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Setting up Trees of Group-Subgroup Relations

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1 Introduction

Already 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, including modern band energy calculations, 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 very 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 relationships between them result from group–subgroup relations between their space groups. These relations, however, were only partially known up to 1965, and a useful form derived by NEUBÜSER & WONDRATESCHEK 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*, Vol. A [2]. And yet, even in the 2002 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, albeit with certain restrictions, is the *Bilbao Crystallographic Server* [4].

In 1980 BÄRNIGHAUSEN presented a procedure to set forth structural relations in crystal chemistry 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*.

2 The Symmetry Principle in Crystal Chemistry

The usefulness of symmetry relations intimately has to do with the symmetry principle in crystal chemistry. This is a principle based on experience which 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 only 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) Peierls distortions; (4) Ordered occupation of like atomic positions by different kinds of atoms; (5) Condensation (freezing) of lattice vibrations (soft modes).

Aspect 3 of the symmetry principle has its origin in an observation of BERNAL. 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* [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 equi-distant 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 other sections of this International School and 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 are the 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 translation 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 if 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 upon 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 type of maximal subgroup and the index of symmetry reduction, using the abbreviations t

[*]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'. No equivalent terms have been found in English. Use the 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

Hermann–Mauguin symbol of the higher symmetric space group $\mathcal{G}$ ⟶ $P\,6/m\,2/m\,2/m$

Al : 1*a*	B : 2*d*
$6/mmm$	$\bar{6}m2$
0	$\frac{1}{3}$
0	$\frac{2}{3}$
0	$\frac{1}{2}$

see note 5

Symbol designating the higher symmetric crystal structure, *e.g.* the chemical formula or mineral name ⟶ $\boxed{AlB_2}$

Type and index of the subgroup $\mathcal{H}$ ⟶ k2

Basis transformation* ⟶ **a**, **b**, 2**c**

Origin shift* ⟶ $0, 0, -\frac{1}{2}$

$x,\ y,\ \frac{1}{2}z+\frac{1}{4}$ ⟵ coordinate transformations

Hermann–Mauguin symbol of the maximal subgroup $\mathcal{H}$ ⟶ $P\,6_3/m\,2/m\,2/c$

Ca : 2*b*	In : 4*f*
$\bar{6}m2$	$3m$
0	$\frac{1}{3}$
0	$\frac{2}{3}$
$\frac{1}{4}$	0.455

see note 5

Symbol designating the lower symmetric crystal structure ⟶ $\boxed{CaIn_2}$

* mentioned only if there is a change

Explanatory notes

1. Possible types 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 translation lattice; 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 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 **a**, **b**, **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.

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 base of he higher symmetric cell.

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*, Vol. A1 (pp. 431 and 433) [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*, whilst 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 for Crystallography*, Volume A1 (p. 430) [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. 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 the *International Tables for Crystallography* offer two possible choices of origin ('origin choice 1' and 'origin choice 2'). In these cases 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 $^{(\mathrm{rh})}$ or $^{(\mathrm{hex})}$. 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 $^{(\mathrm{rev})}$, for example $R\overline{3}^{(\mathrm{rev})}$.

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 provided for every structure. The mere mention of the space groups is insufficient. The atomic coordinates are of especial importance. It is also important to present all structures in such a way that their relations become clearly visible. In particular, all atomic coordinates 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 5. 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 of ignorance or negligence, but also for good reasons. Two of these reasons are the above-mentioned recommendations 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 be 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 really had been well-known or that are mere variations of known structure types. 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 $\mathcal{G}$.

In order to obtain an equivalent coordinate set from another, one makes use of the Euclidean Normalizers listed in Chapter 15 of *International Tables*, Vol. A [2]. The necessary transformation formulae can be found in Tables 15.2.1.3 and 15.2.1.4 of Volume A (pp. 883–898, edition of 2002; 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 $\mathcal{N}_{\mathcal{E}}(\mathcal{G})$. *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.

Example 1

$WOBr_4$ 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 $P^1 4/mmm$ with the basis vectors $\frac{1}{2}(\mathbf{a}-\mathbf{b})$, $\frac{1}{2}(\mathbf{a}+\mathbf{b})$, $\varepsilon\mathbf{c}$ (*cf. International Tables*, Vol. A, Table 15.2.1.4). The index of $P^1 4/mmm$ in $I4$ is $\infty \cdot 2 \cdot 2$, *i.e.* infinite, due to the infinitesimal small basis vector $\varepsilon\mathbf{c}$. 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 can be any arbitrary number. 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. The coordinates are:

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

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.* $\frac{1}{4},\frac{1}{4},\frac{1}{4}$), then the orbit is identical with the *Wyckoff position* (German: *Punktlage*). If, however, one or more coordinates are variable (*e.g.* z in $0,\frac{1}{2},z$), then the Wyckoff position comprises infinite many orbits; they differ in the variable coordinate(s). 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*.

An independent Wyckoff position is designated by the Wyckoff label, for example 4*c*. The 4 is the *multiplicity*; it shows how many points belonging to an orbit of the Wyckoff position in question are contained in one unit cell. The *c* is only an alphabetical label (*a, b, c,*...) according to the listing of the Wyckoff positions in *International Tables for Crystallography*, 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.

In many cases a space group has 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. Atoms fixed on special positions or coordinates that are coupled with each other may become independent.

If atoms on an orbit are to be substituted by atoms of different elements in an ordered way, the Wyckoff position 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; in addition, usually a metric distinction of the base 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 a group and its 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 for Crystallography*, Volume A1, Part 3 [3]. The listed relations are only valid for the mentioned base transformations and origin shifts. For other base 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 in the internet [31]. It requires the input of the space group, subgroup, base transformation and origin shift; it does not work for nonconventional settings.

6 Symmetry relations between crystal structures

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

The relation between pyrite and PdS_2

The space group $Pbca$ of PdS_2 is a *translationengleiche* maximal subgroup of $P2_1/a\overline{3}$, the space group 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 unit cell 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 $Pbca$). As shown in Fig. Abb. 6.1, 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-planarer coordination (electron configuration d^8), whereas the iron atoms in pyrite have octahedral coordination.

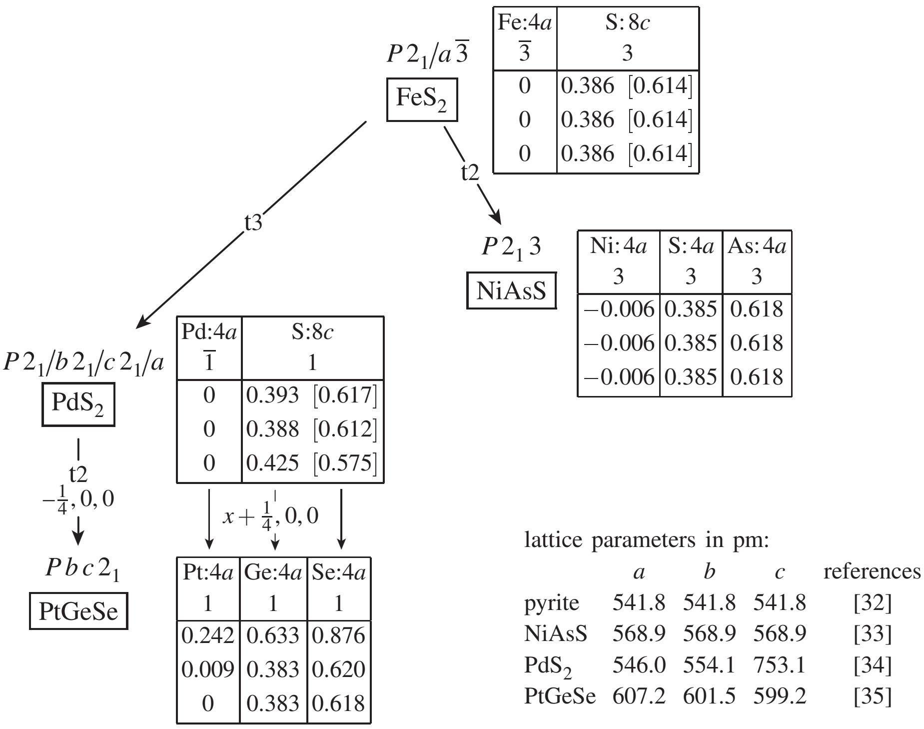


Figure 6.1: Bärnighausen tree for the structural family of pyrite. Coordinates in brackets refer to symmetry equivalent positions

Upon transition from $Pa\overline{3}$ to $Pbca$ none of the occupied Wyckoff positions splits, 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.

Ternary variants of the pyrite type

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 inversions centers of $Pa\overline{3}$ and $Pbca$, respectively, and therefore are of index 2.

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 the site symmetry. In our examples there are small coordinate changes.

The relations between FeS_2, PdS_2, NiAsS and PtGeSe are summarized in Fig. 6.1

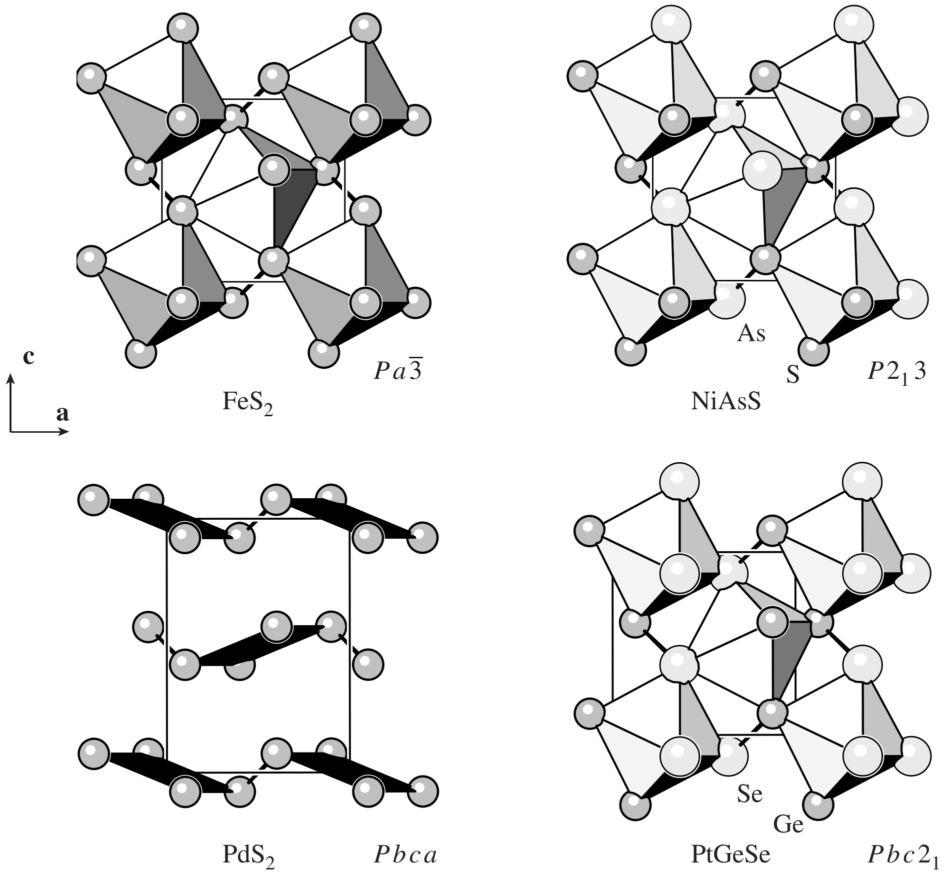


Figure 6.2: View of the unit cells of pyrite, NiAsS, PdS_2 and PtGeSe

according to the scheme presented in page 5. $Pbc2_1$ 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 opposed sign.

The substitution variants 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 $Pbc2_1$ 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.

Two variants of the AlB_2 type

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** aluminium atoms and sheets of boron atoms alternate; the boron sheets are planar like in graphite (Fig. 6.3) [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 middle of the six-membered rings cannot be retained, whereas those in the Al positions 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 in the symmetry reduction from AlB_2 to ZrBeSi. The index is 2: Half of all translations are lost, together with 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 im 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 (Abb. 6.4 left), rendering possible the occupation with atoms of two different elements.

Figs. 6.3 and 6.4 show another peculiarity. $P6/mmm$ has two *different klassengleiche* subgroups of the same type $P6_3/mmc$ with doubled base vector **c**. The second one corresponds to $CaIn_2$ [39, 40]. Here the graphite-like sheets of the AlB_2 type have become

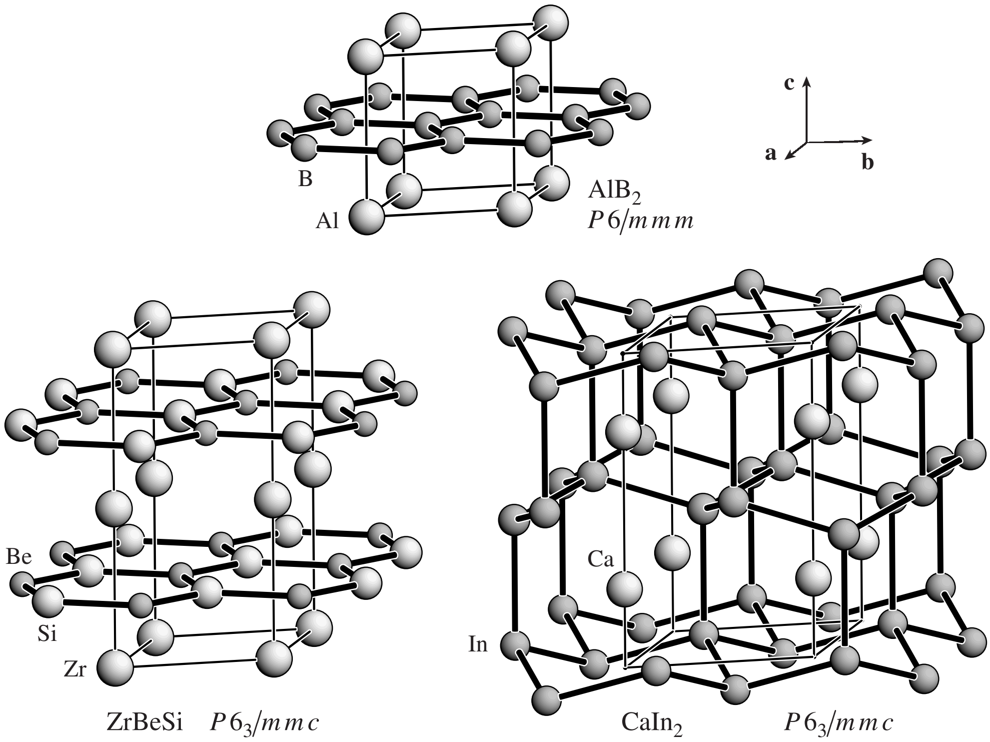


Figure 6.3: The structures of AlB_2, ZrBeSi and $CaIn_2$. The mirror planes perpendicular to **c** in $P6_3/mmc$ are at $z = \frac{1}{4}$ and $z = \frac{3}{4}$

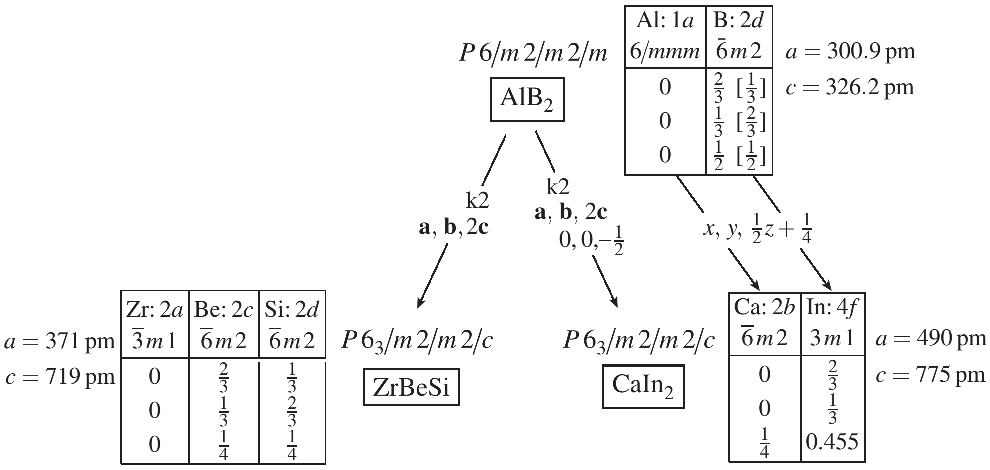


Figure 6.4: Two hettotypes of the AlB_2 type having the same space-group type and a doubled **c** axis, but different origin positions. Due to the doubling of c the z coordinates are halved. The origin shift of $0,0,-\frac{1}{2}$ in the right branch refers to the lattice of the aristotype; as a consequence $\frac{1}{4}$ has to be added to the z coordinates of the hettotype

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 layers 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 being 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 AlB_2 type can be kept when the symmetry is reduced to that of ZrBeSi (*i.e.* it is in an Zr atom). The symmetry reduction to $CaIn_2$, 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. 6.4. 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 $P6/mmm$. The symmetry reduction necessarily requires the atom shift to $z' = 0.455$.

In the relation $AlB_2 \rightarrow$ ZrBeSi the site symmetry $\bar{6}m2$ of the boron atoms is maintained and the Wyckoff position splits. In the relation $AlB_2 \to CaIn_2$ it is the other way round, the position does not split, the atoms remain symmetry-equivalent, but their site symmetry is reduced to $3m1$ and the z coordinate becomes independent.

With *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. They are called Euclidean-equivalent subgroups because they are symmetry-equivalent under a symmetry operation of the Euclidean normalizer of $\mathcal{G}$ [22, 23]. 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].

What has been said for *klassengleiche* subgroups also applies to isomorphic subgroups, since they are a special kind of *klassengleiche* subgroups. The main difference 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].

Large structural families

Using the modular way to put together symmetry relations set forth in the scheme of page 5 and in this chapter, large family trees can be constructed. Headed by an aristotype, they show structural relationships among many different crystal structures. As an example, Fig. 6.5 shows structures that can be derived of the ReO_3 type [41]. Many other trees of this kind have been set up, *e.g.* hettotypes of perovskite [5, 42], rutile [43, 44], CaF_2 [43], NaCl [45], hexagonal closest-packed structures [46], zeolites [47]. Citations concerning many more trees can be found at [6].

Such trees not only serve to show relations between structures. For second-order phase transitions the existence of a direct group–subgroup relation (not necessarily maximal) is mandatory. The tree immediately shows if such a transition is feasible. This is of importance for technical applications using ferroelectric, piezoelectric and other effects that depend on symmetry. Phase transitions that involve a reduction of symmetry are accompanied with the formation of crystal domains. If there is a *translationengleiche* subgroup, twinned crystals are likely to be formed. The number of different twin domains corresponds to the index value, and their relative orientation corresponds to one of the lost symmetry operations. Antiphase domains can appear if there is a *klassengleiche* subgroup.

7 Exercises

To solve the exercises, access to *International Tables*, volumes A [2] and A1 [3] is required.

7.1. Many tetraphenylphosphonium salts with square-pyramidal or octahedral anions crystallize in the space group $P4/n$. For $P(C_6H_5)_4[MoNCl_4]$ the coordinates are (origin choice 2):

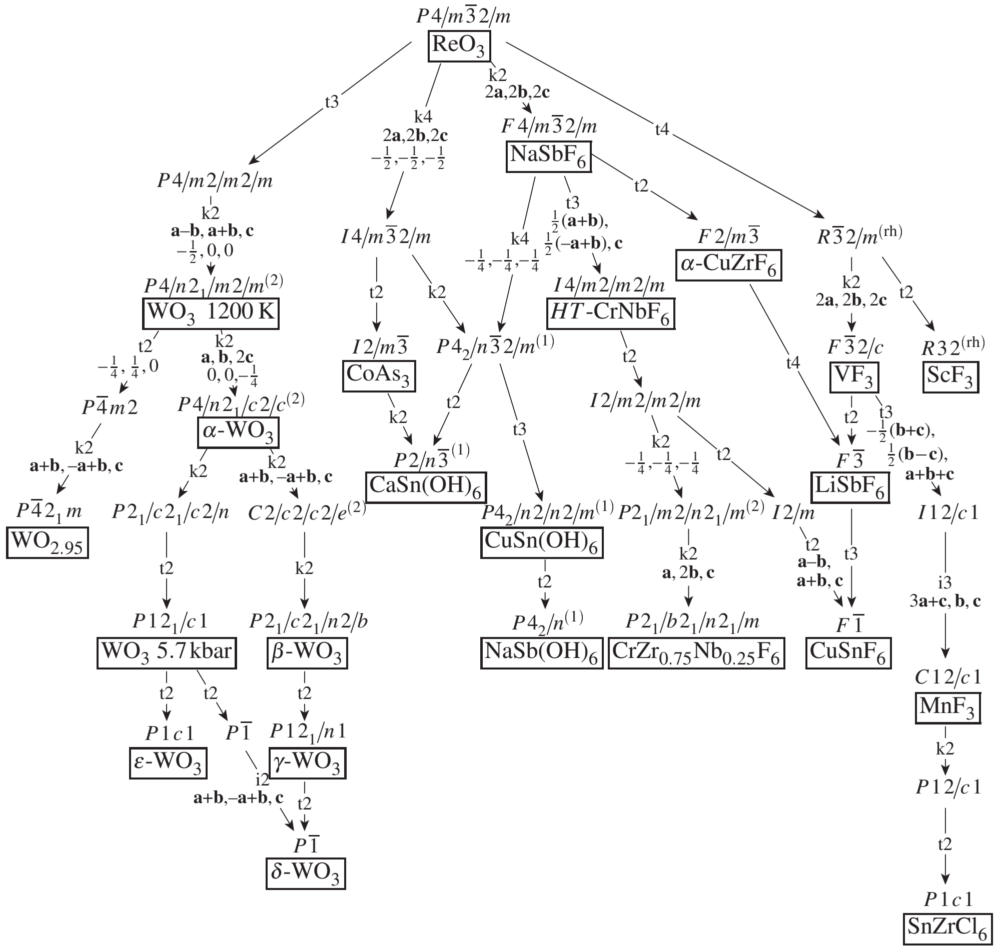


Figure 6.5: Family tree of hettotypes of ReO_3. For the atomic parameters and other crystallographic data see [41]

	x	y	z		x	y	z
P	$\frac{1}{4}$	$\frac{3}{4}$	0	Mo	$\frac{1}{4}$	$\frac{1}{4}$	0.121
C 1	0.362	0.760	0.141	N	$\frac{1}{4}$	$\frac{1}{4}$	–0.093
C 2	0.437	0.836	0.117	Cl	0.400	0.347	0.191

(H atoms and further C atoms omitted)

How many equivalent coordinate sets exist for this structure? What are the corresponding coordinates?

7.2. Take a copy of Fig. 6.2. Include the graphical symbols of all symmetry elements in the style of *International Tables* in the four unit cells. Which symmetry elements are lost in each case?

7.3. The crystal data for *LT*-quartz are $a = 491$ pm, $c = 541$ pm; space group $P3_2 21$; atomic coordinates Si 0.470, 0, $\frac{1}{6}$ and O 0.414, 0.268, 0.286. Upon heating it is converted to *HT*-quartz,

$a = 500$ pm, $c = 546$ pm; space group $P6_222$; coordinates Si $\frac{1}{2}$, 0, $\frac{1}{2}$and O 0.416, 0.208, $\frac{2}{3}$. Set up the corresponding Bärnighausen tree. Which additional degrees of freedom are present in the lower symmetry form?

7.4. The crystal data for α-$AlPO_4$ are:

$P3_121$ $\quad a = 494$ pm, $c = 1095$ pm

	x	y	z		x	y	z
Al	0.466	0	$\frac{1}{3}$	O1	0.417	0.292	0.398
P	0.467	0	$\frac{5}{6}$	O2	0.417	0.257	0.883

What is its relation to quartz? (*cf.* exercise 7.2.)

7.5. Most metals crystallize with one of the following sphere packings.

cubic-closest	hexagonal-closest	body-centered cubic
$Fm\overline{3}m$	$P6_3/mmc$ $\quad c/a = 1.633$	(W-Typ) $\quad Im\overline{3}m$
x y z	x y z	x y z
0 0 0	$\frac{1}{3}$ $\frac{2}{3}$ $\frac{1}{4}$	0 0 0

Derive the structures of Indium, α-mercury, protactinium and α-uranium from the corresponding packings.

In $\quad I4/mmm$	α-Hg $\quad R\overline{3}m$	Pa $\quad I4/mmm$	α-U $\quad Cmcm$
$a = 325.1$ $c = 494.7$	$a = 346.5$ $c = 667.7$	$a = 392.5$ $c = 324.0$	$a = 285.4$ $b = 586.8$
	(hex. axes)		$c = 495.8$ pm
x y z	x y z	x y z	x y z
0 0 0	0 0 0	0 0 0	0 0.398 $\frac{1}{4}$

7.6. Derive the structure of Tl_7Sb_2 from one of the sphere packings mentioned in exercise 7.4.

$Im\overline{3}m$ $\quad a = 1162$ pm

	x	y	z		x	y	z
Tl1	0	0	0	Sb1	0	0.350	0.350
Tl2	0.330	0,330	0.330	Tl3	0,314	0	0

7.7. $TlAlF_4$ exhibits two modifications at different temperatures. Derive the corresponding Bärnighausen tree. What is the difference of the modifications? Although the cell volumes differ by a factor of nearly 4, the index is only 2; how is that possible?

$TlAlF_4$-$tP4$, 300 °C $\quad P4/mmm$
$a = 364.9$ $c = 641.4$ pm

	x	y	z		x	y	z
Tl	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	F1	$\frac{1}{2}$	0	0
Al	0	0	0	F2	0	0	0.274

$TlAlF_4$-$tI8$, 200 °C $\quad I4/mcm$
$a = 514.2$ $c = 1280.7$ pm

	x	y	z		x	y	z
Tl	0	$\frac{1}{2}$	$\frac{1}{4}$	F1	0.276	0.224	0
Al	0	0	0	F2	0	0	0.137

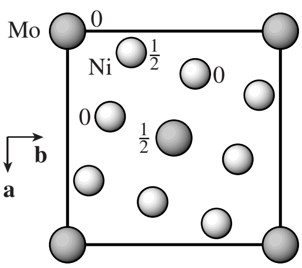
7.8. When the alloy $MoNi_4$ is quenched from 1200 °C, it crystallizes in the Cu type (f.c.c) with disordered distribution of its atoms. After hours at 840 °C it becomes ordered. What is the relation?

$MoNi_4$ Cu type
$Fm\overline{3}m$ $\quad a = 361.2$ pm

		x	y	z
Mo, Ni	4a	0	0	0

$MoNi_4$ ordered
$I4/m$ $\quad a = 572.0$ pm, $c = 356.4$ pm

		x	y	z
Mo	2a	0	0	0
Ni	8h	0.400	0.200	0



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How many independent crystal-structure types are possible for different space groups appearing in a Bärnighausen tree?

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8 Prediction of crystal structure types

In the previous chapters it has been shown how we can find structural relations between *known* structure types with the aid of Bärnighausen trees. Usually, one can find further subgroups of an aristotype for which no structures are known. With the aid of group–subgroup relations one can systematically search for new structural possibilities, *i.e.* one can predict crystal structure types.

The starting point always is an aristotype and a structural principle. 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. Of course, one can only find such structure types that meet these starting conditions.

As an example, we will find out which crystal structure types are possible for a compound of the chemical composition $A_aB_b...X_x$ if the X atoms form a hexagonal-closest packing of spheres and all other atoms occupy octahedral voids. In this case, the aristotype has the space group $P6_3/m2/m2/c$, and the space groups of the sought structure types are subgroups of it. The unit cell of the hexagonal-closest packing contains two X atoms and two octahedral voids. If the unit cell is enlarged by a factor Ξ, this amounts to 2Ξ octahedral voids and 2Ξ X atoms per cell. We treat empty octahedral voids just like occupied octahedral voids; so to say, they are being occupied by Schottky voids (symbol $\square$) or by 'zero atoms'. Then for the chemical composition $A_aB_b...\square_sX_x$ we have: $a+b+\cdots+s=x$.

All numbers $2a\Xi/x$, $2b\Xi/x$, ..., $2s\Xi/x$ must be integral. Therefore, depending on the chemical composition, the unit cell of the sphere packing must be enlarged by an appropriate factor Ξ, say $\Xi=3$ or $\Xi=6,9,\ldots$ for a trihalide $A_1\square_2X_3$.

Therefore, first of all we must consider in what ways the unit cell can be enlarged. Enlargement of the (primitive) unit cell means loss of translation symmetry; *klassengleiche* subgroups must occur. For every kind of cell enlargement we must verify which subgroups are to be considered. In this connection it is essential to pay attention how the relevant Wyckoff positions evolve from group to subgroup. Of special interest are those group–subgroup relations which result in splittings of the Wyckoff positions. In our example we have to follow which and how many independent positions result from the Wyckoff positions of the octahedral voids. The symmetry reduction has to be followed only up to the point where all octahedral voids of the enlarged unit cell have become independent, as long as distorted variants are not considered. Subgroups that show no new splittings of positions need to be considered as intermediate groups only if hierarchically lower space groups cannot be reached in another way.

Let us consider as an example the enlarged rhombohedral unit cell shown in Fig. 8.6 ($2\mathbf{a}+\mathbf{b}$, $-\mathbf{a}+\mathbf{b}$, $3\mathbf{c}$, $\Xi=3$). In the setting with hexagonal axes the cell is enlarged by a factor of 9, but due to the rhombohedral centering the primitive cell is only tripled. The corresponding Bärnighausen tree is shown in Fig. 8.7; the mentioned space groups have been numbered $\mathcal{G}_1$ to $\mathcal{G}_9$. The lowest symmetry subgroup mentioned is $R3$. That is the highest symmetry subgroup of $P6_3/mmc$ in which all octahedral voids have become independent. Additional space groups that could be inserted as intermediate groups between

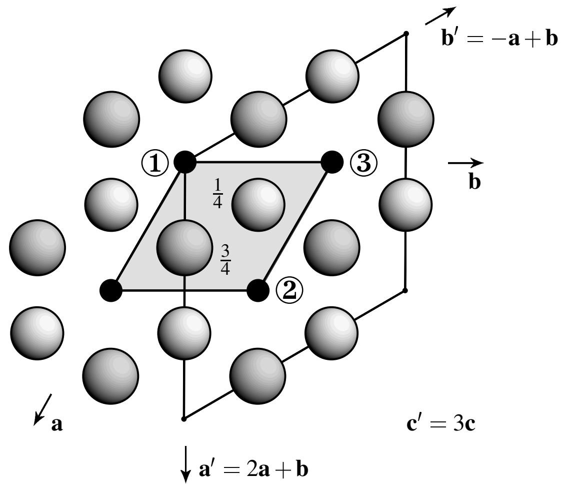

Figure 8.6: Section of a hexagonal-closest packing of spheres. In gray: unit cell, space group $P6_3/m2/m2/c$. Large cell: base plane of the enlarged cell with $\mathbf{c}' = 3\mathbf{c}$ for rhombohedral subgroups (hexagonal axes). The z coordinates of the spheres are referred to the cell of the sphere packing. The dots marked ①, ② and ③ indicate the six octahedral voids in $z = 0$ and $z = \frac{1}{2}$ (for $\mathbf{c}$) and $z = 0$ and $z = \frac{1}{6}$ (for $\mathbf{c}' = 3\mathbf{c}$)

$P6_3/mmc$ and $R3$ have been omitted because they show no new splittings compared to mentioned, hierarchically higher groups. Other space groups than mentioned in Fig. 8.7 cannot occur with the considered kind of cell enlargement, unless there are distortions.

In the maximal *translationengleiche* subgroup $P\overline{3}2/m1$ the octahedral voids are already independent. If we occupy one of them und leave the other one vacant, we obtain the CdI_2 type. This requires no cell enlargement.

The triple unit cell has six octahedral voids. In Fig. 8.7 they are exhibited as six joined boxes and labeled with the corresponding Wyckoff symbols; equal Wyckoff symbols refer to symmetry-equivalent voids, *i.e.* to the same orbit. Horizontally adjacent boxes correspond to edge-sharing octahedra, vertically adjacent boxes to face-sharing octahedra, and diagonally neighboring boxes with a common vertex to vertex-sharing octahedra. The symmetry reduction can be traced by the increasing number of different Wyckoff symbols.

Known representatives are:

> BiI_3 in $R\overline{3}$. It is a layer structure with edge-sharing occupied octahedra (position c_1 in Fig. 8.7).
>
> RhF_3 in $R\overline{3}2/c$. All occupied octahedra share common vertices (position b in Fig 8.7).

There exists a third possible structure type for the composition MX_3, namely in the space group $\mathcal{G}_7 = R32$ if the orbit c_2 is occupied and c_1 and c_3 remain vacant. It has

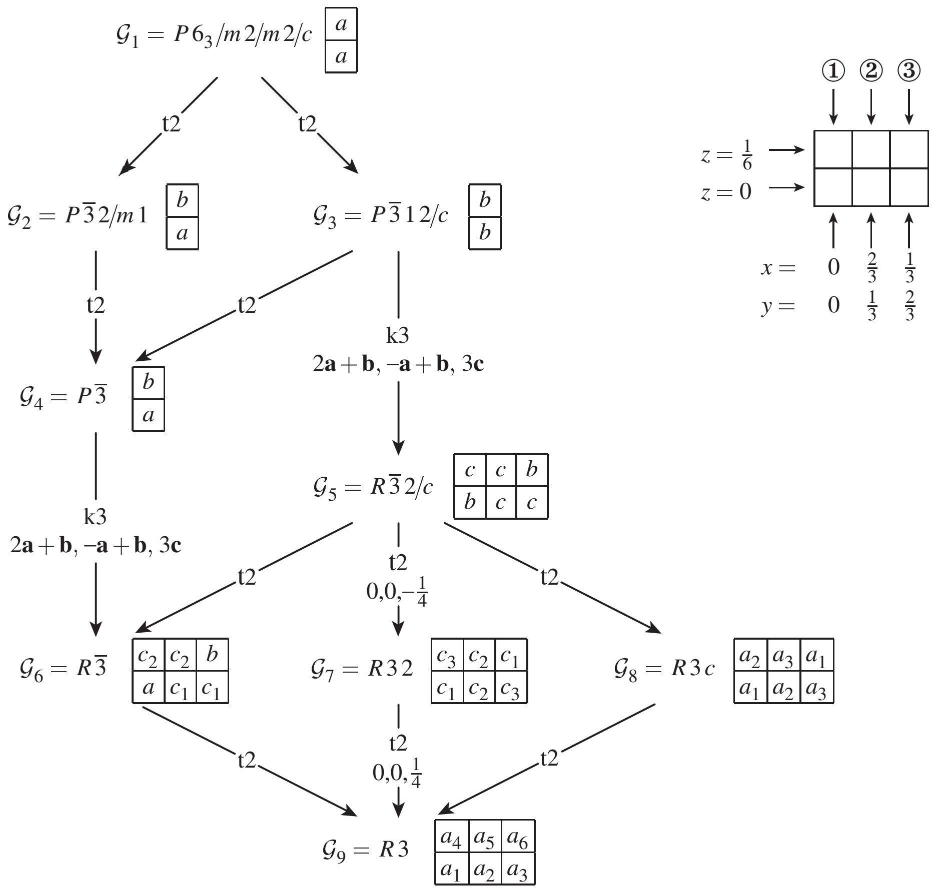

Figure 8.7: Bärnighausen tree relating the hexagonal-closets packing of spheres with some rhombohedral hettotypes. The boxes represent the octahedral voids, letters are Wyckoff labels. The diagram in the upper right corner shows the corresponding coordinates (*cf.* the octahedral voids marked ①, ② and ③ in Fig. 8.6). Different orbits of the same Wyckoff position are distinguished by index numbers (a_1, a_2 etc.)

pairs of face-sharing occupied octahedra that are connected with one another by common vertices (Fig. 8.8). No representative is known for this structure type. A compound that could adopt this structure could be WCl_3. Trivalent tungsten is known for its tendency to form structures with face-sharing octahedra (W≡W bonds). Maybe it is worth searching for such a modification of WCl_3 .

The space groups mentioned in Fig. 8.7 offer some more possible structure types, depending on the occupation of the Wyckoff positions. One is the $LiSbF_6$ typ ($R\overline{3}$, Wyckoff positions a and b occupied). For this composition $AB\square_4X_6$ two more possibilities exist in the space group $R3$: (1) Atom A on a_1, B on a_2; (2) Atom A on a_2, B on a_5. More

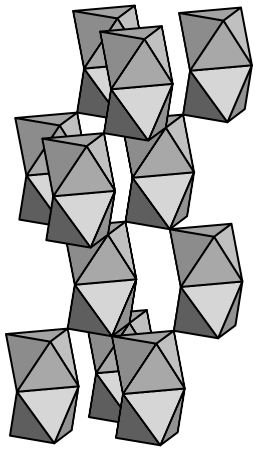

Figure 8.8: Joined octahedra in the hypothetical structure of WCl_3

possibilities do not exist for this composition. If in $R3$ we put A on a_1, B on a_3, the result would be the same structure type as by occupation of a_1 and a_2. The occupation of a_1 and a_6 would result in the $LiSbF_6$ type, which is at a hierarchically higher symmetry level, since this distribution of atoms can already be achieved in the space group $R\overline{3}$. The prediction of possible structure types by occupying the relevant Wyckoff positions therefore requires caution in two ways:

1. Several atom distributions can result in the same structure type; only one of them is to be counted.

2. Some atom distributions can be achieved in space groups at a higher symmetry level and must be assigned to these.

One can avoid errors if one knows how many independent structural possibilities exist for a given chemical composition and space group. This can be calculated, as shown in the next chapter.

9 Calculation of the number of structural possibilities

The total number of possibilities, how to distribute a given number of atom kinds on a given number of orbits can be calculated with the theorem of PÓLYA [48]. This procedure has been used to calculate the number of possible isomers of organic molecules [49, 50]. However, Pólya's method does not distinguish between the symmetry of the different structures, and we will not discuss it here.

With reference to a tree of group–subgroup relations, WHITE has extended Pólya's procedure, so that the number of independent structures depending on symmetry can be calculated. His papers can hardly be understood by non-mathematicians [51], but

MCLARNAN 'translated' them to the language of crystallographers and showed applications [52, 53]; see also [54].

The requisite is a tree of group–subgroup relations and the consideration of the orbits of the relevant atomic positions. Starting from the aristotype, all subgroups have to be included which show new splittings of Wyckoff positions. The tree needs to be extended only up to the point where all atomic positions of interest have become symmetrically independent (as long as distortions are not considered) or until a given limit for the symmetry reduction has been reached.

The space groups (for molecules: the point groups) of the tree are numbered $\mathcal{G}_1, \mathcal{G}_2, \ldots$, taking into account the decreasing symmetry hierarchy. If $i > j$ then $\mathcal{G}_j$ may not be a supergroup of $\mathcal{G}_i$. $\mathcal{G}_1$ is the aristotype. A matrix $\mathbf{M}$ has to be calculated, with the components:

$$m_{ij} = \frac{1}{|\mathcal{G}_j|} \sum_{g \in \mathcal{G}_1} \chi(g\mathcal{G}_i g^{-1} \subseteq \mathcal{G}_j) \qquad (9.1)$$

$$= I_j \frac{[\mathcal{G}_i \subseteq \mathcal{G}_j]}{[\mathcal{G}_i]} \qquad (9.2)$$

$\lvert\mathcal{G}_j\rvert$	= order of the group $\mathcal{G}_j$
g	= symmetry operation of $\mathcal{G}_1$
I_j	$= \dfrac{\lvert\mathcal{G}_1\rvert}{\lvert\mathcal{G}_j\rvert}$ = index of the symmetry reduction from $\mathcal{G}_1$ to $\mathcal{G}_j$
$[\mathcal{G}_i]$	= number of the conjugate subgroups of $\mathcal{G}_i$ in $\mathcal{G}_1$
$[\mathcal{G}_i \subseteq \mathcal{G}_j]$	= number of these conjugate subgroups that are also subgroups of $\mathcal{G}_j$
χ(COND)	= 1, if the condition COND is fulfilled
χ(COND)	= 0, if the condition COND is not fulfilled

χ(COND) is called the 'characteristic function'. In our case the condition is COND = $g\mathcal{G}_i g^{-1} \subseteq \mathcal{G}_j$, *i.e.* it has to be determined if the application of a symmetry operation g of the aristotype on the group $\mathcal{G}_i$ generates the group $\mathcal{G}_j$. For the calculation of the sum in equation (9.1) all symmetry operations of the aristotype have to be covered. For larger trees this is a considerable computational effort that can only be managed with a fast computer.

Equation (9.2) is more suitable if one wants to calculate by hand. For every subgroup, this requires the knowledge of the numbers of its conjugate subgroups in $\mathcal{G}_1$. Conjugate subgroups in $\mathcal{G}_1$ are different subgroups of the same type which are symmetry-equivalent under a symmetry operation of $\mathcal{G}_1$. For example, hexagonal space groups have three conjugate orthorhombic maximal subgroups which are equivalent under the (lost) sixfold axis (Fig. 9.9). Conjugate subgroups only occur if the index is ≥ 3. The number of conjugate subgroups can be determined by a procedure according to KOCH [22, 55].

The matrix $\mathbf{M}$ is triangular, *i.e.* the components above of the main diagonal are $m_{ij} = 0$. All components are integers and the all numbers of the first column are 1.

Consider the Bärnighausen tree of Fig. 8.7. The corresponding matrix is:

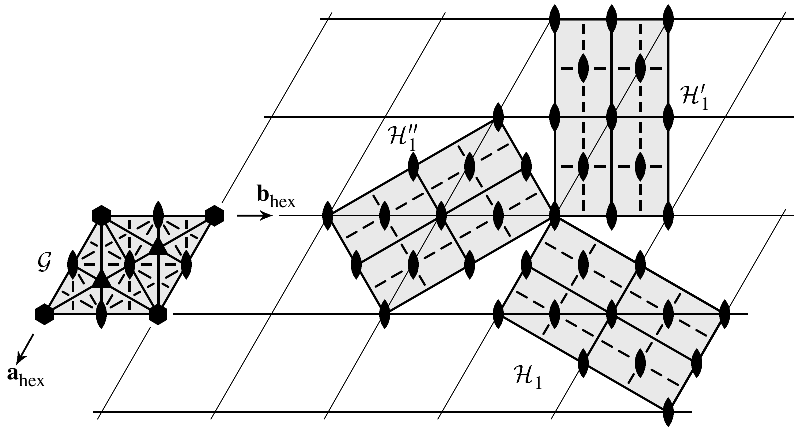

Figure 9.9: Conjugate (C-centered) orthorhombic subgroups ($C\,m\,m\,2$) of a hexagonal subgroup ($P\,6\,m\,m$) with three different orientations

$$\begin{array}{c} \mathcal{G}_1 \\ \mathcal{G}_2 \\ \mathcal{G}_3 \\ \mathcal{G}_4 \\ \mathcal{G}_5 \\ \mathcal{G}_6 \\ \mathcal{G}_7 \\ \mathcal{G}_8 \\ \mathcal{G}_9 \end{array} \begin{pmatrix} 1 &&&&&&&& \\ 1 & 2 &&&&&&& \\ 1 & 0 & 2 &&&&&& \\ 1 & 2 & 2 & 4 &&&&& \\ 1 & 0 & 2 & 0 & 1 &&&& \\ 1 & 2 & 2 & 4 & 1 & 2 &&& \\ 1 & 0 & 2 & 0 & 1 & 0 & 2 && \\ 1 & 0 & 2 & 0 & 3 & 0 & 0 & 6 & \\ 1 & 2 & 2 & 4 & 3 & 6 & 6 & 6 & 12 \end{pmatrix} = \mathbf{M} \tag{9.3}$$

For example, using equation (9.2) we calculate the matrix elements m_{64} and m_{65}:

$I_4 = 2 \cdot 2 = 4$; $\quad I_5 = 2 \cdot 3 = 6$;

$[\mathcal{G}_6] = 6$: $\mathcal{G}_6$ has 6 conjugate groups which are equivalent in $\mathcal{G}_1$; they differ by three positions of their origins (which are translationally equivalent in $\mathcal{G}_1$), each one with two orientations rhombohedral-obverse and reverse;

$[\mathcal{G}_6 \subseteq \mathcal{G}_4] = 6$: all 6 conjugates of $\mathcal{G}_6$ are also subgroups of $\mathcal{G}_4$;

$[\mathcal{G}_6 \subseteq \mathcal{G}_5] = 1$: only one of the conjugates of $\mathcal{G}_6$ is a subgroup of $\mathcal{G}_5$, namely the one with the same origin position and orientation (obverse or reverse)

$$m_{64} = I_4 \frac{[\mathcal{G}_6 \subseteq \mathcal{G}_4]}{[\mathcal{G}_6]} = 4\frac{6}{6} = 4; \qquad m_{65} = I_5 \frac{[\mathcal{G}_6 \subseteq \mathcal{G}_5]}{[\mathcal{G}_6]} = 6\frac{1}{6} = 1$$

An element m_{ij} is always and only zero, if the space group $\mathcal{G}_j$ is not a subgroup of $\mathcal{G}_i$.

The further calculation requires the inverse matrix of **M**, $\mathbf{B} = \mathbf{M}^{-1}$. Since it is a triangular matrix, the matrix inversion is easy to calculate. With some experience it can easily be calculated by mental arithmetic. All diagonal elements of **B** are the reciprocals of the diagonal elements of **M**, $b_{ii} = 1/m_{ii}$. For the other elements we have:

$$b_{ij} = \sum_{k=j}^{i} m_{ik} b_{kj} = 0$$

The inverse matrix of the above-mentioned matrix (9.3) is:

$$\mathbf{B} = \mathbf{M}^{-1} = \begin{pmatrix} 1 \\ -\frac{1}{2} & \frac{1}{2} \\ -\frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{4} & -\frac{1}{4} & -\frac{1}{4} & \frac{1}{4} \\ 0 & 0 & -1 & 0 & 1 \\ 0 & 0 & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ 0 & 0 & 0 & 0 & -\frac{1}{2} & 0 & \frac{1}{2} \\ 0 & 0 & \frac{1}{3} & 0 & -\frac{1}{2} & 0 & 0 & \frac{1}{6} \\ 0 & 0 & -\frac{1}{6} & \frac{1}{6} & \frac{1}{2} & -\frac{1}{4} & -\frac{1}{4} & -\frac{1}{12} & \frac{1}{12} \end{pmatrix}$$

If an element is $m_{ij} = 0$, then $b_{ij} = 0$ also holds. The sum of all b_{ij} in a row of **B** is always 0 (except for the first row).

Aside of the matrix **B**, for a given chemical composition one has to calculate for every space group of the Bärnighausen tree in how many different ways the different kinds of atoms can be distributed among the considered orbits. This is done by the arithmetic rules of combinatorics. For example, in the space group $\mathcal{G}_9$ all six octahedral voids are symmetry-independent; if two of them are to be occupied with two equal atoms, the other four remaining vacant, then we obtain $v_9 = \binom{6}{2} = 15$ combinatorial distributions. In the space group $\mathcal{G}_6 = R\overline{3}$ we obtain the following three possibilities (gray boxes mark the occupied octahedral voids):

c_2	c_2	b
a	c_1	c_1

c_2	c_2	b
a	c_1	c_1

c_2	c_2	b
a	c_1	c_1

For a general formula to calculate the combinatorial numbers see [56].

Thus, for every space group $\mathcal{G}_1$ to $\mathcal{G}_9$ of the Bärnighausen tree we calculate a number v_1 to v_9. These numbers are combined to a column vector $\mathbf{v} = (v_1, \ldots, v_9)$. They represent all of the combinatorial distributions of atoms among the Wyckoff positions of every one of the nine space groups. For low-symmetry space groups they include distributions of higher symmetry, and equivalent structures may have been counted several times. Of the three above-shown possibilities the first one does not belong to the space group

Table 9.1: Numbers of possible structure types (= components of the vectors **z**) depending on space group and chemical composition, for the occupation of octahedral voids in a hexagonal-closest packing of spheres with triple, rhombohedral unit cell. X = atoms of the sphere packing, A, B, C = atoms in the voids, □ = unoccupied voids

	AX		ABX_2 $A\square X_2$		AB_2X_3 $A\square_2X_3$ $\square B_2X_3$		$ABCX_3$ $AB\square X_3$		AB_5X_6 $A\square_5X_6$ $\square B_5X_6$		ABC_4X_6 $AB\square_4X_6$ $A\square C_4X_6$		$AB_2C_3X_6$ $AB_2\square_3X_6$ $A\square_2C_3X_6$ $\square B_2C_3X_6$	
	v	**z**	**v**	**z**	**v**	**z**	**v**	**z**	**v**	**z**	**v**	**z**	**v**	**z**
$\mathcal{G}_1 = P6_3/m2/m2/c$	1	1	0	0	0	0	0	0	0	0	0	0	0	0
$\mathcal{G}_2 = P\overline{3}2/m1$	1	0	2	1	0	0	0	0	0	0	0	0	0	0
$\mathcal{G}_3 = P\overline{3}12/c$	1	0	0	0	0	0	0	0	0	0	0	0	0	0
$\mathcal{G}_4 = P\overline{3}$	1	0	2	0	0	0	0	0	0	0	0	0	0	0
$\mathcal{G}_5 = R\overline{3}2/c$	1	0	0	0	1	1	0	0	0	0	0	0	0	0
$\mathcal{G}_6 = R\overline{3}$	1	0	4	1	3	1	6	3	2	1	2	1	4	2
$\mathcal{G}_7 = R32$	1	0	0	0	3	1	6	3	0	0	0	0	0	0
$\mathcal{G}_8 = R3c$	1	0	0	0	3	0	6	1	0	0	0	0	0	0
$\mathcal{G}_9 = R3$	1	0	20	1	15	0	90	4	6	0	30	2	60	4
sum ($\widehat{=}$ Pólya)		1		3		3		11		1		3		6

$\mathcal{G}_6 = R\overline{3}$, it belongs to the higher symmetry space group $\mathcal{G}_5 = R\overline{3}c$; the last two represent the same structure type, only one of them is to be counted. The numbers $z_1, \ldots z_9$ of mutually *independent* structure types, assigned to the correct space groups follows from:

$$\mathbf{z} = \mathbf{M}^{-1}\mathbf{v} \qquad \text{with} \quad \mathbf{z} = (z_1, \ldots, z_9) \quad \text{column vector}$$

These numbers are given for different chemical compositions in Table 9.1.

To calculate the combinatorial distributions that are combined in the vector **v**, one must know for every space group $\mathcal{G}_i$ how many inequivalent atomic positions have to be considered and what their multiplicities are. Starting from the aristotype, one must follow how the Wyckoff positions develop from group to subgroup, especially how they split into inequivalent positions. The necessary data are listed in *International Tables for Crystallography*, Vol. A1 [3].

9.1 Exercise

9.1. Take the subgroup $I4/m2/m2/m$ of NaCl with a doubled cell (**a**, **b**, 2**c**). Set up the Bärnighausen tree. Calculate how many independent structures are possible in this space group for the compositions $A\square X_2$ (one half of the cation sites vacant), $AB\square_2X_4$ and $A\square_3X_4$ Crystal data: NaCl, $F4/m\overline{3}2/m$; Na 0, 0, 0; Cl $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$.

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TREES OF GROUP–SUBGROUP RELATIONS
Solutions to the Problems

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7.1 The Euclidean normalizer of $P4/n$ is $P4/m2/m2/m$ with base vectors $\frac{1}{2}(\mathbf{a}-\mathbf{b}), \frac{1}{2}(\mathbf{a}+\mathbf{b}), \frac{1}{2}\mathbf{c}$, index 8. There are eight equivalent coordinate sets for the structure. They result by addition of $\frac{1}{2}, \frac{1}{2}, 0$ and $0, 0, \frac{1}{2}$ as well as by the transformation y, x, z. Therefore, the eight coordinate sets are:

	x	y	z	x	y	z	x	y	z	x	y	z
P	$\frac14$	$\frac34$	0	$\frac34$	$\frac14$	0	$\frac14$	$\frac34$	$\frac12$	$\frac34$	$\frac14$	$\frac12$
C 1	0.362	0.760	0.141	0.862	0.260	0.141	0.362	0.760	0.641	0.862	0.260	0.641
C 2	0.,437	0.836	0.117	0.937	0.336	0.117	0.437	0.836	0.617	0.937	0.336	0.617
Mo	$\frac14$	$\frac14$	0.121	$\frac34$	$\frac34$	0.121	$\frac14$	$\frac14$	0.621	$\frac34$	$\frac34$	0.621
N	$\frac14$	$\frac14$	–0.093	$\frac34$	$\frac34$	–0.093	$\frac14$	$\frac14$	0.407	$\frac34$	$\frac34$	0.407
Cl	0.400	0.347	0.191	0.900	0.847	0.191	0.400	0.347	0.691	0.900	0.847	0.691
P	$\frac34$	$\frac14$	0	$\frac14$	$\frac34$	0	$\frac34$	$\frac14$	$\frac12$	$\frac14$	$\frac34$	$\frac12$
C 1	0.760	0.362	0.141	0.260	0.862	0.141	0.760	0.362	0.641	0.260	0.862	0.641
C 2	0.836	0.437	0.117	0.336	0.937	0.117	0.836	0.437	0.617	0.336	0.937	0.617
Mo	$\frac14$	$\frac14$	0.121	$\frac34$	$\frac34$	0.121	$\frac14$	$\frac14$	0.621	$\frac34$	$\frac34$	0.621
N	$\frac14$	$\frac14$	–0.093	$\frac34$	$\frac34$	–0.093	$\frac14$	$\frac14$	0.407	$\frac34$	$\frac34$	0.407
Cl	0.347	0.400	0.191	0.847	0.900	0.191	0.347	0.400	0.691	0.847	0.900	0.691

7.2 The symmetry reduction $P2_1/a\overline{3} \to P2_1/b2_1/c2_1/a$ involves the loss of the threefold rotation axes. From $P2_1/b2_1/c2_1/a$ to $Pbc2_1$ (nonconventional for $Pca2_1$), additionally the inversion centers, the 2_1 axes parallel to a and b and the glide planes perpendicular to c are lost. $P2_1/a\overline{3} \to P2_13$ involves a loss of the inversion centers and the glide planes.

7.3 and **7.4**

$P6_222$

$\boxed{HT\text{-quartz}}$

Si: 3d	O: 6i
222	. . 2
$\frac12$	0,416
0	0,208
$\frac12$	$\frac23$

t2
$0, 0, \frac13$

translationengleiche subgroup;
attention to the origin shift:
add $-\frac13$ to the z coordinates

$P3_221$

$\boxed{LT\text{-quartz}}$

Si: 3b	O: 6c
.2.	1
0,470	0,414
0	0,268
$\frac16$	0,286

The x coordinate of Si and the z coordinate of O become independent, the x and y coordinates of O become independent from each other

i2
$\mathbf{a}, \mathbf{b}, 2\mathbf{c}$
$0, 0, -\frac12$

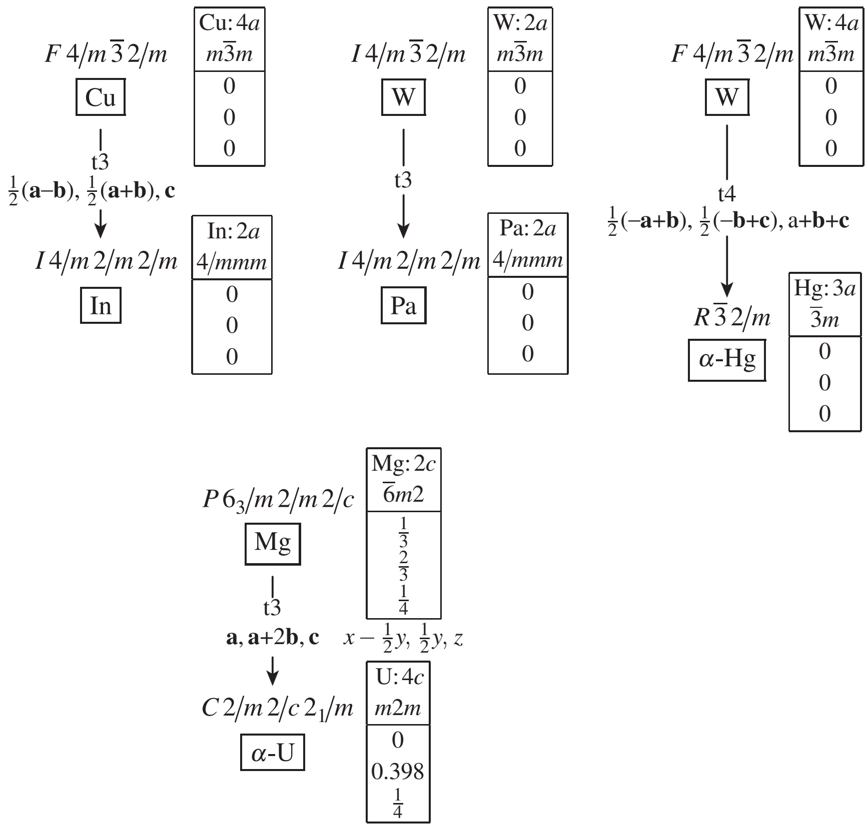
Due to the doubling of c divide the z coordinates with 2, then add $\frac14$ and $\frac34$ to the z coordinates because of the origin shift

$P3_121$

$\boxed{AlPO_4}$

Al: 3a	P: 3b	O1: 6c	O2: 6c
.2.	.2.	1	1
0,466	0,467	0,417	0,417
0	0	0,292	0,257
$\frac13$	$\frac56$	0,398	0,883

7.5 Indium: The relation $Fm\overline{3}m \rightarrow I4/mmm$ requires a basis transformation $a' = \frac{1}{2}(\mathbf{a}-\mathbf{b})$ and thus a ratio $c/a = \sqrt{2}$. For indium $c/a = 1.52$, which is a little larger than $\sqrt{2}$; therefore, it can be described as a cubic-closest packing of spheres with a slight elongation parallel to c.
Protactinium: wit $c/a = 0.83$ it must be described as a compressed body-centered cubic packing of spheres.
Mercury: The relation $Fm\overline{3}m \rightarrow R\overline{3}m$ (hexagonal axes) requires the axes transformation $\frac{1}{2}(-\mathbf{a}+\mathbf{b})$, $\frac{1}{2}(-\mathbf{b}+\mathbf{c})$, $\mathbf{a}+\mathbf{b}+\mathbf{c}$; from this we obtain a ratio $c/a = \sqrt{3}/(\frac{1}{2}\sqrt{2}) = 2.45$. That is slightly larger than the value $c/a = 1.93$ of mercury. It can be described as a trigonally compressed cubic-closest packing of spheres. For $Im\overline{3}m \rightarrow R\overline{3}m$ (hexagonal axes) the transformation would be $-\mathbf{a}+\mathbf{b}$, $-\mathbf{b}+\mathbf{c}$, $\frac{1}{2}(\mathbf{a}+\mathbf{b}+\mathbf{c})$ and thus $c/a = \frac{1}{2}\sqrt{3}/\sqrt{2} = 0.61$.
Uranium: $b/a = 2.06$ instead of $\sqrt{3}$ and $c/a = 1.74$ instead of 1.633; we have a hexagonal-closest packing of spheres which is elongated parallel to b of the orthorhombic cell.



7.6

$I\,4/m\,\overline{3}\,2/m$

$\boxed{\mathrm{W}}$

W:4a
$m\overline{3}m$
0
0
0

i27

$3\mathbf{a}, 3\mathbf{b}, 3\mathbf{c}$

$\frac{1}{3}x,\ \frac{1}{3}y,\ \frac{1}{3}z;\ +(u,v,w),\ u,v,w = 0$ or $\pm\frac{1}{3}$

$I\,4/m\,\overline{3}\,2/m$

$\boxed{\mathrm{Tl_7Sb_2}}$

Tl1:2a	Sb:12e	Tl2:16f	Tl3:24h
$m\overline{3}m$	4mm	3m	mm2
0	0.314	0.330	0.350
0	0	0.330	0.350
0	0	0.330	0

The lattice parameters and the coordinates of $\frac{1}{3}$ show that the cell has to be enlarged by $3 \times 3 \times 3$.
The index 27 is the smallest possible index for an isomorphic subgroup of $I\,m\overline{3}m$.

7.7 The lattice parameters of $\mathrm{TlAlF_4}$-$tI8$ result from those of $\mathrm{TlAlF_4}$-$tP4$ according to $a\sqrt{2} = 364.9\sqrt{2}$ pm $=$ 516.0 pm $\approx$ 514.2 pm and $2c = 2 \cdot 641.4$ pm $=$ 1282.8 pm $\approx$ 1280.7 pm. Since the cell of $\mathrm{TlAlF_4}$-$tI8$ is body-centered, it is double-primitive; the primitive cell has only a doubled volume, in accordance with the index 2. $\mathrm{TlAlF_4}$-$tI8$ no longer has the atoms F2 on reflection planes, the coordination octahedra around the Al atoms are mutually rotated around the direction of c.

$P\,4/m\,2/m\,2/m$

$\boxed{\mathrm{TlAlF_4}\text{-}tP4}$

Al: 1a	Tl: 1d	F1:2f	F2:2g
4/mmm	4/mmm	mmm	4mm
0	$\frac{1}{2}$	$\frac{1}{2}$	0
0	$\frac{1}{2}$	0	0
0	$\frac{1}{2}$	0	0,274

k2

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

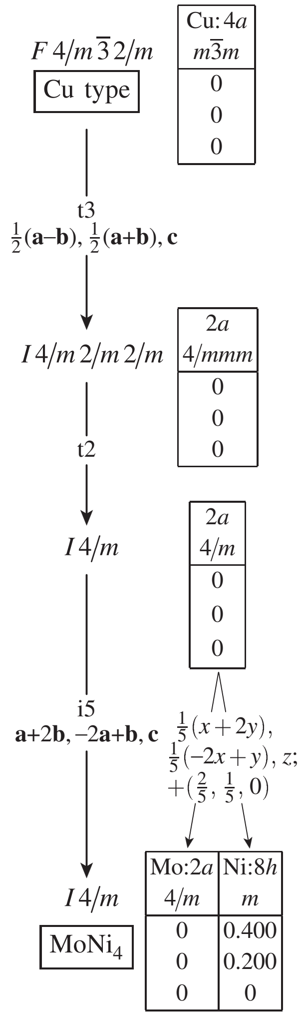
$\frac{1}{2}(x-y),\ \frac{1}{2}(x+y),\ \frac{1}{2}z$

$I\,4/m\,2/c\,2/m$

$\boxed{\mathrm{TlAlF_4}\text{-}tI8}$

Al: 4c	Tl: 4b	F1:8h	F2:8f
4/m	$\overline{4}$2m	m2m	4
0	0	0.276	0
0	$\frac{1}{2}$	0.224	0
0	$\frac{1}{4}$	0	0.137

7.8 The orientation of the face-centered cell of the Cu type is inclined to the cell of $MoNi_4$. One transforms first from the face-centered cell to a body-centered cell and then to the cell of $MoNi_4$:

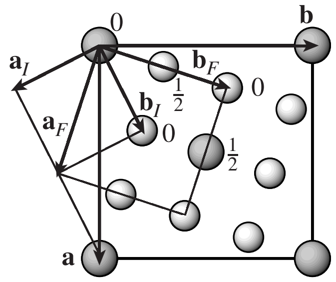


$\mathbf{a}_I = \frac{1}{2}(\mathbf{a}_F - \mathbf{b}_F),\ \mathbf{b}_I = \frac{1}{2}(\mathbf{a}_F + \mathbf{b}_F),\ \mathbf{c}_I = \mathbf{c}_F$

$a_I = a_F/\sqrt{2}$

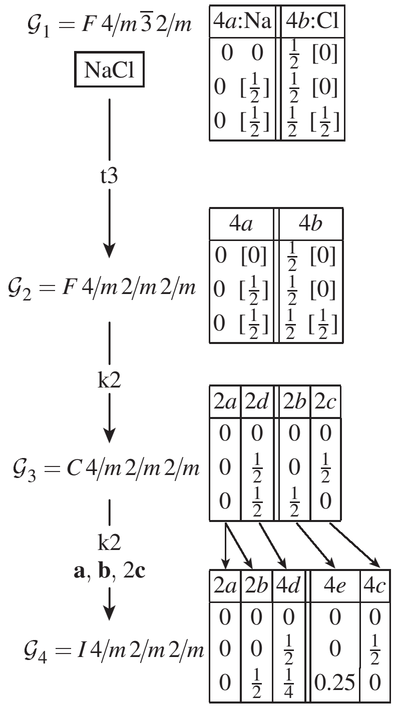
$\mathbf{a} = \mathbf{a}_I + 2\mathbf{b}_I, \quad \mathbf{b} = -2\mathbf{a}_I + \mathbf{b}_I, \quad \mathbf{c} = \mathbf{c}_I$

$a = a_I\sqrt{5} = (a_F/\sqrt{2})\sqrt{5} = 361{,}2\sqrt{\frac{5}{2}}$ pm $= 571{,}1$ pm



The face-centered cell of the Cu type is fourfold primitive and contains $Z = 4$ Cu atoms; the body-centered cell has half the size and is double primitive ($Z = 2$). Compared to the latter, the cell of $MoNi_4$ is enlarged by a factor 5; it contains ten atoms. This is in accord with the experimental value $a = 572.0$ pm. Therefore, there must be a step of symmetry reduction of index 5. An index of 5 is only possible for an isomorphic subgroup of $I\,4/m$; first, there must by a symmetry reduction to $I\,4/m$, which only involves the reduction of site symmetries.

9.1



There are three conjugate subgroups to $\mathcal{G}_2$ in $\mathcal{G}_1$, $[\mathcal{G}_2] = 3$ (corresponding to the three directions of the axes 4 of $\mathcal{G}_1$). The same is valid for $\mathcal{G}_3$, $[\mathcal{G}_3] = 3$. $\mathcal{G}_4$ has six conjugate subgroups in $\mathcal{G}_1$, $[\mathcal{G}_4] = 6$; in addition to the three orientations they can have their origins in the positions $0,0,0$ and $\frac{1}{2},\frac{1}{2},0$ of $\mathcal{G}_1$. Two of them are subgroups of $\mathcal{G}_2$ and $\mathcal{G}_3$. With equation (9.2), p. 22, we obtain:

$$\mathbf{M} = \begin{pmatrix} 1 & & & \\ 1 & 1 & & \\ 1 & 1 & 1 & \\ 1 & 1 & 1 & 2 \end{pmatrix} \qquad \mathbf{B} = \mathbf{M}^{-1} = \begin{pmatrix} 1 & & & \\ -1 & 1 & & \\ 0 & -\frac{1}{2} & \frac{1}{2} & \\ 0 & 0 & -\frac{1}{2} & \frac{1}{2} \end{pmatrix}$$

For the composition A□X_2, the Wyckoff positions of the space groups $\mathcal{G}_1$ and $\mathcal{G}_2$ do not permit an occupation. $\mathcal{G}_3$ ($C4/mmm$) has two combinatorial possibilities: A on $2a$ or A on $2d$ ($2b$ and $2c$ are occupied by X atoms). $\mathcal{G}_4$ ($I4/mmm$) also has two possibilities: A on $2a$ and $2b$ or A on $4d$. Therefore, we have $\mathbf{v} = (0, 0, 2, 2)$ and $\mathbf{z} = \mathbf{B}\mathbf{v} = (0, 0, 1, 0)$. There is only one structural possibility in the space group $\mathcal{G}_3$.

For the composition AB$\square_2X_4$, only $\mathcal{G}_4$ ($I4/mmm$) offers two possibilities of occupation: A on $2a$ and B on $2b$ and vice-versa. Therefore, we have $\mathbf{v} = (0, 0, 0, 2)$ and $\mathbf{z} = \mathbf{B}\mathbf{v} = (0, 0, 0, 1)$. There is only one structural possibility in the space group $\mathcal{G}_4$.

For the composition A$\square_3X_4$ we obtain the same result: A can be placed only on $2a$ or on $2b$ of $\mathcal{G}_4$, $\mathbf{v} = (0, 0, 0, 2)$ and $\mathbf{z} = \mathbf{B}\mathbf{v} = (0, 0, 0, 1)$. This one possibility corresponds to the crystal structure of SnF_4.