In MEF3000 (Functional Materials) a somewhat superficial introduction was given into the operations of symmetry, point groups, lattices and space groups. Neither here shall a complete introduction into all these topics be given. The main thought behind this compendium, as well as of this part of KJM5110, is to give the reader/student an insight into space groups that would be sufficient for description of structures and for the symmetry analysis of the correlations between them. In the first part of this compendium, fundamental concepts and applications of crystallography from the MEF3000 course are recapitulated, in the second part, the understanding of space groups and symmetry operations is taken a bit further, and, in the third part, symmetry-based comparisons of various structures are treated, based on group-subgroup relations.

1. AN EXPANDED REPETITION FROM MEF3000

MATHEMATICAL DESCRIPTION AND NOMENCLATURE

The setup of x-, y- and z-axes for the coordinate system that is used to describe the crystal system of the unit cell is done according to the right-hand rule: Unit-cell vectors \( \mathbf{a}, \mathbf{b}, \mathbf{c} \) that lie in the respective x, y and z axes are taken in the order of thumb, index and the middle finger of the right hand.

A symmetry operator, \( \mathbf{R} \), acts on a point \( \mathbf{r} \) (see Figure 1) so that:

\[
\mathbf{r}' = \mathbf{R} \cdot \mathbf{r},
\]

in which \( \mathbf{R} \) represents a 3×3 matrix:

\[
\begin{pmatrix}
    x' \\
    y' \\
    z'
\end{pmatrix} =
\begin{pmatrix}
    a_{11} & a_{12} & a_{13} \\
    a_{21} & a_{22} & a_{23} \\
    a_{31} & a_{32} & a_{33}
\end{pmatrix}
\begin{pmatrix}
    x \\
    y \\
    z
\end{pmatrix}
\]

---

However, in general, symmetry operations in a three-dimensional lattice are described by the Seitz operator:

\[(R \mid t) = R \cdot r + t\]

Figure 1: A point in space before and after a symmetry operation

For the identity operator \(I\), all \(a_{ij} = 0\) and \(a_{ii} = 1\), and no translation is involved. As a Seitz operator, the operator of identity would be denoted \((1 \mid 0)\). In order to describe a lattice, either centered one with semi-integer translations or a primitive one with integer translations, a Seitz operator \((1 \mid t)\) is used, in which \(t_n = t_1a + t_2b + t_3c\), and \(a, b, c\), are the primitive translation vectors. As an example, for an orthorhombic \(C\)-centered Bravais lattice, \(t_1 = \frac{1}{2}, t_2 = \frac{1}{2}\) and \(t_3 = 0\).

A rotation axis is noted as \(N[uvw]\) depending on its direction in the reference system \((N = 2, 3, 4, \ldots\) describes the order of the axis, \(uvw\) gives the direction). A twofold rotation axis parallel with the \(c\)-axis is described by the \(2[001]\) symbol:

\[
(2[001] \mid 0)(x, y, z) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}
\]

The inversion \((-1)\) operation of symmetry is denoted as:

\[
(-1 \mid 0)(x, y, z) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ -z \end{pmatrix}
\]
A mirror plane \((m)\) is defined according to the direction of its normal vector. As an example, an \(x, \bar{z}\) mirror plane is denominated as \(m[010]\) and acts according to the following matrix operation:

\[
(m[010]) \cdot (x, y, z) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}
\]

With the help of matrix formalism one can in a simple way arrive at what happens when two different (or, for that matter, also identical) operators act subsequently, after each other.

\[
(m[001]) \cdot (2[001]) \cdot (0) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = (-1 | 0)
\]

We see that such a \(2/m\) combination represents an inversion \((-1)\).

A \(b\)-axial glide plane with the \(y, \bar{z}\) reflection (mirror) plane acts as follows:

\[
\left( m[100] \right) \cdot \left( 0, \frac{1}{2}, 0 \right) \cdot r = m[100] r + \left( 0, \frac{1}{2}, 0 \right)
\]

It transforms the point \(x, y, \bar{z}\) into \(-x, \frac{1}{2} + y, \bar{z}\).

Two other types of glide planes have so far been little treated here: diagonal glide planes (symbol \(n\)) and diamond glide planes (symbol \(d\)).

A diagonal glide plane involves translation in two or three directions (not just in one direction as was the case for the axial glide planes). The translations are generally of the types \(a/2 + b/2\), or \(a/2 + c/2\), or \(b/2 + c/2\). In tetragonal and cubic crystal systems, translation of the \(a/2 + b/2 + c/2\) type can occur.

Figure 2 shows a glide plane \(n\) that reflects through a mirror perpendicular to the \(c\)-axis. The point \(x, y, \bar{z}\) is translated by \(a/2 + b/2\) before it is reflected through the plane.

\[
\left( m[001] \right) \cdot \left( \frac{1}{2}, 0, 0 \right) \cdot r = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} + \frac{1}{2} = \begin{bmatrix} 1/2 + x \\ 1/2 + y \\ z \end{bmatrix}
\]
A diamond glide plane involves translations \( \frac{a}{4} + \frac{b}{4} \), or \( \frac{a}{4} + \frac{c}{4} \), or \( \frac{b}{4} + \frac{c}{4} \), as well as \( \frac{a}{4} + \frac{b}{4} + \frac{c}{4} \) in the tetragonal and cubic crystal systems.

Exercise 1. Illustrate how a 4\( _1 \) screw axis parallel to \( z \) acts on the coordinate set \( x, y, z \).

Exercise 2. Write down a Seitz operator and the related matrix operations that show symmetry operation of a 3\( _2 \) screw axis parallel to the \( z \) axis.

**SPACE GROUPS**

Combinations of the 32 crystallographic point groups and the 14 Bravais lattices (which in turn are combinations of the crystal systems and their various possible centering) give rise to the 230 space groups.

A given crystal structure, as a regular spatial arrangement of atoms, is described in terms of space group which defines both its translation symmetry (Bravais lattice) and its rotation symmetry (point group). When crystal structure data are to be presented for a compound, space-group symbol is listed, together with coordinates \( x, y, z \) for atoms at sites of the specified point-group symmetry (see further).

Of the 230 space groups, 73 follow from direct combinations of Bravais lattices with crystallographic point groups without participation of screw axes and glide planes. Such space groups are called *symmorphic* space groups. Consequently there is 157 non-symmmorphic space groups, which must be described by symmetry operators of the \( (R | t) r = R r + t \) type, where \( t \neq 0 \).

Space-group denomination consists of a space-group symbol of the type \( Xefg \), where \( X \) specifies the Bravais lattice, \( (P, F, I, \text{or} \ R, \text{or} \ A, B, C) \), and \( ef \) is the symbol of the crystallographic point group, in which, however, symbols for symmetry operations associated with non-lattice translations, such as screw axes and glide planes, can be introduced instead of the ordinary rotation axes and mirror planes. The non-symmmorphic space groups are thus recognizable by the presence of symbols such as \( a, b, c, d, 2\parallel, 3\parallel, 4\parallel \), etc.
The triclinic crystal system has only $P$ lattices, and consequently only $Pefg$ space groups. The triclinic system can accommodate only very few symmetry elements. If other than identity and inversion symmetry elements were present, the symmetry would increase over what is allowed for triclinic space-group symmetry. There are only two possibilities; a presence of the identity element of symmetry and presence of inversion. The only two space groups in the triclinic system have thus symbols $P1$ and $P\overline{1}$. Within the monoclinic crystal system, both mirror symmetry and twofold rotation axes can be accommodated (point groups $2$, $m$, and $2/m$). Furthermore, a $C$-centering is possible in the monoclinic lattice. This gives rise to altogether 13 monoclinic space groups. In the orthorhombic crystal system there is as much as 59 space groups.

Exercise 3. Show that in the presence of twofold rotation axis the crystal system cannot be triclinic. Prove the same for a mirror.

Exercise 4. Let's have a monoclinic symmetry with a twofold axis and a mirror. How must the mirror be oriented with respect to the twofold axis, so that the monoclinic symmetry is maintained?

Exercise 5. Which of the following is a symmorphic space group: a) $P2_1/m$, b) $Pnma$, c) $P6/mmc$ and d) $I4/mmm$?

Exercise 6. To which crystal systems the following space groups belong: a) $P2$, b) $Pmm2$, c) $Pnma$, d) $R\bar{3}$, e) $Fm\bar{3}m$, f) $I4/mmm$ and g) $P6/mc$.

Exercise 7. Which of the following space groups are centrosymmetric: a) $P2/m$, b) $Pmmm$, c) $P1$, d) $P2_1/e$ and e) $P222$?

**INTERNATIONAL TABLES OF CRYSTALLOGRAPHY**

International Tables of Crystallography, Volume A is an overview of symmetry properties of the 230 space groups. The book is widely used for description of crystal structures.

In the Volume A, the space groups are listed according to the crystal system and the symbol $Xefg$. In many cases, orientations of the axes (directions) can be defined in different ways for a given space group. International Tables give a standard way how to do it, and if the actual orientation is not standard, it is necessary to transform the axes/directions before International Tables are applied correctly.

As a representative example, a data section for the space group $Pnma$ is discussed in the following (the copy of the appropriate page from International Tables is in the Appendix):

The upper line:

\[
Pnma \quad D_{2h}^{16} \quad m \ m \ m \quad \text{Orthorhombic}
\]

is telling us the following: The space group is $Pnma$, the corresponding crystallographic point group is of the Schoenflies symbol $D_{2h}^{16}$ (numbered variants) described by symbol $mmm$ in the alternative Hermann–Maugin nomenclature. The crystal system is orthorhombic.

The next line:

\[
\text{No.62} \quad P2_1/n \quad 2/\bar{1}/m \quad 2/\bar{1}/a \quad \text{Patterson symmetry} \quad Pmmm
\]

gives the number of the space group (numbered from 1 to 230, from triclinic to cubic system), the full space-group symbol (here screw axes occur in addition to the $nma$ in the symbol), and the symbol for
Patterson symmetry which is the symmetry for a special type electron-density map based on Fourier transforms of diffraction data and used for determination of crystal structures. Next:

**Origin** at \(-1\) on 1211

defines the placement of the origin with respect to the symmetry elements. The origin is here at a point with the center of symmetry (at the inversion; a usual case).

**Asymmetric unit**

\[ 0 \leq x \leq \frac{1}{2}; \quad 0 \leq y \leq \frac{1}{4}; \quad 0 \leq z \leq 1 \]

This defines the smallest unit that, when repeated in a given cell by symmetry operations, creates the full symmetry picture of the space group.

**Symmetry operations**

This is a list of the present symmetry elements in a standard notation that describes their placement. If we skip over "Generators selected", the next line is:

**Positions**

<table>
<thead>
<tr>
<th>Multiplicity</th>
<th>Wyckoff letter</th>
<th>Coordinates</th>
<th>Reflection conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Site symmetry</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Multiplicity expresses how many times the given position is repeated upon action of all symmetry operations that belong to the space group. The maximum multiplicity is characteristic of a general position (a point that does not lie on any symmetry element, except identity). This general position is 8-fold for \(Pnma\), and there are three different special positions, all 4-fold. The Wyckoff letter is a running alphabetical description that starts with an “a” for the most special site. The site symmetry gives the point symmetry for the site (for either a general or a special site). The coordinates show how the original coordinates \(x, y, z\) are transformed after all the various symmetry operations have been performed (the number of such coordinates corresponds to multiplicity of the position).

Reflection conditions are conditions for appearance of \(hk\)/Bragg reflections when atoms are placed in the given Wyckoff positions. Bragg reflections that do not fulfill these conditions are extinct.

Some of the remaining items will be explained later (page 17), when more appropriate.

**TYPICAL LISTING OF STRUCTURAL DATA**

Typical structure data for a compound, as found in the literature, are shown in Table 1 on the example of the manganese phosphide, MnP. The appropriate section from the International Tables of Crystallography for the relevant space group \(Pnma\) is shown in the Appendix.

| Table 1: All you need to draw the crystal structure of MnP |
|-----------------------------------------------|-----------------|
| Space Group:                          | \(Pnma\)        |
| Unit cell:                           | \(a = 525.5\) pm, \(b = 318\) pm, \(c = 590.5\) pm |
| Atomic coordinates:                  | Mn in 4c, with \(x = 0.0050\) and \(z = 0.1885\) |
|                                      | P in 4c, with \(x = 0.1850\) and \(z = 0.5670\) |
These data, when applied to the standard symmetry description in the International Tables for Crystallography, describe unambiguously the crystal structure. When the glide plane symbols \( a \) and \( n \) in the space-group symbol are exchanged with ordinary mirror plane \( m \), symbol \( Pnnm \) is obtained that identifies the crystallographic point group \( mmm \) from the orthorhombic crystal system and the primitive lattice \( P \). No angles need to be defined for the unit cell in this case, as all are equal to 90°.

In order to be able to draw the crystal structure from the above data, one has to use the International Tables. One needs to know how the 4c positions are generated. Note that it is not necessary to list a value for \( y \) in 4c, because this is a special position that has \( y \) defined as \( y = \frac{1}{4} \) or \( \frac{3}{4} \). That particular position is situated at a symmetry element, and the symmetry element cannot move freely within the unit cell. On the other hand, \( x \) and \( z \) are completely free parameters that can assume all values between 0 and 1. The listed \( x \) and \( z \) values have been determined from experimental diffraction data.

Making a projection on a chosen plane is often the first step in a “manual” analysis of the structure of interest. It is best to choose the shortest projection axis. In the MnP case, the projection is made on the \( a,c \) plane, since the \( b \) axis is clearly shortest. The two atoms are distinguished by different symbols and the value for the third coordinate may with an advantage be noted with the atom symbol on the projection.

Exercise 8. Draw a projection of the MnP crystal structure on the \( a,c \) plane according to the data in Table 1. How many formula units is in one unit cell? What is the so-called x-ray density of MnP? Which coordination polyhedron is around Mn? What is the average Mn—P bond distance? What bonding relation would you suggest for the Mn Mn interactions based on the calculated shortest distance and comparison with the Mn metal?
2. MORE ON SPACE GROUPS

POINT GROUPS AND SPACE GROUPS

Point group (Gp) of a space group (G) is derived from a set of symmetry operations that are obtained when all translations are set to zero, that is, when the operations are of the (R | 0) type. Of course, the point-group operations of Gp are not those for the space group G. In a symbolical form, the point-group operations are obtained from the space-group operations by

\[(R_j | t_i + t_n) \rightarrow (R_j | 0),\]

where \(t_i\) represents translations associated with the screw axes and glide planes and \(t_n\) represents the lattice translations.

All space groups contain translational symmetry operations of lattice translations (1 | \(t_n\)). These represent a group per se. In addition, there may be symmetry operations of the (R | \(t\)) type present where non-zero \(t\) indicates screw axes or glide planes. The amount of such (R | \(t\)) operations depends on the space group, but the maximum is \(i = 48\).

Operations (R | 0) for a Gp fulfill conditions for a group. Such a group would be one of the 32 crystallographic point groups. In order to describe the essential symmetry operations for a space group, one needs to know both the translation operations and all the j symmetry operations.

GENERAL AND SPECIAL POSITIONS

When an arbitrary point \(x, y, z\) is subject to the \(j\) symmetry operations (R | \(t\)), \(j\) general positions are obtained. If this point is not arbitrary and lies on one or more of the symmetry operations, it is not recreated elsewhere in space by this particular symmetry operation and the position is called special. A special position repeats the point fewer times than the general position.

These considerations concern a primitive cell. For centered cells one finds 2\(j\) for body-centered or one-side centered cells, 3\(j\) for rhombohedrally centered cells in hexagonal setting and 4\(j\) for face centered cells.

DIAGRAMMATIC REPRESENTATION OF SYMMETRY OPERATIONS

The outer shape of the unit cell (the Bravais translational lattice) is drawn in an ab projection. With \(a\) running down the paper side and \(b\) towards right, the right hand rule dictates that \(c\) points out of the projection plane against the observer. This is shown in Figure 3 for the space group \(Pmm2\). Two figures are drawn next to each other; one to the left shows the effect of symmetry operations on a general lattice point, one to the right shows where in the unit cell the various symmetry elements are placed.

The point group \(mm2\) contains symmetry operations 1, \(m[100]\), \(m[010]\), and 2[001]. Their effect on the general point (denoted with a circle) is illustrated in Figure 3. A + sign associated with the circle means that the point lies +\(z\) along the \(c\) axis, hence above the projection plane. A comma in the circle means that the point (the object) is a mirror image of the point with no comma. In a crystal structure, each such point may represent one single atom or a whole collection of atoms.
From symbolism for representation of the point groups we immediately recognize in Figure 3 the symbol for the 2-fold axis, which goes through each lattice point and is parallel with $c$. Furthermore, there are vertical mirror planes denoted by thick full lines. The unit-vector translations in this projection of the primitive orthorhombic lattice are generated by combinations of $(1|a)$ and $(1|b)$ operators, a $(1|a+b)$ as an example. Note that each lattice point has the point-group symmetry $mm2$.

Upon close inspection of Figure 3 one can see that new symmetry elements (denoted as non-essential) have arisen in the unit cell as a result of the interaction between the point-symmetry and translation-symmetry operations. Halfway between the lattice points, new two-fold axes and mirrors appear. Note that both the object (described by the point-group symmetry) and the lattice itself (described by the Bravais lattice) have symmetries compatible with the crystal system, in this case both belong to the orthorhombic crystal system.

**THE TRICLINIC CRYSTAL SYSTEM**

There is only one Bravais lattice for the triclinic crystal system, a primitive lattice. Since only two point groups are compatible with the triclinic symmetry, 1 and -1, there are only two symmorphic triclinic space groups. Any presence of 2-fold axes and mirror planes would automatically bring a higher symmetry. Consequently, there cannot be non-symmorphic triclinic space groups; those would need symmetry operations associated with non-lattice translations such as glide planes and screw axes.

The two space groups $P1$ and $P-1$ are shown schematically in Figure 4. The left-hand portion of the figure shows the point symmetry around the lattice points; the right-hand portion shows the present symmetry elements.

The point-group operation associated with $P1$ is only one; it is the identity operation. Any translations are primitive lattice translations $(1|t)$. The symmetry operator is hence:

$$ (1|0)r = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \text{ and} $$

there is accordingly one general position per unit cell in $P1$. 

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**Figure 3:** The space group $Pmm2$

Effect of symmetry operations on a general point (left)

Location of the symmetry operations in the unit cell (right)
In the space group $P\, 1$ we see operations 1 and -1, and the group is therefore centrosymmetric. Origin is chosen as a rule in the inversion centre, hence:

$$(−1 \mid 0)\mathbf{r} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ -z \end{pmatrix}$$

**Repetition of symmetry operations within the unit cell**

Let’s consider the inversion symmetry for the $P\, 1$ cell in Figure 4. In addition to the mathematical relation above, we see that the point with coordinates $-x$, $1-y$, $-z$ is related to the point $x, y, z$ by a center of inversion placed at $0, \frac{1}{2}, 0$, see Figure 5.
This explains the positioning of the centers of symmetry in Figure 4. Formally, this relationship is expressed by adding a translation (the new inversion center is in \( \frac{1}{2} \) of this translation) to the original expression for the inversion operator:

\[
\begin{pmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
+ \begin{pmatrix}
0 \\
1 \\
0
\end{pmatrix}
= \begin{pmatrix}
-x \\
1-y \\
-z
\end{pmatrix}.
\]

Analogous relationship (where the symmetry element is positioned at \( \frac{1}{2} \) of the required translation) is valid for twofold rotation axes and mirrors. For other symmetry operations, more complex relationships occur, which will not be treated here.

**THE MONOCLINIC SYSTEM**

There are two monoclinic Bravais lattices, one is the primitive lattice \( P \), the other is face-centered lattice \( B \). Actually, the centering symbol depends on the orientation of the monoclinic unit cell; we have chosen \( B \) only because then the \( c \) axis is the unique axis (the one that is perpendicular to the other two axes) and we can look along it at the \( ab \) projection as we are used to. When \( b \) axis is chosen as the unique axis, centering is not possible at the \( ac \) face perpendicular to \( b \). Of the two remaining possibilities (\( C \) centering of the \( ab \) faces, or \( A \) centering of the \( bc \) faces), \( C \) is the standard one. In the \( c \)-unique setting, the \( C \) centering is not possible, and \( B \) is the standard one of two remaining equivalent possibilities, \( A \) or \( B \).

Three crystallographic point groups belong to the monoclinic crystal system; \( 2, m \) and \( 2/m \). Consequently, there are \( 2 \times 3 \) symmorphic space groups\(^4\) \( P2, B2, Pm, Bm, P2/m \) and \( B2/m \). The other monoclinic space groups are nonsymmorphic, hence containing \( 21 \) screw axes and/or glide mirror planes.

Consider a monoclinic unit cell in the \( c \)-unique setting. Plane \( ab \) is perpendicular to \( c \). An eventual twofold rotation or screw axis will be parallel to the unique axis \( c \). Eventual mirrors and glides will be perpendicular to the unique axis \( c \). It is therefore possible to have an \( a \) glide (or equivalently \( b \) glide) in this setting. The possible combinations are then: \( P2, B2, Pb, Bb, P21/m, B21/m, P21/b \) and \( B21/b \). Under closer scrutiny, some of these space groups will be found equivalent.

**The full symbols**

Consider a primitive monoclinic structure (unit cell) with a twofold rotation axis along the unique axis \( c \) as the only symmetry operation. The complete description of the space group will therefore be \( P 1 1 2 \). If there is a glide plane \( b \), it will be perpendicular to the unique axis, and the symbol hence becomes \( P 1 1 2/b \). A careful consideration of the full symbols gives unambiguous information about how the axes are defined. As an example, \( P 1 1 2/b \) means that the \( b \) axis is unique, the angle \( \beta \) between \( a \) and \( c \) is the one that would depart from \( 90^\circ \) and \( 120^\circ \), and that the glide plane is in the \( ac \) plane.

**Monoclinic space groups**

Let’s consider first a simple monoclinic space group in two different settings, in this case we chose \( B2 \) and \( C2 \). For \( B2 \), the \( c \)-axis is unique, and the twofold axis points out of the plane of the paper and is perpendicular to it. The symmetry operations that are present are 1 and 2. In addition there is the \( B \) centering of the lattice which places a lattice point also at \( \frac{1}{2}, 0, \frac{1}{2} \). The top left portion of Figure 6 shows

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\(^2\) not a true Bravais lattice

\(^3\) and equivalent; \( a \) and \( c \) are freely interchangeable, while \( b \) is unique

\(^4\) \( c \)-unique setting for the centered groups

\(^5\) \( a \) and \( b \) are freely interchangeable, while \( c \) is unique
the combined effect of these operations of symmetry on a general point. The point is repeated altogether four times within the unit cell:

\[
\begin{bmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1 \\
\end{bmatrix}
\begin{bmatrix}
x \\
y \\
z 
\end{bmatrix}
= 
\begin{bmatrix}
-x \\
-y \\
z 
\end{bmatrix}.
\]

The other two points are obtained via the centering of the lattice: \(x+\frac{1}{2}, y, z+\frac{1}{2}\) and \(-x+\frac{1}{2}, -y, z+\frac{1}{2}\). Consider now the operation that relates \(x, y, z\) to \(-x+\frac{1}{2}, -y, z+\frac{1}{2}\). In Seitz notation this operation will be described by:

\[
\begin{bmatrix}
\frac{1}{2} - x \\
-y \\
\frac{1}{2} + z 
\end{bmatrix}
= 
\begin{bmatrix}
x \\
y \\
z 
\end{bmatrix}
+ 
\begin{bmatrix}
0 \\
0 \\
\frac{1}{2} 
\end{bmatrix}
= 
\begin{bmatrix}
\frac{1}{2} \\
0 \\
0 
\end{bmatrix}
\]

The coordinate matrix of the second of these two points can be decomposed into several column matrices. The first one represents the effect of the twofold axis at \(x, y, z\), the next column matrix could be a translation along \(c\) in case that the ‘rotation’ axis were not a simple twofold axis, but a twofold screw axis 21. The last one must be associated with the translation that arises because the 21 axis is not at the origin, but at the point \(\frac{1}{2}(\frac{1}{2}, 0, 0)\), hence \(\frac{1}{4}, 0, 0\). The full picture of the distribution of these 2 and 21 axes in the unit cell is shown in the right portion of Figure 6 top.

An analogous derivation for the same symmetry operations, but in the space group \(C2\) will result in space-group diagram that looks completely different. This is because the \(b\) axis is now the unique axis, it is
perpendicular to \( a \) and both are in the plane of the projection, see Figure 6 bottom. The axes 2 and 21 are now parallel with the unique axis \( b \) and lay in the plane of the paper.

We are familiar with symbols for the 2 and 21 axes when these are perpendicular to the plane. When they lie in the plane, the twofold rotation axis is denoted by an arrow in the direction of the rotation axis, and the twofold screw axis is denoted by a half-arrow (Figure 7). Note that symbol \( B2 \) (\( C2 \)) for the space group is sufficient to fully describe the entire symmetry, even though the symmetry elements within the space group include the screw axis. \( B2 \) (\( C2 \)) is therefore equivalent with \( B21 \) (\( C21 \)). The screw axis is hence a result of a simultaneous presence of one twofold rotation axis and the centered Bravais lattice.

For the space group \( Bb \), two symmetry operations occur,\(^6 \) \( 1 \) and \( b \). When these two are combined with the \( B \) centering, 4 general points is obtained. A \( b \) glide generally transforms point \( x, y, z \) to point \( x, \frac{1}{2}+y, -z \) and the \( B \) centering would repeat these two points in respectively \( x+\frac{1}{2}, y, z \) and \( x+\frac{1}{2}, \frac{1}{2}+y, \frac{1}{2}-z \). This repetition pattern is shown in Figure 7 top left.

\[ \begin{bmatrix} x \\ y \\ z \end{bmatrix} \cdot + \begin{bmatrix} \frac{1}{2}+x \\ \frac{1}{2}+y \\ \frac{1}{2}-z \end{bmatrix} = \begin{bmatrix} x \\ y \\ -z \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} + \begin{bmatrix} 0 \\ \frac{1}{2} \\ \frac{1}{2} \end{bmatrix} + \begin{bmatrix} -z \\ y \\ \frac{1}{2} \end{bmatrix} \]

\(^6 \) Also the corresponding point group has two symmetry operations, 1 and \( m \).
R could in this case represent a mirror plane perpendicular to \(c\), as suggested by the first column vector on the right side of the equation. The column vector number 2 and 3 may indicate glide components for this mirror, simultaneously along both \(a\) and \(b\). Hence an \(s\) glide could be present. In such a case, the fourth column vector gives information where the \(n\) glide is located in the unit cell. The \(z\) coordinate of the glide must be situated between those points (in \(z\)) that are related by the glide operation, hence the glide must go through the point \(\frac{1}{2} \cdot (0, 0, \frac{1}{2}) = 0, 0, \frac{1}{4}\). Figure 7 top right shows the symbol which is used to denote such a glide plane. Note that the space group \(Bb\) may therefore also be described as \(Bn\). The space-group diagram of the same space group, but in the setting \(Cc\) is shown in the bottom part of Figure 7.

The last monoclinic space group that will be discussed here is \(P2_1/b\); one of the most common ones, a favorite for organic crystals. The corresponding point group is \(2/m\) and contains four essential symmetry operations 1, -1, 2[001] and \(m[001]\). The translation group is primitive, \(P\), which means that we may expect four general positions.

The space group diagram is drawn in Figure 8.

![Space group P2_1/b](image)

**Figure 8: Space group \(P2_1/b\)**

The \(2_1\) axis of the group symbol repeats the point \(x, y, z\) at \(-x, -y, z+\frac{1}{2}\). The \(b\) glide (perpendicular to \(c\)) repeats \(x, y, z\) at \(x, \frac{1}{2} + y, -z\) and the point \(-x, -y, z+\frac{1}{2}\) at \(-x, \frac{1}{2} - y, \frac{1}{2} - z\), hence four different positions are obtained. Let's evaluate the symmetry relationship between \(x, y, z\) and \(-x, \frac{1}{2} - y, \frac{1}{2} - z\):

\[
R = \begin{pmatrix} x \\ y \\ z \end{pmatrix} + t = \begin{pmatrix} -x \\ \frac{1}{2} - y \\ \frac{1}{2} - z \end{pmatrix} = \begin{pmatrix} 0 \\ -y \\ -z \end{pmatrix} + \begin{pmatrix} 0 \\ \frac{1}{2} \\ \frac{1}{2} \end{pmatrix}
\]

This decomposition of the coordinate matrix of the second point shows that it is related to \(x, y, z\) via a center of symmetry placed at \(\frac{1}{2} \cdot (0, \frac{1}{2}, \frac{1}{2})\), hence 0, \(\frac{1}{4}\), \(\frac{1}{4}\). It proves that this space group is centrosymmetric; and of course also the corresponding point group 2\(/m\) is centrosymmetric.

By convention, origin in space-group diagrams is situated in a center of symmetry. This means that the drawing in Figure 8 must be modified by a shift of the origin. This is done by moving the screw axis so that it passes the point 0, \(\frac{1}{4}\), \(\frac{1}{4}\) and the glide plane is at the height \(z = \frac{1}{4}\) above the projection plane.

Exercise 9. Draw stereographic projection for point groups 2, \(m\) and 2\(/m\). Determine how many general positions each of these point groups has.
Exercise 10. Draw space-group diagram of the space group $P2_1/b$ so that the center of symmetry is in the origin.

Exercise 11. Draw the space-group diagram for the space group $P2_1/c$. Hint: it is analogous to $P2_1/b$, but in a different setting of the unit cell axes.

ORTHORHOMBIC SPACE GROUPS

There are three crystallographic point groups in the orthorhombic crystal system (222, mm2 and mmm), together with four Bravais lattices (P, C, I, and F). In addition, non-symmorphic operations such as 21 axes and axial, diagonal and diamond glides occur. In total, there is 58 orthorhombic space groups: nine with point group 222, twenty one with mm2 and twenty eight with mmm. In this text, we shall look at two of them; $P2_12_12_1$ and $Pnma$.

The letter symbols give symmetry along the three orthogonal directions in the orthorhombic unit cell. For $P2_12_12_1$, this means that there are screw axes along the three unit-cell vectors (a, b and c). The Bravais lattice is primitive and the corresponding point group is 222. This point group has four essential symmetry operations, 1, 2[001], 2[010] and 2[100]. Consequently, $1 \times 4 = 4$ general positions are expected.

How the screw axes repeat coordinates of the general point is dependent on whether or not these axes intersect each other in the unit cell. For $P2_12_12_1$ it is so that the screw axes do not intersect each other. This space group is illustrated in Figure 9.

\[
P2_12_12_1
\]

Figure 9: The space group $P2_12_12_1$

In order to describe this particular space group, a choice must be made for the positioning of the screw axes: The 2[001] axis is chosen to pass through $\frac{1}{4}, 0, 0$. Its operation on the general point $x, y, z$ can be described by the following Seitz notation:

\[
(2[001]) (0,0,1/2) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ 1/2 \end{pmatrix} = \begin{pmatrix} 1/2 - x \\ -y \\ 1/2 + z \end{pmatrix}
\]

If an analogous choice is made for the other two screw axes, i.e., 2[010] through 0, 0, 1/4, and 2[100] through 0, 1/4, 0, four general positions are generated: $x, y, z$, $\frac{1}{2} - x, y, z$, $\frac{1}{2} + x, \frac{1}{2} - y, z$, and $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

It is not without reason that these screw axes are chosen to pass as described. If they intersected each other, other than $P2_12_12_1$ space group would be created, for example $P2_12_2$. 

The last space group that will be discussed here is \textit{Pnma}. Its diagram is given in Figure 10. The Bravais lattice is again primitive and the corresponding point group is \textit{mmm}. This point group has eight symmetry operations, \(1, m[001], m[010], m[100], -1, 2[001], 2[010]\) and \(2[100]\). Consequently, \(1 \times 8 = 8\) general positions occur in this space group.

\[
\begin{pmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
+ 
\begin{pmatrix}
0 \\
\frac{1}{2} \\
\frac{1}{2}
\end{pmatrix}
= 
\begin{pmatrix}
-x \\
\frac{1}{2} + y \\
\frac{1}{2} + z
\end{pmatrix}
\]

However, the origin for this space group is chosen (see below) so that the glide passes through \(\frac{1}{4}, y, z\) and not \(0, y, z\). This means that \(2(\frac{1}{4}, 0, 0)\) is added to the position above, and the equivalent position becomes \(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z\).

The mirror plane \(m\) is perpendicular to \(b\). This means that it operates on \(x, y, z\) as follows:

\[
\begin{pmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
= 
\begin{pmatrix}
x \\
-y \\
z
\end{pmatrix}
\]

In Figure 10 we see that the mirror plane passes through \(x, \frac{1}{4}, z\), and this means that \(2(0, \frac{1}{4}, 0)\) is added to the coordinates generated above so that the equivalent position is \(x, \frac{1}{2}-y, z\).

The axial glide plane \(a\) is perpendicular to \(c\). It operates on \(x, y, z\) as follows:

\[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
+ 
\begin{pmatrix}
\frac{1}{2} \\
0 \\
0
\end{pmatrix}
= 
\begin{pmatrix}
\frac{1}{2} + x \\
y \\
-z
\end{pmatrix}
\]

\textit{Pnma}

Figure 10: The space group \textit{Pnma}
From Figure 10 we see that this axial glide passes through $x, y, \frac{1}{4}$, so that the equivalent position is $\frac{1}{2}+x, y, \frac{1}{2}-z$.

Exercise 12. Show that $Pmna$ is centrosymmetric and locate points of inversion.

**International Tables for Crystallography**

Consider the $Pmna$ space group from the International Tables for Crystallography, the listing of which is reproduced in the Appendix. In total, 8 symmetry operations are listed for this space group, denoted together with their location. Three of them have in detail been explained and described above (that is $n$, $m$, and $\alpha$). Among the remaining ones we see something that looks like a $2[001]$ because it passes through $\frac{1}{4}, 0, z$. However, the in addition present translation term $(0, 0, \frac{1}{2})$ tells us that this actually represents a screw axis $2\alpha$. In a similar manner the remaining symmetry operations can be identified and their location in the unit cell determined.

These 8 symmetry operations generate 8 equivalent general positions, which are numbered. The number, in a round bracket, identifies the equally numbered symmetry operation that created this particular equivalent position by operating on $x, y, z$. However, it is sufficient to choose less, in this case four, symmetry operations as generators for the equivalent points. These operations are $(1), (2), (3)$ and $(5)$ in the list of **Generators selected**. The numbering identifies the following **Symmetry operations**: $1; 2(0, 0, \frac{1}{2})$ at $\frac{1}{4}, 0, z; 2(0, \frac{1}{2}, 0)$ at $0, y, 0; -1$ at $0, 0, 0$, as being the generators.

**Site symmetry**

Site symmetry describes the point-group symmetry around a given position. Such a position represents the point around which the point symmetry performs operations that would repeat the rest of the crystal on itself. The point symmetry is therefore limited to the 32 crystallographic point groups. The general position has the lowest symmetry (point group 1) and the symmetry increases at the special positions.

---

7 The **Generators selected** list always contains the identity operation numbered $(1)$, then the three translations corresponding to the three basic vectors $a, b$ and $c$: $(1, 0, 0), (0, 1, 0)$ and $(0, 0, 1)$ and then the eventual centering translations before it comes to those numbered **Symmetry operations**.
3. GROUPS AND SUBGROUPS – RELATING STRUCTURE TYPES

RELATIONSHIPS BETWEEN POINT GROUP AND A SPACE GROUP

Earlier we have seen how to find the crystallographic point group \( G_p \) that corresponds to a given space group \( G \). This is an example of finding a factor group, in this case \( G/T \), in which all translations are removed (lattice- as well as non-lattice translations) so that only the rotation elements of symmetry remained. This removes the infinite symmetry order of \( G \), and the amount of the remaining symmetry operations is limited to the maximum of 48. For symmorphic groups, the factor group \( G/T \) is identical with the point group and the point group is hence a subgroup of \( G \).

The macroscopic properties of a crystalline material are related to the symmetry of the atomic arrangement. Neumann’s principle states that any macroscopic property (described by a tensor) of a crystal shows at least the symmetry of the point group corresponding to the space group of the structure. Macroscopic physical measurements cannot therefore distinguish between \((R | 0)\) and \((R | t)\). The rotation part \( R \) of the symmetry operations relates points within the crystal that are coupled by chemical bonds, magnetic cooperative interactions, generally over a distance of several Å. As an example, isotropic behavior is observed for cubic crystals, in which the diagonal elements of the property tensor are equal and non-diagonal elements are zero.

SOME DEFINITIONS

**Subgroup**
A group \( S \) is called subgroup to the group \( G \) if all symmetry elements of \( S \) are also present in \( G \) and if the amount of symmetry elements in \( G \) divided by the amount of symmetry elements in \( S \) is an integer.

**Complex**
A complex \( C \) of \( G \) is any set of symmetry elements within a group. A complex \( C \) therefore does need to be a subgroup of \( G \). Complexes can be multiplied: For two complexes \( D \) and \( H \), a product \( DH \) can be expressed as a set of all products between symmetry elements present in \( D \) and \( H \).

**Coset**
If \( p \) is an element of symmetry of \( G \) that is not present in the subgroup \( S \), complexes \( pS \) and \( Sp \) represent the respective left and right cosets of \( S \). Cosets are always formed with respect to a subgroup \( S \), but the cosets \( pS \) and \( Sp \) themselves can never be subgroups of \( G \), because the multiplication by \( p \) removes the identity element, 1, of the subgroup \( S \). Lacking 1, \( pS \) and \( Sp \) do not fulfill requirements for a group.

GROUP–SUBGROUP RELATIONS BETWEEN SPACE GROUPS

In the following part we shall consider how symmetry can be used to clarify relationships between structures and how to derive which structural deformations cause the more symmetric mother structure become the structure of the subgroup. These considerations may eventually be used to judge whether or

---

8 Which originates from the translation group \( T \) having an infinite amount of translations.

9 For non-symmorphic groups, the factor group \( G/T \) is isomorphic with the point group.

10 The symmetry of the macroscopic property may of course be higher, hence be a super-group of that particular point group.
not a structural phase transition can be of a second order, but we will not consider this particular feature of the symmetry relationship in this KJM5110 course.

**Structure chemical considerations**
The group–subgroup relationships are often a valuable aid to present similarity between crystal structures. The symmetry of a real material is not always as high as considered ideally. The reduction in symmetry may arise owing to directional chemical bonds, inert electron pairs, d-electron effects such as Jahn–Teller distortions, ordering of atoms or via soft modes (lattice vibrations).

The reduction in symmetry is often rather small. Sometimes it represents only a nearly infinitesimal step away from the ideally considered structure. In such cases the real structure will be likely to have the maximal subgroup of the ideal space group with higher symmetry.

In many cases the real structure has a space group that is not a maximal subgroup, but a general subgroup of the ideal space group with higher symmetry. In such cases it is desirable to relate the symmetry relationship between the structures by dividing the total symmetry reduction into smaller and more transparent steps, in which the group–maximal subgroup relation would be valid.

**FORMULATION OF THE SYMMETRY REDUCTION, STEP BY STEP**
The symmetry reduction can be described in a relatively simple progression diagram:

Higher symmetry: Symbol of the space group G
the structure description

↓

Type and index of the maximal subgroup

Unit-cell transformation

Shift of origin

Lower symmetry: Symbol of the maximal subgroup S of G
the structure description

There are three possible types of the group–subgroup relations:

1. Those called *translationengleich*; with t as a shorthand. The subgroup S contains all translations of the group G. The crystal class of S has lower symmetry than the crystal class of G.

2. Those called *klassengleich*; the shorthand is k. The subgroup S and group G belong to the same crystal class, but are of different space group type.

3. Those called as “equivalent”; the shorthand is e or i (for isomorphous). Here S and G belong to the same space-group type, but S has lost some translation symmetry relative to G.

Furthermore:
a. The index of the subgroup gives the amount of cosets of $S$ into which $G$ can be decomposed. As a rule are not all symmetry elements of $G$ retained in $S$. The reciprocal value of the index is the fraction of the symmetry elements of $G$ that has been retained in $S$. If the index is a prime number (2, or 3, as an example) the subgroup is maximal.

b. The basis vector for the unit cell with subgroup $S$ obtains as a linear combination of vectors of the unit cell with group $G$.

c. The $x, y, z$ coordinates of the origin for $S$ are expressed in relation to the coordinate system of $G$.

The relations in Figure 11 between space groups $C2/m$, $P2/m$, $C2$ and $C2/m$ may illustrate the concepts of the $\text{klassengleich}$, $\text{translationengleich}$, as well as of the $\text{isomorph}$ (equivalent) group–subgroup relations.

![Figure 11: Relations between the G space group C2/m (top left) and the maximal translationengleich, klassengleich and isomorph subgroups S](image)

**EXAMPLES**

In the following a series of examples will be discussed. These are in general taken from a review paper\(^{11}\) of Hans Bärnighausen (Professor of Inorganic chemistry at the University of Karlsruhe). The group subgroup relations are of various types, and involve cases of:

1. The space group for a given crystal structure is a maximal subgroup of a space group that belongs to an ideal structure whose maximal subgroup is:
   a. $\text{translationengleich}$ (low ↔ high quartz, $\alpha$ ↔ $\beta$-Sn);
   b. $\text{klassengleich}$ (comparison of Rh$_5$Ge$_3$ and Ca$_5$Sb$_3$-type structures);
   c. equivalent or isomorphic (comparison of CuF$_2$ and VO$_2$-type structures).

---

\(^{11}\) Bärnighausen H., MATCH. (1980) 9, 139–175.
2. The space group for a given crystal structure is a general subgroup of another structure (comparison of NiAs and MnP-type structures).

3. Space groups of two or more different structures that have a common supergroup.

**SPACE GROUP OF A GIVEN CRYSTAL STRUCTURE AS MAXIMAL SUBGROUP OF SPACE GROUP OF ANOTHER (IDEAL) STRUCTURE**

Three different cases will be reviewed, of a *translationengleich*, *klassengleich* and an equivalent subgroup, respectively.

**Cases where the maximal subgroup is translationengleich, low ↔ high quartz, α ↔ βSn**

Quartz, SiO₂, undergoes a reversible transformation between the low and high modification at 846 K. The phase transition is displacive, according to Burger’s notation. The two modifications crystallize in the following space groups:

- High quartz: \( P\bar{6}_222 \) (space group No. 182)
- Low quartz: \( P_3221 \) (space group No. 154)

In the International Tables for Crystallography one can find that the space group \( P_3221 \) has \( P\bar{6}_222 \) (not \( P\bar{6}_222 \)) as its minimal non-isomorphic supergroup. The index of the subgroup is 2.

The translation lattice is unchanged and the group–subgroup relation is *translationengleich*. However, one twofold axis is lost under the transition, and low quartz is somewhat deformed by a slight torsion of the tetrahedra. In high quartz, all Si atoms are symmetrically equivalent; in low quartz, there are two crystallographically different Si atoms in the asymmetrical unit.¹²

With the help of the introduced symbolism, the transition can be described as follows:

\[
\begin{align*}
T & \uparrow \\
(K) & \\
P\bar{6}_222 & \downarrow t_2 \\
& \downarrow P_3221
\end{align*}
\]

*Figure 12: Relation between space groups \( P\bar{6}_222 \) and \( P_3221 \) of high- and low-quartz, respectively*

The transformation from β- to α-Sn is a metal–insulator¹³ transition and occurs rather slowly upon cooling through the transition temperature of 286 K. The inverse formation of metallic β-Sn upon heating is supported by pressure. The two structures are compared in Figure 13. The crystal structure of the semiconducting α-Sn (grey tin) is of the diamond type. The relative atomic coordinates \( x, y, z \) of β-Sn are in fact identical to those of α-Sn, but the \( z \) axis is dramatically shortened and the remaining two axes somewhat expanded. As a result, the metallic β form has a significantly higher density than the cubic α form of the diamond type. Such a phase transition is classified as “dilatational” in the Burger’s system of phase transitions.

¹² Which means that upon cooling through the transition, so-called twins will be likely to form. This will have consequences for the piezoelectric properties of the low-quartz whose space group is non-centrosymmetric. The twin formation will act by zeroing the polar components.

¹³ The term metal–insulator transition is often used generally even though the product is a semiconductor as is the present case.
The \( \alpha \)-Sn allotrope adopts space group \( Fd\bar{3}m \) (No. 227), full symbol \( F 4_1/d -3 2/m \), whereas \( \beta \)-Sn crystallizes in \( I4_1/ amd \) (No.141), with full symbol \( I 4_1/a 2/m 2/d \). Some “technical” problems arise in this example, because relationship of these two structures would best be described on an \( F \) unit cell for both (compare in Figure 13). However, tetragonal \( F \) lattice is identical to the Bravais lattice \( I \) and hence not listed in the International Tables for Crystallography. Unit cell parameters are listed in Table 2. For the diamond-type structure, atoms are located in the 8a site, that is, in 000 and \( \frac{1}{2} \frac{1}{2} \frac{1}{2} \) plus those coordinates that follow from the \( F \) centering. These coordinates correspond directly to the \( \beta \)-Sn structure described on the non-conventional \( F \) centered tetragonal cell. The unit cell vectors of the non-conventional \( F \) and conventional \( I \) tetragonal cell of \( \beta \)-Sn are related as follows: 
\[
\begin{align*}
\mathbf{a}_F &= \mathbf{a}_I + \mathbf{b}_I, \\
\mathbf{b}_F &= \mathbf{b}_I - \mathbf{a}_I, \\
\mathbf{c}_F &= \mathbf{c}_I.
\end{align*}
\]

For determination whether the transition is translationengleich or not, the choice of the unit cell is of course irrelevant. However, these two choices bring two different sets of symbols, hence two possible charts that relate \( \alpha \)-Sn and \( \beta \)-Sn:

### Table 2: Unit-cell parameters for \( \alpha \)-Sn and for \( \beta \)-Sn in the non-conventional \( F \) and conventional \( I \) tetragonal cell.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Full symbol of the space group</th>
<th>( a ) (Å)</th>
<th>( b ) (Å)</th>
<th>( c ) (Å)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-Sn</td>
<td>( F 4_1/d -3 2/m )</td>
<td>6.491</td>
<td>6.491</td>
<td>6.491</td>
<td></td>
</tr>
<tr>
<td>( \beta )-Sn</td>
<td>( F 4_1/d 2/d 2/m )</td>
<td>8.23</td>
<td>8.23</td>
<td>3.175</td>
<td>Non-conventional cell</td>
</tr>
<tr>
<td>( \beta )-Sn</td>
<td>( I 4_1/a 2/m 2/d )</td>
<td>5.82</td>
<td>5.82</td>
<td>3.175</td>
<td>Conventional cell</td>
</tr>
</tbody>
</table>

\[14\] In the conventional cell of half the volume, atoms occupy 4a site: 000, \( \frac{1}{2} \frac{1}{2} \frac{1}{2} \), \( \frac{1}{2} \frac{1}{2} \frac{1}{2} \), \( \frac{1}{2} \frac{1}{2} \frac{1}{2} \).
Cases where the maximal subgroup is klassengleich, comparison of the Rh₅Ge₃ and Ca₅Ge₃-type structures

Both Rh₅Ge₃ and Ca₅Ge₃ crystallize in the orthorhombic crystal system. The unit-cell parameters are given in Table 3 and the atomic coordinates in Table 4.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ca₅Ge₃</th>
<th>Ca₅Ge₃</th>
<th>Rh₅Ge₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>12.502</td>
<td>8.287</td>
<td>5.42</td>
</tr>
<tr>
<td>b (Å)</td>
<td>9.512</td>
<td>12.502</td>
<td>10.32</td>
</tr>
<tr>
<td>c (Å)</td>
<td>8.287</td>
<td>9.512</td>
<td>3.96</td>
</tr>
<tr>
<td>Space group</td>
<td>Pnma</td>
<td>Pbnm</td>
<td>Pbam</td>
</tr>
<tr>
<td>Formula units/cell</td>
<td>Z = 4</td>
<td>Z = 4</td>
<td>Z = 2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>in site</th>
<th>general coordinates</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh1</td>
<td>4h</td>
<td>x y ½</td>
<td>0.348</td>
<td>0.280</td>
<td>½</td>
</tr>
<tr>
<td>Rh2</td>
<td>4g</td>
<td>x y 0</td>
<td>0.170</td>
<td>0.107</td>
<td>0</td>
</tr>
<tr>
<td>Rh3</td>
<td>2d</td>
<td>0 ½ ½</td>
<td>0</td>
<td>½</td>
<td>½</td>
</tr>
<tr>
<td>Ge1</td>
<td>2b</td>
<td>0 0 ½</td>
<td>0</td>
<td>0</td>
<td>½</td>
</tr>
<tr>
<td>Ge2</td>
<td>4g</td>
<td>x y 0</td>
<td>0.612</td>
<td>0.152</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 14: Symmetry relations between α-Sn and β-Sn. The conventional cell is applied on the right hand side.
Table 5: Atomic coordinates for Ca₅Ge₃ in the Pbnm setting of Pnma (No.62)

<table>
<thead>
<tr>
<th>Atom</th>
<th>in site</th>
<th>general coordinates</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca1</td>
<td>4c</td>
<td>x y 1/4</td>
<td>0.321</td>
<td>0.272</td>
<td>1/4</td>
</tr>
<tr>
<td>Ca2</td>
<td>8d</td>
<td>x y 1/4</td>
<td>0.193</td>
<td>0.075</td>
<td>0.957</td>
</tr>
<tr>
<td>Ca3</td>
<td>4c</td>
<td>x y 1/4</td>
<td>0.465</td>
<td>0.994</td>
<td>1/4</td>
</tr>
<tr>
<td>Ca4</td>
<td>4c</td>
<td>x y 1/4</td>
<td>0.851</td>
<td>0.211</td>
<td>1/4</td>
</tr>
<tr>
<td>Sb1</td>
<td>4c</td>
<td>x y 1/4</td>
<td>0.079</td>
<td>0.016</td>
<td>1/4</td>
</tr>
<tr>
<td>Sb2</td>
<td>8d</td>
<td>x y 1/4</td>
<td>0.567</td>
<td>0.170</td>
<td>0.015</td>
</tr>
</tbody>
</table>

In order to compare these two structure types, it is reasonable to transform the unit cell for Ca₅Ge₃ (Pnma; No.62) into the non-standard setting Pbnm (Table 3 and 5).

Exercise 13: Draw projections of Ca₅Ge₃ and Rh₅Ge₃ on the bc plane in the respective space groups Pbnm and Pbam. Describe their differences. Identify the symmetry elements (rotational axes, mirror planes, screw axes, glide planes and inversions).

From Table 3 we can see that the unit cell of Ca₅Ge₃ contains 4 formula units, whereas that of Rh₅Ge₃ contains only 2 formula units. This is accomplished by doubling the c axis for Ca₅Ge₃. The index for this classification is 2. Doubling of the c axis removed some of the symmetry elements (as you can see when working on Exercise 13), so that only half of the mirrors, rotation axes and inversions is retained. Accordingly, the Ca₅Ge₃ structure has more degrees of freedom for placement of atoms. This structure can therefore be more deformed than the ideal structure of higher symmetry. According to this reasoning, one can understand the Ca₅Ge₃ structure as a deformed variant of Rh₅Ge₃. The kinship of symmetry between these two structures can be described in the following scheme:

\[
\begin{array}{c}
P b a m \\
\text{Rh₅Ge₃}
\end{array}
\]

\[
\begin{array}{c}
k2 \\
\text{a b 2c}
\end{array}
\]

\[
\begin{array}{c}
P b n m \\
\text{Ca₅Sb₃}
\end{array}
\]

Figure 15: Symmetry relationship between structures of Ca₅Ge₃ and Rh₅Ge₃
**Cases where the maximal subgroup is equivalent (or isomorphic); comparison of the CuF₂ and VO₂ structures**

In order to solve cases when the maximal subgroup is equivalent (or isomorphic), one and the same space group is taken into the group–subgroup considerations (as a set of iso-symbolic space groups). Such situation occurs for CuF₂ and VO₂, which both are deformed variants of the rutile structure. The crystallographic data for these two structures are given in Tables 6, 7 and 8.

<table>
<thead>
<tr>
<th>Table 6: Unit cell parameters for CuF₂ and VO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
</tr>
<tr>
<td>CuF₂</td>
</tr>
<tr>
<td>VO₂</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 7: Atomic coordinates for CuF₂ in the space group ( P2_1/a ) (No.14)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom</td>
</tr>
<tr>
<td>Cu</td>
</tr>
<tr>
<td>F</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 8: Atomic coordinates for VO₂ in the space group ( P2_1/a ) (No.14)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom</td>
</tr>
<tr>
<td>V</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>O</td>
</tr>
</tbody>
</table>

The symmetry relations between these two structures are expressed in the adopted nomenclature as follows:
Cases where the space group of one structure is a general subgroup of another structure; comparison of the structures of NiAs and MnP

In the first chapter of this text, the MnP structure was discussed briefly (page 6). The hexagonal structure of NiAs is known from earlier courses. In the following, we shall describe the kinship between NiAs and MnP-type structures in the light of the group–subgroup considerations. The structure of MnP can be understood as an orthorhombically deformed structure of NiAs, in which deformations cause the metal atoms to come into a closer contact with each other and establish bonding interactions. Several compounds exhibit continuous phase transitions of the second order between the NiAs and MnP-type structures as a function of temperature. According to Burgers nomenclature, this transition is displacive. The crystallographic data for the solid solution MnAs$_{0.90}$P$_{0.10}$, which is a good example of this transition from the MnP to the NiAs type, are listed in Tables 9, 10 and 11.

Table 9: Comparison of the unit-cell parameters for MnAs$_{0.90}$P$_{0.10}$ adopting the NiAs and MnP structure types

<table>
<thead>
<tr>
<th>Structure type</th>
<th>In space-group description</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiAs</td>
<td>$P\overline{6}_3/m\text{m}c$</td>
<td>3.68</td>
<td></td>
<td>5.76</td>
<td>600</td>
</tr>
<tr>
<td>NiAs</td>
<td>$P\ n\ m\ a$</td>
<td></td>
<td>3.68</td>
<td>5.76</td>
<td>600</td>
</tr>
<tr>
<td>MnP</td>
<td>$P\ n\ m\ a$</td>
<td>5.58</td>
<td>3.52</td>
<td>6.22</td>
<td>300</td>
</tr>
</tbody>
</table>

Table 10: Atomic coordinates for MnAs$_{0.90}$P$_{0.10}$ in the space group $P\overline{6}_3/mmc$ (No.194)

<table>
<thead>
<tr>
<th>Atom</th>
<th>in site</th>
<th>general coordinates</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>2a</td>
<td>0 0 0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>As,P</td>
<td>2c</td>
<td>1/3 2/3 1/4</td>
<td>1/3</td>
<td>2/3</td>
<td>1/4</td>
</tr>
</tbody>
</table>
Table 11: Atomic coordinates for MnAs0.90P0.10 in the space group Pnma (No.62)

<table>
<thead>
<tr>
<th>Atom</th>
<th>in site</th>
<th>general coordinates</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>4c</td>
<td>(x = \frac{1}{4} ) (z = 0.01) (\frac{1}{4} = 0.21)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As,P</td>
<td>4c</td>
<td>(x = \frac{1}{4} ) (z = 0.21) (\frac{1}{4} = 0.58)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The MnP and NiAs structures are related via projection that is shown in Figure 17. Figure 18 shows the relation between the unit-cell vectors of a hexagonal lattice and a cell of orthorhombic symmetry that can be chosen in it, the so called orthohexagonal cell. From Figures 17 and 18 we can see that the unit-cell vectors of the MnP and NiAs structures can be related as follows: \(a_{\text{MnP}} = c_{\text{NiAs}}\), \(b_{\text{MnP}} = a_{\text{NiAs}} + b_{\text{NiAs}}\) and \(c_{\text{MnP}} = a_{\text{NiAs}} - b_{\text{NiAs}}\), in matrix notation:

\[
\begin{pmatrix}
a_{\text{MnP}} \\
b_{\text{MnP}} \\
c_{\text{MnP}}
\end{pmatrix} = \begin{pmatrix}
0 & 0 & 1 \\
1 & 1 & 0 \\
1 & -1 & 0
\end{pmatrix}
\begin{pmatrix}
a_{\text{NiAs}} \\
b_{\text{NiAs}} \\
c_{\text{NiAs}}
\end{pmatrix}
\]

From Figure 18 it follows that the ideal orthohexagonal unit-cell dimensions are \(c_{\text{hex}}, a_{\text{hex}}\) and \(a_{\text{hex}} \sqrt{3}\), where the subscript hex refers to the hexagonal cell (compare data for 600 K in Table 9). The formal symmetry reduction from \(P6_3/mmc\) (the full symbol \(P 6_3/m 2/m 2/\bar{1}\)) to \(Pnma\) (the full symbol \(P 2_1/n 2_1/m 2_1/\bar{a}\)) must be done in two steps if one wishes to proceed via maximal subgroups. In order to make this description easier, the space group \(Pnma\) is used in its non-standard setting \(Pmcn\).

![Figure 17: Projections that compare the MnP and NiAs structures.\(^{15}\) The fractions (\(\frac{1}{4}\)) represent relative heights above the projection plane](image)

\(^{15}\) Of course, \(b = a\) in the hexagonal crystal system.
Figure 18: The \textit{Cmcm} orthohexagonal unit cell of the ideal MnP type, drawn in the \textit{ab} plane of a quadruplet of \textit{P6}_3/mmc hexagonal cells of NiAs

Exercise 14: Transform unit-cell parameters and atomic coordinates for MnAs$_{0.90}$P$_{0.10}$ at 300 K from the \textit{Pnma} to the \textit{Pmcn} setting.

The change from the hexagonal to the orthohexagonal cell does not in fact change any of the translations present in the standard hexagonal description of the structure and it is therefore \textit{translationengleich}. It is a mere choice of a larger unit cell. This orthohexagonal cell is \textit{C}-centered, which means that points separated by the translation vector ($\frac{1}{2}$, $\frac{1}{2}$, 0) have identical surroundings. The space group is \textit{Cmcm} (No.63), with the full symbol \textit{C}$_2$/\textit{m}$_2$/\textit{c}$_2$/\textit{m}, and it is a maximal non-isomorphic subgroup to \textit{P6}_3/mmc with index 3, something that can be read in the listing of \textit{P6}_3/mmc (No.194) in the International Tables for Crystallography. The step between the hexagonal and orthohexagonal cell can be described as follows:

\begin{equation}
\begin{array}{c}
P \ 6\overline{3}/m \ 2/m \ 2/c \\
\text{NiAs type} \\
\end{array}
\end{equation}

\begin{equation}
\begin{array}{c}
t_3 \\
\text{orthohexagonal NiAs type} \\
\end{array}
\end{equation}

Figure 19: Symmetry relations between hexagonal and orthohexagonal NiAs

The next step in the symmetry reduction involves removal of the centering \textit{C}. This means that a half of the translations is taken away and the two points no longer have identical surroundings. This relation is hence \textit{classengleich} with index 2, where the latter is read in the listing of \textit{Cmcm} (No.63) in the International Tables for Crystallography.

Both MnP and NiAs structure types are centrosymmetric. However, some of the symmetry centres are lost under way towards the deformed MnP-type structure. From Figure 17 it can be seen that the
symmetry center in the origin of the NiAs-type structure is lost. The origin for the MnP-type structure is therefore chosen in another point, which is centrosymmetric:

\[
C \ 2/m \ 2/c \ 2/m \\
\text{orthohexagonal NiAs type}
\]

\[
k2 \\
\frac{1}{4}, -\frac{1}{4}, 0
\]

\[
P \ 2_1/m \ 2_1/c \ 2_1/n \\
\text{NiAs type}
\]

**Figure 20:** Origin shift between the orthohexagonal NiAs type and the MnP type structure

**A case where two or several different structures have a common supergroup**

Consider symmetry relations between space groups \(C\ 2/m\), \(I\ 2/c\) and \(P\ 2_1/a\) in Figure 21:

\[
C \ 2/m \ 1 \\
| \\
k2 \\
\text{a b 2c}
\]

\[
I \ 2/c \ 1 \\
\text{RbAuCl}_4
\]

\[
P \ 2_1/a \ 1 \\
\text{RbAuBr}_4
\]

**Figure 21:** Relation between \(I\ 2/c\) structure of RbAuCl\(_4\) and \(P\ 2_1/a\) structure of RbAuBr\(_4\)

The crystal structures of RbAuCl\(_4\) and RbAuBr\(_4\) have clearly similar features. Their space groups have a common supergroup, \(C\ 2/m\). This means that both \(I\ 2/c\) and \(P\ 2_1/a\) are maximal subgroups of \(C\ 2/m\). In this case it would be possible to construct a common ideal mother structure from which both RbAuCl\(_4\) and RbAuBr\(_4\) structures can be derived by suitable deformations.

**BÄRNIGHAUSEN’S FAMILY TREES OF STRUCTURES**

The group–subgroup considerations can be used to create so called family trees of crystallographically related structures. These diagrams are able to relate structures irrespective of small deviations of composition, purely on symmetry basis. Two examples are shown in Figures 22 and 23, respectively, both for perovskite-type structures.
Figure 22: Family tree of perovskite-type structures of composition ABX₃; after Bärnighausen
Since these early times, these family tries have been revisited. Modified and updated versions, as well as those that include more complex perovskite variants, can be found, for example, in Bock and Müller, Acta Cryst. (2002) B58, 594–606.
Appendix: An example of the space-group listing from the International Tables for Crystallography

\[ P \overline{n} m a \qquad D_{2h}^{16} \qquad m m m \quad \text{Orthorhombic} \]

No. 62 \quad P 2_1/n 2_1/m 2_1/a

Patterson symmetry \( P \overline{m} m m \)

\[
\begin{align*}
\text{Origin at } & \begin{array}{l}
1 \\
\text{on } 12, 1 \\
\end{array} \\
\text{Asymmetric unit } & \begin{array}{l}
0 \leq x \leq 1; \quad 0 \leq y \leq 1; \quad 0 \leq z \leq 1 \\
\end{array}
\end{align*}
\]

Symmetry operations

\begin{align*}
(1) & \begin{array}{ll}
1 & 1 \\
\end{array} \\
(2) & \begin{array}{ll}
2(0,0,1) & 1,0,z \\
\end{array} \\
(3) & \begin{array}{ll}
2(0,1,0) & 0,y,0 \\
\end{array} \\
(4) & \begin{array}{ll}
2(1,0,0) & x,1,z \\
\end{array} \\
(5) & \begin{array}{ll}
0,0,0 & 1,0,0 \\
\end{array} \\
(6) & \begin{array}{ll}
x,y,1 \\
\end{array} \\
(7) & \begin{array}{ll}
x,1,z \\
\end{array} \\
(8) & \begin{array}{ll}
2(0,1,1) & 1,y,0 \\
\end{array}
\end{align*}
CONTINUED

No. 62

Pnma

Generators selected (1); t(1,0,0); t(0,1,0); t(0,0,1); (2); (3); (5)

Positions

Multiplicity, Wyckoff letter, Site symmetry

Coordinates

\[
\begin{align*}
8 & d \begin{array}{l} \{1\} x,y,z \end{array} \\
& \begin{array}{l} \{2\} x+y, z+\frac{1}{2} \\
& \{3\} x, y+\frac{1}{2}, z \\
& \{4\} x+\frac{1}{2}, y+z+\frac{1}{2} \\
& \{5\} x, y, z \\
& \{6\} x+y+z+\frac{1}{2} \\
& \{7\} x, y+\frac{1}{2}, z \\
& \{8\} x+\frac{1}{2}, y+z+\frac{1}{2}
\end{array}
\end{align*}
\]

Reflection conditions

General:

\[
\begin{align*}
0kl & : k+l = 2n \\
hk0 & : k = 2n \\
h00 & : h = 2n \\
o0l & : k = 2n \\
o00 & : l = 2n
\end{align*}
\]

Special: as above, plus

no extra conditions

\[
\begin{align*}
hkl & : h+1, k = 2n \\
hkl & : h+1, k = 2n
\end{align*}
\]

Symmetry of special projections

Along [001] \( p2g_m \)

\[
\begin{align*}
a' &= a \\
b' &= b
\end{align*}
\]

Origin at 0,0,0

Along [100] \( c 2m\)

\[
\begin{align*}
a' &= b \\
b' &= c
\end{align*}
\]

Origin at \( x, 1, 1 \)

Maximal non-isomorphic subgroups

\[
\begin{array}{|c|c|c|}
\hline
\text{I} & [2] P 2_1 2_1 2_1 & 1; 2; 3; 4 \\
& [2] P 1 1 2_1 /a (P 2_1 /c) & 1; 2; 3; 5; 7 \\
& [2] P 1 1 2_1 /m (P 2_1 /m) & 1; 3; 5; 7 \\
& [2] P 2_1 /m 1 1 (P 2_1 /c) & 1; 4; 5; 8 \\
& [2] P m n 2_1 (P m n 2_1) & 1; 2; 7; 8 \\
& [2] M n 2_1 (P n 2_1) & 1; 3; 5; 7 \\
& [2] P 2_1 m a (P m c 2_1) & 1; 4; 6; 7 \\
\hline
\end{array}
\]

Ha none

Hb none

Maximal isomorphic subgroups of lowest index

\[
\begin{align*}
\text{Ic} & \quad [3] P n m a (a' = 3a); [3] P n m a (b' = 3b); [3] P n m a (c' = 3c)
\end{align*}
\]

Minimal non-isomorphic supergroups

\[
\begin{align*}
\text{I} & \quad \text{none}
\end{align*}
\]

\[
\begin{align*}
\text{II} & \quad [2] A m m a (C m m c) ; [2] B b m m (C m c m) ; [2] C m b (C m c a) ; [2] I m m a ; [2] P n m m (2a' = a)(P m m n) ; \\
& \quad [2] P c m a (2b' = b)(P b m a) ; [2] P b m a (2c' = c)(P b c m)
\end{align*}
\]