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# Symmetry Relations between Crystal Structures

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This manuscript has many predecessors. It is based on lectures and courses that repeatedly have been held since 1975 in Germany, Italy and France. Parts of this script were adopted from course scripts and other material by Hartmut Bärnighausen (University of Karlsruhe). I am grateful to him for his generosity and for numerous discussions and suggestions.

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## Part 1: Trees of Group–subgroup Relations

### 1 Introduction

In the early days of crystal structure determinations it became clear that the laws governing the packing of atoms and molecules must be understood, that crystal structures have to be classified and ordered, and that relations between them must be recognized. Meanwhile more than 400000 crystal structures have been deposited in databases. Without ordering principles it would be a hopeless undertaking to master this flood of data.

Many conceptions have been developed to this end, such as the famous rules of PAULING on ionic radii, coordination polyhedra and the joining of polyhedra or the Zintl-Klemm-Busmann rules. These and other principles have served in textbooks and other publications to classify crystal structures. However, in most cases symmetry considerations have not been considered at all or only as a secondary tool. This is astonishing, since symmetry is indispensable for the determination and the description of a specific crystal structure. There is a reason for this discrepancy: Related crystal structures often have different space groups, and the relations between them result from group–subgroup relations between their space groups. These relations were only partially known up to 1965, and a useful form derived by NEUBÜSER & WONDRADESCHEK was not generally accessible for another 18 years [1]. For the first time, they were included in the 1983 edition of *International Tables for Crystallography*, Volume A [2]. And yet, even in the 2005 edition, the listing of the subgroups in Volume A is incomplete. The complete listing finally has become available in 2004 in the additional Volume A1 [3].

In addition, two essential kinds of information are missing in Volume A: (1) One must not only know the subgroups of the space groups, but also which coordinate transformations are involved; (2) The relations between the positions occupied by atoms in the space groups in question must be known. In principle, this information can be extracted from Volume A, but that is a cumbersome task prone to errors. In the new Volume A1 all this information is now completely available (for all of the infinite many subgroups). Another source of information is the *Bilbao Crystallographic Server* [4].

In 1980 BÄRNIGHAUSEN presented a procedure to set forth structural relations between crystal structures with the aid of symmetry relations between space groups [5]. For a recent review on this subject see [6]. Short descriptions can be found at [7] and [8]. 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 partial substitutions of atoms. A tree of group–subgroup relations between the involved space groups, now called a *Bärnighausen tree*, serves as the main guideline. The highly symmetrical starting structure is called the *aristotype* after MEGAW [9] or *basic structure* after BUERGER [10, 11]. The derived structures are the *hettotypes* or *derivative structures*.

Aside from their usefulness in systematic crystal chemistry, group–subgroup relations have other applications: They help understanding the domain structures of twinned crystals, they are indispensable to treat second-order phase transitions and they even help in the determination of protein crystal structures.

## 2 The Symmetry Principle in Crystal Chemistry

The usefulness of symmetry relations intimately has to do with the symmetry principle in crystal chemistry. This principle is based on experience and has been worded during its long history in rather different ways. BÄRNIGHAUSEN summarized it in the following way [5]:

### The Symmetry Principle in Crystal Chemistry

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 may prevent the attainment of the highest possible symmetry. However, in most cases the deviations from the ideal symmetry are small (key-word pseudosymmetry).
3. During phase transitions and solid state reactions which result in products of lower symmetry, the higher symmetry of the starting material is indirectly preserved by the formation of oriented domains.

Another wording which stresses aspect 1 is due to BRUNNER [12]:

Atoms of the same kind tend to occupy equivalent positions.

This wording gives us a hint to the physical reasons governing the symmetry principle: 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 favorable surrounding for atoms of a given kind which all of these atoms strive to attain. According to quantum theory, atoms of the same kind are indistinguishable, but in a crystal this is only ensured if they are symmetry-equivalent.

Aspect 2 of the symmetry principle is exploited in the following chapters. 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 like atomic positions by different kinds of atoms; (6) Condensation of lattice vibrations (soft modes); (7) Ordering of atoms in a disordered structure.

Aspect 3 of the symmetry principle has its origin in an observation of BERNAL. He noted that in the solid state reaction  $\text{Mn}(\text{OH})_2 \rightarrow \text{MnOOH} \rightarrow \text{MnO}_2$  the starting and the product crystal had the same orientation. Such reactions are called *topotactic reactions* [13, 14]. In a paper by BERNAL & MACKAY we find the sentence [15]:

“One of the controlling factors of topotactic reactions is, of course, symmetry.

This can be treated at various levels of sophistication, but we find that the simple concept of Buridan’s ass illumines most cases.”

According to the metaphor of BURIDAN (French philosopher, died ca. 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 behavior would correspond to an absence of phase transitions or solid-state reactions if there are more than one energetic equivalent orientations of the domains of the products. Crystals, of course, do not behave like the ass; they take both.

### 3 Subgroups of space groups

The theory of space groups is dealt with in the literature [3, 16, 17, 18]. However, for the understanding of the following sections I repeat a few important terms.

A space group is a group according to group theory. The symmetry operations (not the symmetry elements) are the group elements that make up the space group. A group that results by the removal of some of the symmetry operations is a subgroup. If there exists no intermediate group between a space group and one of its subgroups, then this subgroup is a maximal subgroup. The index (of the symmetry reduction) is the factor, by which the number of symmetry operations has been reduced; it always is an integer. The index of a maximal subgroup always is a prime number  $p$  or a power of a prime number  $p^2$  or  $p^3$ .

According to Hermann's theorem, a maximal subgroup is either a *translationengleiche*\* or a *klassengleiche* subgroup. A *translationengleiche* subgroup still has the complete translation lattice; its primitive unit cell has an unchanged volume. A *klassengleiche* subgroup belongs to the same crystal class; it has lost translational symmetry, *i.e.* the conventional unit cell is either enlarged or it has lost centering translations. *Isomorphic* subgroups are a special kind of *klassengleiche* subgroups which belong to the same space-group type (same Hermann-Mauguin symbol) or to the enantiomorphic space-group type (*e.g.*  $P4_1$  and  $P4_3$ ). Every space group has an infinity of maximal isomorphic subgroups.

### 4 Bärnighausen trees

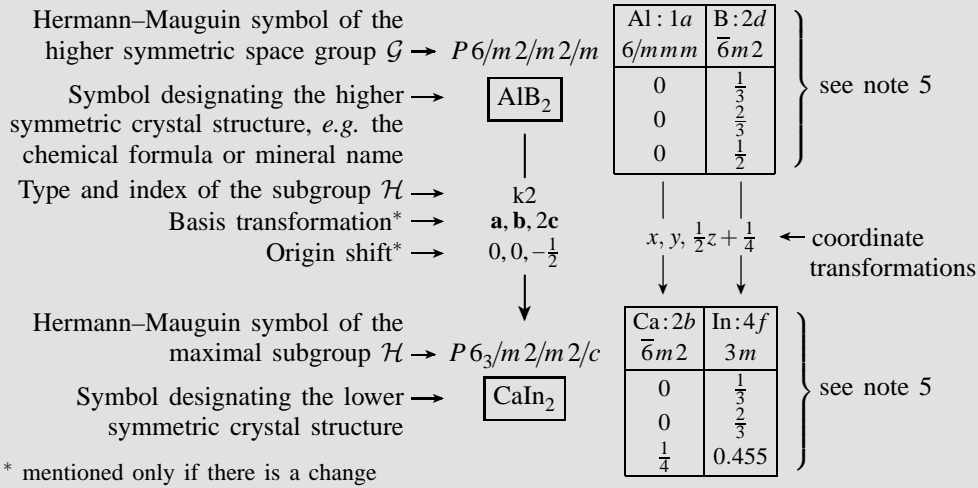
The aforementioned notions permit us to represent symmetry relations between different crystal structures in a concise manner. Beginning with the space group of the aristotype at its top, we construct a tree of group-subgroup relations in a modular design, each module representing one step of symmetry reduction to a maximal subgroup. Therefore, we only have to discuss one of these modules in detail.

For two structures we want to interrelate, we place their space-group symbols one under the other and indicate the direction of the symmetry reduction by an arrow pointing downwards (scheme on the following page). In the middle of this 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 size of the unit cell or its setting changes, we also insert the new basis vectors expressed as vector sums of the basis vectors of the higher symmetric 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 basis of the higher symmetric cell. *Any change of the basis vectors and the origin is essential information that should never be omitted.*

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\*called *zellengleiche* subgroups by HERMANN, but now called *translationengleiche* subgroups to avoid certain misunderstandings. German *translationengleiche* means 'with the same translations'. *Klassengleiche* means 'of the same (crystal) class'. A committee of experts of the International Union of Crystallography was not able to agree upon equivalent English terms and decided to keep the German terms; however, some authors use the terms 'equi-translational' and 'equi-class'. Use the German terms with terminal -e irrespective of the declension endings that would be used in German.

**Scheme of the general formulation of the smallest step of symmetry reduction  
connecting two related crystal structures**



**Explanatory notes**

1. Possible types of maximal subgroups  $\mathcal{H}$  of a given space group  $\mathcal{G}$ :

symbol	term	meaning
t	<i>translationen-gleiche</i>	$\mathcal{G}$ and $\mathcal{H}$ have the same translational lattice; the crystal class of $\mathcal{H}$ is of lower symmetry than that of $\mathcal{G}$
k	<i>klassengleiche</i>	$\mathcal{G}$ and $\mathcal{H}$ belong the same crystal class; $\mathcal{H}$ has lost translational symmetry, its primitive 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  $\mathcal{G}$ .
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  $\mathcal{G}$ .
4. Origin shift: The coordinate triplet of the origin of  $\mathcal{H}$  is given in the coordinate system of  $\mathcal{G}$ .
5. Additional information: Space permitting, the atomic positions are given in a box next to the space group symbol in the following way:

element symbol: Wyckoff label site symmetry
$x$
$y$
$z$

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

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 highly 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, *i.e.* to use space-group symbols that do not correspond to the standard settings of *International Tables for Crystallography*. Since they are more informative, it is advisable to use only the full Hermann–Mauguin symbols. For the differences between conventional and nonconventional settings see Sections 3.1.4 and 3.1.6 of *International Tables for Crystallography*, Volume A1 [3].

Origin shifts often cause problems and also tend to obscure relations. However, usually they cannot be avoided. There is no point to deviate from the standard origin settings of *International Tables for Crystallography*, because otherwise much additional information would be required for an unequivocal description. *Attention:* The coordinate triplet specifying the origin shift in the group–subgroup arrow refers to the *axes system of the higher symmetry space group*, while the corresponding changes of the atomic coordinates refer to the coordinate system of the subgroup and therefore always are different. Details are given in Section 3.1.3 of *International Tables*, Volume A1 [3]. Pay also attention that in the tables of Parts 2 and 3 of Volume A1 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 only given as parts of the coordinate transformations, *i.e.* in the coordinate systems of the subgroups. Unfortunately, the chosen origin shifts themselves (there are always different possible choices) also differ in Parts 2 and 3, which means that a coordinate transformation taken from Part 3 does not correspond to the one given in Part 2 for the same group–subgroup pair. In case of need, one has to calculate the corresponding values with the formulae of Section 3.1.3 of Volume A1.

For some space groups *International Tables* offer two possible choices of origin ('origin choice 1' and 'origin choice 2'). In these cases the choice is specified by a superscript <sup>(1)</sup> or <sup>(2)</sup> after the space-group symbol, for example  $P4/n^{(2)}$ . The setting of rhombohedral space groups is specified, if necessary, by superscript <sup>(rh)</sup> or <sup>(hex)</sup>. Occasionally it may be useful to use a nonconventional rhombohedral 'reverse' setting, *i.e.* with the centering 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 <sup>(rev)</sup>, for example  $R\bar{3}^{(rev)}$ .

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

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 absolutely 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. Unfortunately, for nearly all space groups there exist several different equivalent sets of coordinates describing one and the same structure, so

that one often is forced to transform coordinates from one set to another to attain the necessary correspondence (*cf.* next section).

If the space permits it, it is useful to list the site symmetries and the coordinates of the atoms next to the space groups in the Bärnighausen tree, such as shown in the scheme on page 6. If the space is not sufficient, this information must be listed in a separate table.

## 5 Atomic positions and Wyckoff positions

The use of a standardized description of crystal structures has been recommended to obtain comparable sets of data [19, 20, 21]. However, the corresponding rules have often been disregarded, not only because of ignorance or negligence, but also for good reasons. Two of these reasons are the above-mentioned recommendation to avoid cell transformations, if possible, and to observe a strict correspondence of atomic parameters of structures that are to be compared. Furthermore, even if the standardization rules are observed, there often are several possibilities to describe one and the same structure.

It is by no means a simple matter to recognize if two differently documented structures are alike or not. The literature abounds with examples of ‘new’ structures that in reality had been well known. For all space groups, except  $Im\bar{3}m$  and  $Ia\bar{3}d$ , there always exist several different equivalent sets of atomic coordinates for exactly the same crystal structure with an unchanged setting of the space group. For the space group  $\mathcal{G}$  the number of equivalent coordinate sets is  $e$ ;  $e$  is the index of  $\mathcal{G}$  in its *Euclidean normalizer*  $\mathcal{N}_{\mathcal{E}}(\mathcal{G})$  [22, 23].  $\mathcal{N}_{\mathcal{E}}(\mathcal{G})$  is a supergroup of  $\mathcal{G}$ .

A procedure to obtain one equivalent coordinate set from another is described in Section 15.3 of *International Tables*, Volume A [2]; see also [24]. One takes advantage of the Euclidean Normalizers, using the transformation formulae given in Tables 15.2.1.3 and 15.2.1.4 of Volume A (editions of 2002 and 2005; Table 15.3.2 in the editions of 1987 to 1995) under the heading ‘Additional generators of  $\mathcal{N}_{\mathcal{E}}(\mathcal{G})$ ’. The last column of the tables contains the indices  $e$  of  $\mathcal{G}$  in  $\mathcal{N}_{\mathcal{E}}(\mathcal{G})$ . *Cf.* example on the next page. *Attention:* For chiral space groups like  $P3_1$  one obtains only equivalent sets of coordinates without a change of chirality; for chiral structures in non-chiral Sohncke space groups [25] like  $P2_12_12_1$  the sets of coordinates include the enantiomeric pairs.

The infinitely large set of symmetry-equivalent points in a space group is called a (*crystallographic*) *orbit* [27, 28, 29]. If the corresponding coordinates are completely fixed by symmetry (*e.g.*  $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ ), the orbit is identical with the *Wyckoff position* (German: *Punktlage*). If, however, one or more coordinates are variable (*e.g.*  $z$  in  $0, \frac{1}{2}, z$ ), the Wyckoff position comprises infinite many orbits; they differ in the variable coordinate. The set of points that is symmetry-equivalent to, say,  $0, \frac{1}{2}, 0.391$  makes up one orbit. The set of points corresponding to  $0, \frac{1}{2}, 0.468$  belongs to the same Wyckoff position, but to a different orbit. Therefore, the Wyckoff position may comprise many orbits (do not get irritated by the singular form of the words orbit, Wyckoff position and *Punktlage*).

A Wyckoff position is designated by the Wyckoff label, for example 4c. The 4 is the *multiplicity*; it shows how many points belonging to an orbit of the Wyckoff position



**Example 1**

WOB<sub>4</sub> crystallizes in the space group  $I4$  with the following atomic coordinates [26]:

	$x$	$y$	$z$
W	0	0	0.078
O	0	0	0.529
Br	0.260	0.069	0.0

The Euclidean Normalizer of  $I4$  is  $P^14/mmm$  with the basis vectors  $\frac{1}{2}(\mathbf{a}-\mathbf{b})$ ,  $\frac{1}{2}(\mathbf{a}+\mathbf{b})$ ,  $\epsilon\mathbf{c}$  (cf. *International Tables*, Volume A, Table 15.2.1.4). The index of  $P^14/mmm$  in  $I4$  is  $\infty \cdot 2 \cdot 2$ , i.e. infinite, due to the infinitesimal small basis vector  $\epsilon\mathbf{c}$ . By addition of  $0,0,t$  to the coordinates of all atoms one obtains one out of an infinity of new equivalent coordinate sets, because  $t$  may have any arbitrary value. The index  $\infty \cdot 2 \cdot 2$  expresses that for each of these infinite many coordinate sets there are four equivalent sets. They result by inversion at  $0,0,0$  and by the transformation  $y, x, z$ . The obtained equivalent coordinate sets include the enantiomeric pairs:

W	0	0	0.078 + $t$	0	0	-0.078 - $t$	
O	0	0	0.529 + $t$	0	0	-0.529 - $t$	
Br	0.260	0.069	0,0 + $t$	-0.260	-0.069	0,0 - $t$	
W	0	0	0.078 + $t$	0	0	-0.078 - $t$	
O	0	0	0.529 + $t$	0	0	-0.529 - $t$	
Br	0.069	0.260	0,0 + $t$	-0.069	-0.260	0,0 - $t$	with $t =$ arbitrary

in question are contained in one unit cell. The  $c$  is an alphabetical label ( $a, b, c, \dots$ ) according to the listing of the Wyckoff positions in *International Tables*, Volume A [2].

A consequence of this kind of labeling is its dependence on the size of the chosen unit cell. For example, the multiplicities of rhombohedral space groups are larger by a factor of three if the unit cell is not referred to rhombohedral but to hexagonal axes.

Many space groups have several equivalent Wyckoff positions that commonly make up a *Wyckoff set*. These Wyckoff positions have the same site symmetries. For example, all positions on all twofold rotation axes of the space group  $I222$  form a Wyckoff set.

Between the points of an orbit and the corresponding points of a subgroup there exists a one-to-one relation. Both orbits have the same magnitude. Upon symmetry reduction, a Wyckoff position will either split into several symmetry-independent positions, or its site symmetry is reduced, or both happen [30]. If there is a splitting, some or all positions can keep their site symmetries. Atomic coordinates fixed on special positions or coupled with each other may become independent.

If atoms of an orbit are to be substituted by atoms of different elements in an ordered way, it must split. Distortions of the structure require a reduction of the site symmetry, unless it is already low enough. Upon distortion, the coordinates of some or all atoms may or must deviate from the ideal parameters of the undistorted structure. In addition, usually a metric distinction of the basis vectors takes place.

The relations between the Wyckoff positions of a group and a subgroup are uniquely determined as long as the relative positions of the unit cells of group and subgroup are

uniquely determined. Usually there are several (arbitrary) possibilities for the relative positions of the cells, and the relations of the Wyckoff positions may differ.

How the Wyckoff positions of the space groups are transformed to the Wyckoff positions of their subgroups is completely listed in *International Tables*, Volume A1 [3]. The listed relations are only valid for the mentioned basis transformations and origin shifts. For other basis transformations or origin shifts interchanges within the Wyckoff sets may have to be performed. The relations of the Wyckoff positions can also be obtained with the computer program WYCKSPLIT, which is accessible via internet at the Bilbao Crystallographic Server [31]. It requires the input of the space group, subgroup, basis transformation and origin shift; it does not work for non-conventional settings unless transformation matrices are given to convert to standard settings.

## 6 Symmetry relations between crystal structures

In this chapter the different kinds of group-subgroup relations are explained with the aid of simple examples.

### 6.1 Translationengleiche maximal subgroups

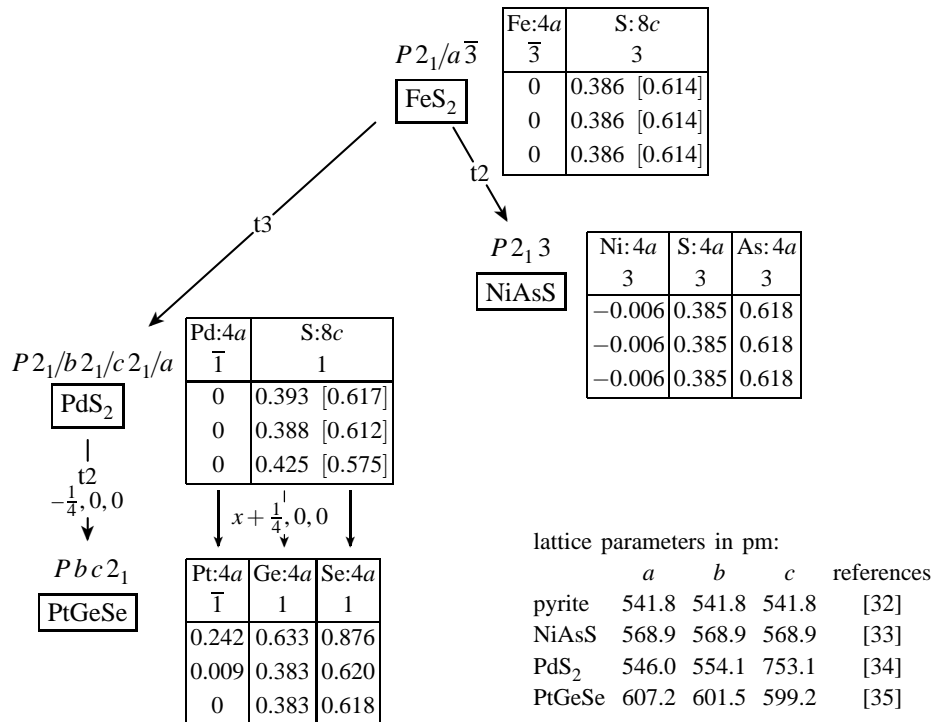
The space group  $Pbca$  of  $PdS_2$  is a *translationengleiche* maximal subgroup of  $Pa\bar{3}$ , the space group of pyrite ( $FeS_2$ ). The threefold axes of the cubic space group are lost, the index is 3. The twofold screw axes parallel to the edges of the cube and the glide planes are retained, but they no longer are equivalent in the orthorhombic subgroup, so that they all have to be mentioned now in the Hermann–Mauguin symbol  $P2_1/b2_1/c2_1/a$  (short symbol  $Pbca$ ). As shown in Fig. 1, the atomic coordinates have not changed much. However, the two structures differ, 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.

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

If the positions of the sulfur atoms of pyrite or  $PdS_2$  are substituted by two different kinds of atoms in an ordered 1 : 1 ratio, this enforces a symmetry reduction to subgroups. These may only be subgroups in which the sulfur positions split into symmetrically independent positions. In the chosen examples NiAsS and PtGeSe the symmetry reductions consist in the loss of the inversion centers of  $Pa\bar{3}$  and  $Pbca$ .

In both examples the site symmetries of the splitting Wyckoff positions are kept (site symmetry 3 for NiAsS, 1 for PtGeSe). For subgroups of index 2 it always holds that a position either splits or suffers a site symmetry reduction. Coordinate changes are not necessary, but may occur depending on site symmetry. In our examples there are small coordinate changes.

The relations between  $FeS_2$ ,  $PdS_2$ , NiAsS and PtGeSe are summarized in Fig. 1 according to the scheme presented on page 6.  $Pbc2_1$  corresponds to  $Pca2_1$  after inter-



**Figure 1:** Bärnighausen tree for the structural family of pyrite. Coordinates in brackets (not stated normally) refer to symmetry equivalent positions

change of the axes  $a$  and  $b$ . Mind the origin shift from PdS<sub>2</sub> 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 opposed sign. The unit cells are depicted in Fig. 2.

The substitution variants NiAsS and PtGeSe can only be connected by the common supergroup  $P2_1/a\bar{3}$ . A direct group-subgroup relation from  $P2_13$  to  $Pbc2_1$  is not possible, since  $P2_13$  has no glide planes. The difference between NiAsS and PtGeSe is due to the different distributions of the atoms.

## 6.2 Klassengleiche maximal subgroups

Let us consider two variants of the  $AlB_2$  type as an example of *klassengleiche* subgroups [36].  $AlB_2$  has a simple hexagonal structure in the space group  $P6/mmm$ . In the direction of  $c$  aluminum atoms and sheets of boron atoms alternate; the boron sheets are planar like in graphite (Fig. 3) [37]. The  $ZrBeSi$  type has a similar structure [38], but the sheets consist of Be and Si atoms. As a consequence, the inversion centers in the middles of the six-membered rings cannot be retained, whereas those in the Al positions

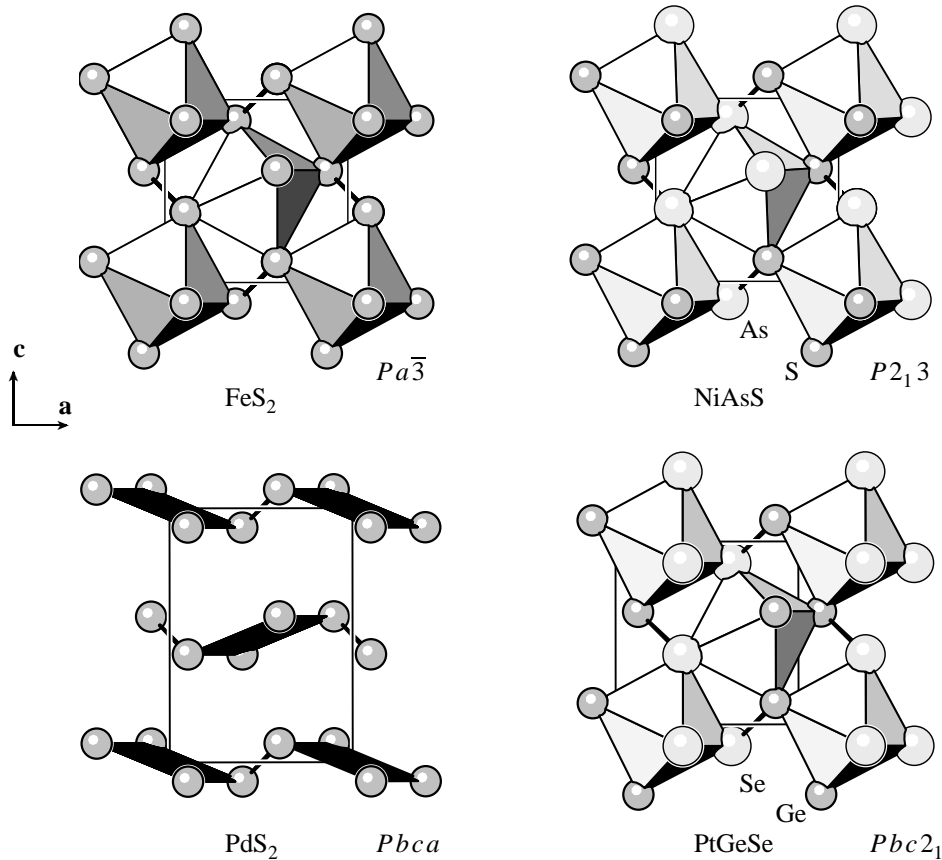
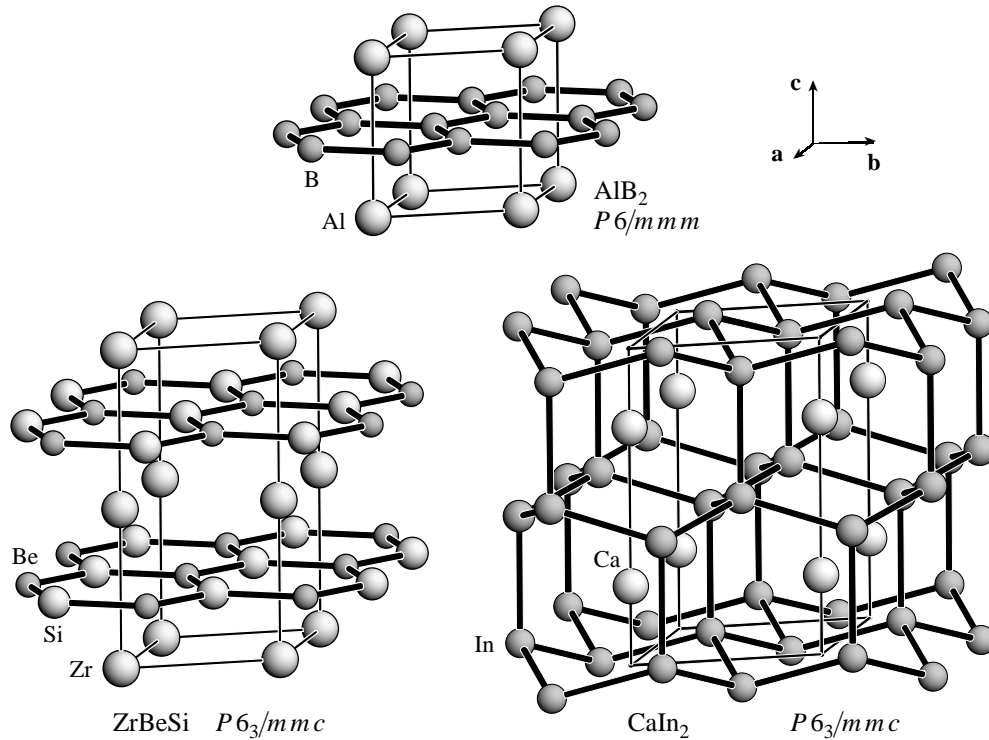


Figure 2: Views of the unit cells of pyrite, NiAsS, PdS<sub>2</sub> and PtGeSe

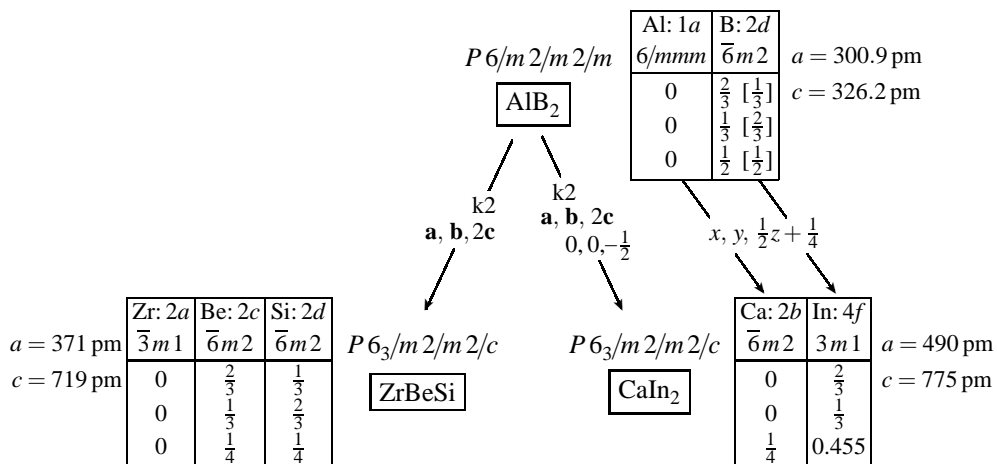
are retained in the Zr positions. This enforces a symmetry reduction to the *klassengleiche* subgroup  $P6_3/mmc$  with doubled  $c$  vector.

The doubling of  $c$  is the essential aspect of the symmetry reduction. The index is 2: Half of all translations are lost, half of the inversion centers, half of the symmetry axes perpendicular to  $c$  and half of the mirror planes perpendicular to  $c$ . Instead of the mirror planes perpendicular to  $[210]$  (last  $m$  in the Hermann-Mauguin-Symbol) there are glide planes  $c$ . 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. 4 left), rendering possible the occupation with atoms of two different elements.

Figs. 3 and 4 show us another peculiarity.  $P6/mmm$  has two *different klassengleiche* subgroups of the same type  $P6_3/mmc$  with doubled basis vector  $c$ . The second one corresponds to  $CaIn_2$  [39, 40]. Here the graphite-like sheets of the  $AlB_2$  type have become puckered layers of indium atoms; the In atoms of adjacent layers have shifted parallel to  $c$  and have come close to each other in pairs, so that the result is a three-dimensional network as in lonsdaleite ('hexagonal diamond'). The alternating shift of the atoms no longer permits the existence of mirror planes in the layers; however, neighboring lay-



**Figure 3:** The structures of  $\text{AlB}_2$ ,  $\text{ZrBeSi}$  and  $\text{CaIn}_2$ . The mirror planes perpendicular to  $c$  of  $P6_3/mmc$  are at  $z = \frac{1}{4}$  and  $z = \frac{3}{4}$



**Figure 4:** Two hettotypes of the  $\text{AlB}_2$  type having the same space-group type and a doubled  $c$  axis, but different origin positions. Due to the doubling of  $c$  the  $z$  coordinates are halved. The origin shift of  $0, 0, -\frac{1}{2}$  in the right branch refers to the lattice of the aristotype; as a consequence,  $\frac{1}{4}$  has to be added to the  $z$  coordinates of the hettotype

ers are mutually mirror-symmetrical. The calcium atoms are on the mirror planes, but no longer on inversion centers. The difference between the two subgroups  $P6_3/mmc$  consists in the selection of the symmetry operations that are lost with the doubling of  $c$ .

The conventional description of the space groups according to *International Tables* requires an inversion center to be at the origin of space group  $P6_3/mmc$ . The position of the origin in an Al atom of the  $\text{AlB}_2$  type can be kept when the symmetry is reduced to that of  $\text{ZrBeSi}$  (*i.e.* it is on a Zr atom). The symmetry reduction to  $\text{CaIn}_2$ , however, requires an origin shift to the center of one of the six-membered rings. In terms of the unit cell of the aristotype that is a shift by  $0, 0, -\frac{1}{2}$ , and this way it is marked in the group-subgroup arrow in Fig. 4. For the new atomic coordinates, which are referred to the axes system of the subgroup, the origin shift results in the addition of  $+\frac{1}{4}$  to the  $z$  coordinates, *i.e.* with *opposite* sign, compared to the value given in the group-subgroup arrow; in addition, due to the doubling of  $c$ , the  $z$  coordinates of the aristotype have to be halved. The new  $z$  coordinate of the In atom therefore is approximately  $z' \approx \frac{1}{2}z + \frac{1}{4} = \frac{1}{2} \cdot \frac{1}{2} + \frac{1}{4}$ . It cannot be exactly this value, because then there would have been no symmetry reduction and the space group would still be  $P6/mmm$ .

In the relation  $\text{AlB}_2 \rightarrow \text{ZrBeSi}$  the site symmetry  $\bar{6}m2$  of the boron atoms is maintained and the Wyckoff position splits. In the relation  $\text{AlB}_2 \rightarrow \text{CaIn}_2$  it is the other way, the position does not split, the atoms remain symmetry-equivalent, but their site symmetry is reduced to  $3m1$  and the  $z$  coordinate becomes independent.

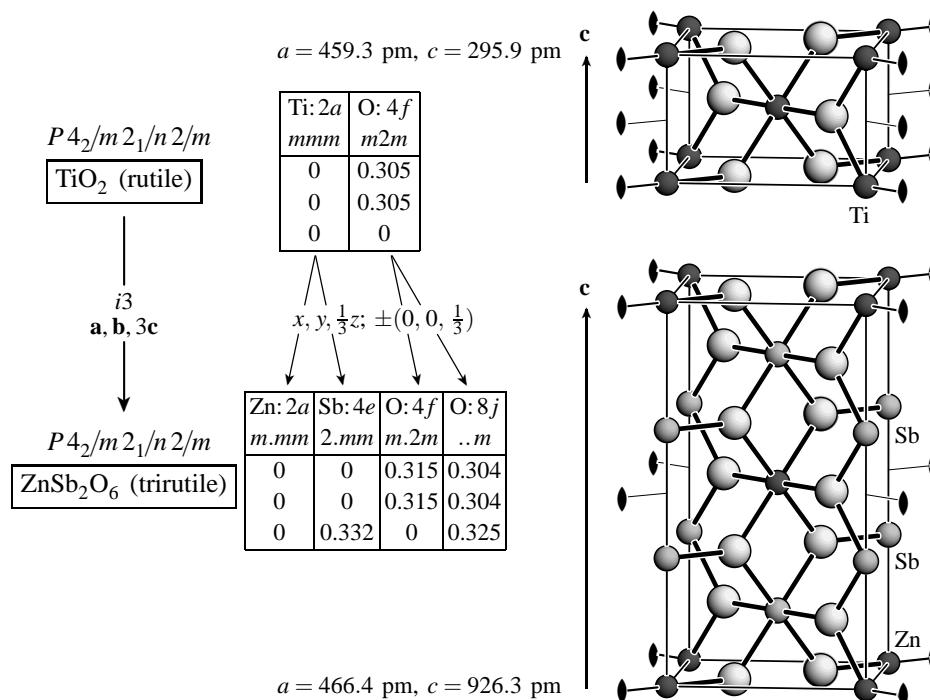
Among *klassengleiche* subgroups of index 2 there often exist two or four different subgroups of the same space-group type which differ in their origin positions. It is important to choose the correct one of them, with the correct origin shift. In *International Tables*, Volume A1 [3], all of these subgroups are listed, but not so in Volume A [2].

### 6.3 Isomorphic maximal subgroups

Isomorphic subgroups are a special kind of *klassengleiche* subgroups. The main particularity is that each space group has infinite many isomorphic subgroups. Their indices may be prime numbers  $p$  or powers  $p^2$  or  $p^3$ , but often only certain prime numbers are permitted [3]. The index agrees with the factor by which the unit cell has been enlarged.

A classical example concerns the trirutile structure. The space group of rutile,  $P4_2/mnm$ , has an isomorphic subgroup of index 3, but none of index 2. By triplication of  $\mathbf{c}$  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  $\text{ZnSb}_2\text{O}_6$  (Fig. 5). 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. A space group includes a specific translational lattice and is used to designate the symmetry of a given crystal structure. The space group type, however, is independent of the lattice metrics.



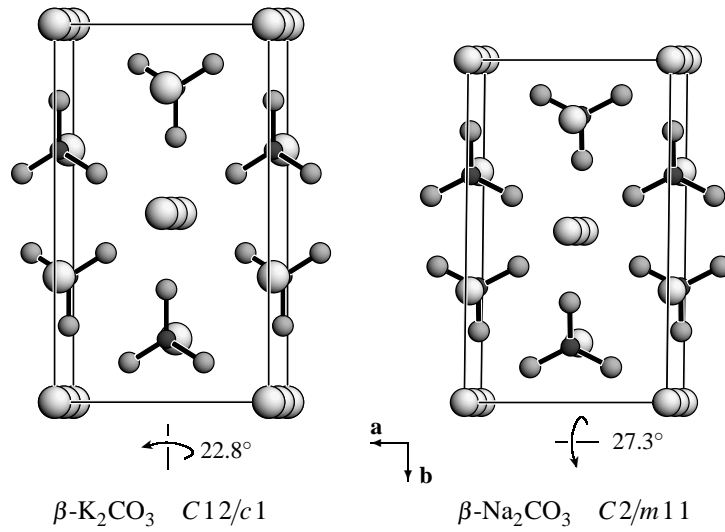
**Figure 5:** The group–subgroup relation rutile–trirutile. The twofold rotation axes depicted in the unit cells show that only one third of them are retained upon the symmetry reduction

#### 6.4 The space groups of two structures have a common supergroup

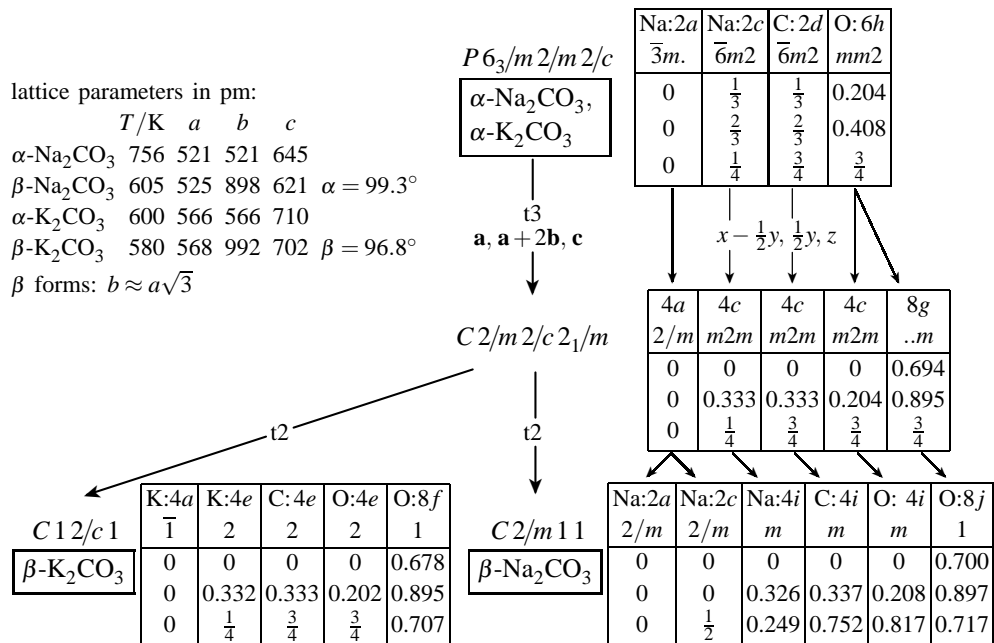
Two crystal structures can be intimately related even when there is no direct group–subgroup relation between their space groups. Instead, there may exist a common supergroup. The above-mentioned structures of NiAsS and PtGeSe offer an example. In that case, the pyrite type corresponds to the common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

$\beta\text{-K}_2\text{CO}_3$  and  $\beta\text{-Na}_2\text{CO}_3$  have similar structures and unit cells (Fig. 6). The planes of the carbonate ions are not aligned perpendicular to  $c$ ; compared to the perpendicular orientation, in  $\beta\text{-K}_2\text{CO}_3$ , they are rotated about  $b$  by  $22.8^\circ$  and those of  $\beta\text{-Na}_2\text{CO}_3$  are rotated about  $a$  by  $27.3^\circ$ . There is no group–subgroup relation between the space groups  $C12/c1$  and  $C2/m11$  of the two structures (the nonconventional setting  $C2/m11$  chosen for  $\beta\text{-Na}_2\text{CO}_3$  ensures a correspondence between the cells of both structures).

Looking for common minimal supergroups of  $C12/c1$  and  $C2/m11$  one can find two candidates:  $Cmcm$  and  $Cmce$ . Since the atomic coordinates of  $\beta\text{-K}_2\text{CO}_3$  and  $\beta\text{-Na}_2\text{CO}_3$  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, neither in Volume A nor Volume A1 of *International Tables*. One has to look up the subgroups of  $Cmcm$  and  $Cmce$  in Volume A1 and check in which cases the origin shifts coincide. One finds that the relation  $Cmce \rightarrow C12/c1$  requires an origin shift



**Figure 6:** The unit cells of  $\beta\text{-K}_2\text{CO}_3$  and  $\beta\text{-Na}_2\text{CO}_3$ . The angles of tilt of the  $\text{CO}_3^{2-}$  ions are referred relative to a plane perpendicular to  $c$ .



**Figure 7:** Group-subgroup relations among some modifications of the alkali metal carbonates [41]



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 (Fig. 7).

No structure with space group  $Cmcm$  is known that can be related to the discussed carbonate structures. Could there be any other structure with an even higher symmetry? A supergroup of  $Cmcm$  is  $P6_3/mmc$  and, in fact,  $\alpha\text{-K}_2\text{CO}_3$  and  $\alpha\text{-Na}_2\text{CO}_3$  are high-temperature modifications that crystallize in this space group. They have the carbonate groups perpendicular to  $c$ . 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.

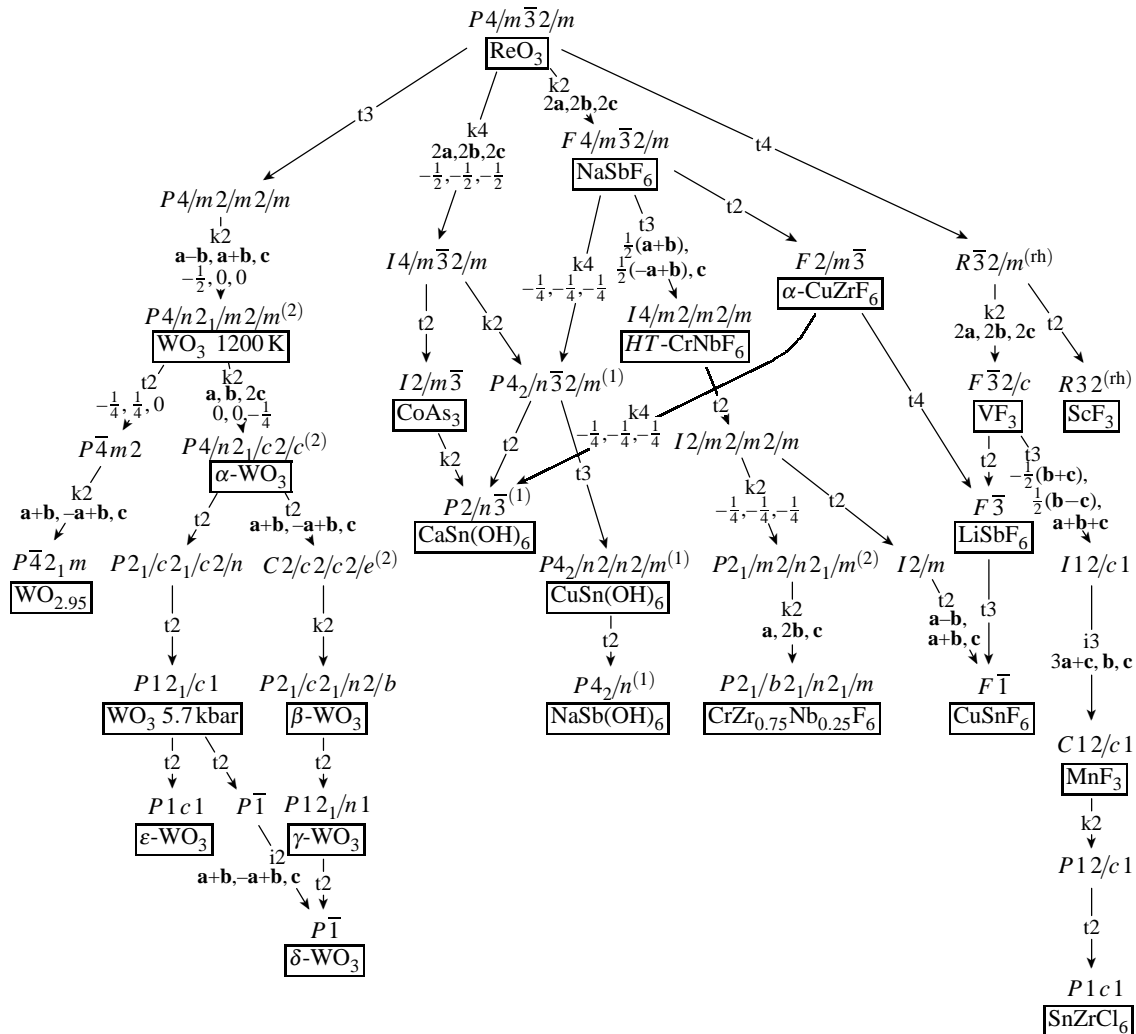
## 6.5 Large families of structures

Using the modular way to put together symmetry relations set forth in the scheme of page 6 and in the preceding sections, large family trees can be constructed. Headed by an aristotype, they show structural relationships among many different crystal structures. As an example, Fig. 8 shows structures that can be derived of the  $\text{ReO}_3$  type [42]. The left part of Fig. 8 refers to only one compound,  $\text{WO}_3$ , and shows relations between different polymorphic forms of this compound. The right part of Fig. 8 lists relations between substitution derivatives of  $\text{ReO}_3$  and their distorted variants due to the Jahn-Teller effect, hydrogen bonds, differing atom sizes etc. Many other trees of this kind have been set up, *e.g.* hettotypes of perovskite [5, 43], rutile [44],  $\text{CaF}_2$  [45],  $\text{NaCl}$  [46], hexagonal closest-packed structures [47], zeolites [48]. For more citations *cf.* [6].

In addition to show 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 [46, 49]. 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 can be such as 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. Two examples of predictions are presented in Section 14.1. For every space group appearing in the Bärnighausen tree, one can calculate how many different structure types are possible for a given chemical composition [50, 51, 52].

## 7 A warning and appeal to use group–subgroup relations with circumspection

Using the tables of *International Tables*, Volume A1, or using computer programs as offered by the Bilbao Crystallographic Server, it may be easy to search for group–subgroup relations between space groups of crystal structures. *This should only be done bearing in*



**Figure 8:** Family tree of hettotypes of  $\text{ReO}_3$ . For the atomic parameters and other crystallographic data cf. [42]

*mind and explicitly stating a crystallographic, physical or chemical context.* It is senseless to construct relations in a purely formal manner, without a sound crystal-chemical or physical foundation. Crystallographic, chemical and physical common sense and knowledge should always be kept in mind.

Group theory is a useful tool, but don't try to subordinate physics and chemistry under formal conceptions, inventing relations that don't really exist. It has to be the other way: Experimental evidence always has priority, and group theory may then be used to interpret the results with circumspection. In Section 9, page 21, I mention an example of how group theory may not be applied.

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 for the mere sake to cling on 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 (this is a frequent and serious error); skipping intermediate space groups; 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 be the cause for subsequent errors and misunderstandings.

## Part 2: Symmetry Relations at Phase Transitions, Domain Structures and Topotactic Reactions

### 8 Phase transitions in the solid state

A phase transition is an event which entails a discontinuous (sudden) change of at least one property of a material.

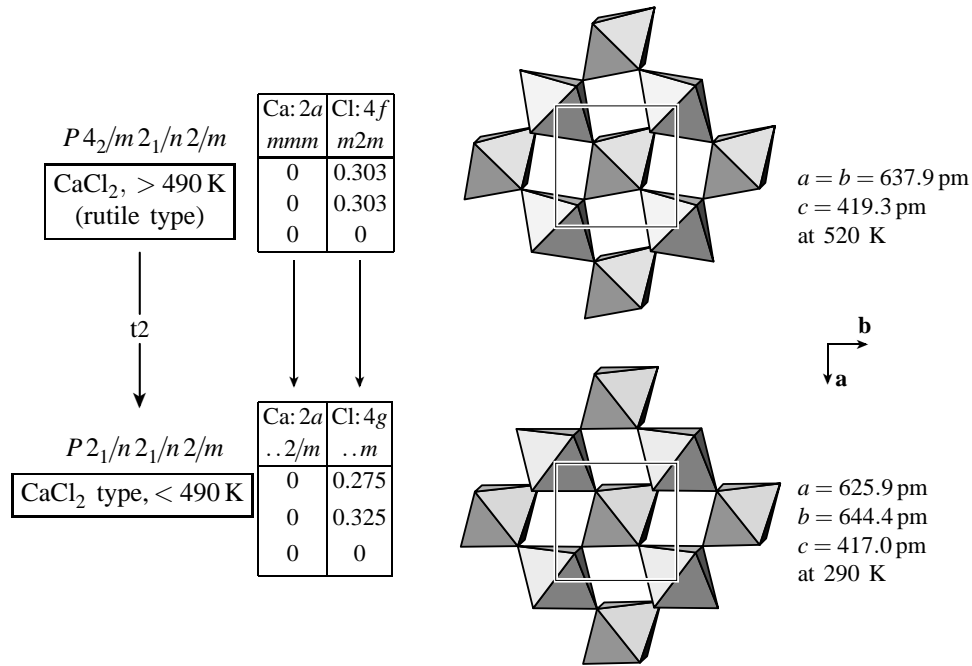
If the sudden change concerns the volume or the entropy, *i.e.* if one of the first derivatives of the free enthalpy is not zero,  $\Delta V \neq 0$ ,  $\Delta S \neq 0$ ,  $\Delta H = T\Delta S \neq 0$ , it is termed, after Ehrenfest, a *first order* phase transition. First order phase transitions always exhibit hysteresis; they proceed in a more or less sluggish manner and during the transition the old and the new phases coexist. It proceeds by nucleation and growth. All structural changes occur at and only at an advancing interface between the receding old and the growing new phase. If crystalline, the two phases may be related by a group–subgroup relation of their space groups, but often this not the case.

Reconstructive phase transitions, which involve the breaking and rejoining of chemical bonds, always are first-order transitions.

If the first derivatives of the free enthalpy show no discontinuity, but the second derivatives do, the phase transition is termed to be of *second order*. There is no sudden volume change and no latent heat ( $\Delta V = 0$ ,  $\Delta S = 0$ ,  $\Delta H = T\Delta S = 0$ ). Structural changes at second order phase transitions are continuous. Driven by certain lattice vibrations, the so-called soft modes, the atoms are displaced in a synchronous (‘military’) fashion in all unit cells of the crystal. It is mandatory that the space groups of the two phases are related by a group–subgroup relation (not necessarily a maximal one). Landau theory has been very successful at the interpretation of second order transitions.

Calcium chloride undergoes a second-order phase transition at  $T_c = 490$  K (Fig. 9) [53, 54]. At  $T > 490$  K it is tetragonal, rutile type, space group  $P4_2/m2/n2/m$ . When cooled from higher temperatures, at 490 K, a mutual rotation of the coordination octahedra sets in. The rotation angle increases continuously the more the temperature is lowered. As soon as the slightest rotation has taken place, the symmetry can no longer be tetragonal; among others, the reflection planes that run diagonal through the unit cell cannot be retained. The symmetry is reduced to that of an orthorhombic subgroup of  $P4_2/m2/n2/m$  in which these reflection planes are not present; this subgroup is  $P2_1/n2_1/n2/m$ . The tetragonal-to-orthorhombic symmetry reduction involves a differentiation of the lattice parameters  $a$  and  $b$ . If we keep the labels of the directions, either  $a < b$  or  $a > b$  holds.

Inevitable temperature and pressure gradients in the crystal, the mosaic structure of real crystals, crystal imperfections, and fluctuations that occur close to the transition point cause that even in a second-order transition in reality not all of the crystal transforms uniformly at the same moment. Rather, we obtain different domains, some of them having  $a < b$ , others  $a > b$ . The result is a twinned crystal of the low temperature form.

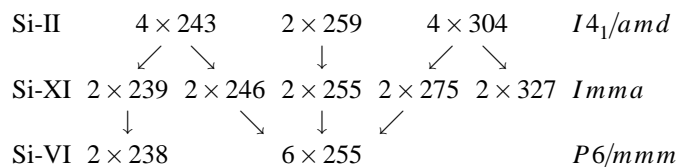


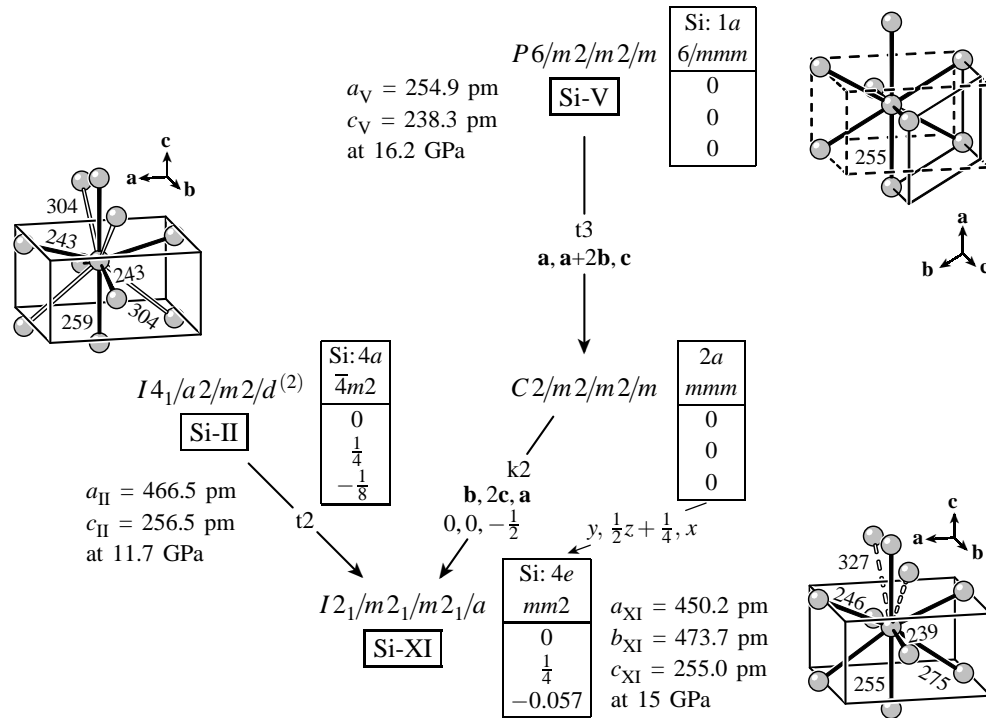
**Figure 9:** Group–subgroup relation between two modifications of calcium chloride and the mutual rotation of the coordination octahedra.

## 9 A first-order phase transition via a common subgroup, is that possible?

When pressure is exerted upon silicon, it first transforms to a modification with the  $\beta$ -tin structure (Si-II,  $I4_1/amd$ ). Then it is transformed to silicon-XI [55]. At even higher pressures it is converted to silicon-V which has been described with a primitive 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 and Si-V (Fig. 10). If there were no atomic displacements, 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 half-way between. The metric deviations of the lattices are small; taking into account the basis transformations given in Fig. 10, 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.

The mentioned phase transitions of silicon are *displacive*, with *small* atomic displacements. The coordination of a Si atom shows this (contact distances < 340 pm):





**Figure 10:** Symmetry relations among three high-pressure modifications of silicon.

The lattice parameter  $c$  of the hexagonal structure is approximately half the value of  $a$  of tetragonal Si-II. The volume jumps are small (0.2 % and 0.5 %). 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. Taken all these facts (and assuming that Si-V really has the ascribed unusual simple hexagonal structure), a group-theoretical relation between Si-II and Si-V exists via the common subgroup of Si-XI.

However, the situation is completely different at reconstructive phase transitions when there is no group-subgroup relation between the space groups of the two phases. The success of Landau theory in the treatment of second-order transitions has led, with some success, to extend the theory to first-order transitions. A mandatory requirement of Landau theory is the existence of a group-subgroup relation. If there is no such a relation, a way out seems to be to assume a two-step mechanism. Similar to the transformation of Si-II to Si-V via Si-XI, two consecutive transitions via an intermediate phase have been assumed. The hypothetical intermediate is supposed to have a space group that is a common subgroup of the initial and the final phase.

Reconstructive phase transitions are always first-order transitions and exhibit hysteresis. Hysteresis completely rules out a synchronous (military) motion of the atoms. The transition proceeds by nucleation and growth. Any intermediate state is restricted to the interface between the growing new and the receding old phase.

On either side of the interface the space groups are different. There exists no symmetry operation that can map one space group onto another one. Therefore, at the interface, there can be no symmetry and, much less, a three-dimensional space-group. In addition, a space group is something static. In a snapshot of, say, a few femtoseconds duration, no crystal ever fulfills a space group because nearly all of the vibrating atoms are displaced from their equilibrium positions. It is only after a longer view that one can recognize mean atomic positions which allow the assignment of a space group. During a phase transition, the interface advances through the crystal, the atoms are in motion; there, no mean atomic positions exist.

Invented “transformation paths” for reconstructive phase transitions via hypothetical intermediate structures having common crystallographic subgroups do not reflect physical reality. Nevertheless, quite a few papers were published that postulate such paths. In some papers, detailed pictures of the assumed atomic motions are shown, depicted in one cell. However, since the synchronous atomic displacement is ruled out for a first-order transition, *the depicted one cell should not be confounded with a crystallographic unit cell*. The assumed displacements can take place only in one or a few cells at a time, followed one by one by more cells like in a row of falling dominoes, *i.e.* by nucleation and growth. The assignment of a space group to a short-lived transient state existing in only one cell is in contradiction to the definition of a space group.

## 10 Domain structures

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 [5, 56, 57, 58].

A domain structure is the result of nucleation and growth processes. If the crystal lattices of the two phases are not too different, the orientation of the new phase depends on the orientation of the old one. 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 (military) 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 in the course of the nucleation process. The crystallites that result from the subsequent growth of the nuclei maintain their orientations. The resulting system of intergrown crystals is called a *topotactic texture* after W. Kleber [59]. Under these circumstances, aspect 3 of the symmetry principle, as stated on page 4, is fully effective. A phase transition that is connected with a symmetry reduction will result in new phases that consist of

- twin domains*,
- if the formed phase belongs to a crystal class with reduced symmetry,
- 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. 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. 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 sometimes are called *ferroic* transitions, those between *klassengleiche* space groups are *non-ferroic*.

Among phase transitions induced by a change of temperature, as a rule, the high-temperature modification has the higher symmetry. No such a rule can be stated for pressure-induced phase transitions.

## 11 Twinned crystals

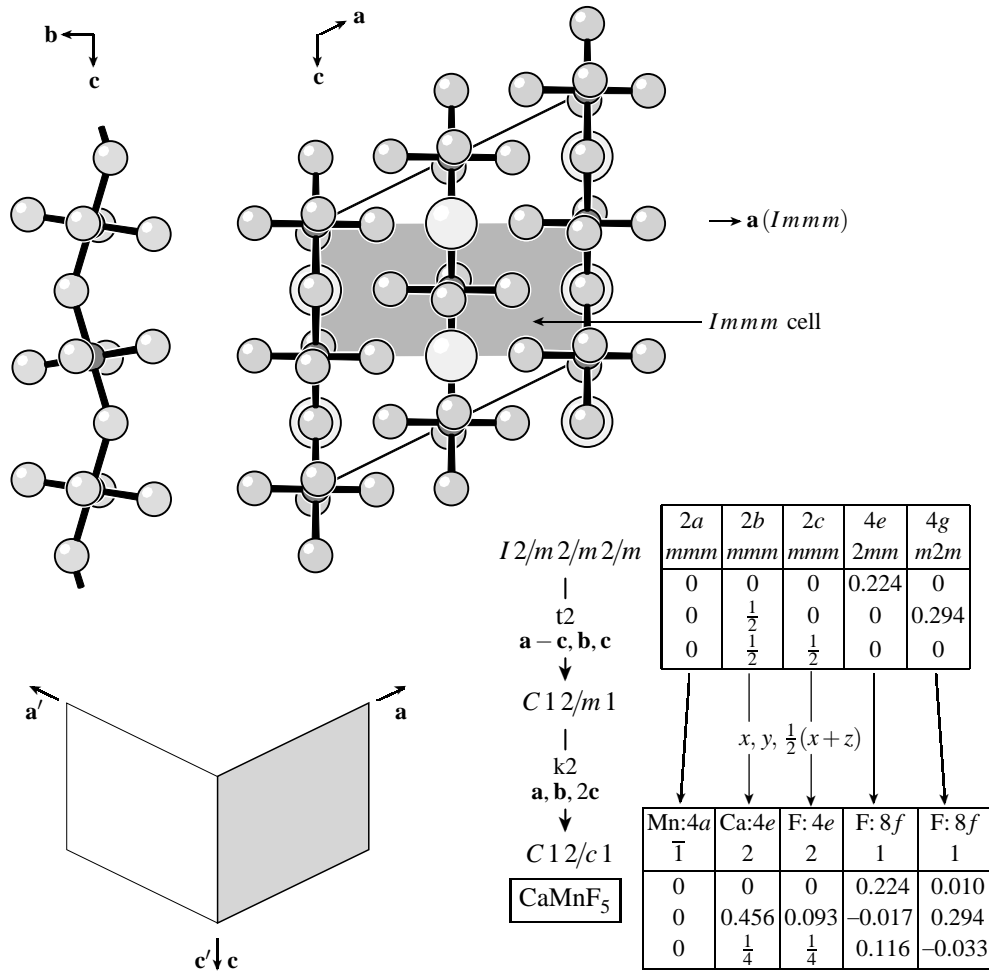
An intergrowth of two or more macroscopic individuals of the same crystal species is a twin, if the orientation relations between the individuals conform to crystallographic laws. The individuals are called twin components or twin domains. They are related by a *twin operation* which is a symmetry operation that does not belong to the point or space group of the crystal.

Growth and transformation twins have to be distinguished. For twins that are formed during the growth of the crystal from a solution or melt, the conditions of nucleation determine how the individuals are intergrown. Group–subgroup relations are of no importance in this case. For example, the ubiquitous growth twins of the cubic mineral fluorite ( $\text{CaF}_2$ ) show two cubes rotated exactly by  $180^\circ$  about the twin axis [111] (obverse–reverse twins). They started growth from a common nucleus, but this has nothing to do with a group–subgroup relation.

Transformation twins arise from phase transitions in the solid state when there is a symmetry reduction with a *translationengleiche* subgroup. The twinning operation is one of the symmetry operations that are lost during the symmetry reduction.

Usually, chemical reactions in the solid state require high temperatures. If a substance forms several polymorphic forms, at first a high-temperature form is obtained. Subsequent cooling may then result in unnoticed phase transitions with symmetry reductions. If this involves a *translationengleiche* group–subgroup relation, twinned crystals may result. In X-ray diffraction, the reflections of the twin domains will be superposed in such a way that the higher symmetry of the high-temperature form may be feigned. The structure determination, assuming a space group of too high symmetry, will yield a faulty struc-





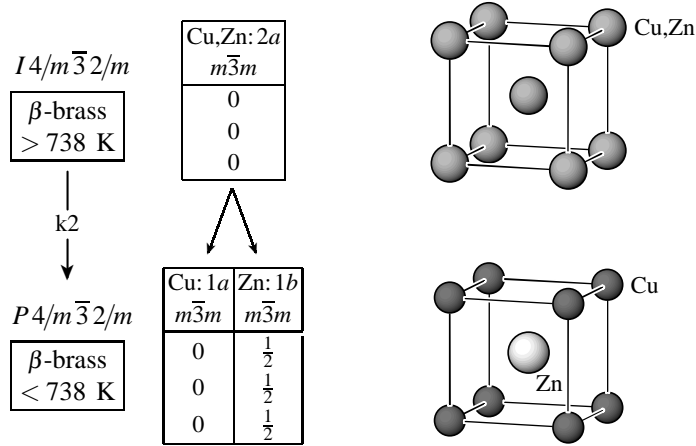
**Figure 11:** Structure of the compounds  $CaCrF_5$ ,  $CaMnF_5$  and  $CdMnF_5$  and group-subgroup relations derived from the presumed high-temperature form. Top left: section of a chain of vertex-sharing octahedra; in the high-temperature form the chain is linear. Bottom left: mutual orientation of the unit cells of the twins

tural model. However, as the following example shows, it can also occur that the lower symmetry of a subgroup is feigned.

Taken from literature, the following table lists the space groups and lattice parameters of three compounds; all three have the same structure (Fig. 11):

	$a/\text{pm}$	$b/\text{pm}$	$c/\text{pm}$	$\beta/^\circ$	ref.
$CaCrF_5$	$C2/c$	900.5	647.2	753.3	115.9 [60]
$CaMnF_5$	$P2/c$	893.8	636.9	783.0	116.2 [61]
$CdMnF_5$	$P2_1/n$	884.8	629.3	780.2	116.6 [62]

The occurrence of three different space groups for the same structure, with nearly equal



**Figure 12:** The relation between disordered and ordered  $\beta$ -brass

lattice parameters, is absolutely improbable. It should be easy to distinguish the three space groups  $C2/c$ ,  $P2/c$  and  $P2_1/n$  from their X-ray reflection extinctions. There seems to be a fundamental error. Twins are the cause, and group-subgroup relations help to resolve the problem. The actual space group is  $C2/c$  [63].

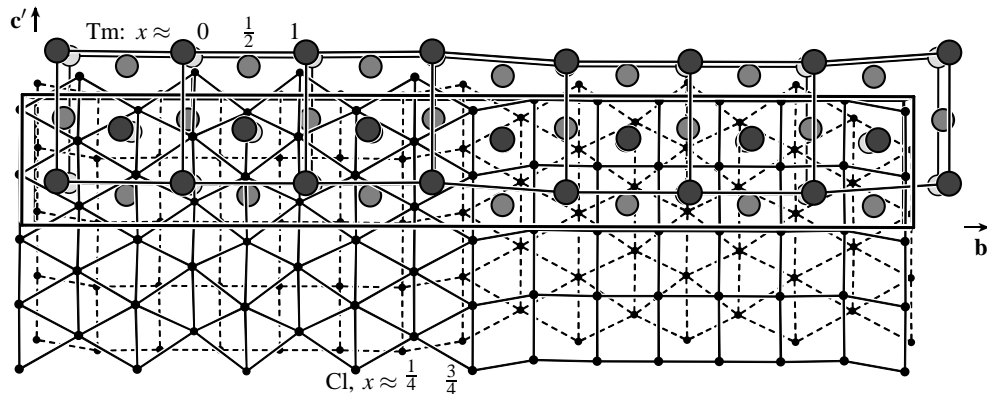
The structure contains  $MF_5^{2-}$  zigzag chains. With linear chains, the symmetry increases to  $I2/m2/m2/m$  with half the unit cell size. This seems to be the symmetry at the high-temperature preparation conditions. Upon cooling, a phase transition with symmetry reduction to  $C2/c$  takes place (Fig. 11). The *translationengleiche* relation of index 2 shows the appearance of twins with two orientations. Corresponding to the orthorhombic cell of the supergroup, the metric relations of the monoclinic cells are such that X-ray reflections of one twin domain are superposed on those of the other one. Part of the reflections of one domain appear exactly at the places of extinct reflections of the other domain. As a consequence, the  $C$  centering of the space group  $C2/c$  cannot be recognized by the extinction condition  $h+k=2n+1$ .

The refinement of the structure of  $CaMnF_5$  with the wrong space group  $P2/c$ , a subgroup of  $C2/c$ , yielded unreliable atomic coordinates and bond lengths.

## 12 Antiphase domains

At high temperatures,  $\beta$ -brass has a disordered structure with the space group  $Im\bar{3}m$ . Upon cooling, the atoms become ordered, resulting in the *klassengleiche* subgroup  $Pm\bar{3}m$  of index 2 (Fig. 12). Therefore, we can expect the formation of antiphase domains.

Consider a nucleus of crystallization of the ordered phase and its growth. Let us assume copper atoms at the vertices and zinc atoms in the centers of the unit cells of the growing nucleus. At some other place in the crystal a second nucleus forms and grows, but let it have a shifted origin, *i.e.* a copper atom in the center of the initial cell. At some place the growing domains will meet. Even though their unit cells have the same



**Figure 13:** The vernier structure of  $\text{Tm}_7\text{Cl}_{15}$ . In the upper part seven pseudo-face-centered ‘cells’ of Tm atoms are shown. The Cl atoms are located at the knots of the drawn nets; in the lower part only the nets are depicted. Seven rows of Cl atoms in the pseudo-square array are on top of eight rows in the pseudo-hexagonal array

orientation and size, they do not harmonize because their origins are mutually shifted by half of the cube diagonal. The result is a domain boundary at which copper atoms are aside copper atoms or zinc atoms aside zinc atoms. This is an antiphase boundary.

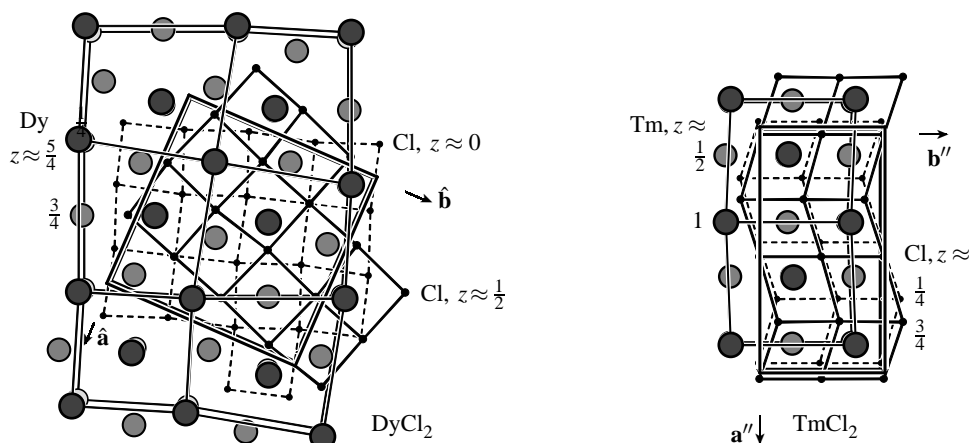
Contrary to twins, antiphase domains cause no problems in X-ray diffraction (unless the domains are very small, causing diffuse scattering instead of Bragg reflections). Antiphase boundaries are visible in the electron microscope.

### 13 Topotactic reactions

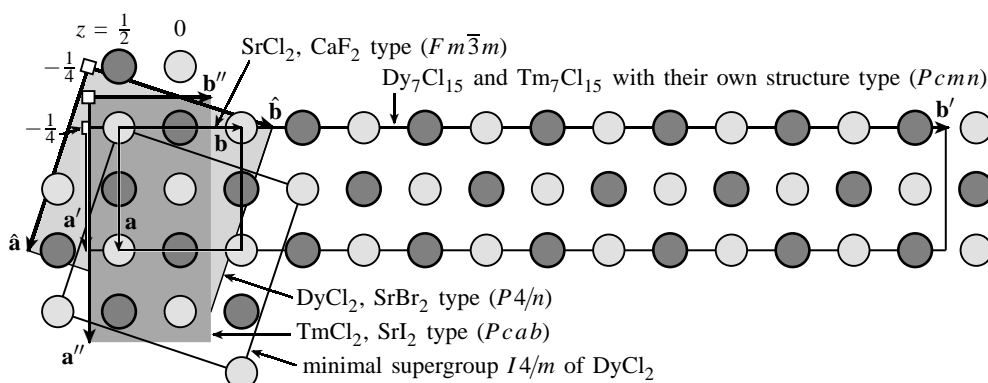
A chemical reaction that takes place in a solid in such a way that the orientation of the product crystal is determined by the orientation of the initial crystal, is called a topotactic reaction. In many topotactic reactions, there exists *no* crystallographic group–subgroup relation between the educt and the product. The orientational relation in the topotactic texture results from the orientation of the nuclei of crystallization which have a preferred orientation in the matrix of the starting crystal.

$\text{Mg}(\text{OH})_2$ , brucite, is homeotypic to  $\text{CdI}_2$ ; it has a hexagonal closest packing of O atoms in the space group  $P\bar{3}m1$ . Upon thermal dehydration, a single crystal of  $\text{Mg}(\text{OH})_2$  is transformed to MgO (periclase), NaCl type, space group  $Fm\bar{3}m$ , with cubic closest packing of O atoms. The topotactic texture obtained consists of a very large number of MgO crystallites. They are strictly oriented like the domains of cubic [111] growth twins, with the [111] direction pointing in the *c* direction of the initial  $\text{Mg}(\text{OH})_2$  (obverse–reverse twins) [64]. This is due to the nucleation process; nuclei of the orientations obverse and reverse are formed randomly on energetically equivalent sites in the initial crystal. There is no group–subgroup relation between brucite and periclase.

In other cases of topotactic reactions, there exist group–subgroup relations. The reduction of rare earth trihalides with the corresponding metals at high temperatures yields



**Figure 14:** The crystal structures of  $\text{DyCl}_2$  ( $\text{SrBr}_2$  type) and  $\text{TmCl}_2$  ( $\text{SrI}_2$  type). Six pseudo-face-centered 'cells' of metal atoms are shown for  $\text{DyCl}_2$ , and two for  $\text{TmCl}_2$ . The Cl atoms are located at the knots of the drawn nets



**Figure 15:** Structural relations between strontium halides and the vernier structure  $\text{Ln}_7\text{Cl}_{15}$ . Only the metal atom positions of the  $\text{CaF}_2$  type are shown.  $\hat{c} \approx c'' \approx c' \approx c$  are in the direction of view

subhalides of the general formula  $\text{Ln}_x\text{X}_{2x+1}$ . Their crystal structures are so-called vernier structures. The halogen atoms alternate in more and less dense rows like in a vernier. The metal atoms are arranged approximately like in a face-centered cubic lattice (Fig. 13) [65, 66]. The structures of the dihalides  $\text{DyCl}_2$  ( $\text{SrBr}_2$  type,  $P4/n$ ) (Fig. 14) [67, 68, 69] and  $\text{TmCl}_2$  ( $\text{SrI}_2$  type,  $Pcab$ ) [70, 71] and of the vernier structures can be derived from the  $\text{CaF}_2$  type. The vernier compounds, however, have a slight excess of halogen atoms.

How their unit cells are related to the  $\text{CaF}_2$  type is shown in Fig. 15. The corresponding lattice parameters (in pm) can be calculated as follows, assuming  $a = b = c = 682$  pm (Dy compounds) and  $a = b = c = 678$  pm (Tm compounds) for the  $\text{CaF}_2$  type:

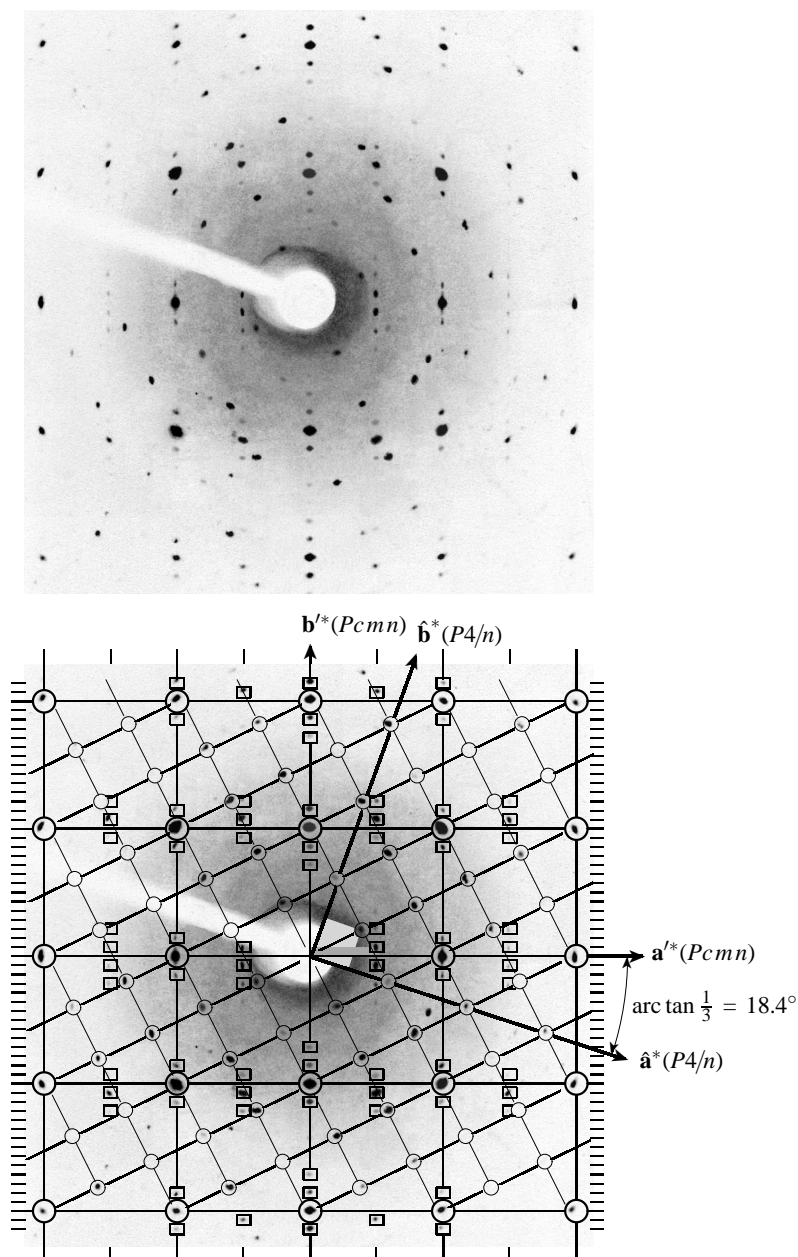
DyCl <sub>2</sub> P4/n		Dy <sub>7</sub> Cl <sub>15</sub> Pcmn		Tm <sub>7</sub> Cl <sub>15</sub> Pcmn		TmCl <sub>2</sub> Pcab	
calculated	obs.[65]	calculated	obs.[66]	calculated	obs.[66]	calculated	obs.[71]
$\hat{a} = \frac{1}{2}\sqrt{10}a = 1078$	1077.5	$a' = a = 682$	667.4	$a' = a = 678$	657.1	$a'' = 2a = 1356$	1318.1
$\hat{b} = \frac{1}{2}\sqrt{10}a = 1078$	1077.5	$b' = 7b = 4774$	4818	$b' = 7b = 4746$	4767.7	$b'' = b = 678$	671.4
$\hat{c} = c = 682$	664.3	$c' = c = 682$	709.7	$c' = c = 678$	700.1	$c'' = c = 678$	697.7

Upon heating, the partial structure of the anions melts before the proper melting point; *i.e.* there is a phase transition, the cations retaining their positions as in the CaF<sub>2</sub> type, while the anions in between begin to float. The quasi-liquid state of the anions at the high preparation temperatures of the vernier compounds permits a nonstoichiometric composition. When cooled, the anions become ordered within the array of the cations. Depending on composition, several compounds crystallize simultaneously, with intergrown crystals in definite orientations. For example, starting from a high-temperature phase of the composition DyCl<sub>2,08</sub>, DyCl<sub>2</sub> and Dy<sub>7</sub>Cl<sub>15</sub> (= DyCl<sub>2,14</sub>) crystallize simultaneously.

The X-ray diffractogram of such a crystal, at a first glance, is confusing (Fig. 16, top). However, with the orientation relations according to Fig. 15 and the group-subgroup relations (Fig. 17), the diagram can be interpreted as an intergrowth of DyCl<sub>2</sub> and Dy<sub>7</sub>Cl<sub>15</sub> (Fig. 16, bottom). The tetragonal  $c^*$  axis of DyCl<sub>2</sub> coincides exactly with a reciprocal axis of Dy<sub>7</sub>Cl<sub>15</sub>, which therefore has been chosen as its  $c^*$  axis; this is the reason for the unconventional setting of the space group *Pcmn* (conventional *Pnma*).

The strong reflections in Fig. 16 result from a superposition from both compounds; they correspond to the CaF<sub>2</sub> type, which, however, is not present.

A similar topotactic intergrowth occurs with TmCl<sub>2</sub> and Tm<sub>7</sub>Cl<sub>15</sub>. The relative positions of the unit cells shown in Fig. 15 can be discerned clearly in the diffractograms (Fig. 18). The basis vectors of both compounds have exactly the same directions. Pay attention to the reflections 040 and 440 of TmCl<sub>2</sub> in Fig. 18 next to 0280 and 2280 of Tm<sub>7</sub>Cl<sub>15</sub>. They do not coincide exactly because  $b(\text{TmCl}_2) = 671.4 \text{ pm} < \frac{1}{7}b(\text{Tm}_7\text{Cl}_{15}) = 681.1 \text{ pm}$ .  $\frac{1}{2}a(\text{TmCl}_2) = 659.05 \text{ pm}$  is marginally larger than  $a(\text{Tm}_7\text{Cl}_{15}) = 657.1 \text{ pm}$ , *cf.* the slight horizontal shift of 840 of TmCl<sub>2</sub> *vs.* 4280 of Tm<sub>7</sub>Cl<sub>15</sub>.



**Figure 16:** Buerger precession diffractogram ( $hk0$  reflections) of a 'single crystal' of  $\text{DyCl}_x$  with  $x \approx 2.08$  [65]

Bottom: interpretation as a topotactic texture of  $\text{DyCl}_2$  and  $\text{Dy}_7\text{Cl}_{15}$ . Small circles:  $\text{DyCl}_2$ ,  $\text{SrBr}_2$  type ( $P4/n$ ); rectangles:  $\text{Dy}_7\text{Cl}_{15}$ ,  $\text{Tm}_7\text{Cl}_{15}$  type ( $Pcmn$ ); large circles: superimposed reflections of both substances. Due to the  $n$  glide planes all reflections with  $h+k=2n+1$  are extinct

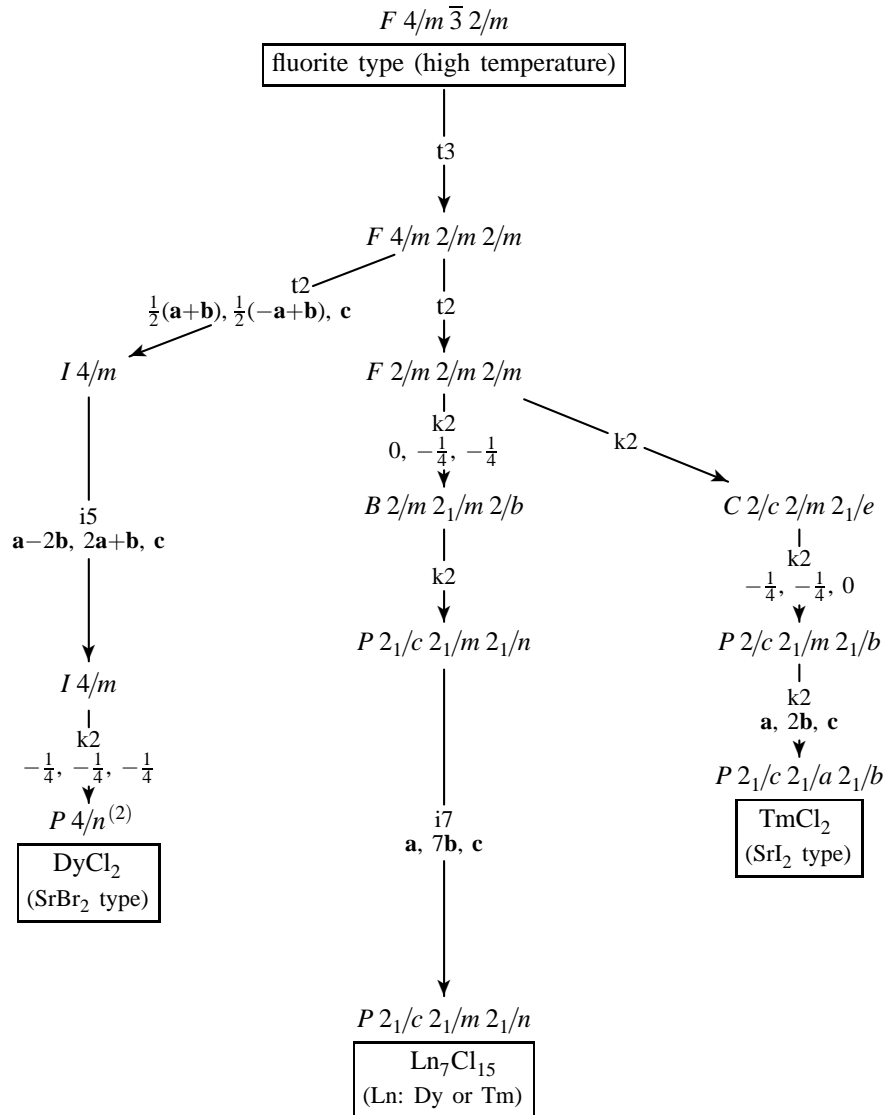
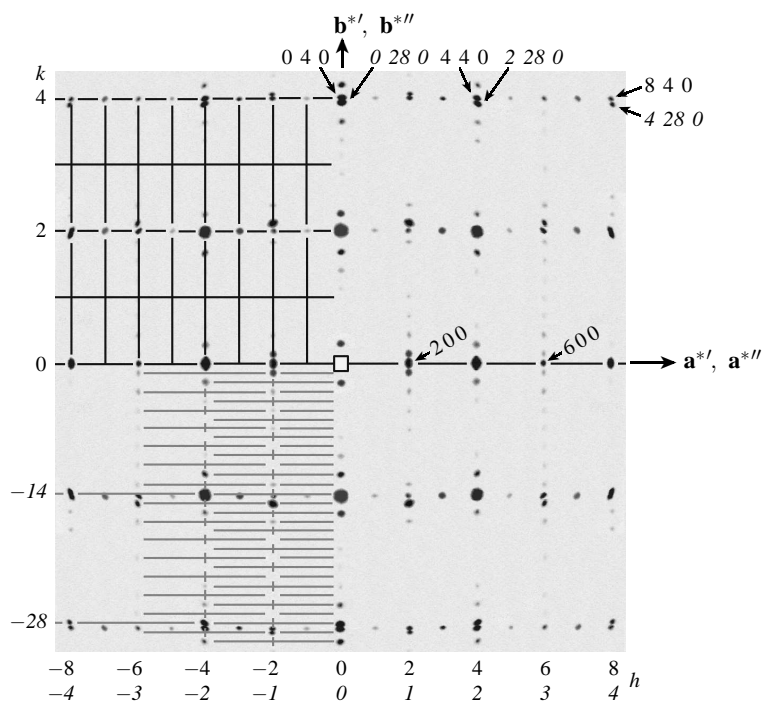


Figure 17: Derivation of the crystal structures of some rare earth halides [65, 66]



**Figure 18:** Simulated precession diagram of the reflections  $hk0$  of a topotactic texture of  $\text{TmCl}_2$  and  $\text{Tm}_7\text{Cl}_{15}$ . Top left quadrant: reciprocal grid lines of  $\text{TmCl}_2$ . Bottom left quadrant: reciprocal grid lines of  $\text{Tm}_7\text{Cl}_{15}$ . Simulation deduced from measured data of a ‘single crystal’ [65]. Reflections  $h+k=2n+1$  of  $\text{Tm}_7\text{Cl}_{15}$  ( $Pcmn$ ) are extinct; Reflections  $k=2n+1$  and  $h00$  with  $h=2n+1$  of  $\text{TmCl}_2$  ( $Pcab$ ) are extinct. Miller indices in italics refer to  $\text{Tm}_7\text{Cl}_{15}$



## Part 3: Symmetry Aspects of Close-packed Structures and Molecular Structures

### 14 Occupation of voids in closest packings of spheres

To comprehend the huge amount of known crystal structure types, chemists very successfully have developed quite a few concepts. One of them is the wide-spread 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, that the occupation of voids is treated like a substitution of ‘zero atoms’ by real atoms.

The topotactical occupation of voids can actually be performed in diverse cases. Examples are the intercalation compounds and the large number of metal hydrides  $MH_x$  that can be prepared by diffusion of hydrogen into the metals. However, in many cases the occupation of voids, just like the substitution of atoms in a crystal, is not a real but a mental process. It is a very helpful descriptive approach.

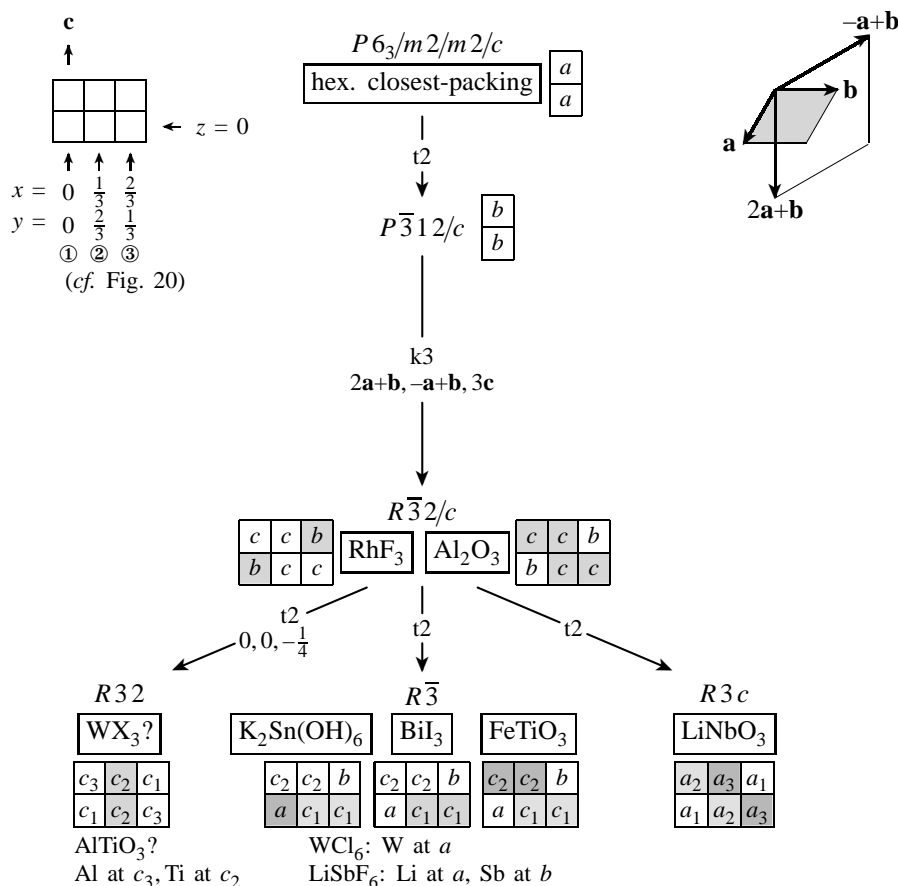
Many inorganic crystal structures can be derived from closest-packings of spheres in which a part of the octahedral or tetrahedral voids have been occupied. Consider a hexagonal closest-packing of spheres with a partial occupation of the octahedral voids. In all closest-packings of spheres the number of octahedral voids is equal to the number of spheres. The chemical composition determines what fraction of the voids is occupied. In a trihalide  $AX_3$  whose halogen (X) atoms form the packing of spheres, with A atoms in its octahedral voids, exactly one third of the voids must be occupied. The unit cell of the hexagonal closest-packing of spheres contains two spheres and two octahedral voids. In order to be able to occupy one third of the voids, the unit cell has to be enlarged by a factor of three or a multiple of 3. Cell enlargement means loss of translational symmetry, and further symmetry elements may have to be removed. That means: the space groups of the derived structures are subgroups of the space group of the packing of spheres.

#### 14.1 Rhombohedral hettotypes of hexagonal closest-packing

The Bärnighausen tree in Fig. 19 shows the derivation of certain rhombohedral structures from a hexagonal closest-packing of spheres. Fig. 20 depicts the corresponding section of the packing of spheres. A triplication of the primitive unit cell is necessary.

The unit cell of the aristotype contains two spheres at the Wyckoff position  $2d$ ,  $\pm(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$ , and two octahedral voids at  $2a$ ,  $0,0,0$  and  $0,0,\frac{1}{2}$ . After triplication, the unit cell contains six octahedral voids. They are represented in Fig. 19 by little boxes and labeled by their Wyckoff letters. Symmetry-equivalent voids have the same letter. Boxes next to each other correspond to octahedra having a common edge, boxes one on top of the other to face-sharing octahedra, and diagonally adjacent boxes to vertex-sharing octahedra.

With the successive symmetry reduction the number of symmetrically independent octahedral voids increases, as can be seen by the increasing number of different Wyckoff symbols.



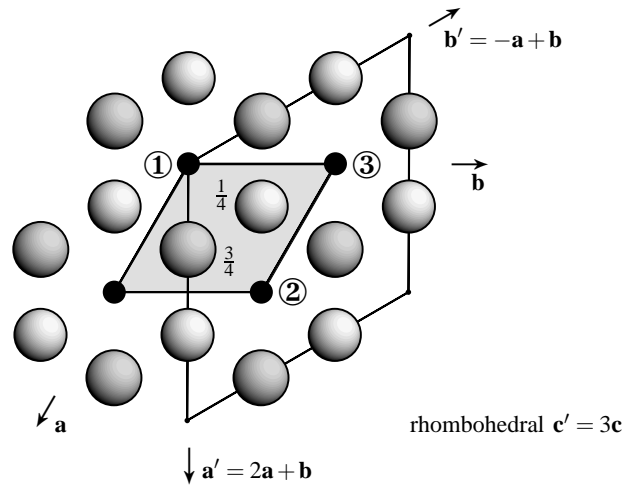
**Figure 19:** Bärnighausen tree for rhombohedral hettotypes of a hexagonal closest-packing of spheres. Boxes represent the octahedral voids, the letters are Wyckoff letters. The scheme in the upper left shows the corresponding coordinates (cf. the octahedral voids marked ①, ② and ③ in Fig. 20). Different orbits of the same Wyckoff position are distinguished by indices ( $a_1, a_2, \dots$ ). Gray boxes refer to occupied voids

If we are interested in compounds of the composition  $\text{AX}_3$  (X atoms form the packing of spheres), then two of the six octahedral voids have to be occupied by A atoms. We express this by the formula  $\text{A}_2\Box_4\text{X}_6$  or  $\text{A}\Box_2\text{X}_3$ . The corresponding known structure types are:

$\text{BiI}_3$ ,  $R\bar{3}$ . It is a layer structure; occupied octahedra share edges (position  $c_1$  in Fig. 19).

$\text{RhF}_3$ ,  $R\bar{3}2/c$ . All occupied octahedra share vertices (position  $b$  in Fig. 19).

If we exchange occupied and vacant octahedral voids of the  $\text{RhF}_3$  type, the space group  $R\bar{3}2/c$  is not altered. Now, four voids are occupied (position  $c$ ) and two are vacant; the composition is  $\Box_2\text{A}_2\text{X}_3$ , and this corresponds to the structure type of corundum



**Figure 20:** Section from a hexagonal closest-packing of spheres. Gray: unit cell, space group  $P6_3/m2/m2/c$ . Large cell: triplicated cell with  $c' = 3c$  for rhombohedral subgroups (hexagonal axis setting). The  $z$  coordinates of the spheres refer to the small hexagonal cell. The dots marked ①, ② and ③ indicate six octahedral voids at  $z = 0$  and  $z = \frac{1}{2}$  of the hexagonal cell or  $z = \frac{1}{6}$  of the rhombohedral cell

( $\alpha$ - $\text{Al}_2\text{O}_3$ ). Regarded this way,  $\text{RhF}_3$  and  $\alpha$ - $\text{Al}_2\text{O}_3$  formally have equivalent structures. Crystal-chemically they are not equivalent:  $\alpha$ - $\text{Al}_2\text{O}_3$  has face- and edge-sharing octahedra, while they only share vertices in  $\text{RhF}_3$ .

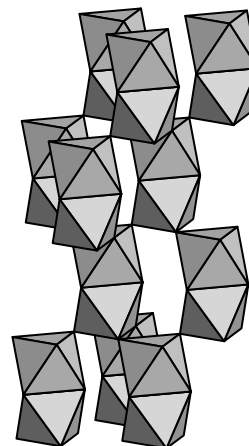
All aluminum positions of  $\alpha$ - $\text{Al}_2\text{O}_3$  are symmetry-equivalent. By symmetry reduction from  $R\bar{3}2/c$  to  $R\bar{3}$  the corresponding Wyckoff position  $c$  splits; the two resulting independent positions can be occupied by different elements. Ilmenite,  $\text{FeTiO}_3$ , has this structure. It has edge-sharing octahedra (boxes side by side) that are occupied by atoms of the same element. Occupation of the edge-sharing octahedra by different elements is possible in  $R3c$  (positions  $a_2$  and  $a_3$  in Fig. 19); this is the structure of  $\text{LiNbO}_3$ .

The structures of some more compounds correspond to space groups of this Bärnighausen tree.  $\text{WCl}_6$  has one sixth of the octahedral voids occupied with W atoms in a hexagonal closest-packing of chlorine atoms. The space group  $R\bar{3}$  is the only appropriate one of this tree; the Wyckoff position  $a$  is occupied, the others remain vacant.

Except for the  $\text{RhF}_3$  and  $\text{BiI}_3$  type, there is a further possible structure for the composition  $\text{AX}_3$ , namely in the space group  $R32$ , marked  $\text{WX}_3$  in Fig. 19; it has the orbit  $c_2$  occupied, and  $c_1$  and  $c_3$  remain vacant. This structure has pairs of occupied octahedra sharing a face, and these pairs share vertices (Fig. 23). Thus far, no representative is known for this structure type. A compound that could adopt this structure is  $\text{WCl}_3$ . Trivalent tungsten is known for its tendency to form structures with face-sharing octahedra, as in the  $\text{W}_2\text{Cl}_9^{3-}$  ion. May be it is worthwhile to search for such a modification of  $\text{WCl}_3$  (another modification having  $\text{W}_6\text{Cl}_{18}$  clusters is known).

The space group  $R32$  also allows a structural variant of ilmenite, which could be adopted by the yet unknown compound  $\text{AlTiO}_3$ . With Ti on  $c_2$  and Al on  $c_3$  the octahedra joining would be like in ilmenite. The Ti atoms would be located in pairs of face-sharing octahedra. In  $\text{AlTiO}_3$  titanium would be trivalent and still would have a valence electron per atom; this would favor the occupation of face-sharing octahedra, with formation of Ti–Ti bonds.

The examples of the postulated possible structures of  $\text{WCl}_3$  and  $\text{AlTiO}_3$  show how Bärnighausen trees can be used to predict structure types.



**Fig. 21:** Octahedra linking in the predicted structure of  $\text{WCl}_3$

## 15 Crystal structures of molecular compounds

The treatment of inorganic compounds in the previous chapters should not give the impression that group–subgroup relations may not be appropriate for compounds consisting of complicated molecules. In fact, crystals of such compounds frequently have low-symmetry space groups, with molecules occupying positions with the site symmetries 1 oder  $\bar{1}$ . The most frequent space group is  $P2_1/c$  (Table 1), and for chiral molecules, which may only adopt one of the 65 Sohncke space groups [25], it is  $P2_12_12_1$ . For this reason, a principle of ‘symmetry avoidance’ has even been postulated for molecular compounds. As the following examples show, this is not true. Rather, the symmetry principle

**Table 1:** Frequency of the space groups among known crystal structures of molecular compounds and frequency of the occurring point symmetries of the molecules (only organic compounds with only one kind of molecule, approx. 96000 compounds) [77]

space group	frequency %	symmetry of occupied sites in this space group %				point group	frequency among molecules %
		1	$\bar{1}$	2	3		
$P2_1/c$	40.0	86	14			70.9	
$P\bar{1}$	17.4	81	19			8.1	
$P2_12_12_1^*$	11.6	100				7.5	
$C2/c$	7.1	48	10	42		6.5	
$P2_1^*$	5.8	100				2.1	
$Pbca$	4.8	88	12			1.7	
$Pna2_1$	1.6	100				0.6	
$Pnma$	1.3	2	1	97		0.5	
$Pbcn$	1.0	36	4	60		0.3	
146 others	9.4	55				0.3	

\* Sohncke space group

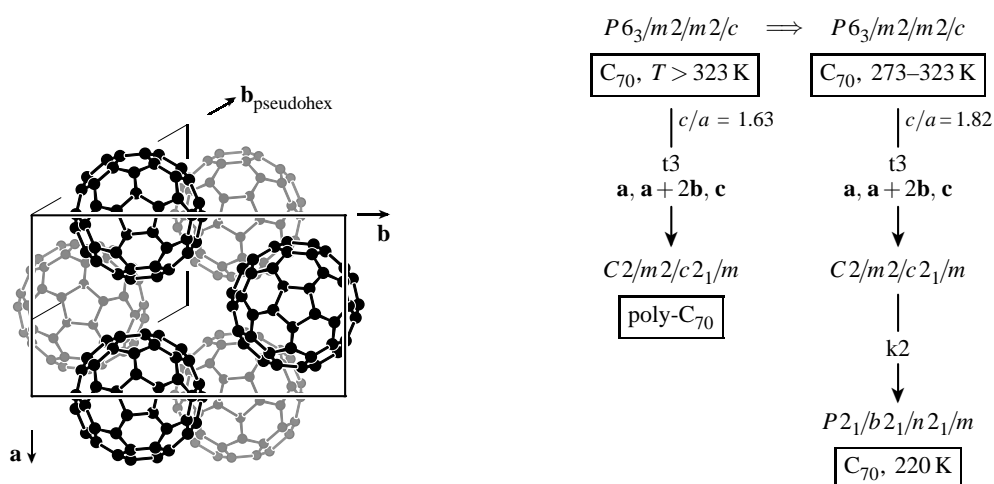
also holds for these compounds. However, aspect number 2, as stated on page 4, has primary importance. The low molecular symmetry often does not permit packings with molecules occupying special positions and enforces a corresponding symmetry reduction.

According to experience and detailed studies [78, 79, 80], molecules strive to attain the densest packing possible. The statistics also show: centrosymmetrical molecules in more than 99 % of all cases adopt centrosymmetrical space groups and predominantly occupy centrosymmetrical positions [81]. If the molecule has a twofold rotation axis, this is retained in the crystal in 59 % of all cases. Space groups with mirror planes, as a rule, occur only if at least one kind of molecule is situated on a mirror plane [77].

### 15.1 Molecules packed as in closest-packings of spheres

Some molecules have an approximately spherical shape. They tend to pack themselves like in a packing of spheres.  $C_{60}$  molecules arrange themselves as in a cubic closest-packing of spheres, space group  $F4/m\bar{3}2/m$  [82]. The molecules rotate in the crystal, although with a preferred orientation that corresponds to the site symmetry  $2/m\bar{3}$ .  $2/m\bar{3}$  is the common subgroup of the molecular symmetry  $2/m\bar{3}5$  (icosahedral symmetry) and the site symmetry  $4/m\bar{3}2/m$  of  $F4/m\bar{3}2/m$ . If all molecules were ordered, the space group would be  $F2/m\bar{3}$ , a maximal subgroup of  $F4/m\bar{3}2/m$  [83]. Below 249 K the molecules become ordered in the subgroup  $P2/a\bar{3}$  and the site symmetry is reduced to  $\bar{3}$  [84].

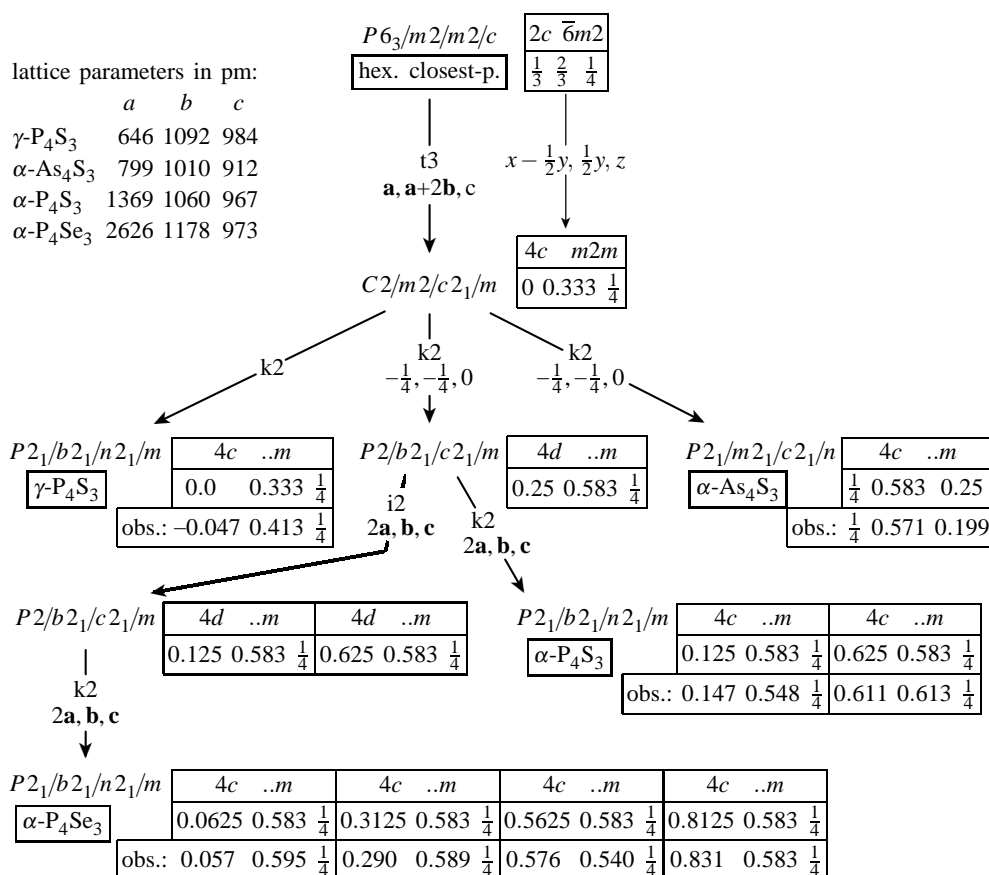
In crystals of the fullerene  $C_{70}$ , obtained by sublimation, the molecules adopt a hexagonal closest-packing of spheres ( $P6_3/m2/m2/c$ ) with the ideal  $c/a$  ratio of 1.63; in the mean, the rotating molecules are spherical [85]. Upon cooling, at  $\sim 50^\circ\text{C}$ , a first-order phase transition takes place; the structure retains the hexagonal space group, now with



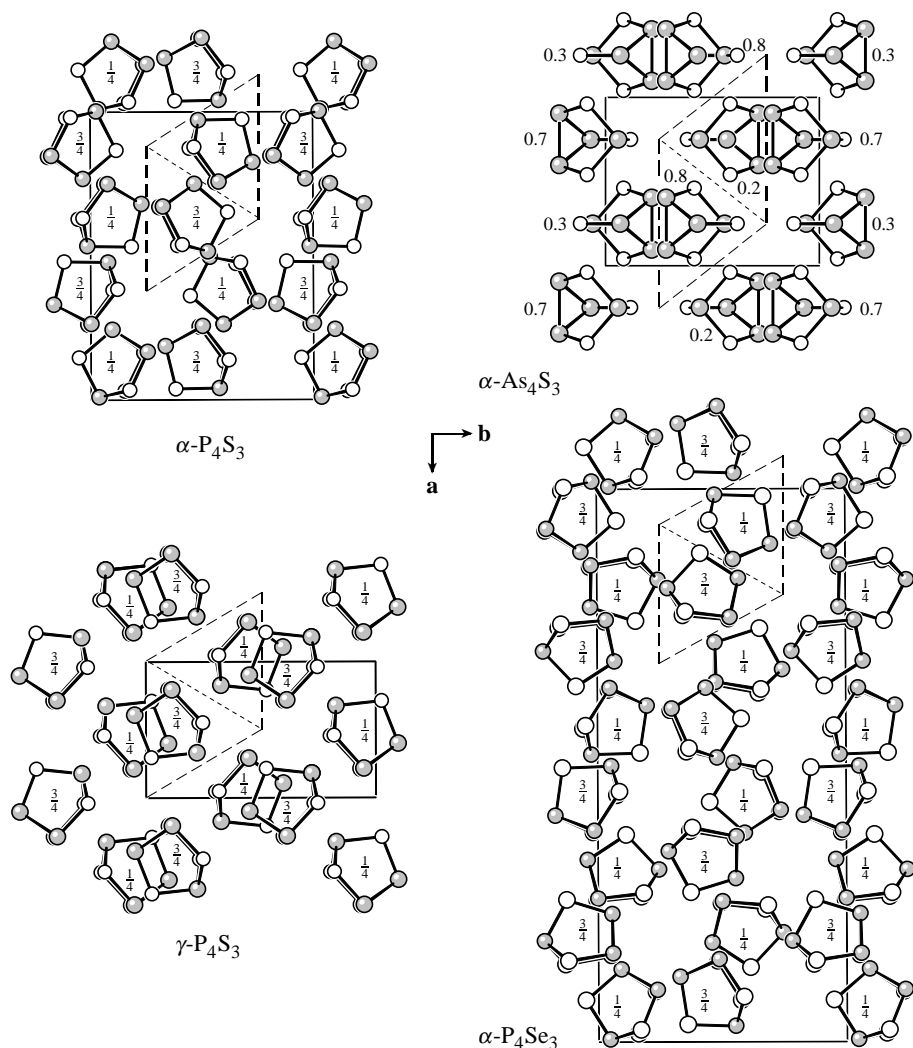
**Figure 22:** The low-temperature modification of  $C_{70}$ , space group  $P2_1/b2_1/n2_1/m$ .  $a = 1001.6$  pm,  $b = 1735$  pm  $= a\sqrt{3}$ ,  $c = 1853$  pm. View along the pseudo-hexagonal axis. Symmetry relations between the  $C_{70}$  modifications

$c/a = 1.82$ . There is no group-subgroup relation. The slightly elongated molecules now are aligned parallel to the hexagonal axis and only rotate about this direction. At  $\sim 20^\circ\text{C}$  this rotation freezes. Due to the molecular symmetry  $\overline{10}2m$  ( $D_{5h}$ ), the crystal symmetry cannot continue to be hexagonal, it becomes orthorhombic, space group  $P2_1/b2_1/n2_1/m$  (Fig. 22). The symmetry reduction includes a *translationengleiche* subgroup relation of index 3, and accordingly twinned crystals with three kinds of domains are formed. The intermediate space group  $C2/m2/c2_1/m$  is not adopted because the molecules are rotated about their pentagonal axis in such a way that the orientation of their twofold axes does not coincide with those of  $C2/m2/c2_1/m$ . However, the space group  $C2/m2/c2_1/m$  is adopted by polymeric  $C_{70}$ ; this is obtained by a topotactic polymerization (under pressure at  $300^\circ\text{C}$ ), the  $C_{70}$  molecules being joined in the  $c$  direction [86].

The less spherical cage molecules of  $P_4S_3$ ,  $P_4Se_3$  and  $As_4S_3$  crystallize like in a hexagonal closest-packing of spheres. Several polymorphic forms occur, which is an ex-



**Figure 23:** Bärnighausen tree relating a hexagonal closest-packing of spheres with polymorphic forms of  $P_4S_3$  and  $As_4S_3$  [87]. Only coordinates of the molecular centers are mentioned.  $Pm\overline{c}n$  and  $Pbnm$  are nonconventional settings of  $Pnma$ .



**Figure 24:** Packing of four modifications of cage-like molecules  $E_4X_3$ . Dotted lines: pseudo-hexagonal unit cells. Numbers:  $z$  coordinates of the centers of the molecules.

pression that no good packing of the molecules is possible; they are somewhat jammed in each of the modifications. The four modifications mentioned in Fig. 23 have four different space groups, all of which belong to the space-group type  $Pnma$ . The non-spherical shape of the molecules is taken care of in different ways: Slight shifts from the ideal positions at  $\gamma\text{-P}_4\text{S}_3$  (cf.  $y$  coordinates in Fig. 23; Fig. 24), distortion of the lattice at  $\alpha\text{-P}_4\text{S}_3$  and  $\alpha\text{-As}_4\text{S}_3$  (elongation along **a**) with two different molecular orientations.  $\alpha\text{-P}_4\text{Se}_3$  has the least deviations from the ideal packing of spheres, but it requires four symmetry-independent, mutually rotated molecules [87].

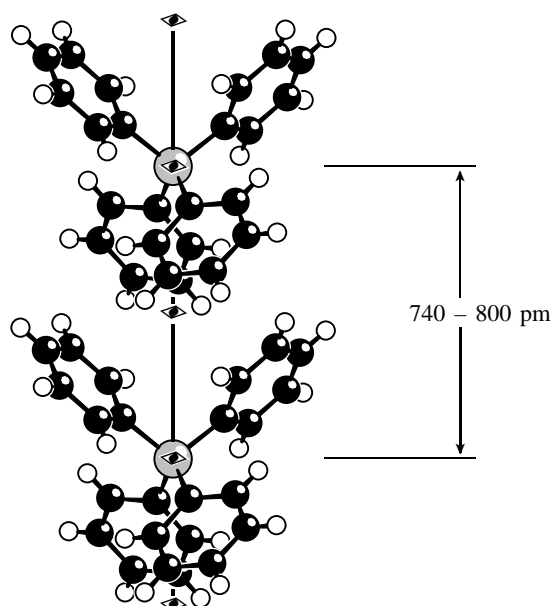


Figure 25: Piles of  $\text{P}(\text{C}_6\text{H}_5)_4^+$  ions in columns

## 15.2 The packing in tetraphenylphosphonium salts

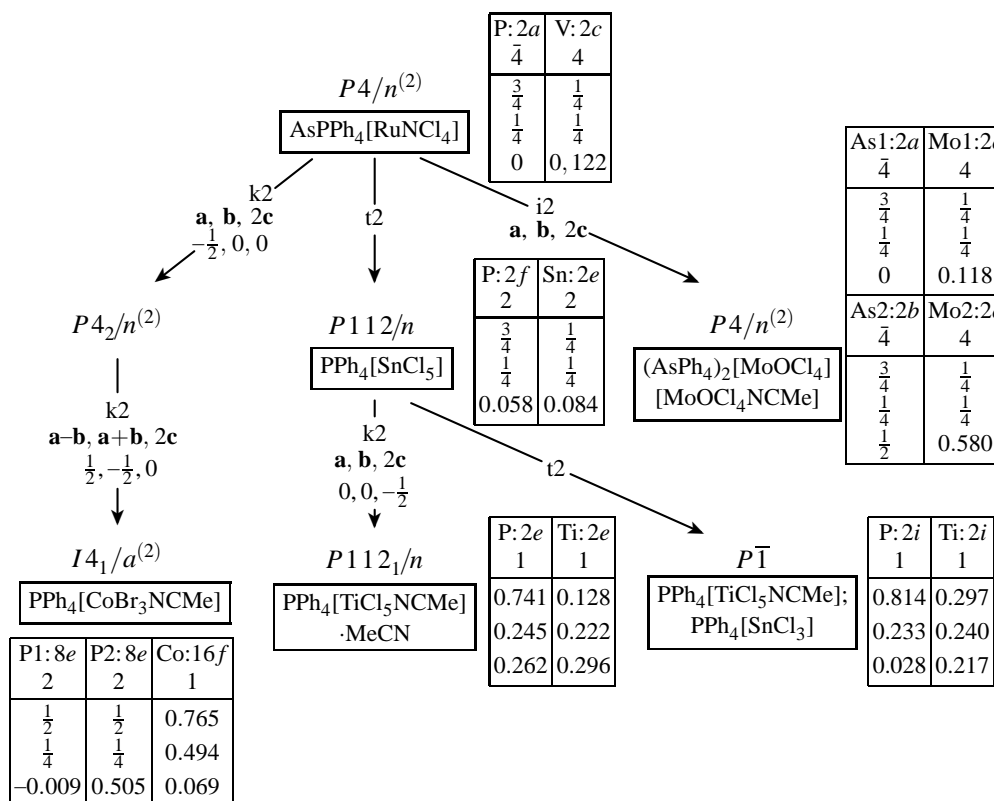
The  $\text{P}(\text{C}_6\text{H}_5)_4^+$  ions in crystalline tetraphenylphosphonium salts frequently are piled to columns parallel to  $c$  (Fig. 25). The distance between neighboring ions is 740 to 800 pm. The most frequent packing is tetragonal, space group  $P4/n$ . The positions of the  $\text{P}(\text{C}_6\text{H}_5)_4^+$  ions have site symmetry  $\bar{4}$ , whereas the anions are located on fourfold rotation axes (site symmetry 4). This kind of packing is observed when the anions have a fourfold rotation axis, namely with square anions like  $\text{AuCl}_4^-$ , square-pyramidal anions like  $\text{VOCl}_4^-$  or octahedral anions like  $\text{SbCl}_6^-$  (Figs. 26 and 27).

What happens if the symmetry of the anions is not compatible with the site symmetry 4? Then the symmetry is reduced, the space group being a subgroup of  $P4/n$  with the correspondingly reduced site symmetry for the anions [6, 88]. Examples:

$\text{SnCl}_5^-$  ions have a trigonal-bipyramidal structure, point group  $\bar{6}2m$ . This symmetry is compatible with the packing if the space-group symmetry is reduced from  $P4/n$  to  $P2/n$ , the  $\text{SnCl}_5^-$  ions being aligned with one of their twofold axes along the previously fourfold axis [89]. If the anions have no twofold axes, the symmetry must be reduced even more. With  $\text{SnCl}_3^-$  ions the packing remains essentially unchanged, but the space group symmetry is reduced to  $P\bar{1}$  (Fig. 26) [90].

The  $[\text{TiCl}_5(\text{NCCH}_3)]^-$  ion still has a fourfold axis (point group  $4mm$ , not taking into account the H atoms). However, it is 1060 pm long and does not fit along the fourfold rotation axis, the translation period being restricted to 800 pm by the columns of  $\text{PPh}_4^+$  ions. Nevertheless, the packing remains, but with inclined  $[\text{TiCl}_5(\text{NCCH}_3)]^-$  ions. This



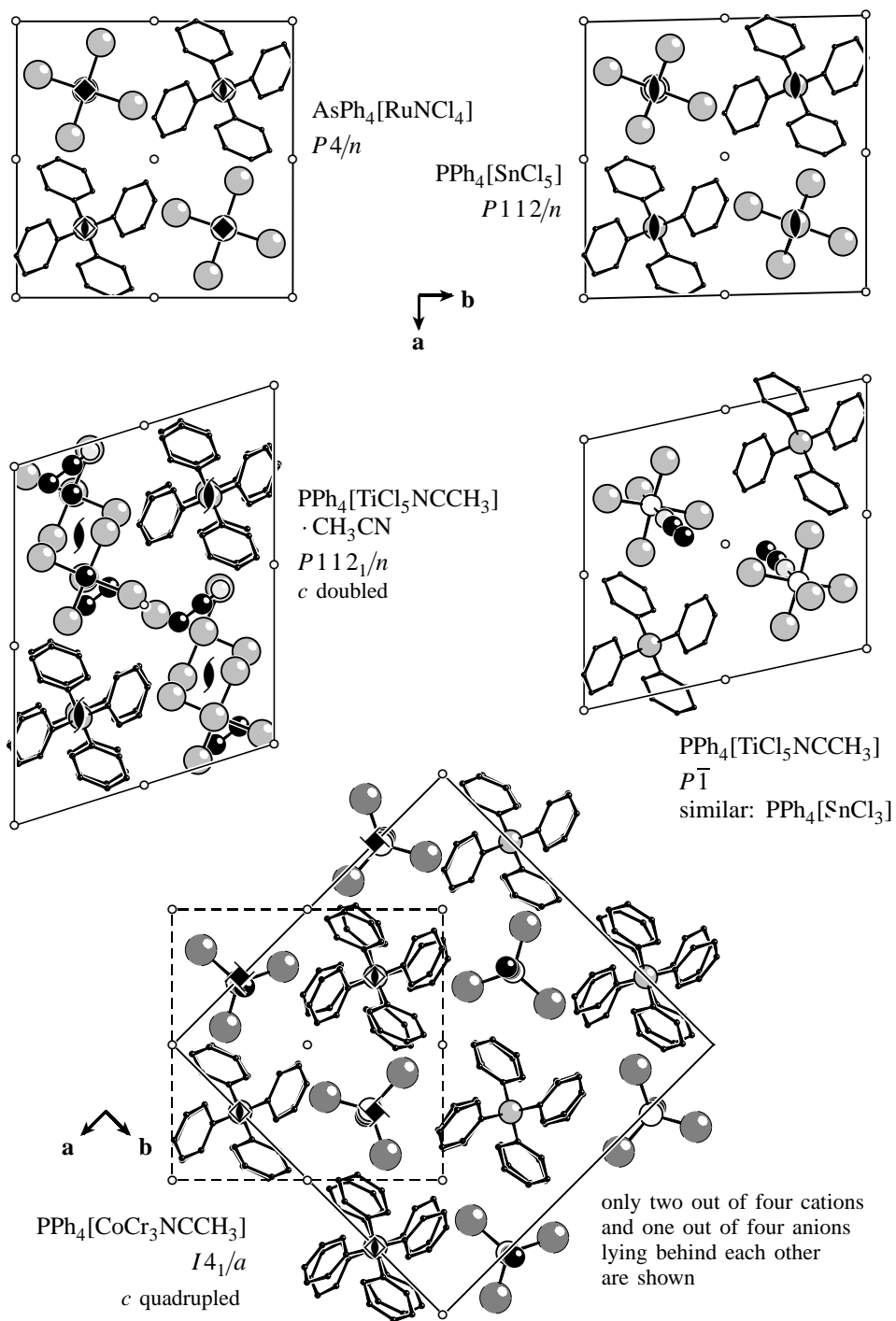


**Figure 26:** Bärnighausen tree relating diverse tetraphenylphosphonium salts.

ruins the fourfold rotational symmetry, the space group symmetry is reduced to  $P\bar{1}$  (Figs. 26 and 27) [91].

Even  $PPh_4[TiCl_5(NCCH_3)] \cdot CH_3CN$  keeps the same packing principle. To accommodate the additional acetonitrile molecules, the columns of  $PPh_4^+$  ions move apart and the  $[TiCl_5(NCCH_3)]^-$  ions move away from the 4 axes. After the symmetry reduction  $P4/n \rightarrow P2/n - 2c \rightarrow P2_1/n$ , the  $[TiCl_5(NCCH_3)]^-$  ions are located alternately on two sides of a  $2_1$  axis [91].

$P\bar{1}$  and  $P2_1/n$  are the most common space group types for molecular compounds. Both,  $PPh_4[TiCl_5(NCCH_3)]$  and  $PPh_4[TiCl_5(NCCH_3)] \cdot CH_3CN$ , have no particle on a special position, and the metrics of the unit cells are way off from being tetragonal. And yet, in both cases the intimate relation to the tetragonal aristotype is obvious, the molecular packing still is pseudo-tetragonal. We cannot state a ‘principle of symmetry avoidance’.



**Figure 27:** Unit cells of diverse tetraphenylphosphonium salts

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