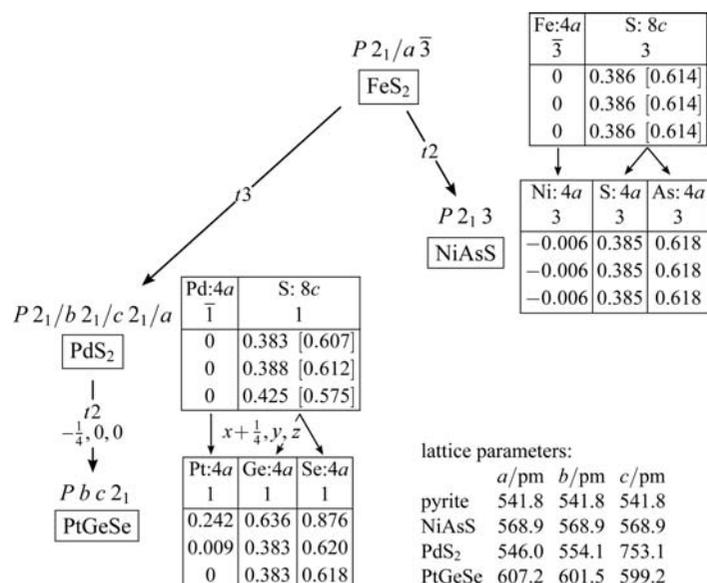|	a/pm	b/pm	c/pm
pyrite	541.8	541.8	541.8
NiAsS	568.9	568.9	568.9
PdS_2	546.0	554.1	753.1
PtGeSe	607.2	601.5	599.2

Fig. 1.6.4.1. Bärnighausen tree for the family of structures of pyrite. Coordinates in brackets (not stated normally) refer to symmetry-equivalent positions. Lattice parameters are taken from Ramsdell (1925) and Brostigen & Kjeskhus (1969) for pyrite; from Ramsdell (1925), Steger *et al.* (1974) and Foecker & Jeitschko (2001) for NiAsS; from Grønvold & Røst (1957) for PdS_2; and from Entner & Parthé (1973) for PtGeSe.

left), rendering possible occupation by atoms of two different species.

Figs. 1.6.4.2 and 1.6.4.3 show another peculiarity. $P6/mmm$ has two *different klassengleiche* maximal subgroups of the same type $P6_3/mmc$ with doubled basis vector $\mathbf{c}$. The second one corresponds to $CaIn_2$ (Iandelli, 1964; Wendorff & Roehr, 2005). Here the graphite-like sheets of the AlB_2 type have become puckered layers of indium atoms; the indium atoms of adjacent layers have shifted parallel to $\mathbf{c}$ and have come close to each other in pairs, so that the result is a network as in lonsdaleite (hexagonal diamond). The alternating shift of the atoms no longer permits the existence of mirror planes in the layers; however, neighbouring layers are mutually mirror-symmetrical. The calcium atoms are on the mirror planes, but no longer on inversion centres. The difference between the two subgroups $P6_3/mmc$ consists of the selection of the symmetry operations that are being lost with the doubling of $\mathbf{c}$.

The conventional description of the space groups requires an inversion centre to be at the origin of space group $P6_3/mmc$. The position of the origin at an Al atom of the AlB_2 type can be kept when the symmetry is reduced to that of ZrBeSi (*i.e.* Zr at the origin). The symmetry reduction to $CaIn_2$, however, requires an origin shift to the centre of one of the six-membered rings. In the coordinate system of the aristotype that is a shift by 0, 0, $-\frac{1}{2}$, as marked in the middle of the group–subgroup arrow in Fig. 1.6.4.3. For the new atomic coordinates (in the coordinate system of the subgroup), the origin shift results in the addition of $+\frac{1}{4}$ to the z coordinates; in addition, due to the doubling of c, the z coordinates of the aristotype have to be halved. Therefore, the new z coordinate of the In atom is approximately $z' \simeq \frac{1}{2}z + \frac{1}{4} = \frac{1}{2} \times \frac{1}{2} + \frac{1}{4} = 0.5$. It cannot be exactly this value, because then there would have been no symmetry reduction and the space group would still be $P6/mmm$. The symmetry reduction requires the atom shift to $z' = 0.452$.

In the relation $AlB_2 \rightarrow$ ZrBeSi, the site symmetry $\overline{6}m2$ of the boron atoms is retained and the Wyckoff position splits. In the relation $AlB_2 \rightarrow CaIn_2$ it is the other way; the position does

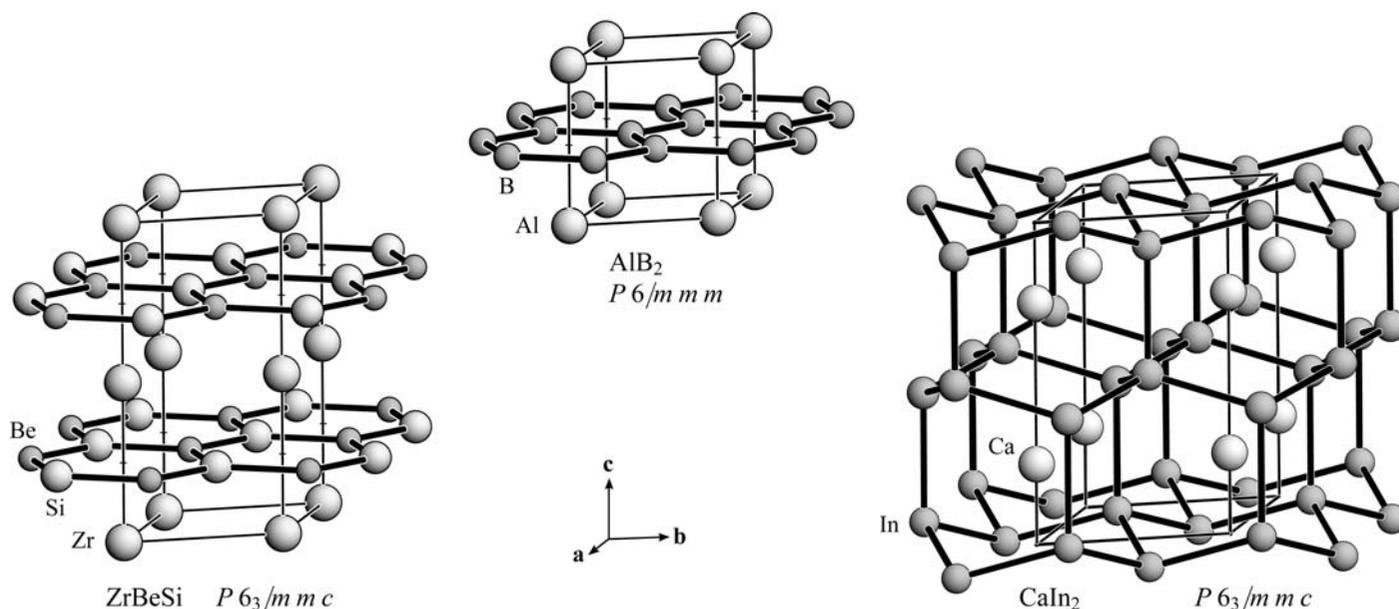Fig. 1.6.4.2. The structures of AlB_2, ZrBeSi and $CaIn_2$. The mirror planes of $P6_3/mmc$ perpendicular to **c** are at $z = \frac{1}{4}$ and $z = \frac{3}{4}$.
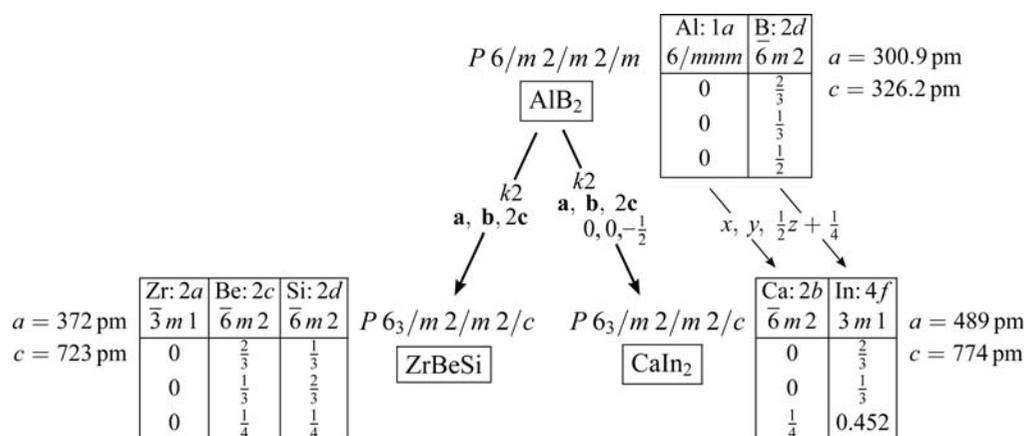

Fig. 1.6.4.3. Both hettotypes of the AlB_2 type have the same space-group type and a doubled c axis, but the space groups are different due to different origin positions relative to the origin of the aristotype.

not split, the atoms remain symmetry-equivalent, but their site symmetry is reduced to $3m1$ and the z coordinate becomes variable.

Among *klassengleiche* subgroups there often exist two and sometimes four or even eight nonconjugate subgroups of the same space-group type with different origin positions. It is important to choose the correct one, with the correct origin shift. All of these subgroups are listed in this volume if they are maximal.

Compared to AlB_2, ZrBeSi and $CaIn_2$ have so-called 'super-structures' (they have additional reflections in the X-ray diffraction patterns). Whereas the term superstructure gives only a qualitative, informal outline of the facts, the group-theoretical approach permits a precise treatment.

1.6.4.3. Isomorphic maximal subgroups

Isomorphic subgroups comprise a special category of *klassengleiche* subgroups. Every space group has an infinity of isomorphic maximal subgroups. The index agrees with the factor by which the unit cell has been enlarged. The indices are prime numbers; squares of prime numbers may occur in the case of

tetragonal, hexagonal and trigonal space groups, and for cubic space groups only cubes of prime numbers ($\geq 3^3$) are possible. For many space groups, not all prime numbers are permitted. The prime number 2 is often excluded, and additional restrictions may apply. In the tables in Parts 2 and 3 of this volume all permitted isomorphic maximal subgroups are listed.

Usually, in accordance with the symmetry principle, only small index values are observed (mostly 2 and 3, sometimes 4, less frequently 5, 7 or 9). However, seemingly curious values like 13, 19, 31 or 37 do occur [for examples with indices of 13 and 37, discovered by Bärnighausen, see Müller (2004)].

A classic example of a relation between isomorphic space groups concerns trirutile (Billiet, 1973). The space group of rutile, $P4_2/mnm$, has an isomorphic subgroup of index 3, but none of index 2. By triplication of **c** it becomes possible to substitute the titanium-atom positions of rutile by two different kinds of atoms in a ratio of 1:2, as for example in $ZnSb_2O_6$ (Fig. 1.6.4.4; Byström *et al.*, 1941; Ercit *et al.*, 2001). Since the space group $P4_2/mnm$ has no isomorphic subgroup of index 2, a 'dirutile' with this space-group type cannot exist.

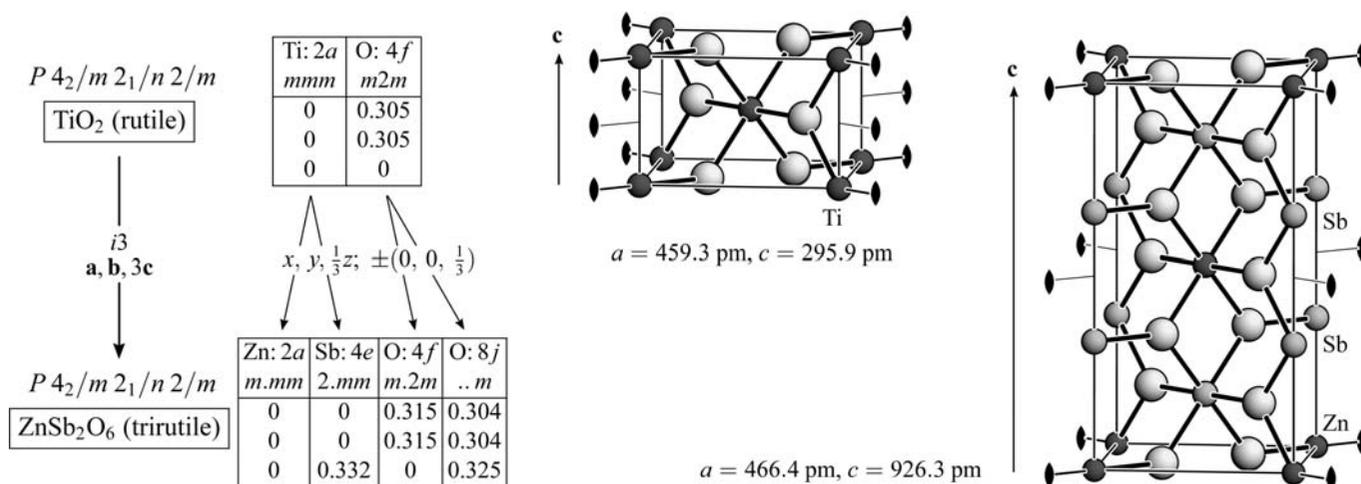Note that rutile and trirutile have *different* space groups of the same space-group type.

Fig. 1.6.4.4. The group–subgroup relation rutile–trirutile. The twofold rotation axes have been included in the plots of the unit cells, showing that only one third of them are retained upon the symmetry reduction.

1.6.4.4. The space groups of two structures having a common supergroup

Two crystal structures can be intimately related even when there is no direct group–subgroup relation between their space groups. Instead, there may exist a common supergroup. The structures of NiAsS and PtGeSe, presented in Section 1.6.4.1, offer an example. In this case, the pyrite type corresponds to the common supergroup. Even if there is no known representative, it can be useful to look for a common supergroup.

β-K_2CO_3 and β-Na_2CO_3 have similar structures and unit cells (Fig. 1.6.4.5; Jansen & Feldmann, 2000). The planes of the carbonate ions are not aligned exactly perpendicular to **c**; compared to the perpendicular orientation, in the case of β-K_2CO_3, they are rotated about **b** by 22.8° and those of β-Na_2CO_3 are rotated about **a** by 27.3°. There is no group–subgroup relation between the space groups $C12/c1$ and $C2/m11$ of the two structures (the nonconventional setting $C2/m11$ has been chosen for β-Na_2CO_3 to ensure a correspondence between the cells of both structures). Looking for common minimal supergroups of $C12/c1$ and $C2/m11$ one can find two candidates: $Cmcm$, No. 63, and $Cmce$, No. 64. Since the atomic coordinates of β-K_2CO_3 and β-Na_2CO_3 are very similar, any origin shifts in the relations from the common supergroup to $C12/c1$ as well as $C2/m11$ must be the

same. In the listings of the supergroups the origin shifts are not mentioned either in Volume A or in this volume. Therefore, one has to look up the subgroups of $Cmcm$ and $Cmce$ in this volume and check in which cases the origin shifts coincide. One finds that the relation $Cmce \rightarrow C12/c1$ requires an origin shift of $\frac{1}{4}, \frac{1}{4}, 0$ (or $-\frac{1}{4}, -\frac{1}{4}, 0$), while all other relations ($Cmcm \rightarrow C12/c1$, $Cmcm \rightarrow C2/m11$, $Cmce \rightarrow C2/m11$) require no origin shifts. As a consequence, only $Cmcm$ and not $Cmce$ can be the common supergroup.

No structure is known that has the space group $Cmcm$ and that can be related to these carbonate structures. Could there be any other structure with even higher symmetry? A supergroup of $Cmcm$ is $P6_3/mmc$ and, in fact, α-K_2CO_3 and α-Na_2CO_3 are high-temperature modifications that crystallize in this space group. They have the carbonate groups perpendicular to **c**. The group–subgroup relations are depicted in Fig. 1.6.4.6. In this case there exists a higher-symmetry structure that can be chosen as the common aristotype. In other cases, however, the common supergroup refers to a hypothetical structure; one can speculate why it does not exist or one can try to prepare a compound having this structure.

Among the alkali metal carbonates several other modifications are known which we do not discuss here.
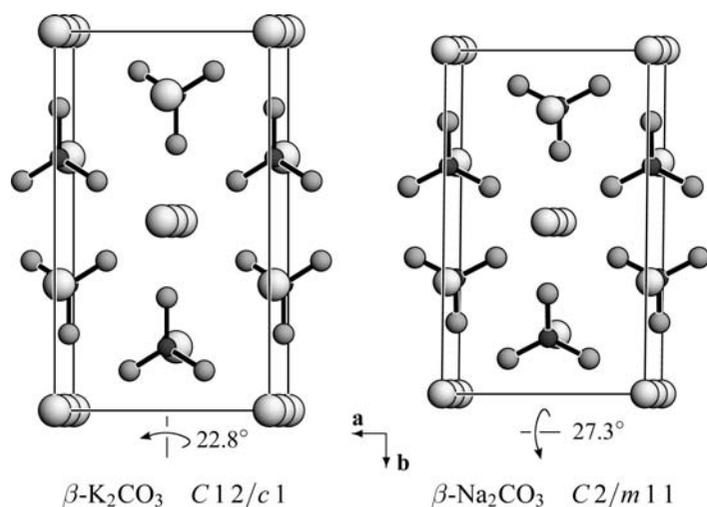
1.6.4.5. Can a structure be related to two aristotypes?

Occasionally a crystal structure shows a pronounced distortion compared to a chosen aristotype and another aristotype can be chosen just as well with a comparable distortion.

When pressure is exerted upon silicon, it first transforms to a modification with the β-tin structure (Si-II, $I4_1/amd$). Then it is transformed to silicon-XI (McMahon *et al.*, 1994). At even higher pressures it is converted to silicon-V forming a simple hexagonal structure ($P6/mmm$). The space group of Si-XI, $Imma$, is a subgroup of both $I4_1/amd$ and $P6/mmm$, and the structure of Si-XI can be related to either Si-II or Si-V (Fig. 1.6.4.7). Assuming no distortions, the calculated coordinates of a silicon atom of Si-XI would be $0, \frac{1}{4}, -0.125$ when derived from Si-II, and $0, \frac{1}{4}, 0.0$ when derived from Si-V. The actual coordinates are halfway between. The metric deviations of the lattices are small; taking into account the basis transformations given in Fig. 1.6.4.7, the expected lattice parameters for Si-XI, calculated from those of Si-V, would be $a_{XI} = a_V \sqrt{3} = 441.5$ pm, $b_{XI} = 2c_V = 476.6$ pm and $c_{XI} = a_V = 254.9$ pm.

Fig. 1.6.4.5. The unit cells of β-K_2CO_3 and β-Na_2CO_3. The angles of tilt of the CO_3^{2-} ions are referred relative to a plane perpendicular to **c**.

$P\,6_3/m\,2/m\,2/c$

α-Na$_2$CO$_3$, α-K$_2$CO$_3$

	Na:2a	Na:2c	C:2d	O:6h
	$\bar{3}m.$	$\bar{6}m2$	$\bar{6}m2$	$mm2$
	0	$\frac{1}{3}$	$\frac{1}{3}$	0.204
	0	$\frac{2}{3}$	$\frac{2}{3}$	0.408
	0	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{3}{4}$

lattice parameters in pm:

	T/K	a	$a\sqrt{3}$	b	c	
α-Na$_2$CO$_3$	756	521		521	645	
β-Na$_2$CO$_3$	605	525	898 = 898	621		$\alpha = 99.3°$
α-K$_2$CO$_3$	600	566		566	710	
β-K$_2$CO$_3$	580	568	984 ≈ 992	702		$\beta = 96.8°$

$t3$
$\mathbf{a},\ \mathbf{a+2b},\ \mathbf{c}$

$C\,2/m\,2/c\,2_1/m$

$x - \tfrac{1}{2}y,\ \tfrac{1}{2}y,\ z$

	4a	4c	4c	4c	8g
	$2/m$	$m2m$	$m2m$	$m2m$	$..m$
	0	0	0	0	0.694
	0	0.333	0.333	0.204	0.895
	0	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$

$t2$

$C\,1\,2/c\,1$

β-K$_2$CO$_3$

	K:4a	K:4e	C:4e	O:4e	O:8f
	$\bar{1}$	2	2	2	1
	0	0	0	0	0.678
	0	0.332	0.333	0.202	0.895
	0	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	0.707

$t2$

$C\,2/m\,1\,1$

β-Na$_2$CO$_3$

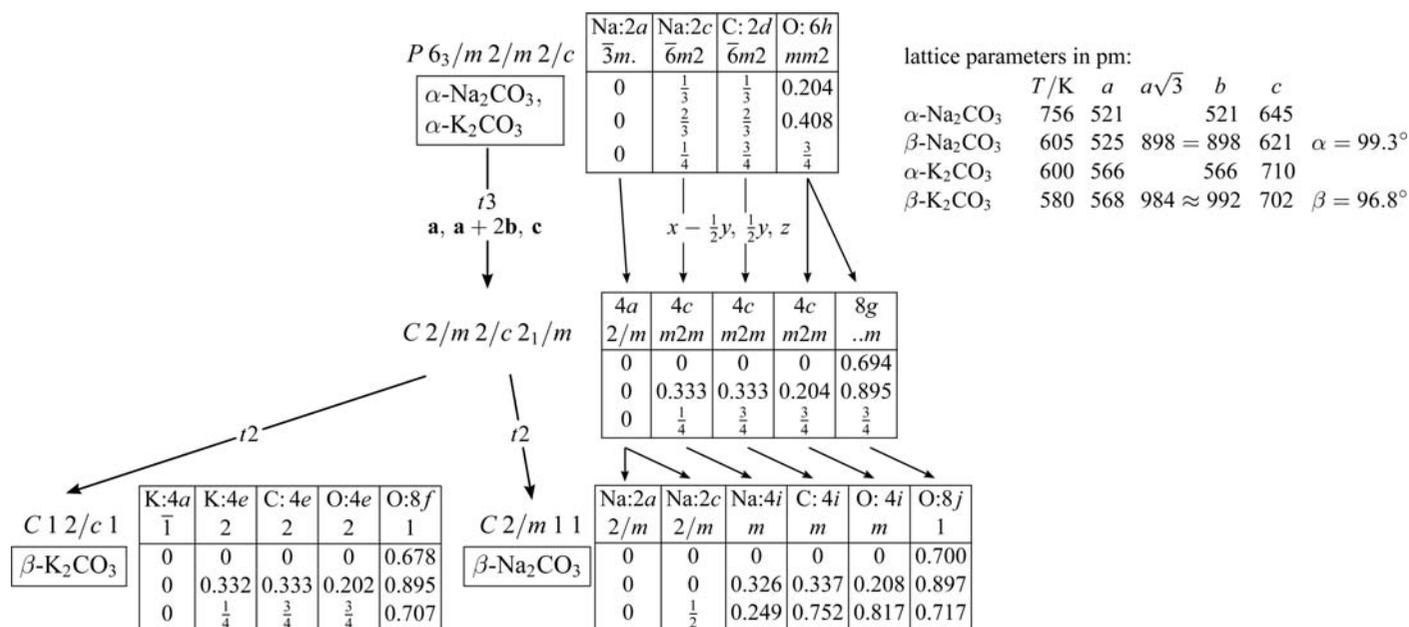|	Na:2a	Na:2c	Na:4i	C:4i	O:4i	O:8j
	$2/m$	$2/m$	m	m	m	1
	0	0	0	0	0	0.700
	0	0	0.326	0.337	0.208	0.897
	0	$\frac{1}{2}$	0.249	0.752	0.817	0.717

Fig. 1.6.4.6. Group–subgroup relations among some modifications of the alkali metal carbonates. Lattice parameters for α- and β-Na$_2$CO$_3$ are taken from Swainson *et al.* (1995) and those for α- and β-K$_2$CO$_3$ are taken from Becht & Struikmans (1976).

These phase transitions of silicon involve small atomic displacements and small volume changes. The lattice parameter c of the hexagonal structure is approximately half the value of a of tetragonal Si-II. There are two separate experimentally observable phase transitions. In a certain pressure range, the whole crystal actually consists of stable Si-XI; it is not just a hypothetical intermediate. Taking all these facts together, a group-theoretical relation between Si-II and Si-V exists *via* the common subgroup of Si-XI.

Usually, however, there is no point in relating two structures *via* a common subgroup. Two space groups always have an infinity of common subgroups, and it may be easy to set up relations *via* common subgroups in a purely formal manner; this can be quite meaningless unless it is based on well founded physical or chemical evidence. See also the statements on this matter in Section 1.6.4.6, at the end of Section 1.6.6 and in Section 1.6.7.

1.6.4.6. Treating voids like atoms

To comprehend the huge amount of known crystal-structure types, chemists have very successfully developed quite a few concepts. One of them is the widespread description of structures as packings of spheres with occupied interstices. Group–subgroup relations can help to rationalize this. This requires that unoccupied interstices be treated like atoms, *i.e.* that the occupation of voids is treated like a substitution of 'zero atoms' by real atoms.

The crystal structure of FeF$_3$ (VF$_3$ type) can be derived from the ReO$_3$ type by a mutual rotation of the coordination octahedra about the threefold rotation axes parallel to one of the four diagonals of the cubic unit cell of the space group $Pm\bar{3}m$ (Fig. 1.6.4.8). This involves a symmetry reduction by two steps to a rhombohedral hettotype with the space group $R\bar{3}c$ (Fig. 1.6.4.9, left).

FeF$_3$ can also be described as a hexagonal closest packing of fluorine atoms in which one third of the octahedral voids have been occupied by Fe atoms (Fig. 1.6.4.9, right). This is a more

$P\,6/m\,2/m\,2/m$

Si-V

$a_V = 254.9$ pm
$c_V = 238.3$ pm
at 16.2 GPa

	Si: 2a
	$6/mmm$
	0
	0
	0

$t3$
$\mathbf{a},\ \mathbf{a+2b},\ \mathbf{c}$

$C\,2/m\,2/m\,2/m$

	2a
	mmm
	0
	0
	0

$I\,4_1/a\,2/m\,2/d^{(2)}$

Si-II

$a_{II} = 466.5$ pm
$c_{II} = 256.5$ pm
at 11.7 GPa

	Si: 4a
	$\bar{4}m2$
	0
	$\frac{1}{4}$
	$-\frac{1}{8}$

$t2$

$k2$
$\mathbf{b},\mathbf{2c},\mathbf{a}$
$0,0,-\tfrac{1}{2}$

$y,\ \tfrac{1}{2}z + \tfrac{1}{4},\ x$

$I\,2_1/m\,2_1/m\,2_1/a$

Si-XI

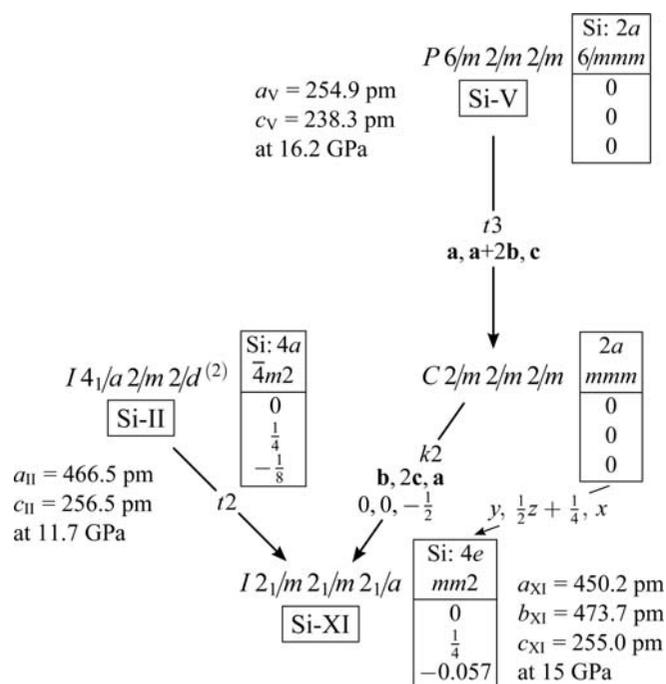|	Si: 4e	
	$mm2$	$a_{XI} = 450.2$ pm
	0	$b_{XI} = 473.7$ pm
	$\frac{1}{4}$	$c_{XI} = 255.0$ pm
	-0.057	at 15 GPa

Fig. 1.6.4.7. The structure of the high-pressure modification Si-XI is related to the structures of both Si-II and Si-V.
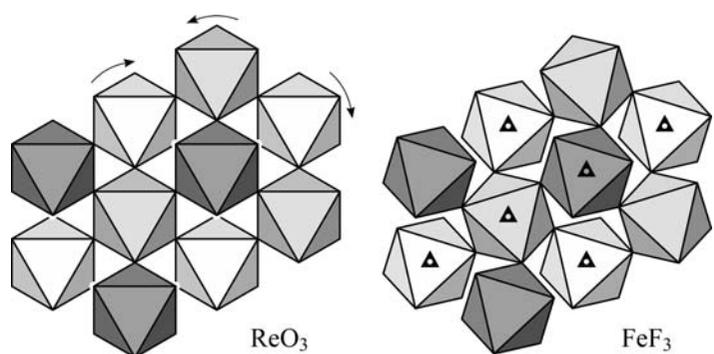

Fig. 1.6.4.8. The connected coordination octahedra in ReO$_3$ and FeF$_3$ (VF$_3$ type). Light, medium and dark grey refer to octahedron centres at $z = 0$, $z = \tfrac{1}{3}$ and $z = \tfrac{2}{3}$, respectively (hexagonal setting).

descriptive and more formal point of view, because the number of atoms and the kind of linkage between them are altered.

The calculated ideal x coordinates of the fluorine atoms of FeF_3, assuming no distortions, are $x = 0.5$ when derived from ReO_3 and $x = 0.333$ when derived from the packing of spheres. The actual value at ambient pressure is $x = 0.412$, i.e. halfway in between. When FeF_3 is subjected to high pressures, the coordination octahedra experience a mutual rotation which causes the structure to come closer to a hexagonal closest packing of fluorine atoms; at 9 GPa this is a nearly undistorted closest packing with the x parameter and the $c/(a\sqrt{3})$ ratio close to the ideal values of 0.333 and 1.633 (Table 1.6.4.1).

Therefore, at high pressures the hexagonal closest packing of spheres could be regarded as the more appropriate aristotype. This, however, is only true from the descriptive point of view, i.e. if one accepts that the positions of voids can be treated like atoms. If one studies the mutual rotation of the octahedra in FeF_3 or if phase transitions from the ReO_3 type to the VF_3 type are of interest, there is no point in allowing a change of the occupation of the octahedra; in this case only the group–subgroup relations given in the left part of Fig. 1.6.4.9 should be considered.

However, if one wants to derive structures from a hexagonal closest packing of spheres and point out similarities among them, the group–subgroup relations given in the right part of Fig. 1.6.4.9 are useful. For example, the occupation of the octahedral voids in the Wyckoff position $12c$ instead of $6b$ of $R\bar{3}c$ (Fig. 1.6.4.9, lower right) results in the structure of corundum (α-Al_2O_3); this shows that both the VF_3 type and corundum have the same kind of packing of their anions, even though the linkage of their coordination octahedra is quite different and the number of occupied positions does not coincide.

It should also be kept in mind that the occupation of voids in a packing of atoms can actually be achieved in certain cases. Examples are the intercalation compounds and the large number

Table 1.6.4.1. *Crystal data for FeF_3 at different pressures*

The observed lattice parameters a and c, the x coordinates of the F atoms and the angles of rotation of the coordination octahedra ($0° = ReO_3$ type, $30° =$ hexagonal closest packing) are given (Sowa & Ahsbahs, 1998; Jørgenson & Smith, 2006).

Pressure /GPa	a/pm	c/pm	$c/(a\sqrt{3})$	x	Angle /°
10^{-4}	520.5	1332.1	1.48	0.412	17.0
1.54	503.6	1340.7	1.54	0.385	21.7
4.01	484.7	1348.3	1.61	0.357	26.4
6.42	476	1348	1.64	0.345	28.2
9.0	469.5	1349	1.66	0.335	29.8

of metal hydrides MH_x that can be prepared by diffusion of hydrogen into the metals. The hydrides often keep the closest packed structures of the metals while the hydrogen atoms occupy the tetrahedral or octahedral voids.

It is not recommended to plot group–subgroup relations in which FeF_3 is depicted as a common subgroup of both the ReO_3 type and the hexagonal closest packing of spheres. This would mix up two quite different points of view.

1.6.4.7. Large families of structures. Prediction of crystal-structure types

Large trees can be constructed using the modular way to put together Bärnighausen trees, as set forth in Fig. 1.6.3.1 and in the preceding sections. Headed by an aristotype, they show structural relations among many different crystal structures belonging to a family of structures. As an example, Fig. 1.6.4.10 shows structures that can be derived from the ReO_3 type (Bock & Müller, 2002b). Many other trees of this kind have been set up, for example hettotypes of perovskite (Bärnighausen, 1975, 1980; Bock & Müller, 2002a), rutile (Baur, 1994, 2007; Meyer, 1981), CaF_2 (Meyer, 1981), hexagonal closest packed structures (Müller, 1998), AlB_2 (Pöttgen & Hoffmann, 2001), zeolites (Baur & Fischer, 2000, 2002, 2006) and tetraphenylphosphonium salts (Müller, 1980, 2004).

In the left branch of Fig. 1.6.4.10 only one compound is mentioned, WO_3. This is an example showing the symmetry relations among different polymorphic forms of a compound. The right branch of the tree shows the relations for substitution derivatives, including distortions caused by the Jahn–Teller effect, hydrogen bonds and different relative sizes of the atoms.

In addition to showing relations between known structure types, one can also find subgroups of an aristotype for which no structures are known. This can be exploited in a systematic manner to search for new structural possibilities, i.e. one can predict crystal-structure types. For this purpose, one starts from an aristotype in conjunction with a structural principle and certain additional restrictions. For example, the aristotype can be a hexagonal closest packing of spheres and the structural principle can be the partial occupation of octahedral voids in this packing. Additional restrictions could be things like the chemical composition, a given molecular configuration or a maximal size of the unit cell. Of course, one can only find such structure types that meet these starting conditions. For every space group appearing in the Bärnighausen tree, one can calculate how many different structure types are possible for a given chemical composition (McLarnan, 1981a,b,c; Müller, 1992).

Examples of studies of structural possibilities include compounds AX_3, AX_6, $A_aB_bX_6$ (with the X atoms forming the packing of spheres and atoms A and B occupying the octahedral voids; $a + b < 6$; Müller, 1998), molecular compounds $(MX_5)_2$ (Müller, 1978), chain structures MX_4 (Müller, 1981) and MX_5
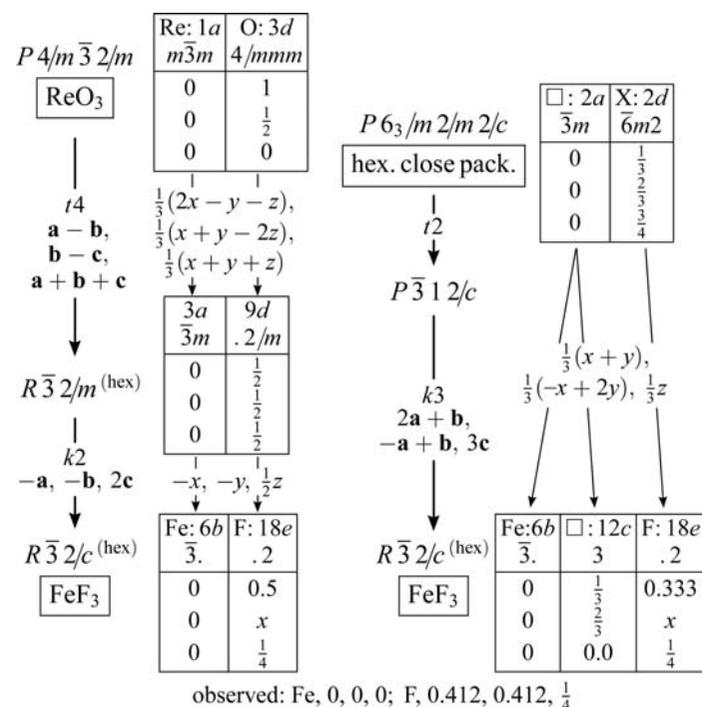

Fig. 1.6.4.9. Derivation of the FeF_3 structure either from the ReO_3 type or from the hexagonal closest packing of spheres. The coordinates for FeF_3 given in the boxes are ideal values calculated from the aristotypes assuming no distortions. A y coordinate given as x means $y = x$. The Schottky symbol □ designates an unoccupied octahedral void.
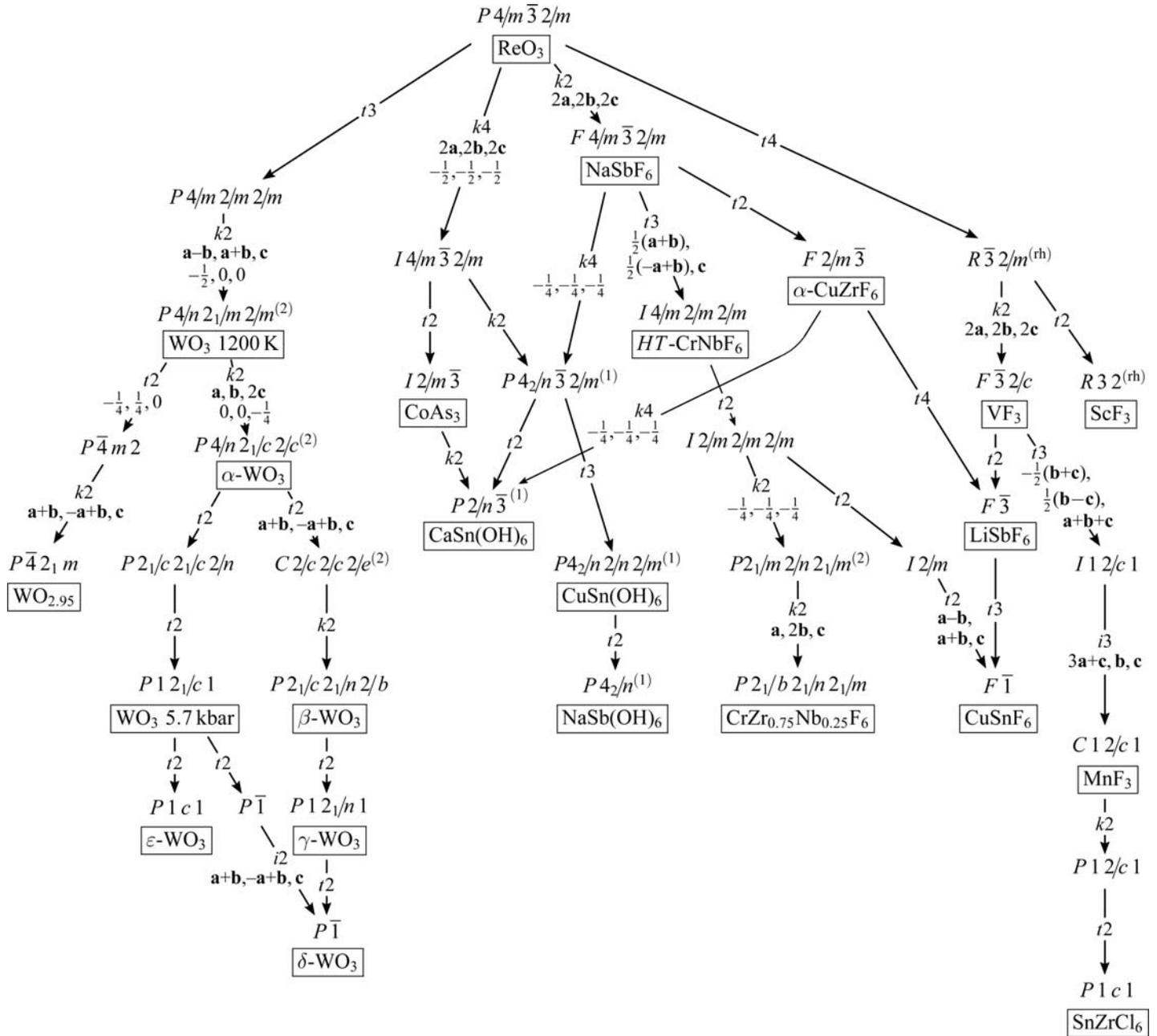
1. SPACE GROUPS AND THEIR SUBGROUPS

Fig. 1.6.4.10. Bärnighausen tree of hettotypes of the ReO_3 type. For the atomic parameters and other crystallographic data see Bock & Müller (2002b). $F\bar{3}2/c$ and $F\bar{3}$ are nonconventional face-centred settings of $R\bar{3}2/c$ and $R\bar{3}$, respectively, with rhombohedral-axes setting and nearly cubic metric, $F\bar{1}$ is a nearly cubic setting of $P\bar{1}$. Every space-group symbol corresponds to one space group (not space-group type) belonging to a specific crystal structure. Note that the vertical distances between space-group symbols are proportional to the logarithms of the indices.

(Müller, 1986), wurtzite derivatives (Baur & McLarnan, 1982) and NaCl derivatives with doubled cell (Sens & Müller, 2003).

1.6.5. Handling cell transformations

It is important to keep track of the coordinate transformations in a sequence of group–subgroup relations. A Bärnighausen tree can only be correct if every atomic position of every hettotype can be derived from the corresponding positions of the aristotype. The mathematical tools are described in Sections 1.2.2.3, 1.2.2.4 and 1.2.2.7 of this volume and in Part 5 of Volume A.

A basis transformation and an origin shift are mentioned in the middle of a group–subgroup arrow. This is a shorthand notation for the matrix–column pair (Seitz symbol; Section 1.2.2.3) or the 4×4 matrix (augmented matrix, Section 1.2.2.4) to be used to calculate the basis vectors, origin shift and coordinates of a maximal subgroup from those of the preceding space group. If there is a sequence of several transformations, the overall changes can be calculated by multiplication of the 4×4 matrices.

Let $\mathbb{P}_1, \mathbb{P}_2, \ldots$ be the 4×4 matrices expressing the basis vector and origin changes of several consecutive cell transformations. $\mathbb{P}_1^{-1}, \mathbb{P}_2^{-1}, \ldots$ are the corresponding inverse matrices. Let $\mathbf{a}, \mathbf{b}, \mathbf{c}$ be the starting (old) basis vectors and $\mathbf{a}', \mathbf{b}', \mathbf{c}'$ be the (new) basis vectors after the consecutive transformations. Let $\mathbb{x}$ and $\mathbb{x}'$ be the augmented columns of the atomic coordinates before and after the transformations. Then the following relations hold:

$$(\mathbf{a}', \mathbf{b}', \mathbf{c}', \boldsymbol{p}) = (\mathbf{a}, \mathbf{b}, \mathbf{c}, \boldsymbol{o})\,\mathbb{P}_1\mathbb{P}_2, \ldots \quad \text{and} \quad \mathbb{x}' = \ldots \mathbb{P}_2^{-1}\mathbb{P}_1^{-1}\mathbb{x}.$$

$\boldsymbol{p}$ is the vector of the origin shift, $i.e.$ its components are the coordinates of the origin of the new cell expressed in the coor-

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dinate system of the old cell; o is a zero vector. Note that the inverse matrices have to be multiplied in the reverse order.

Example 1.6.5.1

Take a transformation from a cubic to a rhombohedral unit cell (hexagonal setting) combined with an origin shift of $p_1 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ (in the cubic coordinate system), followed by transformation to a monoclinic cell with a second origin shift of $p_2 = (-\frac{1}{2}, -\frac{1}{2}, 0)$ (in the hexagonal coordinate system). From Fig. 1.6.5.1 (left) we can deduce

$$\mathbf{a}_{hx} = \mathbf{a}_{cb} - \mathbf{b}_{cb}, \quad \mathbf{b}_{hx} = \mathbf{b}_{cb} - \mathbf{c}_{cb}, \quad \mathbf{c}_{hx} = \mathbf{a}_{cb} + \mathbf{b}_{cb} + \mathbf{c}_{cb},$$

which in matrix notation is

$$(\mathbf{a}_{hx}, \mathbf{b}_{hx}, \mathbf{c}_{hx}) = (\mathbf{a}_{cb}, \mathbf{b}_{cb}, \mathbf{c}_{cb})P_1$$

$$= (\mathbf{a}_{cb}, \mathbf{b}_{cb}, \mathbf{c}_{cb})\begin{pmatrix} 1 & 0 & 1 \\ -1 & 1 & 1 \\ 0 & -1 & 1 \end{pmatrix}.$$

In the fourth column of the 4×4 matrix $\mathbb{P}_1$ we include the components of the origin shift, $p_1 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$:

$$\mathbb{P}_1 = \left(\begin{array}{c|c} P_1 & p_1 \\ \hline o & 1 \end{array}\right) = \left(\begin{array}{ccc|c} 1 & 0 & 1 & \frac{1}{4} \\ -1 & 1 & 1 & \frac{1}{4} \\ 0 & -1 & 1 & \frac{1}{4} \\ \hline 0 & 0 & 0 & 1 \end{array}\right).$$

The inverse matrix P_1^{-1} can be calculated by matrix inversion, but it is more straightforward to deduce it from Fig. 1.6.5.1; it is the matrix that converts the hexagonal basis vectors back to the cubic basis vectors:

$$\mathbf{a}_{cb} = \frac{2}{3}\mathbf{a}_{hx} + \frac{1}{3}\mathbf{b}_{hx} + \frac{1}{3}\mathbf{c}_{hx}, \quad \mathbf{b}_{cb} = -\frac{1}{3}\mathbf{a}_{hx} + \frac{1}{3}\mathbf{b}_{hx} + \frac{1}{3}\mathbf{c}_{hx},$$
$$\mathbf{c}_{cb} = -\frac{1}{3}\mathbf{a}_{hx} - \frac{2}{3}\mathbf{b}_{hx} + \frac{1}{3}\mathbf{c}_{hx},$$

$$(\mathbf{a}_{cb}, \mathbf{b}_{cb}, \mathbf{c}_{cb}) = (\mathbf{a}_{hx}, \mathbf{b}_{hx}, \mathbf{c}_{hx})P_1^{-1}$$

$$= (\mathbf{a}_{hx}, \mathbf{b}_{hx}, \mathbf{c}_{hx})\begin{pmatrix} \frac{2}{3} & -\frac{1}{3} & -\frac{1}{3} \\ \frac{1}{3} & \frac{1}{3} & -\frac{2}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{pmatrix}.$$

The column part (fourth column) of the inverse matrix $\mathbb{P}_1^{-1}$ is $-P_1^{-1}p_1$ (*cf.* equation 1.2.2.6):

$$-P_1^{-1}p_1 = -\begin{pmatrix} \frac{2}{3} & -\frac{1}{3} & -\frac{1}{3} \\ \frac{1}{3} & \frac{1}{3} & -\frac{2}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{pmatrix}\begin{pmatrix} \frac{1}{4} \\ \frac{1}{4} \\ \frac{1}{4} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ -\frac{1}{4} \end{pmatrix}.$$

Therefore, $\mathbb{P}_1^{-1}$ is

$$\mathbb{P}_1^{-1} = \left(\begin{array}{c|c} P_1^{-1} & -P_1^{-1}p_1 \\ \hline o & 1 \end{array}\right) = \left(\begin{array}{ccc|c} \frac{2}{3} & -\frac{1}{3} & -\frac{1}{3} & 0 \\ \frac{1}{3} & \frac{1}{3} & -\frac{2}{3} & 0 \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} & -\frac{1}{4} \\ \hline 0 & 0 & 0 & 1 \end{array}\right).$$

Similarly, for the second (hexagonal to monoclinic) transformation, we deduce the matrices P_2, P_2^{-1} and the column part of $\mathbb{P}_2^{-1}$, $-P_2^{-1}p_2$, from the right image of Fig. 1.6.5.1:
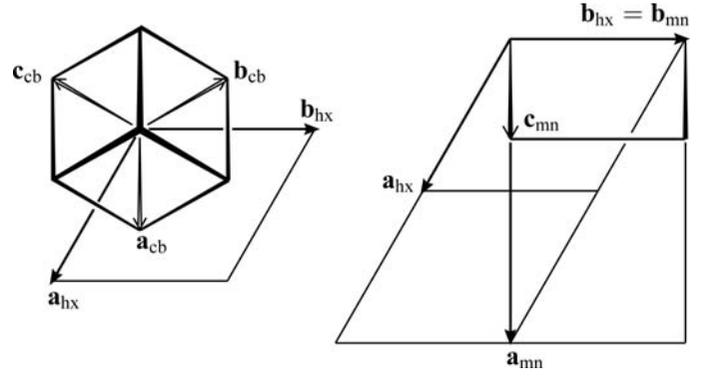

Fig. 1.6.5.1. Relative orientations of a cubic to a rhombohedral cell (hexagonal setting) (left) and of a rhombohedral cell (hexagonal setting) to a monoclinic cell (the monoclinic cell has an acute angle β).

$$(\mathbf{a}_{mn}, \mathbf{b}_{mn}, \mathbf{c}_{mn}) = (\mathbf{a}_{hx}, \mathbf{b}_{hx}, \mathbf{c}_{hx})P_2$$

$$= (\mathbf{a}_{hx}, \mathbf{b}_{hx}, \mathbf{c}_{hx})\begin{pmatrix} 2 & 0 & \frac{2}{3} \\ 1 & 1 & \frac{1}{3} \\ 0 & 0 & \frac{1}{3} \end{pmatrix}$$

$$(\mathbf{a}_{hx}, \mathbf{b}_{hx}, \mathbf{c}_{hx}) = (\mathbf{a}_{mn}, \mathbf{b}_{mn}, \mathbf{c}_{mn})P_2^{-1}$$

$$= (\mathbf{a}_{mn}, \mathbf{b}_{mn}, \mathbf{c}_{mn})\begin{pmatrix} \frac{1}{2} & 0 & -1 \\ -\frac{1}{2} & 1 & 0 \\ 0 & 0 & 3 \end{pmatrix}$$

$$-P_2^{-1}p_2 = -\begin{pmatrix} \frac{1}{2} & 0 & -1 \\ -\frac{1}{2} & 1 & 0 \\ 0 & 0 & 3 \end{pmatrix}\begin{pmatrix} -\frac{1}{2} \\ -\frac{1}{2} \\ 0 \end{pmatrix} = \begin{pmatrix} \frac{1}{4} \\ \frac{1}{4} \\ 0 \end{pmatrix}.$$

For the basis vectors of the two consecutive transformations we calculate:

$$\mathbb{P}_1\mathbb{P}_2 = \left(\begin{array}{ccc|c} 1 & 0 & 1 & \frac{1}{4} \\ -1 & 1 & 1 & \frac{1}{4} \\ 0 & -1 & 1 & \frac{1}{4} \\ \hline 0 & 0 & 0 & 1 \end{array}\right)\left(\begin{array}{ccc|c} 2 & 0 & \frac{2}{3} & -\frac{1}{2} \\ 1 & 1 & \frac{1}{3} & -\frac{1}{2} \\ 0 & 0 & \frac{1}{3} & 0 \\ \hline 0 & 0 & 0 & 1 \end{array}\right)$$

$$= \left(\begin{array}{ccc|c} 2 & 0 & 1 & -\frac{1}{4} \\ -1 & 1 & 0 & \frac{1}{4} \\ -1 & -1 & 0 & \frac{3}{4} \\ \hline 0 & 0 & 0 & 1 \end{array}\right),$$

$$(\mathbf{a}_{mn}, \mathbf{b}_{mn}, \mathbf{c}_{mn}, p) = (\mathbf{a}_{cb}, \mathbf{b}_{cb}, \mathbf{c}_{cb}, o)\mathbb{P}_1\mathbb{P}_2$$

$$= (\mathbf{a}_{cb}, \mathbf{b}_{cb}, \mathbf{c}_{cb}, o)\left(\begin{array}{ccc|c} 2 & 0 & 1 & -\frac{1}{4} \\ -1 & 1 & 0 & \frac{1}{4} \\ -1 & -1 & 0 & \frac{3}{4} \\ \hline 0 & 0 & 0 & 1 \end{array}\right),$$

which corresponds to

$$\mathbf{a}_{mn} = 2\mathbf{a}_{cb} - \mathbf{b}_{cb} - \mathbf{c}_{cb}, \quad \mathbf{b}_{mn} = \mathbf{b}_{cb} - \mathbf{c}_{cb}, \quad \mathbf{c}_{mn} = \mathbf{a}_{cb}$$

and an origin shift of $p = (-\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$ in the cubic coordinate system. The corresponding (cubic to monoclinic) coordinate transformations result from

$$\mathbb{X}_{mn} = \mathbb{P}_2^{-1}\mathbb{P}_1^{-1}\mathbb{X}_{cb}$$

$$
\begin{pmatrix} x_{mn} \\ y_{mn} \\ z_{mn} \\ \hline 1 \end{pmatrix} =
\left(\begin{array}{ccc|c} \frac{1}{2} & 0 & -1 & \frac{1}{4} \\ -\frac{1}{2} & 1 & 0 & \frac{1}{4} \\ 0 & 0 & 3 & 0 \\ \hline 0 & 0 & 0 & 1 \end{array} \right)
\left(\begin{array}{ccc|c} \frac{2}{3} & -\frac{1}{3} & -\frac{1}{3} & 0 \\ \frac{1}{3} & \frac{1}{3} & -\frac{2}{3} & 0 \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} & -\frac{1}{4} \\ \hline 0 & 0 & 0 & 1 \end{array} \right)
\begin{pmatrix} x_{cb} \\ y_{cb} \\ z_{cb} \\ \hline 1 \end{pmatrix}
$$

$$
= \left(\begin{array}{ccc|c} 0 & -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ 0 & \frac{1}{2} & -\frac{1}{2} & \frac{1}{4} \\ 1 & 1 & 1 & -\frac{3}{4} \\ \hline 0 & 0 & 0 & 1 \end{array} \right)
\begin{pmatrix} x_{cb} \\ y_{cb} \\ z_{cb} \\ \hline 1 \end{pmatrix},
$$

which is the same as

$$x_{mn} = -\tfrac{1}{2}y_{cb} - \tfrac{1}{2}z_{cb} + \tfrac{1}{2}, \quad y_{mn} = \tfrac{1}{2}y_{cb} - \tfrac{1}{2}z_{cb} + \tfrac{1}{4},$$
$$z_{mn} = x_{cb} + y_{cb} + z_{cb} - \tfrac{3}{4}.$$

1.6.6. Comments concerning phase transitions and twin domains

When a compound forms several polymorphic forms, a Bärnighausen tree can serve to show whether second-order phase transitions are feasible between them and what kinds of twin domains may be formed during such a transition. The possible kinds of domains can also be deduced for first-order phase transitions involving a group–subgroup relation and for topotactic reactions.

Second-order (continuous) phase transitions are only possible if there is a direct (not necessarily maximal) group–subgroup relation between the space groups of the two phases. If there is no such relation, for example, if two polymorphic forms can be related only by a common supergroup, the phase transformation can only be of first order. The condition of a direct group–subgroup relation is a necessary but not a sufficient condition; the phase transition can still be of first order.

The domain structure of crystalline phases that often results at solid-state phase transitions and during topotactic reactions can be transparently interpreted with the aid of symmetry considerations (Section 1.2.7; Bärnighausen, 1980; Janovec & Přívratská, 2003; van Tendeloo & Amelinckx, 1974; Wondratschek & Jeitschko, 1976). A domain structure is the result of nucleation and growth processes. The orientational relations between the phases before and after the transformation, as a rule, are not the result of a homogeneous process involving a simultaneous motion of the atoms in a single crystal. The crystalline matrix of the substrate rather governs the preferred orientation adopted by the nuclei that are formed during the course of the nucleation process. The crystallites that result from the subsequent growth of the nuclei maintain their orientations. Under these circumstances, aspect 3 of the symmetry principle, as stated in Section 1.6.2, is fully effective. A phase transition that is connected with a symmetry reduction will result in new phases that consist of

(i) *twin domains* if the formed phase belongs to a crystal class with reduced symmetry, or

(ii) *antiphase domains* (translational domains) if translational symmetry is lost.

The total number of domains, of course, depends on the number of nucleation sites. The number of different domain kinds, however, is ruled by the index of the symmetry reduction. At a *translationengleiche* symmetry reduction of index 3 (*t3* group–subgroup relation) we can expect twins with three kinds of domains, having three different orientations. An isomorphic subgroup of index 5 (*i5* relation), since it is a *klassengleiche* symmetry reduction, will entail five kinds of antiphase domains. If the symmetry reduction includes several steps (in a chain of several maximal subgroups), the domain structure will become more complicated. With two *t2* group–subgroup relations, we can expect twins of twins with two kinds of domains each. In the example of Fig. 1.2.7.1, we have a sequence of one *t2* and one *k2* step; therefore, as explained in a more rigorous manner in Example 1.2.7.3.4, we can expect two kinds of twin domains having two different orientations and, in addition, two kinds of antiphase domains. The actual number of observable domain kinds may be less than expected if a domain kind is not formed during nucleation. This can be controlled by the nucleation conditions; for example, an external electric field can suppress the formation of more than one kind of differently oriented ferroelectric domains.

In the physical literature, phase transitions between *translationengleiche* space groups are sometimes called *ferroic* transitions, those between *klassengleiche* space groups are *non-ferroic*.

As mentioned at the end of Section 1.6.4.5, a common subgroup of two space groups usually is not suitable for relating two crystal structures. Just so, a common crystallographic subgroup is unfit to explain the mechanism for a reconstructive, first-order phase transition. Such mechanisms have been proposed repeatedly (see, *e.g.*, Capillas *et al.*, 2007, and references therein). Like in a second-order transition, continuous atomic movements have been assumed, leading first to a structure with the reduced symmetry of a common subgroup, followed by a symmetry increase to the space group of the second phase. However, a first-order transition always shows hysteresis, which means that the initial and the final phase coexist during the transition and that there is a phase boundary between them. The transition begins at a nucleation site, followed by the growth of the nucleus (see, *e.g.*, Binder, 1987; Chaitkin & Lubensky, 1995; Chandra Shekar & Gavinda Rajan, 2001; Christian, 2002; Doherty, 1996; Gunton, 1984; Herbstein, 2006; Jena & Chaturvedi, 1992; Wayman & Bhadeshia, 1996). The reconstruction of the structure and the necessary atomic motions occur at the phase boundary between the receding old phase and the growing new phase. Any intermediate state is restricted to this interface between the two phases. *It is impossible to assign a three-dimensional space group to an interface.* In addition, while the interface advances through the crystal, the atoms at the interface do not linger in a static state. A space group can only be assigned to a static state (time-dependent phenomena are not covered by space-group theory).

1.6.7. Exercising care in the use of group–subgroup relations

Using the tables of this volume or from other sources or using computer programs as offered by the Bilbao Crystallographic Server (see Chapter 1.7), it may be easy to search for group–subgroup relations between space groups of crystal structures. This should only be done bearing in mind and explicitly stating a crystallographic, physical or chemical context. It is senseless to construct relations in a purely formal manner, 'just for fun', without a sound crystal-chemical or physical foundation. There exist no clear criteria to determine what is a 'sound foundation', but crystallographic, chemical and physical common sense and knowledge should always be taken into consideration.

In addition, by experience we know that setting up trees of group–subgroup relations is susceptible to pitfalls. Some sources of errors are: not taking into account necessary origin shifts; wrong origin shifts; wrong basis and/or coordinate transformations; unnecessary basis transformations just for the sake of clinging on to standard space-group settings; lack of distinction between space groups and space-group types; lack of keeping track of the development of the atomic positions from group to subgroup; using different space-group or coordinate settings for like structures. If the group–subgroup relations are correct, but origin shifts or basis transformations have not been stated, this can cause subsequent errors and misunderstandings.

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