GROUP-SUBGROUP RELATIONS BETWEEN SPACE GROUPS:
A USEFUL TOOL IN CRYSTAL CHEMISTRY

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Summary

One of the main objectives of crystal chemistry is to order the wealth of known structures and to elucidate general principles. Quite obviously relations of cognate structures have to play a major rôle in such endeavors. If two structures are topologically equivalent these relations can be conveniently and clearly expressed by group-subgroup relations between their space groups. Graphic representation of these relations leads to a hierarchic ordering resembling a 'f a m-i l y   t r e e'. At the top of each tree resides a highly symmetrical structure, the so-called 'a r i s t o t y p e', from which the other structures of the tree can be derived along certain pathways of symmetry reduction . In order to describe the relations precisely, the symmetry reductions are broken down into minimal steps so that a space group is always followed only by m a x i m a l subgroups. These are appropriately characterized by the terms 'translationen-gleich', 'klassengleich' or 'äquivalent' and by their index of symmetry reduction. Examples from crystal chemistry demonstrate various applications and show the wealth of information contained in the details. The prime reason for this success of the abstract framework of group theory in crystal chemistry evidently lies in the so-called symmetry principle. In the first chapter a comprehensive formulation of this empirical principle is given, and important steps of its historical development are outlined.

Contents

1. The symmetry principle in crystal chemistry.

I should like to start with a general question: Why is it possible to apply the abstract framework of group theory to such an empirical discipline as crystal chemistry? The answer can only be given in a qualitative manner, but I hope that the following elucidations will be convincing. In crystal chemistry many experimentally derived facts can be explained from certain basic principles. This was emphasized repeatedly by LAVES [1], [2]. Here we are only interested in one of these basic principles, the so-called 'symmetry principle'. It has a long history, but the earlier formulations are somewhat vague and of limited value for practical applications. Thus, I shall present at first a more detailed version of this principle by putting emphasis on three important aspects.

(i)   In the solid state the arrangement of atoms reveals a pronounced tendency towards the highest possible symmetry.

(ii)   Several counteracting factors may prevent the attainment of the highest possible symmetry, but in most cases the deviations from the ideal arrangement are only small, and frequently the observed symmetry reduction even corresponds to the smallest possible step.

(iii)   During a solid state reaction which results in one or more products of lower symmetry very often the higher symmetry of the starting material is indirectly preserved by the orientation of domains formed within the crystalline matrix.

After this presentation of my own version of the symmetry principle some historical remarks are appropriate. As far as I know FEDOROV [3], [4] was the first scientist who had recognized the true nature of the symmetry principle. From extensive studies of the morphology of crystals he deduced the following 'symmetry law': "All crystals are either cubic or hexagonal, at least approximately". Obviously, this statement corresponds to aspect (i) mentioned above. Also aspect (ii) has already been expressed by FEDOROV [3] in 1904: "The main value of the symmetry law is that the greater the measurable deviation is from either the cubic or the hexagonal symmetry, the fewer representatives are known".

In the twenties the famous Swiss mineralogist NIGGLI [5] supported FEDOROV's view emphatically. He restricted the 'symmetry law' only in so far as he pointed out that there is no rigorous proof of it. Consequently, he characterized the symmetry principle as a 'philosophical doctrine' or as a 'working hypothesis'. Furthermore, he added the important viewpoint that sometimes reminiscences to more than one

symmetry can be found. As an example he mentioned the mineral marcasite.

The first and to the best of my knowledge the only one who applied the symmetry principle to X-ray crystallography and crystal chemistry was LAVES [1]. But even LAVES used the symmetry principle in a rather restricted sense [2]: "A tendency to form arrangements of high symmetry is observable". Note that this statement is in accordance with my first aspect (i) only. Somewhat later I shall come back to the surprising phenomenon of such a restricted use and I will mention the presumable reason for it.

Some people do not like a 'philosophical doctrine' such as the symmetry principle. Therefore I will quote a formulation given by BRUNNER [6] in 1971 that sounds more precise: "Atoms of the same type tend to be in equivalent positions". After some reflection you will see that the symmetry principle and BRUNNER's statement are equivalent. Incidentally, BRUNNER has pointed out that this sentence is nothing but a simplified expression of the old WIENER-SOHNCKE principle: "Points are disposed around each point in the same way as around every other". As a good example of the equivalence between the symmetry principle and BRUNNER's statement note that his statement picks out, from among all closest sphere packings, the hexagonal two-layer structure and the cubic three-layer structure as the only packings with equivalent sites.

Until now my excursion into history has shown that the aspects (i) and (ii) of the symmetry principle were already known although somewhat vaguely. Aspect (iii) was mentioned by BERNAL & MACKAY [7] in 1965 as follows: "One of the controlling factors in topotactic reactions is, of course, symmetry. This can be treated at various levels of sophistication, ranging from Lyubarskii's to ours, where we find that the simple concept of Buridan's Ass illumines most cases". Probably you know very well the metaphor of 'Buridan's Ass', but nevertheless I will repeat its meaning here. 'Buridan's Ass' is a dog, not an ass[*], dying of hunger between two equal amounts of food, because it could not decide between them. Crystals, of course, are not such donkeys, they take both.

Beyond doubt the three aspects of the symmetry principle are based on a deep-rooted inherent law of the solid state. In my opinion the term 'symmetry principle' is well-coined, because it is like a signal for the application of space-group theory. Now the question arises: Why can we find hardly any papers deal-

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[*] This transfer was done by antagonists of Buridan's doctrine.

ing with problems of this kind? Perhaps you are surprised at my question. You might think at first that space-group theory is already quite solidly anchored in crystal chemistry, and you are right if you refer to the widespread use of the International Tables for X-ray Crystallography [8] in determining and describing crystal structures. But do not forget that symmetry aspects have attracted little attention beyond the description of single, isolated structures. You will find proof of this claim by paging through the major current text books of crystal chemistry. Ignoring space group symbols when making comparisons between different structures is almost a characteristic feature of these books. Surely there are various reasons for this one-sided, only geometry-based view. One reason might be that our scientific community has downright forgotten the ordering principle in FEDO-ROV's lifework 'Das Krystallreich' [4] published in 1920. The main reason, however, is that the group-theoretical tools to improve this situation only became available in a comprehensive form in 1966. By stating 1966 I am referring to a paper by NEUBÜSER & WONDRATSCHEK [9] entitled 'Subgroups of the space groups'. Some problems in this field of mathematical crystallography had already been solved in the thirties by HERMANN & HEESCH (see [10]) and also been tackled in the 'Internationale Tabellen zur Bestimmung von Kristallstrukturen' of 1935 [10]. Because HERMANN & HEESCH had restricted their treatment to a special type of subgroup, the so-called 'zellengleiche Untergruppen' *) (lattice-equivalent subgroups), a broad application of their results was not possible. Our experiences in recent years have shown that a second category of subgroups, the so-called 'klassengleiche Untergruppen' (class-equivalent subgroups), are of equal if not greater significance for crystal chemistry. In the above mentioned 1966 paper NEUBÜSER & WONDRATSCHEK [9] presented the full compilation of the maximal subgroups of both categories. I was lucky enough to come into closer contact with Professor WONDRATSCHEK through my appointment to Karlsruhe at this time. To him I am indebted for many stimulating discussions and for receiving a preprint of his subgroup tables [11]. Without this contact the practical value of the field would not have come to my knowledge as a chemist. During the last six years I tried repeatedly to pass along my own experience in this field by presenting papers (for instance [12]) and by organizing two summer schools at Karlsruhe [13] in concert with Dr. KLEE and Professor WONDRATSCHEK.

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*) There is now a general agreement that this term should no longer be used, because it is somewhat misleading. The term 'translationengleiche Untergruppen' was recommended instead [13] and will be used throughout this paper.

2. The group-theoretical representation of crystal-chemical relationships.

To demonstrate relationships between cognate crystal structures and to present the results in a straightforward and comprehensive form is one of the main purposes of crystal chemistry. Only thus can we ensure that the overall perspective is not swept away by the growing flood of structural information. Everybody who publishes crystal structures can help in this endeavor by trying to classify his new structures within the framework of what is already known. The literature abounds with examples where so-called 'new' structures reveal themselves at a closer look as mere variations of well-known basic structure types. Below I will illustrate this assertion along with my examples.

Our experiences of the last 6 years have shown that group-subgroup relations are a valuable aid for presentation of essential similarities between different crystal structures in a rational and straightforward way. This success is not surprising, if one bears in mind the symmetry principle. By the same token one can say that the success can be considered as a direct proof of this principle, especially with reference to the second aspect (ii). It was indeed found that frequently a real crystal structure does not reach the highest possible symmetry, because there are counteracting factors like

I)   directed chemical bonds between the atoms (so-called covalent bonds),

II) atoms containing outer electrons that do not participate in chemical bonds (so-called lone-pair electrons),

III) atoms having a non-spherical electron density distribution as trigger of the so-called Jahn-Teller distortion,

IV) weakly-bounded or quasi-free electrons,

V)   diffusion-controlled ordering between atoms of different kinds, often observed with alloys during annealing,

VI) condensed lattice vibrations (so-called soft modes).

It is, however, an experimentally proven fact that the influence of these counteracting factors is relatively small. In many cases the observed symmetry reduction represents the smallest possible step, i.e. the space group of a crystal structure is a m a x i m a l subgroup of a higher symmetric one which might be possible for this structure. Thus, the great practical value of the NEUBÜSER – WONDRATSCHEK tables [11] is evident. Note that these tables are confined to maximal subgroups of the categories 'translationengleich' and 'klassengleich'

whereas maximal e q u i v a l e n t subgroups are omitted. The reason for this omission is obvious: Every space group has an infinity of maximal equivalent subgroups. Such subgroups, however, are also very important in crystal chemistry. Fortunately, the identification of equivalent subgroups is not a difficult task, particularly since the index of the subgroup is often low. Very recently a tabulation of maximal equivalent subgroups of lowest index was given by BERTAUT & BILLIET [14].

If the crystal structure in question has a space group which is not a maximal but a general subgroup of a higher symmetric one, it is very convenient to resolve the total symmetry reduction into a series of usually very few sequential steps, in the course of which every step represents the transition to a maximal subgroup. Again the NEUBÜSER-WONDRATSCHEK tables are useful. In addition to the group-subgroup compilation one often needs the reverse listing, namely the group-supergroup compilation [11].

In a general way our style of representation of symmetry relations between different crystal structures is based on the modular-design principle where the smallest possible step is like a module of a construction set. Thus, we only have to discuss this step in greater detail. We place the space groups of two structures which we want to compare one upon the other and indicate the direction of the symmetry reduction by an arrow (Table 1). In the middle of this arrow we state the type of the maximal subgroup and the index of the symmetry reduction, using the abbreviations t for 'translationengleich', k for 'klassengleich', and e for 'equivalent'. If the size of the unit cell and its conventional setting changes, we add the basis vectors of the maximal subgroup as a linear combination of the basis vectors of the higher symmetric unit cell. For clearness it is recommended to use unit-cell transformations as rarely as possible. It is much better to fully exploit the Hermann-Mauguin symbol in formulating space groups and to choose space-group symbols which do not correspond to the standard setting of the 'International Tables' [8]. In many cases cognate crystal structures can be described with a common origin. Sometimes, however, it is advisable to accept an origin shift, since otherwise the space-group description deviates considerably from the standard setting of the 'International Tables' [8]. Problems of this kind were studied in detail by BILLIET [15]. In the present paper the origin problem will be discussed along with one of the examples (see Chapter 4.).

TABLE 1.   General formulation of the smallest possible step connecting symmetry relations between cognate crystal structures.

Hermann-Mauguin symbol of the higher symmetric space group G

Shortened symbol for characterizing the higher symmetric crystal structure. Often the chemical formula of the compound in question is appropriate.

Type and index of the maximal subgroup U

Unit cell transformation
Origin shift

Hermann-Mauguin symbol of the maximal subgroup U of G

Shortened symbol for characterizing the lower symmetric crystal structure. Often the chemical formula of the compound in question is appropriate.

Explanations

1. Possible types of maximal subgroups U of a given space group G.

Abbreviation	Term	Meaning
t	'translationengleich' (lattice-equivalent)	U contains all the translations of G. The crystal class of U is of lower symmetry than that of G.
k	'klassengleich' (class-equivalent)	G and U have the same crystal class, but belong to different space-group types. Thus U has lost translational symmetry, i.e. the primitive cell of U is larger than that of G.
e	equivalent [*]	G and U belong to the same space-group type. As in the 'klassengleich' case, U has lost translational symmetry.

2. Index

The index of a subgroup U is the number of cosets of U in G.

3. Unit cell transformation

The three basis vectors of the unit cell belonging to U are given as linear combinations of the basis vectors of the unit cell belonging to G.

4. Origin shift

The three coordinates of the origin belonging to U are given with respect to the system of coordinates belonging to G.

[*] More precisely: crystallographically equivalent

At the end of this chapter it should be mentioned that the formulation of structure relations as developed here has the advantage to be concise, but the disadvantage to be without further content. This lack is, however, fundamental according to a theorem known from logic about the reciprocity of extent and contents of a concept: The larger the extent of a notion, the smaller its contents and vice versa. If structure correlations by means of symmetry relations between space groups are to be of practical value, a collection of the usual crystallographic data for related structures has to be provided. It is important to present these structures in such a way that their relations become clearly visible. In particular, the atoms of the asymmetric units should exhibit strict correspondence, so that their positional parameters can immediately be compared. Some examples in the following chapters have been prepared according to this suggestion.

3. Examples for the simplest possibility of a symmetry relation between cognate crystal structures: The space group of one crystal structure is a maximal subgroup of the space group of another structure.

3.1. The maximal subgroup is lattice-equivalent ("translationengleich").

3.1.1. The structural relationship between high quartz and low quartz.

It is known since a long time that the mineral quartz (chemical composition SiO_2) undergoes a reversible phase transition at $573^{\circ}C$ accompanied by small shifts of the atoms. Crystallographic details of the low-temperature modification (called low quartz) and of the high-temperature modification (called high quartz) as well as additional details concerning the mechanism of the phase transition (displacive transformation after BUERGER [16]) are given in many textbooks (see for instance [17], [18]). Here we are mainly interested in the fact that the space group $P 3_2 2 1$ of low quartz is a maximal lattice-equivalent subgroup of $P 6_2 2 2$, the space group of high quartz. The twofold axis in the [210]-direction is lost, thus the index of the subgroup $P 3_2 2 1$ is 2. Together with the subgroup type 'translationengleich' (called t for short) this number is given with the arrow (Fig. 1). Note that this phase transition entails extensive twinning because the higher symmetry of the starting material is indirectly preserved, as one should expect from the third aspect (iii) of the symmetry principle (Chapter 1.) From the rough sketch (Fig. 1) you can imagine the distor-

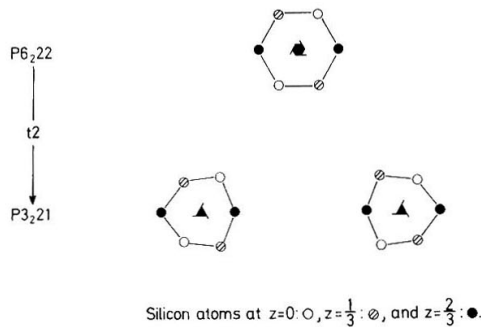Silicon atoms at $z=0$: ○, $z=\frac{1}{3}$: ⊘, and $z=\frac{2}{3}$: ●.

FIG. 1. Genesis of Dauphiné twins during the transition from high quartz (upper line) to low quartz (lower line).

tion of the crystal structure of high quartz during the transition, but note that the shifts of the silicon atoms (oxygen atoms have been omitted) are rather small. In Fig. 1 these shifts are multiplied by the factor 2 for better elucidation. The twin domains are the well-known Dauphiné twins. If they are present in low quartz the crystal cannot be used as piezoelectric component in electronics, because the polar twofold axes compensate each other.

3.1.2. The structural relationship between α- and β-tin.

According to TAMMANN [19] grey tin (α-Sn) is transformed to white tin (β-Sn) by application of high pressure. The reverse transformation which takes place at low temperatures is also known ('tin pest'). At first sight a comparison of the crystal data of the two Sn-modifications does not reveal any relationship, but none the less both modifications are topologically equivalent. The structure of β-Sn is derived from the structure of α-Sn — which is of the diamond type — by shortening of one of the cube edges and elongation of the other two without change of the relative coordinates x, y, and z of the Sn atoms (Fig. 2). A phase transition of this kind is a so-called dil-

α-tin (F d 3 m)   β-tin (F 4₁/d d m or 1 4₁/a m d standard setting)
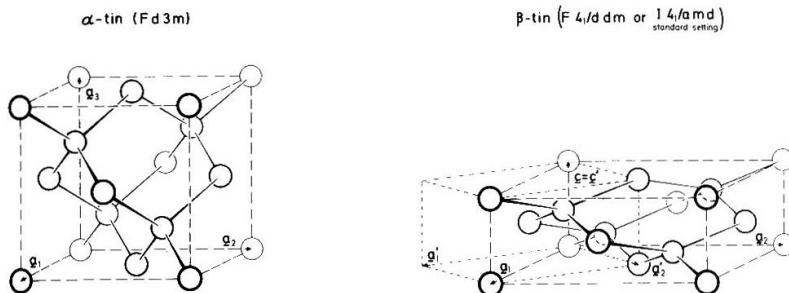
FIG. 2. Perspective views of the unit cells of α- and β-tin. The unit cell of α-Sn is cubic with a = 649.12 pm [20]. For β-Sn the non-conventional setting of the tetragonal unit cell with $a_1 = a_2 = 823.03$ pm and c = 317.49 pm is preferred, however the conventional tetragonal cell with $a_1' = a_2' = 581.97$ pm and $c' = 317.49$ pm is also shown [20].

atational transformation (BUERGER [21]). The metrical differences between α- and β-Sn are rather large. As a result one observes a volume decrease of about 21% during the transformation. Moreover the coordination number of tin in

creases from 4 to 6. The two additional neighbors are translation-equivalent atoms along [001] and [00$\bar{1}$] , but for better comparison between the left and the right hand side of Fig. 2 the corresponding chemical bonds are not drawn. It is worth to mention that the crystallographic phase transition is associated with a semiconductor-metal transition.

In group-theoretical terms the transformation of α-Sn to β-Sn corresponds to the transition to a lattice-equivalent maximal subgroup of index 3 according to the notation F 4_1/d $\bar{3}$ 2/m — t3 ⟶ F 4_1/d $\bar{1}$ 2/m. Because of the compression along [001] the crystal system changes from cubic to tetragonal, and hence the space-group symbol of the subgroup has to be changed according to the usual setting of the tetragonal system. The transition α-Sn ⟶ β-Sn then is described by the relation shown in Fig. 3 (a). Instead of the face-centered cell a body-centered cell containing half the
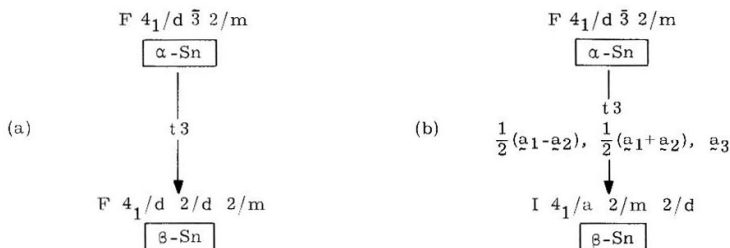
$$\text{(a)} \qquad \begin{array}{c} \text{F } 4_1/\text{d } \bar{3} \text{ 2/m} \\ \boxed{\alpha\text{-Sn}} \\ | \\ \text{t 3} \\ | \\ \text{F } 4_1/\text{d } 2/\text{d } 2/\text{m} \\ \boxed{\beta\text{-Sn}} \end{array} \qquad \text{(b)} \qquad \begin{array}{c} \text{F } 4_1/\text{d } \bar{3} \text{ 2/m} \\ \boxed{\alpha\text{-Sn}} \\ | \\ \text{t 3} \\ \tfrac{1}{2}(\underline{a}_1 - \underline{a}_2), \ \tfrac{1}{2}(\underline{a}_1 + \underline{a}_2), \ \underline{a}_3 \\ | \\ \text{I } 4_1/\text{a } 2/\text{m } 2/\text{d} \\ \boxed{\beta\text{-Sn}} \end{array}$$

FIG. 3. Symmetry relationship between grey tin (α-Sn) and white tin (β-Sn). For clarity the group-theoretical representation is given in two different ways using a non-conventional setting of the space group of β-Sn (a) and the conventional one (b).

number of atoms can be chosen as smallest unit cell. The axes $\underline{a}_1'$ and $\underline{a}_2'$ of the small cell point along the face diagonals of the previous cell. For the conventional description of β-Sn via the smallest possible unit cell the space-group symbol must be changed to I 4_1/a m d (short Hermann-Mauguin symbol). In the representation as suggested for group-subgroup relations (see Table 1.) the transition between α-Sn and β-Sn is formulated in the way shown in Fig. 3 (b).

This example stresses the difficulties which may arise from the use of the term 'zellengleich' instead of 'translationengleich'. As shown in Fig. 3 (b) the size of the unit cell has changed, but none the less I 4_1/a m d is 'zellengleich' with the minimal supergroup F d 3 m . This contradiction is resolved if one bears in mind that HERMANN [10] has related the term 'zellengleich' to the primitive unit cell which

actually is of equal size for both the fourfold primitive F-cell and the twofold primitive I-cell.

3.1.3. The structural relationship between diamond and sphalerite.

So far we have compared pairs of crystal structures which were chemically related. It may, however, also be useful to compare structures which are completely different from a chemical point of view. A classic example is the relation between the diamond type and the sphalerite type, as shown in Fig. 4. The atoms of both structures have identical coordinates, the difference being that the diamond structure con-
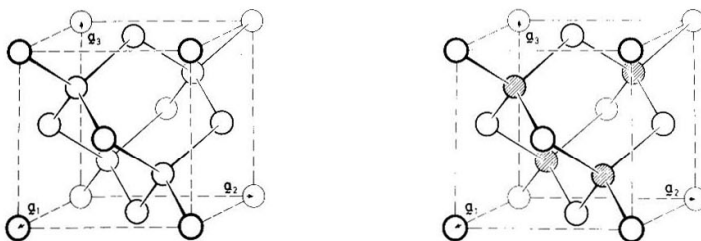

FIG. 4. Comparison between the crystal structures of diamond (left) and sphalerite (right). Diamond consists of C-atoms; the chemical formula of the mineral sphalerite is ZnS (sulfur atoms are hatched).

tains only one type of atoms, whereas the sphalerite structure contains two types which are distributed in an ordered way. The symmetry relation between the two structures is of the form

$$F \ 4_1/d \ \bar{3} \ 2/m \xrightarrow{\quad t2 \quad} F \ \bar{4} \ 3 \ m$$

$$\boxed{\text{diamond type}} \qquad\qquad \boxed{\text{sphalerite type}}$$
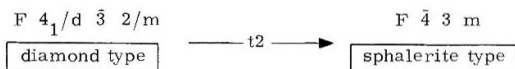
The transition, 'translationengleich' of index 2, leads from a centrosymmetric to a non-centrosymmetric space group. The loss of the inversion centers is easy to understand, because in the diamond structure these centers lie exactly half way between neighboring atoms which in Fig. 4 are connected by straight lines.

3.2. The maximal subgroup is class-equivalent ('klassengleich').

3.2.1. The structural relationship between Rh_5Ge_3 and Ca_5Sb_3.

The crystal structure of Ca_5Sb_3 was published in 1974 [23]. The authors had found no relationship with any known structure, but they were kind enough to send me a copy of the manuscript parallel with submission to the journal. Because I had some training in recognizing symmetry relationships between the space groups I saw very soon that in fact another closely related structure existed, Rh_5Ge_3 [24]. This came just in time to be added as a note in proof. Table 2 shows the crystal data of both compounds. How could I have suspected a relationship, if the structures apparently have so little in common? Well, the space group P b n m, obtained from P n m a by cyclic permutation of the lattice constants is a class-equivalent subgroup of P b a m with index 2. The symmetry reduction while re-
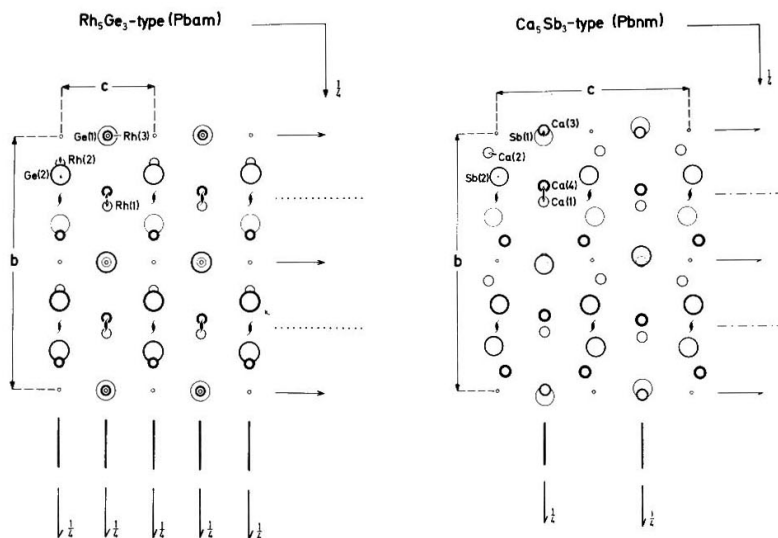

FIG. 5. Schematic representation of the crystal structures of two M_5X_3-compounds. All symmetry elements of the respective space groups are included in order to show the way of thinning ('Auslichtung') during the symmetry reduction. For further crystallographic details see Table 2 and 3.

TABLE 2. Comparison between the crystal data of two orthorhombic M_5X_3-compounds and their symmetry relationship.

	Ca_5Sb_3 [23]	Rh_5Ge_3 [24]	Ca_5Sb_3 (rearranged)
a (pm)	1250.2	542	828.7
b (pm)	951.2	1032	1250.2
c (pm)	828.7	396	951.2
Ratio of the axes	1.31 : 1 : 1.15	0.53 : 1 : 0.38	0.66 : 1 : 0.76
Z	4	2	4
Space group	P n m a	P b a m	P b n m

P b a m

Rh_5Ge_3

k2
$\underline{a}$, $\underline{b}$, $2\underline{c}$

P b n m

Ca_5Sb_3

TABLE 3. Positional parameters of the atoms for two related M_5X_3-compounds.

(I) Rh_5Ge_3 :   space group $P\ 2_1/b\ 2_1/a\ 2/m$ (No. 55) ;
Rh(1) in 4h m ;   Rh(2) and Ge(2) in 4g m ;
Rh(3) in 2d 2/m ; Ge(1) in 2b 2/m .

(II) Ca_5Sb_3 :   space group $P\ 2_1/b\ 2_1/n\ 2_1/m$ (No. 62) ;
Ca(1), Ca(3), Ca(4), and Sb(1) in 4c m ;
Ca(2) and Sb(2) in 8d 1 .

Atom [*]	x(I)	x(II)	y(I)	y(II)	z(I)	z(II) [**]
M(1)	0.348	0.3213	0.280	0.2725	0.5	0.25
M(2)	0.170	0.1930	0.107	0.0753	0	-0.0425
M(3)	0.5	0.4645	0	-0.0063	0.5	0.25
M(4) or [M(1')]	[0.848]	0.8515	[0.220]	0.2106	[0.5]	0.25
X(1)	0	0.0785	0	0.0168	0.5	0.25
X(2)	0.612	0.5668	0.152	0.1704	0	0.0146

[*]   Atoms and their parameters in square brackets are symmetry related to other ones given earlier.

[**]   The values of z(II) are strictly or approximately one-half of the corresponding values z(I), because the lattice constant c of Ca_5Sb_3 is about two times larger than that of Rh_5Ge_3 .

taining the crystal class requires a doubled axis c. For Rh_5Ge_3 and Ca_5Sb_3 this is in fact true when the axes-ratios are compared. When I looked at the atomic positions my suspicion was confirmed. Fig. 5 illustrates how striking the relationship between the structures really is when we arrange them in a way appropriate to symmetry. For Rh_5Ge_3 two adjacent unit cells are shown. All atoms lie on the mirror planes perpendicular to the c-axis. If one reduces the symmetry by the index 2 by leaving out half of the translations in the c-direction - which is equivalent to doubling the c-axis -, only one half of the mirror planes, one half of the inversion centres and one half of the screw axes can be retained. Thus the atoms in the structure acquire additional degrees of freedom for positional shifts, but the magnitude of the shifts is quite small (see Table 3). We have here a common phenomenon in crystal chemistry: Very often to a highly symmetrical structure deformed or distorted structures are associated. Of course this is nothing new. New is only the way we comprehend and assign a distorted structure. The rather general and meaningless term 'd i s t o r t e d' by means of group-subgroup relations receives a precise and reproducible meaning. Let me only mention that also the assignment of equivalent atoms is greatly facilitated and that some consequences for better documentation result (Table 3).

3.2.2. Formation of antiphase domains in hexacelsian during a class - equivalent phase transition.

It was shown in Chapter 3.1.1. that a solid-state phase transition results in twin d o m a i n s , when the growing phase belongs to a l a t t i c e - e q u i v a l e n t subgroup of the space group of the starting material. In the present chapter it will be demonstrated that with a c l a s s - e q u i v a l e n t symmetry reduction so-called a n t i - p h a s e d o m a i n s [25] may be created. Again I would like to draw your attention to aspect (iii) of the symmetry principle, key-word 'indirect preserving of symmetry' (Chapter 1.).

The formation of antiphase domains can easily be understood from the example shown in Fig. 6. This example looks like a hypothetical one, but there is every reason to believe that it may stand for a high-temperature phase transition observed with 'hexacelsian', a synthetic product of the chemical composition $BaAl_2Si_2O_8$ [26]. As can be seen from Fig. 6 the symmetry reduction is 'klassengleich', since translational symmetry is lost during the transformation to the low-temperature modification. As the growth of the latter phase starts
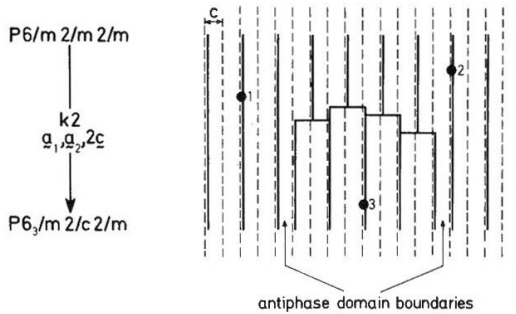
FIG. 6. Genesis of antiphase domains during a phase transition which is asso-
ciated with a loss of translational symmetry. 1, 2, and 3 are independent
nuclei for crystal growth of the lower symmetric phase (bold lines)
within the crystalline matrix of the higher symmetric starting mate-
rial (dashed lines).

at different nuclei which are independent of each other, the growing crys-
tals will be to some extent 'in phase' with respect to the new translation $2\underline{c}$, but
just as often 'out of phase'; e.g. starting at point 1 and 2 in Fig. 6 the growing
crystals are in phase, but starting at point 1 and 3 as well as 2 and 3 they are
out of phase. Thus the latter will form antiphase domain boundaries. For hexa-
celsian such boundaries are shown in Fig. 7. This picture was taken by MÜLLER
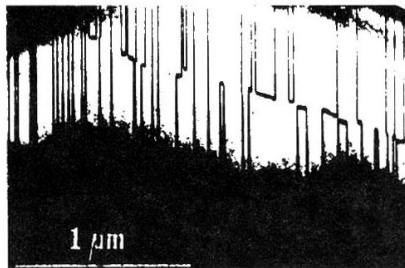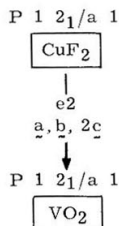[26] with the aid of transmission electron microscopy.

FIG. 7. Antiphase domains in hexacelsian after MÜLLER [26].

3.3. The maximal subgroup is equivalent.

The transition to an equivalent subgroup is illustrated via the comparison between the CuF_2 and the VO_2 structures. In the concise nomenclature of Table 1 (Chapter 2.) we have

P 1 2_1/a 1
$$\boxed{CuF_2}$$
$|$
e2
$\underset{\sim}{a}, \underset{\sim}{b}, 2\underset{\sim}{c}$
$\downarrow$
P 1 2_1/a 1
$$\boxed{VO_2}$$

From Fig.8 it may be seen how the transition $CuF_2 \longrightarrow VO_2$, which involves doubling of the c axis, leads to the elimination ('Auslichtung') of half of the symmetry elements. In VO_2 only every other row of inversion centres and screw axes parallel to the a axis are retained. The arrows which are attached to the

CuF₂ (P 2₁/a)   VO₂ (P 2₁/a) at 298 K
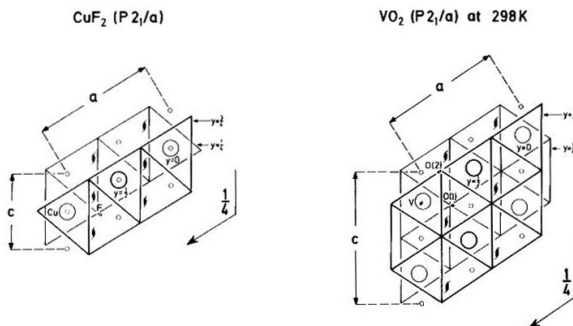

FIG. 8. Comparison between the crystal structures of CuF_2 and VO_2. The crystallographic details can be found in Table 4.

atoms of the asymmetric unit show how small the displacements from the ideal structure really are. The ideal structure in this case is not the rutile structure but a hypothetical one in which the anions are arranged as in the hexagonal closest sphere packing.

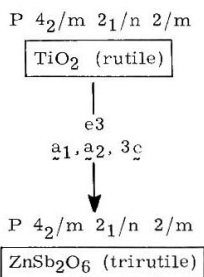TABLE 4. Crystallographic data of CuF_2 [27] and VO_2 [28] .

(I) CuF_2 : space group $P \ 1 \ 2_1/a \ 1$ (No.14) ; $Z = 2$;
a = 536.2 , b = 456.9 , c = 330.9 pm , $\beta = 121.11^O$;
Cu in 2b $\bar{1}$; F in 4e 1 .

(II) VO_2 : space group $P \ 1 \ 2_1/a \ 1$ (No.14) ; $Z = 4$;
a = 538.25 , b = 453.78 , c = 575.17 pm , $\beta = 122.65^O$;
V, O(1), and O(2) in 4e 1 .

Atom *)	x(I)	x(II)	y(I)	y(II)	z(I)	z(II) **)
Cu or V	0	0.02646	0	0.02106	0.5	0.23947
F or O(1)	0.2951	0.29884	0.2968	0.29742	0.7558	0.40051
[F'] or O(2)	[0.2049]	0.20859	[0.7968]	0.78815	[0.2442]	0.10616

*) Atoms and their parameters in square brackets are symmetry related to other ones given earlier.

**) The values of z(II) are approximately one-half of the corresponding values z(I), because the lattice constant c of VO_2 is about two times larger than that of CuF_2 .

Another simple case of a symmetry relation between equivalent space groups was discussed as early as 1973 by BILLIET [29], but note that BILLIET used the designation 'isosymbolic space groups'. Applying our nomenclature (see Table 1) BILLIET's example looks as follows:

$$P \ 4_2/m \ 2_1/n \ 2/m$$

TiO$_2$ (rutile)

e3

$\underset{\sim}{a}_1, \underset{\sim}{a}_2, 3\underset{\sim}{c}$

$$P \ 4_2/m \ 2_1/n \ 2/m$$

ZnSb$_2$O$_6$ (trirutile)

The most interesting point in this context is the fact that compounds are known which undergo an order – disorder transition between the trirutile and the rutile structure. For further details see [30] .

4. Examples for more complex cases of symmetry relations between cognate crystal structures: The space group of one crystal structure is a general subgroup of the space group of another structure.

4.1. The structural relationship between NiAs and MnP.

The example I should like to present because of its clarity deals with the intensively studied phase transition from the NiAs-type into the MnP-type known for many compounds. Crystallographic data for one of these are given in Table 5. Formal symmetry reduction here has to follow two steps because we only want to allow transitions into maximal subgroups (Fig. 9). In the first step we disturb hexagonality, for example by changing the angle of 120°. Now on symmetry
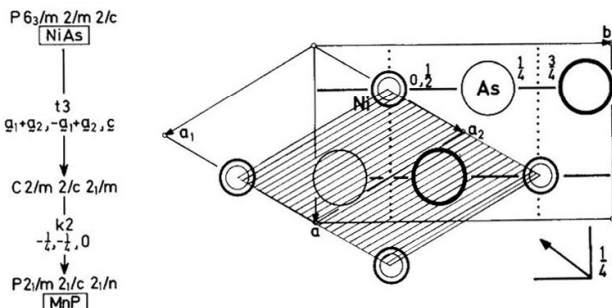
FIG. 9. The symmetry relation between NiAs and MnP as well as a schematic representation of the corresponding structural relationship. The hatched area means the unit cell of the NiAs-type structure; the basis vectors $\underline{a}$ and $\underline{b}$ refer to the unit cell of the MnP-type structure. Note that there is an origin shift and that only some symmetry elements are shown.

grounds we have to use an orthorhombic C-centered cell in order to comply with conventional notation. This new choice of axes of course makes no change in the translations, so the first step is 'translationengleich'. The second step involves the destruction of the face-centering of the intermediate space group C m c m. This implies losing one-half of the translations, thus we have a class-equivalent reduction of index 2.

NiAs and MnP are centrosymmetric. We have to be careful about which of the crystallographically non-equivalent inversion centres is destroyed during reduction. Fig. 9 shows that it is precisely the one which is usually chosen as the origin of the NiAs-cell (hatched in Fig. 9). Actually the problem is quite trivial. Nevertheless I want to point it out because experience shows that fixing the origin is a common source of error.

With a great number of examples we have found a guide-line that works in many cases: Very often with symmetry-reducing centrosymmetric structures, that inversion centre is retained which is in the orbit of lowest site symmetry. For our example of the NiAs-MnP transition we have: the inversion centre of the orbit (6g) with site symmetry $2/m$ is retained, the one of the orbit (2a) with site symmetry $\bar{3}$ m disappears (compare Table 5.).

The atomic shifts from the ideal positions during symmetry reduction are quite small. So there is good reason to describe MnP as a distorted NiAs-type. It can

TABLE 5. Crystallographic data of the high- and low-temperature modification of $(Mn_{0.9}Fe_{0.1})As$ [31].

	$(Mn_{0.9}Fe_{0.1})As$ at 673 K (NiAs - type)	Hypothetical intermediate structure	$(Mn_{0.9}Fe_{0.1})As$ at 293 K (MnP - type)
Crystal system	hexagonal	orthorhombic	orthorhombic
Lattice constants (pm)	a_1 = 370 a_2 = 370 c = 578	a ≈ 370 b ≈ 641 c ≈ 578	a = 358.9 b = 625.2 c = 561.5
Space group	P 6_3/m $2/m$ $2/c$ (No. 194)	C $2/m$ $2/c$ $2_1/m$ (No. 63)	P $2_1/m$ $2_1/c$ $2_1/n$ (No. 62)
Atomic positions and site symmetry	Ni in 2a $\bar{3}$ m As in 2c $\bar{6}$ m 2	M in 4a $2/m$ X in 4c m m	Mn and P in 4c m
$(Mn_{0.9}Fe_{0.1})$ x y z	0.25 0.25 *) 0	0.25 0.25 *) 0	0.25 0.2138 0.0126
As x y z	0.25 0.5833 *) 0.25	0.25 ≈ 0.583 *) 0.25	0.25 0.5811 0.2073

*) These positional parameters are not the original ones but transformed values. They are related to the unit cell of the MnP-type structure for better comparison.

be regarded in the sense of BUERGER [16] as a 'derivative structure'. Let me
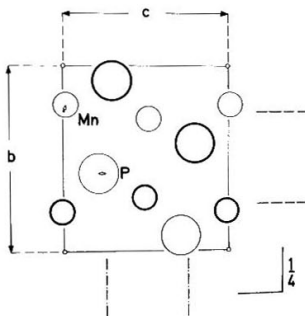show you the extent of distortion in MnP from Fig.10.

FIG. 10. The crystal structure of the MnP-type. All atoms are located at the
height x = 1/4 (light circles) or x = 3/4 (heavy circles). Only
some symmetry elements are shown.

In this figure the structure is projected along the a-axis because free parame-
ters occur only in the b- and c-direction. The displacement from the ideal posi-
tions is indicated by the length of the arrows. Incidentally, because of symmetry
it is sufficient to draw the arrows for the asymmetric unit only. In the litera-
ture quite often the whole picture is speckled with arrows which in my opinion
does not make for clarity. Along with the pair NiAs-MnP I want to mention an-
other case studied by SELTE, KJEKSHUS & ANDRESEN [31] which backs up my
thesis that group-theoretical presentations of this type are really warranted. For
$(Mn_{0.9}Fe_{0.1})As$ the authors have shown not only that the compound undergoes
a MnP-NiAs-type transition - there are many examples of it — but also how
this transition proceeds. In a series of structure determinations of the compound
in transition the authors could show that the positional parameters of the atoms
as well as the lattice constants vary continuously between the MnP-type and the
NiAs-type, in other words a diffusionless phase transition of second or higher
order takes place. One can assume that other phase transitions not so well in-
vestigated proceed in this diffusionless manner, provided that direct group-sub-
group relations between the phases exist .

4.2. The disorder-order transition of the alloy $MoNi_4$.

The example of this chapter stands for the large field of transitions between dis-
ordered and ordered structures. Quite generally, structures with a statistical

distribution of different atoms on specific orbits belong to the space group of higher symmetry. Therefore, the ordering process that takes place in many alloys when annealed is always associated with a transition into a subgroup. One of the alloys which has been subject to thorough investigation is $MoNi_4$. At higher temperatures the metal atoms are distributed statistically on the sites of the cubic closest sphere packing. Slow cooling gives rise to diffusion-controlled ordering, the result of which is the structure shown in Fig. 11 . For a crystal-

Atoms at z=0: light drawn circles,
$z=\frac{1}{2}$: bold drawn circles.
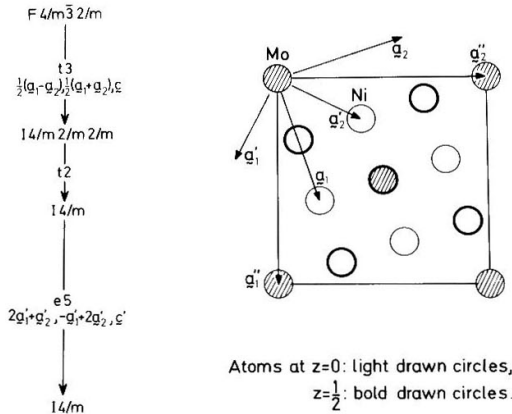
FIG. 11. The symmetry relation between the disordered high temperature structure of $MoNi_4$ and the ordered low temperature structure. The latter is shown in rough outlines. For further details see Table 6.

lographic description we need a strangely enlarged cell of tetragonal symmetry. With respect to the old cell of statistical distribution (basis vectors of the unit cell a_1, a_2, and $a_3 = c$, see Fig. 11) the volume of the new cell (basis vectors a_1'', a_2'', and c) has increased by a factor of 5/2. For this phenomenon the terms 'superlattice' or 'superstructure' are often used, but these are very bad terms and should be discarded (BERTAUT [32]), because a subgroup derives from a group by a loss of symmetry operations. The terms 'sublattice' or 'substructure' seem to be more appropriate. The group-theoretical treatment is especially instructive here, because the important cell-enlarging step involves a transition to an equivalent subgroup.

The single steps of symmetry reduction correspond to certain particularities in the crystalline texture of the ordered alloys. With the lattice-equivalent steps in view, one can easily understand that the textured alloy structure shows twin-

ning. One only has to keep in mind that the mechanism for ordered alloy formation is governed by two processes, nucleation and growth of nuclei. As in the first step the loss of the threefold axis of the cubic system creates three energetically equivalent alternatives for the orientation of the incipient tetragonal structure, they have to form triple twins or triplets. Each of these triplets in the second step is subject of another twinning process. The reason for this is analogous to the one before. The first mentioned triple twins have been called

TABLE 6. Crystallographic data of the disordered and ordered alloy $MoNi_4$ [33].

	Disordered $MoNi_4$ (Cu-type structure)	Ordered $MoNi_4$ (own structure type)
Crystal system	cubic	tetragonal
Lattice constants (pm)	$a = 361.2$	$a = 572.0$; $c = 356.4$
Space group	$F\ 4/m\ \bar{3}\ 2/m$ (No.225)	$I\ 4/m$ (No. 87)
Atomic positions and site symmetry	all atoms in 4a m3m	Mo in 2a 4/m Ni in 8h m with free parameters $x = 0.200$ (5) and $y = 0.400$ (5)

'perpendicular twins' [34], because the c axes of the three individuals are almost perpendicular to each other; they correspond, of course, to the basis vectors a_1, a_2, and a_3 of the cubic unit cell of the disordered structure. The above mentioned twins which are formed during the second step of symmetry reduction (cf. Fig. 11) have been called 'antiparallel twins' [34], because the c axes of the two individuals are parallel, but pointing in opposite directions. The essential feature of the symmetry reduction in the third step is the formation of antiphase domains, which cannot be understood without considering the loss of translations. With four-fifths of the translations lost, i.e. one-fifth retained or - in other words - with index 5, one expects a corresponding variety of antiphase domains, and in fact in 1971 the group around AMELINCKX [34] showed that 4 different types of antiphase boundaries occur with $MoNi_4$. Accordingly in their experiments they observed the triple and double twins. Thus, the texture of this alloy is like a 'finger-print' for the intermediate space groups (see Fig. 11) . In 1974 VAN TENDELOO & AMELINCKX [35] gave an explanation for the apparently quite complicated textures of ordered alloys, using

group-theoretical concepts. The presentation they gave is quite correct but unnecessarily complicated. Somewhat later WONDRATSCHEK & JEITSCHKO [36] showed that these relationships can be presented in an equally correct but far simpler way with the aid of lattice-equivalent and class-equivalent subgroups of the space groups. Our example $MoNi_4$ is intended as an illustration of how simple the application of the concept really is. Before leaving this example I wish to repeat a general and easily remembered statement from the paper of WONDRATSCHEK & JEITSCHKO [36] : Whenever a phase transition involves a change in symmetry one observes twin domains when the new phase belongs to a crystal class of lower symmetry and antiphase domains when translations as symmetry operations are lost.

5. An example for another frequently observed possibility of a symmetry relation between cognate crystal structures: The space groups of two (or more) different crystal structures have a common supergroup.

The example of this chapter will show that structural relationships between different crystal structures can be elucidated by finding the common supergroup of their space groups. In addition it will illustrate the fact that this procedure can even be of advantage when only the crystal data of the compounds, that is the lattice constants and space groups, are known.

In his Ph. D. thesis on alkaline halogeno-aurates at the university of Freiburg SLEATER [37] found that the rubidium and caesium compounds cannot all be isotypic, contrary to the results of PENFIELD's excellent morphological investigation of 1892 [38]. By appropriately modifying SLEATER's conventional setting of the monoclinic compounds (cf. Table 7) one arrives at an elegant solution of this contradiction [39]. If one compares the crystal data of $RbAuCl_4$ and $RbAuBr_4$ in the n e w setting, the metrics of the unit cells show a close relationship. Because the data match quite well save for a doubled lattice constant c of $RbAuCl_4$, a class-equivalent symmetry reduction is at hand. In fact, both space groups I 2/c and P 2_1/a can be derived by class-equivalent symmetry reduction from the common supergroup C 2/m :

C 1 2/m 1

k2
$\underline{a}, \underline{b}, 2\underline{c}$

k2

I 1 2/c 1

$\boxed{RbAuCl_4}$
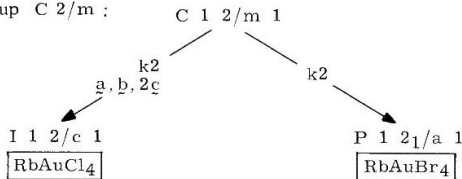
P 1 2_1/a 1

$\boxed{RbAuBr_4}$

TABLE 7. Comparison between the crystal data of $RbAuCl_4$ and $RbAuBr_4$ in two different settings.

Relations between the basis vectors of the unit cells for

$RbAuCl_4$: $\underline{a} = -\underline{a}' - \underline{c}'$; $\underline{b} = \underline{b}'$; $\underline{c} = 2\underline{a}' + \underline{c}'$.

$RbAuBr_4$: $\underline{a} = \underline{c}'$; $\underline{b} = -\underline{b}'$; $\underline{c} = \underline{a}'$.

	Conventional setting [37]		Unconventional setting [39]	
	$RbAuCl_4$	$RbAuBr_4$	$RbAuCl_4$	$RbAuBr_4$
Lattice constants in pm	$a' = 1251$	$a' = 743$	$a = 976.0$	$a = 1029.9$
	$b' = 590$	$b' = 622$	$b = 590.2$	$b = 621.4$
	$c' = 1744$	$c' = 1029$	$c = 1411.6$	$c = 743.6$
Angle in degree	$\beta' = 146.9$	$\beta' = 121.3$	$\beta = 120.05$	$\beta = 121.33$
Ratio of the axes	$2.120:1:2.956$	$1.195:1:1.654$	$1.654:1:2.392$	$1.657:1:1.197$
Z	4	2	4	2
Space group	$C\ 1\ 2/c\ 1$	$P\ 1\ 2_1/c\ 1$	$I\ 1\ 2/c\ 1$	$P\ 1\ 2_1/a\ 1$

TABLE 8. Crystallographic data of $RbAuCl_4$ and $RbAuBr_4$ compared with corresponding data of a more symmetrical but hypothetical structure $MM'X_4$.

		$RbAuCl_4$ [40]		$RbAuBr_4$ [41]	$MM'X_4$
Space group		$I\ 1\ 2/c\ 1$ (No.15)		$P\ 1\ 2_1/a\ 1$ (No.14)	$C\ 1\ 2/m\ 1$ (No.12)
Atomic positions and site symmetry		Rb in 4e 2		Rb in 2d $\bar{1}$	M in 2d 2/m
		Au in 4a $\bar{1}$		Au in 2a $\bar{1}$	M' in 2a 2/m
		Cl(1) in 8f 1		Br(1) in 4e 1	X(1) in 4i m
		Cl(2) in 8f 1		Br(2) in 4e 1	X(2) in 4e $\bar{1}$
Rb or M	x	0		0	0
	y	0.4763		0.5	0.5
	z	0.25	*)	0.5	0.5
Au or M'	x	0		0	0
	y	0		0	0
	z	0	*)	0	0
Cl(1), Br(1) or X(1)	x	0.1161		0.1183	0.117
	y	-0.0210		-0.0165	0
	z	0.1855	*)	0.3783	0.374
Cl(2), Br(2) or X(2)	x	0.1633		0.1691	0.25
	y	0.2943		0.2949	0.25
	z	0.0187	*)	0.0419	0

*) These z-values are strictly or approximately one-half of the corresponding values of $RbAuBr_4$, because the lattice constant c of $RbAuCl_4$ is about two times larger than that of $RbAuBr_4$ (cf. Table 7) .

As can be seen from the scheme, in both cases the symmetry of the space group C 2/m is reduced by the loss of translations. During the step to the class-equivalent maximal subgroup P 2_1/a the face-centering C is lost; going to the class-equivalent maximal subgroup I 2/c only every other point along the c-axis is generated by translational symmetry.

One suspects that the structures of both RbAuCl$_4$ and RbAuBr$_4$ can be derived from one hypothetical parent structure of higher symmetry (C 2/m) by applying two different minor distortions. After some trial and error I developed a model for this parent structure in C 2/m. In this space group, for Rb and Au and for one of the two crystallographically different halogen atoms only sites with three fixed parameters are possible (Table 8). The free x- and z-parameters of the other halogen atom follow directly from space-filling considerations. After the hypothetical model had been obtained it became clear why it could not serve as a solution of the structural problem in itself. In the supergroup C 2/m the trivalent gold atom would have to be octahedrally coordinated, whereas its electronic d^8-configuration requires square planar surroundings. Fig. 12 shows how the octahedral environment, which the gold atom would have in the supergroup, can be shifted into a square planar coordination by small displacements of the atoms. Two alternatives are shown; they are related by mirror symmetry. The structure of RbAuBr$_4$ is now generated by repeating the upper part of the right-hand side of Fig. 12 in a direction tilted approximately 30° off the viewing direction. With RbAuCl$_4$ nearly the same thing happens, except that both the upper and the lower part appear alternately along the viewing direction. This explains the necessity to double the c-axis immediately. Fig. 13 shows the two model structures in a different viewing direction. The square planar halogeno-aurate ions are drawn schematically as squares. While tilted equilaterally along c for RbAuBr$_4$, the two alternatives 'zig-zag' for RbAuCl$_4$. The two models were directly fed into the computer, and the coordinates were already good enough for the refinement to converge. Credit and my thanks should be given to Prof. STRÄHLE, who has done all the practical work of measuring data sets, and refining and evaluating details of the structures.

The example above leaves one question open: Although there is a good reason why the halogeno-aurate structures in the supergroup C 2/m are not realized, it could still be that a similar compound assumes this more symmetrical structure. A trivalent cation with a tendency to octahedral coordination would be likely to do this, and in fact the example we looked for exists with the structure type of
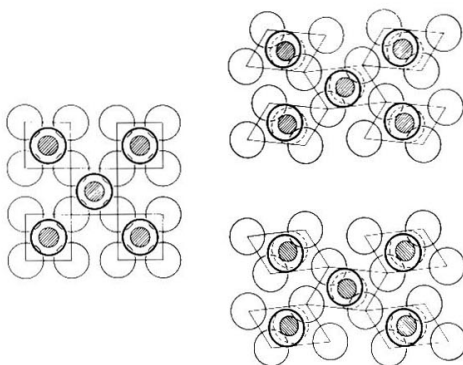
FIG. 12. The $[M'X_4]$-layer as the main structural unit of a hypothetical crystal structure with the composition $MM'X_4$ (on the left) and two distorted versions known from $RbAuCl_4$ (on the right). The atoms M' and Au, resp., are represented by hatched circles, the atoms X or Cl by open ones. The drawing plane is (001).

RbAuCl$_4$ (I2/c)   RbAuBr$_4$ (P2$_1$/a)

FIG. 13. Comparison between the crystal structures of $RbAuCl_4$ and $RbAuBr_4$. Open circles: Au-atoms; hatched circles: Rb-atoms; Cl- or Br-atoms at the corners of the inclined squares. For crystallographic details see Table 8 .

$KAlF_4$. **Its** octahedral framework is so perfect that symmetry $P4/m\,m\,m$, even higher than $C\,2/m$, is possible. In this paper I want to dispense with further particulars.

6. General application of group-subgroup relations.

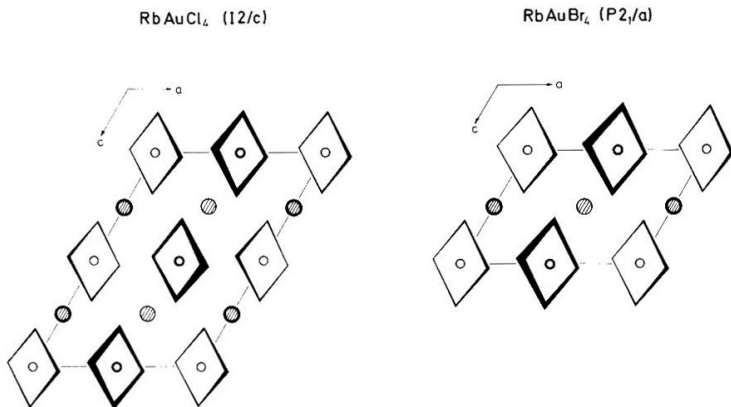### 6.1. Synopsis of symmetry-related crystal structures: Compounds with the same formula type.

For clarity I have limited myself so far to a relatively narrow range of applications of group-subgroup relationships. In the last section of this paper I would like to show that this range can be considerably broadened. I would even venture to say that it is of special advantage to observe group-theoretical aspects within a wide range of crystal chemistry. From experience we know that many structures can be treated as distortion variants of other structures. Thus, there is good reason to look for structures which can no longer be derived from, or linked with, other structures. The number of basic structures [16] will still remain on a comprehensible scale. To date it is a question of personal preference how far one wants to carry this method of classifying crystal structures. As an experimental scientist I am inclined to regard crystal chemistry as an experimental field, and to see what will turn out to be feasible. To illustrate my train of thought about basic structures, let me show you a picture by the Dutch designer ESCHER [42]. No doubt the curl of black and white reptiles in the centre of Fig.14 represents a complicated structure. The far-
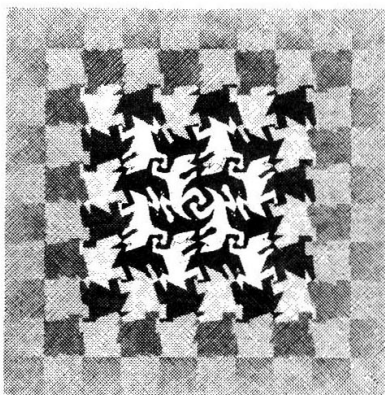
FIG. 14. M.C. ESCHER [42] : "Development I".

ther we follow the curls into the margin, the more clearly the basic structure of the picture reveals itself as a checkerboard. In the reverse direction we see how every single reptile can be thought of as being distorted from a square. If you look into the margin itself you will see that even the checkerboard disappears. Translated into crystal chemistry this corresponds for example to the step from sphalerite to diamond (cf. Chapter 3.1.3.).

As an illustration of the basic idea of this chapter a synopsis for the so-called perovskite-family is given in Fig. 15 [61]. Only those structure types are consid-

FIG. 15. The "family tree" of perovskite-type structures with chemical formula MM'X$_3$. Structures which may not be reliable are marked by *). PrAlO$_3$ has been questioned by BIRGENAU et al. [59], PbZrO$_3$ by MEGAW [60].

ered which may be regarded as derivative structures of the cubic perovskite with formula MM'X$_3$. Thus, structures which are characterized by an ordered distribution of different cations on the M sites as well as the M' sites are excluded, but

they can be treated in a similar way. SALJE [62] has also studied symmetry re-
lations between perovskites, but his approach is formally different since he works
with irreducible representations of the space groups. The 18 variants of the basic
perovskite structure shown in Fig.15 are arranged according to the group-sub-
group relations of their respective space groups. As can be seen the group-theo-
retical connection of these structures results in a hierarchical order resembling
a 'family tree'. Incidentally this term harmonizes very nicely with the definition
of structure families as given by MEGAW [63]. For the structure of highest sym-
metry within a structure family MEGAW has coined the term 'aristotype' which
in my opinion is rather appropriate. Those structures which can be derived from
the aristotype may be called the 'hettotypes', a term which has also been pro-
posed by MEGAW. The new terms, of course, are in correlation with BUERGER's
expressions 'basic structure' and 'derivative structure' [16]. Problems of nomen-
clature, however, should not be over-estimated. Another statement concerning
Fig.15 is really much more important. Considering the fact that every space
group has an infinity of subgroups, it is somewhat surprising that all the perovs-
kite-like structures are placed within such a small area as Fig.15. In my opin-
ion this result can be regarded as a strong manifestation of the symmetry princi-
ple, especially of the aspect (ii) (see Chapter 1.) . If you allow a metaphor, I
would like to say: In crystal chemistry we are only confronted with the 'tip of
the iceberg'.

The presentation of all the structural data of the above mentioned perovskites
would be beyond the scope of this paper. Nevertheless it is advisable to give at
least the crystal data (see Table 9), because our setting of the compounds
(Fig. 15) differs frequently from the standard setting of the space groups.
Finally it should be mentioned that BILLIET [64] has recently published some
comments on the 'family tree' of the perovskite-like structures [61].

Summing up, it may be said that considerations of group-subgroup relations may
help to put the science of crystal chemistry on a more logical basis. This im-
pression is based on our own work (MX_2- and $MM'X_4$-compounds, unpublished
results) as well as on the work of EYSEL [65] ($A_2[BX_4]$- and $A_2[BX_3]$-com-
pounds) and MÜLLER (M_2X_{10}-compounds [66] and MX_6-compounds [67]).

TABLE 9. Crystal data of the compounds MM′X$_3$ shown in Fig. 15.

Compound		References	Lattice dimensions a (pm)	b (pm)	c (pm)	Angle (degree)	Space group		Z
NaNbO$_3$	(993 K)	[43],[44]	395.8				P m 3 m	(No.221)	1
NaNbO$_3$, T$_2$	(873 K)	[43],[44]	556.39		394.28		P 4/m b m	(No.127)	2
NaNbO$_3$, T$_1$	(803 K)	[43],[45]	786.42	785.50	786.96		C c m m	(No.63)	8
NaNbO$_3$, S	(773 K)	[43],[45]	786.08	785.56	786.06		P n m m	(No.59)	8
NaNbO$_3$, P	(298 K)	[46],[47]	550.6	556.6	1552.0		P b c m	(No.57)	8
NaNbO$_3$, Q	(298 K)	[48]	552.39	558.07	776.70	γ=90.065	P 1 1 m	(No.6)	4
NaNbO$_3$, N	(123 K)	[47]	781.66			α=89.22	F 3 c	(No.161)	8
BaTiO$_3$	(298 K)	[49]	399.45		403.35		P 4 m m	(No.99)	1
BaTiO$_3$	(263 K)	[50]	568.2	566.9	399.0		C 2 m m	(No.38)	2
SrTiO$_3$	(78 K)	[51]	≈551.5*		≈780.4*		I 4/m c m	(No.140)	4
BaPbO$_3$	(4.2 K)	[52]	606.3	600.7	847.6	α=90.35	I c m m	(No.74)	4
PrAlO$_3$	(293 K)	[53]	753.9				F 3̄ c	(No.167)	8
PrAlO$_3$	(172 K)	[53]	534.7	532.2	748.1	β=90.0	I 2/m	(No.12)	4
PrAlO$_3$	(135 K)	[53]	533.5	531.7	747.7	α≈β≈90.0,γ=90.67	I 1̄	(No.2)	4
GdFeO$_3$		[54]	534.9	561.1	766.9		P b n m	(No.62)	4
LaYbO$_3$		[55]	581	601	839		P b n 2$_1$	(No.33)	4
KCuF$_3$	(type a)	[56]	828.20		784.74		F 4/m m c	(No.140)	8
CsGeCl$_3$		[57]	544.4			α=89.63	R 3 m	(No.160)	1
PbZrO$_3$		[58]	588.4	1176.8	822.0		P b a 2	(No.32)	8

*) only c/a precisely known

6.2. Synopsis of symmetry-related crystal structures: Compounds with different formula types.

In the last section of this paper it will be shown that group-subgroup relations are also of advantage when the compounds have different stoichiometry.

Fig. 16 gives a simple example. Three apparently different crystal structures

CoSn-type (P6/mmm)

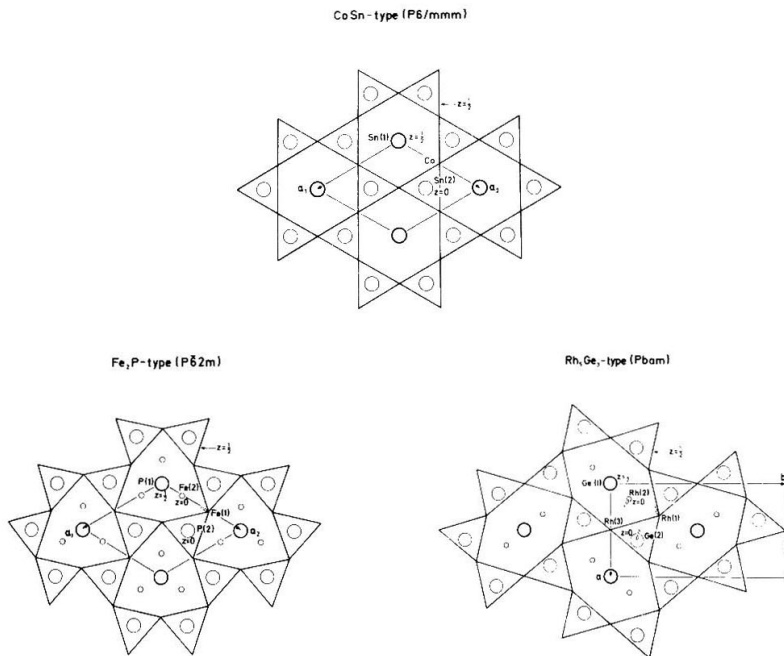Fe₂P-type (Pδ2m)   Rh₅Ge₃-type (Pbam)

FIG. 16. Schematic representation of three different, but nevertheless related crystal structures. Some crystallographic data and references are given in Table 10.

are shown, the relationship of which is made evident by linking the atoms concerned with bold lines. The highly symmetrical hexagonal structure is the CoSn-type. In the sense of MEGAW [63] it can be called 'aristotype'. Imagine the Co-atoms at the intersection points of the so-called Kagomé-net with the Schläfli-symbol 3636. Whereas the Sn(1)-atoms are in the same plane as the Co-atoms of the net, the Sn(2)-atoms are half way between two nets, adjacent Sn(2)-atoms being translationally equivalent along the viewing direction. Space filling in the inter-
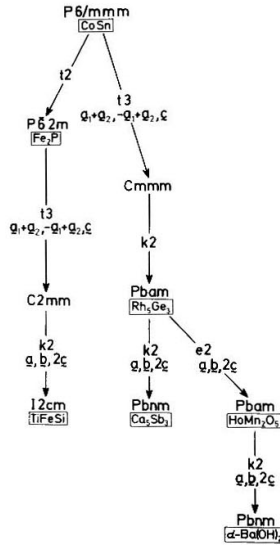
P6/mmm
[CoSn]

t2

t3
$q_1+q_2, -q_1+q_2, c$

P $\bar{6}$ 2m
[Fe₂P]

Cmmm

t3
$q_1+q_2, -q_1+q_2, c$

k2

C2mm

Pbam
[Rh₅Ge₃]

k2
$a, b, 2c$

k2
$a, b, 2c$

e2
$a, b, 2c$

I2cm
[TiFeSi]

Pbnm
[Ca₅Sb₃]

Pbam
[HoMn₂O₅]

k2
$a, b, 2c$

Pbnm
[α-Ba(OH)₂]

FIG. 17. Symmetry relationships between some apparently different crystal structures. Note that the compounds Rh_5Ge_3 and Ca_5Sb_3 have already been discussed in greater detail (Chapter 3.2.1.).

TABLE 10. Crystal data of some compounds shown in Fig. 17.

Note that corresponding data for Rh_5Ge_3 and Ca_5Sb_3 can be found in Chapter 3.2.1., Table 2. For better comparison the hexagonal structures of CoSn and Fe₂P are described in the orthohexagonal setting [8].

	CoSn [68]	Fe₂P [69]	TiFeSi [70]	HoMn₂O₅ [71]	α-Ba(OH)₂ [72]
a (pm)	527.9	586.75	628.7	736	710.5
b (pm)	914.3	1016.3	1083.0	849	1102.3
c (pm)	425.8	345.81	699.7	569	1651.5
Ratio of the axes	0.58 : 1 : 0.47	0.58 : 1 : 0.34	0.58 : 1 : 0.65	0.87 : 1 : 0.67	0.64 : 1 : 1.50
Z	6	6	12	4	20
Space group	P 6/m m m (No. 191)	P $\bar{6}$ 2 m (No. 189)	I 2 c m (No. 46)	P b a m (No. 55)	P b n m (No. 62)

metallic compound CoSn is relatively low, only 55%. Not surprisingly we have a num-
ber of variants of this structure type, created by filling the large hexagonal chan-
nels around the Sn(1)-atoms. Two such variants are shown. Stuffing three atoms
into each channel - that is 3 atoms per unit cell - hexagonality can be retained,
and one obtains the Fe_2P-type. The resulting distortion of the Kagomé-net is geo-
metrically plausible. It corresponds to a lattice-equivalent symmetry reduction
of index 2. Stuffing only t w o atoms into each channel or unit cell necessarily
destroys the hexagonal symmetry, and one obtains the Rh_5Ge_3-type with a differ-
ent distortion of the Kagomé-net, which is also quite plausible. Thus the basic
idea becomes clear: Despite differing stoichiometry, the structural relationship
of different compounds can be close enough to warrant the search for a common
basic structure (aristotype) in order to improve a systematic treatment of crystal
chemistry. It takes but a little courage to integrate more structures into this ex-
ample and to encompass a wider area of crystal chemistry. For instance our ex-
ample can easily be expanded beyond the Fe_2P-type and the Rh_5Ge_3-type as shown
in Fig. 17. Some crystallographic data as well as references are given in Table 10,
but for reasons of space a discussion of more details is inappropriate.

Some of you may be disturbed at the way in which we brushed aside stoichio-
metry, and thus the chemistry of the compounds in this example. But let me
remind you that interpretation of one structure as a stuffed variant or
vacancy variant of another structure has always belonged to the inventory of crys-
tal chemistry. In addition to what is already known I wanted to show how
group-subgroup relations give a more precise description. A special advantage
seems to lie in the hierarchical structure of the group-theoretical description. Con-
sequent application of the 'family-tree principle' could help to make crystal chem-
istry more comprehensible than it is today.

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