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EXERCISES

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Chapter 1

Space-group symmetry data in International Tables for Crystallography, Volume A and Volume A1: Basic concepts and notation

1.1 Crystallographic Symmetry Operations

In order to describe the symmetry operations analytically one introduces a coordinate system $\{O, \mathbf{a}, \mathbf{b}, \mathbf{c}\}$, consisting of a set of basis vectors \mathbf{a} , \mathbf{b} , \mathbf{c} and an origin O. A symmetry operation can be regarded as an instruction of how to calculate the coordinates \tilde{x} , \tilde{y} , \tilde{z} of the image point \tilde{X} from the coordinates x, y, z of the original point X.

The equations are

$$\tilde{x} = W_{11} x + W_{12} y + W_{13} z + w_1
\tilde{y} = W_{21} x + W_{22} y + W_{23} z + w_2
\tilde{z} = W_{31} x + W_{32} y + W_{33} z + w_3,$$
(1.1.1)

These equations can be written using the matrix formalism:

$$\tilde{\boldsymbol{x}} = \boldsymbol{W} \boldsymbol{x} + \boldsymbol{w} = (\boldsymbol{W}, \boldsymbol{w}) \boldsymbol{x}$$
 where

the symmetry operations $(\boldsymbol{W}, \boldsymbol{w})$ are given in a matrix-column form consisting of a (3×3) matrix (linear) part \boldsymbol{W} and a (3×1) -column(translation) part \boldsymbol{w} :

$$(\boldsymbol{W}, \boldsymbol{w}) = \begin{pmatrix} W_{11} & W_{12} & W_{13} & w_1 \\ W_{21} & W_{22} & W_{23} & w_2 \\ W_{31} & W_{32} & W_{33} & w_3 \end{pmatrix}$$
(1.1.2)

Apart from the matrix-column pair presentation of $(\boldsymbol{W}, \boldsymbol{w})$ often the so-called *short-hand notation* for the symmetry operations is used. It is obtained from the left-hand side of equ. (1.1.1) by omitting the terms with coefficients 0 and writing in one line the three different rows of equ.(1.1.1), separated by commas.

For example, the matrix-column pair $(\boldsymbol{W}, \boldsymbol{w}) = \begin{pmatrix} \bar{1} & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ 1/2 \end{pmatrix}$ is represented in short-

hand notation by the coordinate triplet: $\overline{x} + y, y, \overline{z} + 1/2$. This is the entry (11) of the General positions of the space group $P6_522$, No. 179 (cf. the space-group tables of International Tables for Crystallography, Volume A: Space-group symmetry, referred to as ITA).

1.1.1 Crystallographic Symmetry Operations and Their Representations by Matrices

Geometric meaning of matrix-column pairs (W, w)

The geometric meaning of a matrix-column pair (\mathbf{W}, \mathbf{w}) can be determined only if the reference coordinate system is known. The following procedure indicates the necessary steps for the complete geometric characterization of (\mathbf{W}, \mathbf{w}) .

Procedure for the geometric interpretation of (W, w)

- 1. W -information
 - (a) Type of isometry: the types 1,2,3,4,6 or $\overline{1},\overline{2},\overline{3},\overline{4},\overline{6}$ can be determined by the matrix invariants: det(W) and tr(W)

		$\det($	W)	= -	+1		det	(W)	= -	1
$\mathrm{tr}(\boldsymbol{W})$	3	2	1	0	-1	-3	-2	-1	0	1
type	1	6	4	3	2	Ī	$\overline{6}$	$\overline{4}$	$\bar{3}$	$\bar{2} = m$
order	1	6	4	3	2	2	6	4	6	2

- (b) Direction of \boldsymbol{u} the rotation or rotoinversion axis or the normal of the reflection plane
 - i. Rotations: Calculate the matrix $\mathbf{Y}(\mathbf{W}) = \mathbf{W}^{k-1} + \mathbf{W}^{k-2} + \ldots + \mathbf{W} + \mathbf{I}$. The elements of any non-zero column of \mathbf{Y} give the components of the vector \mathbf{u} with respect to the reference co-ordinate system.
 - ii. Rotoinversions: Calculate the matrix Y(-W). The elements of any non-zero column of Y give the components of the vector u with respect to the reference co-ordinate system. For $\overline{2} = m$, Y(-W) = -W + I.
- (c) Sense of rotation (for rotations or rotoinversions with k > 2): The sense of rotation is determined by the sign of the determinant of the matrix \mathbf{Z} , given by $\mathbf{Z} = [\mathbf{u}|\mathbf{x}|(\det \mathbf{W})\mathbf{W}\mathbf{x}]$, where \mathbf{u} is the vector of 1b and \mathbf{x} is a non-parallel vector of \mathbf{u} , e.g. one of the basis vectors.
- 2. \boldsymbol{w} -information
 - (a) Intrinsic translation part (screw or glide component) t/k
 - i. Screw rotations

$$t/k = \frac{1}{k} \boldsymbol{Y} \boldsymbol{w}, \text{where } \boldsymbol{W}^k = \boldsymbol{I}$$
 (1.1.3)

ii. Glide reflections

$$\boldsymbol{t}/k = \frac{1}{2}(\boldsymbol{W} + \boldsymbol{I})\boldsymbol{w}$$
(1.1.4)

(b) Location of the symmetry elements (fixed points x_F)

ii. $t/k \neq 0$

i.
$$\boldsymbol{t}/k = 0$$

 $(\boldsymbol{W}, \boldsymbol{w})\boldsymbol{x}_F = \boldsymbol{x}_F.$ (1.1.5)

$$(\boldsymbol{W}, \boldsymbol{w}_{lp})\boldsymbol{x}_F = \boldsymbol{x}_F. \tag{1.1.6}$$

The column $w_{lp} = w - t/k$ is the so-called *location part* as it determines the position of the rotation or screw-rotation axis or of the reflection or glide-reflection plane in space.

The formulæ of this section enable the user to find the geometric contents of any symmetry operation. In reality, *ITA* have provided the necessary information for all symmetry operations which are listed in the plane–group or space–group tables. The entries of the *General position* are numbered. The geometric meaning of these entries is listed under the same number in the block **Symmetry operations** in the tables of *ITA*. The explanation of the symbols for the symmetry operations is found in Sections 2.9 and 11.2 of *ITA*.

1.1.2 Symmetry Operations and Symmetry Elements

The definitions of *symmetry elements*, *geometric elements* and the related *element sets* of symmetry operations for crystallographic space groups and point groups are summarised in the following table.

Name of symmetry element	Geometric element	Defining operation (d.o)	Operations in element set
Mirror plane	Plane A	Reflection in A	D.o. and its coplanar equivalents [*]
Glide plane	Plane A	Glide reflection in A; $2\nu \pmod{\nu}$ a lattice translation	D.o. and its coplanar equivalents [*]
Rotation axis	Line b	Rotation around b, angle $2\pi/n$ n = 2, 3, 4 or 6	1st,, $(n-1)$ th powers of d.o. and their coaxial equivalents [†]
Screw axis	Line b	Screw rotation around b, angle $2\pi/n$, u = j/n times shortest lattice translation along b, right-hand screw, $n = 2, 3, 4$ or $6, j = 1, \dots, (n-1)$	1st,, $(n-1)$ th powers of d.o. and their coaxial equivalents [†]
Rotoinversion axis	Line b and point P on b	Rotoinversion: rotation around b , angle $2\pi/n$, and inversion through P , $n = 3, 4$ or 6	D.o. and its inverse
Center	Point P	Inversion through P	D.o. only

 Table 1.1.1
 Symmetry elements in point and space groups

* That is, all glide reflections with the same reflection plane, with glide vectors \mathbf{v} differing from that of d.o. (taken to be zero for reflections) by a lattice translation vector. The glide planes a, b, c, d and e are distinguished.

[†] That is, all rotations and screw rotations with the same axis b, the same angle and sense of rotation and the same screw vector **u** (zero for rotation) up to a lattice translation vector.

^{\ddagger} Eg, g is replaced by a, b, c, n, dor e for specific kinds of glide planes.

Examples

1. Glide planes

The element set of a glide plane with a glide vector \mathbf{v} consists of infinitely many different glide reflections with glide vectors that are obtained from \mathbf{v} by adding any lattice translation parallel to the glide plane, including centring translations of the centred cells. If, however, among the infinitely many glide reflections of the element set of the same plane there exists one operation with zero glide vector, then this operation is taken as *defining operation*, *i. e.* the symmetry element is a mirror plane.

- (a) The symmetry operation x + 5/2, y 7/2, -z + 3 is a glide reflection. Its geometric element is a the plane x, y, 3/2. Its symmetry element is a glide plane in space group *Pmmn* because there is no lattice translation by which the glide vector can be changed to o. If, however, the same mapping is a symmetry operation of space group *Cmmm*, then its symmetry element is a reflection plane, because the glide vector with components 5/2, -7/2 can be cancelled through a translation $(2 + 1/2)\mathbf{a} + (-4 + 1/2)\mathbf{b}$ which is a lattice translation in a *C* lattice. Evidently, the correct specification of the symmetry element is possible only with respect to a specific translation lattice.
- (b) Similarly, in *Cmma* with an *a*-glide reflection x + 1/2, y, \overline{z} also the *b*-glide reflection $x, y + 1/2, \overline{z}$ occurs. The geometric element is the plane x, y, 0 and the symmetry element is an *e*-glide plane.
- (c) More general, all vectors $(u + \frac{1}{2})\mathbf{a} + v\mathbf{b} + \frac{1}{2}k(\mathbf{a} + \mathbf{b})$, u, v, k integers, are glide vectors of *a*-glide reflections through the (001) plane of a space group with a *C*-centered lattice. Among them one finds a glide reflection *b* with a glide vector $\frac{1}{2}\mathbf{b}$ related to $\frac{1}{2}\mathbf{a}$ by the centring translation; an *a*-glide reflection and a *b*-glide reflection share the same plane as a geometric element. Their symmetry element is thus an *e*-glide plane.
- 2. Screw axes

The element set of a screw axis is formed by a screw rotation of angle $2\pi/n$, its (n-1)th powers and all their co-axial equivalents that include all rotations and screw rotations with the same axis, the same angle and the same screw vector up to lattice translation vector (*i. e.* any screw vector obtained by adding a lattice translation vector, parallel to the screw axis). If any of the screw vectors is zero, then the symmetry element is a rotation axis.

- (a) $2_1 \parallel [001]$ in a primitive cell: The element set is formed by all twofold screw rotations with screw vectors of the type $(u \frac{1}{2})\mathbf{c}$, *i. e.* screw components as $\frac{1}{2}\mathbf{c}$, $-\frac{1}{2}\mathbf{c}$, $\frac{3}{2}\mathbf{c}$, *etc.*
- (b) The symmetry operation 4 x, -2 y, z + 5/2 is a screw rotation of space group $P222_1$. Its geometric element is the line 2, -1, z and its symmetry element is a screw axis.
- (c) The determination of the complete element set of a geometric element is important for the correct designation of the corresponding symmetry element. For example, the symmetry element of a twofold screw rotation with an axis through the origin is a twofold screw axis in the space group $P222_1$ but a fourfold screw axis in $P4_1$.

1.2 Site symmetry: General and Special positions

The concept of *Site symmetry*, *i.e.* the set of symmetry operations that leave a given point fixed, allows to define *General* and *Special positions* for space groups.

Let \mathcal{G} be a space group and X a point. The subgroup $\mathcal{S}_X = \{(\boldsymbol{W}, \boldsymbol{w})\}$ of all $(\boldsymbol{W}, \boldsymbol{w}) \in \mathcal{G}$ that leave X fixed, *i.e.* for which $(\boldsymbol{W}, \boldsymbol{w})X = X$ holds, is called the *site symmetry group* \mathcal{S}_X of \mathcal{G} for the point X.

!!

The group $S_X < \mathcal{G}$ is of finite order. If $S_X = \{I\}$, *i.e.* only the identity operation maps X onto itself, X is called a point of *General position*. Otherwise, if $S_X > \{I\}$, X is called a point of *Special position*. Each point X_i of a \mathcal{G} -orbit has its site symmetry group $S_i < \mathcal{G}$. The site symmetry groups S_i and S_j of two points X_i and X_j of the same \mathcal{G} -orbit are conjugate subgroups of \mathcal{G} : if $X_j = (\mathbf{W}, \mathbf{w})X_i$, $(\mathbf{W}, \mathbf{w}) \in \mathcal{G}$, then $S_j = (\mathbf{W}, \mathbf{w})S_i(\mathbf{W}, \mathbf{w})^{-1}$. For this reason, all points of one special position in *IT*A are described by the same site-symmetry symbol.

In *ITA* the so-called *oriented site-symmetry symbols* are used to show how the symmetry elements at a site are related to the symmetry elements of the crystal lattice. The oriented site-symmetry symbols of the site-symmetry groups display the same sequence of symmetry directions as the space-group symbol. Sets of equivalent symmetry directions that do not contribute any element to the site-symmetry group are represented by a dot.

1.3 Metric tensors. Simple crystallographic calculations: Distances and angles

When considering crystal structures, idealized as crystal patterns, frequently the values of distances between the atoms (bond lengths) and of the angles between atomic bonds (bonding angles) are required. In this section the necessary formulae for such calculations are derived.

1.3.1 Bond lengths

Let assume that the crystal structure is given by the coordinates of the atoms (better: of their centers) in a conventional coordinate system. Then the vectors between the points can be calculated by the differences of the point coordinates.

Let $XY = \mathbf{r} = r_1 \mathbf{a}_1 + r_2 \mathbf{a}_2 + r_3 \mathbf{a}_3$ be the vector from point X to point Y, $r_i = y_i - x_i$. The scalar product (\mathbf{r}, \mathbf{r}) of \mathbf{r} with itself is the square of the length r of \mathbf{r} . Thus

$$r^{2} = (\mathbf{r}, \mathbf{r}) = ((r_{1}\mathbf{a}_{1} + r_{2}\mathbf{a}_{2} + r_{3}\mathbf{a}_{3}), (r_{1}\mathbf{a}_{1} + r_{2}\mathbf{a}_{2} + r_{3}\mathbf{a}_{3})).$$

Because of the rules for scalar products, this can be written

$$r^{2} = (r_{1}\mathbf{a}_{1}, r_{1}\mathbf{a}_{1}) + (r_{2}\mathbf{a}_{2}, r_{2}\mathbf{a}_{2}) + (r_{3}\mathbf{a}_{3}, r_{3}\mathbf{a}_{3}) + 2(r_{2}\mathbf{a}_{2}, r_{3}\mathbf{a}_{3}) + 2(r_{3}\mathbf{a}_{3}, r_{1}\mathbf{a}_{1}) + 2(r_{1}\mathbf{a}_{1}, r_{2}\mathbf{a}_{2}).$$

It follows for the distance between the points X and Y

$$r^{2} = r_{1}^{2} a_{1}^{2} + r_{2}^{2} a_{2}^{2} + r_{3}^{2} a_{3}^{2} + 2 r_{2} r_{3} a_{2} a_{3} \cos \alpha_{1} + 2 r_{3} r_{1} a_{3} a_{1} \cos \alpha_{2} + 2 r_{1} r_{2} a_{1} a_{2} \cos \alpha_{3}.$$
(1.3.7)

Using this equation, bond distances can be calculated if the coefficients of the bond vector and the lattice constants of the crystal are known.

The general formula (1.3.7) becomes much simpler for the higher symmetric crystal systems. For example, referred to an orthonormal basis, equation (1.3.7) is reduced to

$$r^2 = r_1^2 + r_2^2 + r_3^2. (1.3.8)$$

Abbreviating $(\mathbf{a}_i, \mathbf{a}_k) = G_{ik} = a_i a_k \cos \alpha_j$ (j is defined for $i \neq k$: then $k \neq j \neq i$), this formula can be written as

$$r^{2} = \sum_{i,k=1}^{3} G_{ik} r_{i} r_{k}.$$
(1.3.9)

This result can be expressed in a matrix form introducing the so-called *metric tensor* (fundamental matrix) G of the coordinate basis. The scalar products of the basis vectors, designated by G_{ik} , i, k = 1, 2, 3, form the

fundamental matrix of the coordinate basis $\mathbf{G} = \begin{pmatrix} G_{11} & G_{12} & G_{13} \\ G_{21} & G_{22} & G_{23} \\ G_{31} & G_{32} & G_{33} \end{pmatrix}$. Because of $G_{ik} = G_{ki}$, \mathbf{G} is a

symmetric matrix.

Using the multiplication with rows and columns, the matrix form of the result (1.3.9) is given by:

$$r^2 = \boldsymbol{r}^{\mathrm{T}} \boldsymbol{G} \boldsymbol{r}, \qquad \text{with} \tag{1.3.10}$$

$$\boldsymbol{G} = \begin{pmatrix} a_1^2 & a_1 a_2 \cos \gamma & a_1 a_3 \cos \beta \\ a_1 a_2 \cos \gamma & a_2^2 & a_2 a_3 \cos \alpha \\ a_1 a_3 \cos \beta & a_2 a_3 \cos \alpha & a_3^2 \end{pmatrix}.$$
(1.3.11)

For orthonormal bases, because of G = I equation (1.3.11) becomes very simple:

$$r^2 = \boldsymbol{r}^{\mathrm{T}} \, \boldsymbol{r}. \tag{1.3.12}$$

1.3.2 Bonding angles

The (bonding) angle Φ between the (bond) vectors $\overrightarrow{SX} = \mathbf{r}$ and $\overrightarrow{SY} = \mathbf{t}$ is calculated using the equation

 $(\mathbf{r}, \mathbf{t}) = |\mathbf{r}| |\mathbf{t}| \cos \Phi = r t \cos \Phi$, see Fig. 1.3.2.1.



One obtains

$$r t \cos \Phi = r_1 t_1 a_1^2 + r_2 t_2 a_2^2 + r_3 t_3 a_3^2 + (r_2 t_3 + r_3 t_2) a_2 a_3 \cos \alpha_1 + (r_3 t_1 + r_1 t_3) a_1 a_3 \cos \alpha_2 + (r_1 t_2 + r_2 t_1) a_1 a_2 \cos \alpha_3.$$
(1.3.13)

Again one can use the coefficients G_{ik} to obtain,

$$\cos \Phi = \left(\sum_{i,k=1}^{3} G_{ik} r_i r_k\right)^{-1/2} \left(\sum_{i,k=1}^{3} G_{ik} t_i t_k\right)^{-1/2} \sum_{i,k=1}^{3} G_{ik} r_i t_k.$$
(1.3.14)

For orthonormal bases, equation (1.3.13) is reduced to

$$rt\cos\Phi = r_1t_1 + r_2t_2 + r_3t_3, \tag{1.3.15}$$

and equation 1.3.14 is replaced by

$$\cos \Phi = \frac{r_1 t_1 + r_2 t_2 + r_3 t_3}{r \ t}.$$
(1.3.16)

The "matrix" formula for the angle Φ between the vectors $(\overrightarrow{SX}) = \mathbf{r}$ and $(\overrightarrow{SY}) = \mathbf{t}$

is given by
$$rt \cos \Phi = \mathbf{r}^{\mathrm{T}} \mathbf{G} \mathbf{t}$$
, see Fig. 1.3.2.1, or

$$\cos \Phi = (\mathbf{r}^{\mathrm{T}} \mathbf{G} \mathbf{r})^{-1/2} (\mathbf{t}^{\mathrm{T}} \mathbf{G} \mathbf{t})^{-1/2} \mathbf{r}^{\mathrm{T}} \mathbf{G} \mathbf{t}.$$
 (1.3.17)

1.3.3 The volume of the unit cell

The volume V of the unit cell of a crystal structure, *i. e.* the body containing all points with coordinates $0 \le x_1, x_2, x_3 < 1$, can be calculated by the formula

$$\det(\boldsymbol{G}) = V^2. \tag{1.3.18}$$

In the general case one obtains

$$V^{2} = \begin{vmatrix} G_{11} & G_{12} & G_{13} \\ G_{21} & G_{22} & G_{23} \\ G_{31} & G_{32} & G_{33} \end{vmatrix} = a^{2} b^{2} c^{2} (1 - \cos^{2} \alpha - \cos^{2} \beta - \cos^{2} \gamma + 2 \cos \alpha \cos \beta \cos \gamma).$$
(1.3.19)

The formula (1.3.19) becomes simpler depending on the crystallographic symmetry, *i. e.* on the crystal system.

1.4 Coordinate Transformations: basic results

Let a coordinate system be given with a basis $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ and an origin O. The general transformation (affine transformation) of the coordinate system consists of two parts, a linear part and a shift of the origin. The transformation is uniquely defined by the (3×3) matrix P of the linear part and the (3×1) column matrix p containing the components of the shift vector p.

1. The linear part is described by a (3×3) matrix

$$\boldsymbol{P} = \begin{pmatrix} P_{11} \ P_{12} \ P_{13} \\ P_{21} \ P_{22} \ P_{23} \\ P_{31} \ P_{32} \ P_{33} \end{pmatrix}$$

i.e. the matrix which relates the new basis $(\mathbf{a}'_1, \mathbf{a}'_2, \mathbf{a}'_3)$ to the old basis $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ according to

$$(\mathbf{a}_{1}', \mathbf{a}_{2}', \mathbf{a}_{3}') = (\mathbf{a}_{1}, \mathbf{a}_{2}, \mathbf{a}_{3}) \mathbf{P} = (\mathbf{a}_{1}, \mathbf{a}_{2}, \mathbf{a}_{3}) \begin{pmatrix} P_{11} P_{12} P_{13} \\ P_{21} P_{22} P_{23} \\ P_{31} P_{32} P_{33} \end{pmatrix}.$$
 (1.4.20)

2. A shift of the origin is defined by the *shift vector*

$$p = (p_1 \mathbf{a}_1, p_2 \mathbf{a}_2, p_3 \mathbf{a}_3)$$

The basis vectors \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 are fixed at the origin O; the new basis vectors $(\mathbf{a}'_1, \mathbf{a}'_2, \mathbf{a}'_3)$ are fixed at the new origin O' that has the coordinates (p_1, p_2, p_3) in the old coordinate system.

The general affine transformation of the coordinates of a point X in direct space (given by the column $\boldsymbol{x} = (x_1, x_2, x_3)$) is given by the following formula:

$$x' = (P, p)^{-1}x = P^{-1}x - P^{-1}p = P^{-1}(x - p).$$
 (1.4.21)

The metric tensor G of the unit cell in direct lattice is transformed by the matrix P as follows:

$$\boldsymbol{G}' = \boldsymbol{P}^t \boldsymbol{G} \boldsymbol{P} \tag{1.4.22}$$

where P^t is the transposed matrix of P.

The volume of the unit cell V changes with the transformation. The volume of the new unit cell V' is obtained by

$$V' = \det(\boldsymbol{P})V \tag{1.4.23}$$

with $det(\mathbf{P})$ being the determinant of the matrix \mathbf{P} .

Also, the matrix-column pairs of the symmetry operations are changed by a change of the coordinate system. If a symmetry operation is described in the "old" (unprimed) coordinate system by the matrix-column pair (\mathbf{W}, \mathbf{w}) and in the "new" (primed) coordinate system by the pair $(\mathbf{W}', \mathbf{w}')$, then the relation between the pairs (\mathbf{W}, \mathbf{w}) and $(\mathbf{W}', \mathbf{w}')$ is given by:

$$(\mathbf{W}', \mathbf{w}') = (\mathbf{P}, \mathbf{p})^{-1} (\mathbf{W}, \mathbf{w}) (\mathbf{P}, \mathbf{p})$$
 (1.4.24)

The coordinate systems of the space groups used by the programs and database on the Bilbao Crystallographic Server (referred to as *standard* or *default* settings) for the presentation of the space-group data coincide with the conventional space-group descriptions found in *ITA*. For space groups with more than one description in *ITA*, the following settings are chosen as standard: *unique axis b* setting, *cell choice* 1 for monoclinic groups, *hexagonal axes* setting for rhombohedral groups, and *origin choice* 2 (origin in $\overline{1}$) for the centrosymmetric groups listed with respect to two origins in *ITA*. Optionally certain applications allow the usage of the so-called *ITA* settings which include all conventional settings applied in *ITA* (*e.g. rhombohedral axes* setting for rhombohedral groups, and *origin choice* 1 for the centrosymmetric groups) and the great variety of about 530 settings of monoclinic and orthorhombic groups listed in Table 4.3.2.1 of *ITA*. Settings different from the standard ones and the *ITA* settings are designated as *non-conventional*.

1.5 Group-subgroup relations of space groups

1.5.1 Basic definitions

A subset \mathcal{H} of elements of a group \mathcal{G} is called a *subgroup* of \mathcal{G} , $\mathcal{G} > \mathcal{H}$ if it fulfills the group postulates with respect to the law of composition of \mathcal{G} . In general, the group \mathcal{G} itself is included among the set of subgroups of \mathcal{G} , *i.e.* $\mathcal{G} \geq \mathcal{H}$. If $\mathcal{G} > \mathcal{H}$ is fulfilled, then the subgroup \mathcal{H} is called a *proper* subgroup of \mathcal{G} . In a relation $\mathcal{G} \geq \mathcal{H}$ or $\mathcal{G} > \mathcal{H}$, \mathcal{G} is called a *supergroup* of \mathcal{H} . A subgroup $\mathcal{H} < \mathcal{G}$ is a *maximal subgroup* if no group \mathcal{Z} exists for which $\mathcal{H} < \mathcal{Z} < \mathcal{G}$ holds. If \mathcal{H} is a maximal subgroup of \mathcal{G} , then \mathcal{G} is a *minimal supergroup* of \mathcal{H} .

Let $\mathcal{H} < \mathcal{G}$ be a subgroup of \mathcal{G} of order $|\mathcal{H}|$. Because \mathcal{H} is a proper subgroup of \mathcal{G} there must be elements $g_q \in \mathcal{G}$ which are not elements of \mathcal{H} . Let $g_2 \in \mathcal{G}$ be one of them. Then the set of elements $g_2 \mathcal{H} = \{g_2 h_j \mid h_j \in \mathcal{H}\}^1$ is a subset of elements of \mathcal{G} with the property that all its elements are different and that the sets \mathcal{H} and $g_2 \mathcal{H}$ have no element in common. Thus, also the set $g_2 \mathcal{H}$ contains $|\mathcal{H}|$ elements of \mathcal{G} . If there is another element $g_3 \in \mathcal{G}$ which does belong neither to \mathcal{H} nor to $g_2 \mathcal{H}$, one can form another

¹The formulation $g_2 \mathcal{H} = \{g_2 h_i \mid h_i \in \mathcal{H}\}$ means: $g_2 \mathcal{H}$ is the set of the products $g_2 h_i$ of g_2 with all elements $h_i \in \mathcal{H}$.

set $g_3 \mathcal{H} = \{g_3 h_j \mid h_j \in \mathcal{H}\}$. All elements of $g_3 \mathcal{H}$ are different and no one occurs already in \mathcal{H} or in $g_2 \mathcal{H}$. This procedure can be continued until each element $g_r \in \mathcal{G}$ belongs to one of these sets. In this way the group \mathcal{G} can be partitioned, such that each element $g \in \mathcal{G}$ belongs to exactly one of these sets.

The partition just described is called a *decomposition* ($\mathcal{G} : \mathcal{H}$) *into left cosets* of the group \mathcal{G} relative to the group \mathcal{H} .

$$\mathcal{G} = \mathcal{H} \cup g_2 \mathcal{H} \cup \dots \cup g_i \mathcal{H} \tag{1.5.25}$$

The sets $g_p \mathcal{H}$, $p = 1, \ldots, i$ are called *left cosets*, because the elements $h_j \in \mathcal{H}$ are multiplied with the new elements from the left-hand side. The procedure is called a *decomposition into right cosets* $\mathcal{H} g_s$ if the elements $h_j \in \mathcal{H}$ are multiplied with the new elements g_s from the right-hand side.

$$\mathcal{G} = \mathcal{H} \cup \mathcal{H} g_2 \cup \dots \cup \mathcal{H} g_i \tag{1.5.26}$$

The elements g_p or g_s are called the *coset representatives*. The number of cosets is called the *index* $[i] = |\mathcal{G} : \mathcal{H}|$ of \mathcal{H} in \mathcal{G} .

Two subgroups $\mathcal{H}_j, \mathcal{H}_k < \mathcal{G}$ are called *conjugate* if there is an element $g_q \in \mathcal{G}$ such that $g_q^{-1}\mathcal{H}_j g_q = \mathcal{H}_k$ holds. In this way, the subgroups of \mathcal{G} are distributed into classes of conjugate subgroups that are also called *conjugacy classes of subgroups*. Subgroups in the same conjugacy class are isomorphic and thus have the same order. Different conjugacy classes of subgroups may contain different numbers of subgroups, *i.e.* have different lengths.

A subgroup \mathcal{H} of a group \mathcal{G} is a normal subgroup $\mathcal{H} \triangleleft \mathcal{G}$ if it is identical with all of its conjugates, $g_q^{-1}\mathcal{H}g_q = \mathcal{H}$, for all $g_q \in \mathcal{G}$, *i.e.* if its conjugacy class consists of the one subgroup \mathcal{H} only.

1.5.2 Subgroups of space groups

The set of all symmetry operations of a three-dimensional crystal pattern forms its symmetry group, which is the *space group* of this crystal pattern. An essential feature of a crystal pattern is its periodicity which indicates that there are translations among its symmetry operations. The infinite number of translations determines the infinite order of any space group. The set of all translations of a space group \mathcal{G} forms the infinite translation subgroup $\mathcal{T}(\mathcal{G}) \triangleleft \mathcal{G}$ which is a normal subgroup of \mathcal{G} of finite index. Consider the right coset decomposition of \mathcal{G} relative to $\mathcal{T}(\mathcal{G})$.

Obviously, the coset representatives of the decomposition $(\mathcal{G} : \mathcal{T}(\mathcal{G}))$ represent in a clear and compact way the infinite number of elements of the space group \mathcal{G} . And this is one of the ways of presenting the space groups in *ITA* and also in the Bilbao Crystallographic Server, *i.e.* by the matrices of the coset representatives of $(\mathcal{G} : \mathcal{T}(\mathcal{G}))$ listed in the *General position*.

Each coset in the decomposition $(\mathcal{G}: \mathcal{T}(\mathcal{G}))$ is characterized by its linear part. One can show that the set of linear parts, represented by the set of matrices W_j , forms a group which is called the *point group* $\mathcal{P}_{\mathcal{G}}$ of the space group \mathcal{G} . The point groups which can belong to space groups are called *crystallographic point groups*.

The following types of subgroups of space groups are to be distinguished:

- A subgroup \mathcal{H} of a space group \mathcal{G} is called a *translationengleiche subgroup* or a *t*-subgroup of \mathcal{G} if the set $\mathcal{T}(\mathcal{G})$ of translations is retained, *i.e.* $\mathcal{T}(\mathcal{H}) = \mathcal{T}(\mathcal{G})$, but the number of cosets of the decomposition $(\mathcal{G}: \mathcal{T}(\mathcal{G}))$, *i.e.* the order of the point group $\mathcal{P}_{\mathcal{G}}$ is reduced.
- A subgroup $\mathcal{H} < \mathcal{G}$ of a space group \mathcal{G} is called a *klassengleiche subgroup* or a *k*-subgroup if the set $\mathcal{T}(\mathcal{G})$ of all translations of \mathcal{G} is reduced to $\mathcal{T}(\mathcal{H}) < \mathcal{T}(\mathcal{G})$ but all linear parts of \mathcal{G} are retained. Then the number of cosets of the decompositions $(\mathcal{H} : \mathcal{T}(\mathcal{H}))$ and $(\mathcal{G} : \mathcal{T}(\mathcal{G}))$ is the same, *i.e.* the order of the point group $\mathcal{P}_{\mathcal{H}}$ is the same as that of $\mathcal{P}_{\mathcal{G}}$.
- A klassengleiche or k-subgroup $\mathcal{H} < \mathcal{G}$ is called *isomorphic* or an *isomorphic subgroup* if it belongs to the same affine space-group type (isomorphism type) as \mathcal{G} does.
- A subgroup of a space group is called *general* or a *general subgroup* if it is neither a *translationengleiche* nor a *klassengleiche* subgroup. It has lost translations as well as linear parts, *i.e.* point-group symmetry.

Any subgroup \mathcal{H} of a group \mathcal{G} is related to a specific subset of elements of \mathcal{G} and this subset defines the subgroup uniquely: different subgroups of \mathcal{G} , even those isomorphic to \mathcal{H} , correspond to different subsets of the elements of \mathcal{G} . For example, the listing of the maximal *t*-subgroups of the space groups in *ITA* is based on this fact: apart from the space-group type and index, each *t*-subgroup \mathcal{H} is specified by the set of coordinate triplets of the general position of \mathcal{G} which are retained in \mathcal{H} .

In the Bilbao Crystallographic Server any subgroup \mathcal{H} of a space group \mathcal{G} is specified by its *ITA*-number, the index in the group \mathcal{G} and the transformation matrix-column pair $(\boldsymbol{P}, \boldsymbol{p})$ that relates the standard bases $(\mathbf{a}, \mathbf{b}, \mathbf{c})_{\mathcal{H}}$ of \mathcal{H} and $(\mathbf{a}, \mathbf{b}, \mathbf{c})_{\mathcal{G}}$ of \mathcal{G} :

$$(\mathbf{a}, \mathbf{b}, \mathbf{c})_{\mathcal{H}} = (\mathbf{a}, \mathbf{b}, \mathbf{c})_{\mathcal{C}} \boldsymbol{P}$$
 (1.5.27)

The column $\boldsymbol{p} = (p_1, p_2, p_3)$ of coordinates of the origin $O_{\mathcal{H}}$ of \mathcal{H} is referred to the coordinate system of \mathcal{G} .

The subgroup data listed in the server, *i.e.* the space-group type of \mathcal{H} and the transformation matrix (\mathbf{P}, \mathbf{p}) , are completely sufficient to define the subgroup uniquely: the transformation of the coordinate triplets of general-position of \mathcal{H} (in standard setting) to the coordinate system of \mathcal{G} by $(\mathbf{P}, \mathbf{p})^{-1}$ yields exactly the subset of elements of \mathcal{G} corresponding to \mathcal{H} .

A very important result on group-subgroup relations between space groups is given by Hermann's theorem: For any group–subgroup chain $\mathcal{G} > \mathcal{H}$ between space groups there exists a uniquely defined space group \mathcal{M} with $\mathcal{G} \geq \mathcal{M} \geq \mathcal{H}$, where \mathcal{M} is a *translationengleiche* subgroup of \mathcal{G} and \mathcal{H} is a *klassengleiche* subgroup of \mathcal{M} . The decisive point is that any group-subgroup chain between space groups $\mathcal{G} > \mathcal{H}$ of index [i] can be split into a *translationengleiche* subgroup chain between the space groups \mathcal{G} and \mathcal{M} of index $[i_P]$ and a *klassengleiche* subgroup chain between the space groups \mathcal{G} and \mathcal{H} of index $[i] = [i_P] \cdot [i_L]$. The first one, also called *t*-chain $\mathcal{G} \stackrel{i_P}{>} \mathcal{M}$, is related to the reduction of the point-group symmetry in the subgroup. The second one $\mathcal{M} \stackrel{i_L}{>} \mathcal{H}_j$ is known also as *k*-chain and it takes account of the loss of translations.

It may happen, that either $\mathcal{G} = \mathcal{M}$ or $\mathcal{H} = \mathcal{M}$ holds. In particular, one of these equations must hold if $\mathcal{H} < \mathcal{G}$ is a maximal subgroup of \mathcal{G} . In other words, a maximal subgroup of a space group is either a *translationengleiche* subgroup or a *klassengleiche* subgroup, never a general subgroup.

If the maximal subgroups are known for each space group, then in principle each non-maximal subgroup of a space group \mathcal{G} with finite index can be obtained from the data on maximal subgroups. A nonmaximal subgroup $\mathcal{H} < \mathcal{G}$ of finite index [i] is connected with the original group \mathcal{G} through a chain $\mathcal{H} = \mathcal{Z}_k < \mathcal{Z}_{k-1} < \cdots < \mathcal{Z}_1 < \mathcal{Z}_0 = \mathcal{G}$, where each group $\mathcal{Z}_j < \mathcal{Z}_{j-1}$ is a maximal subgroup of \mathcal{Z}_{j-1} , with the index $[i_j] = |\mathcal{Z}_{j-1} : \mathcal{Z}_j|, j = 1, \dots, k$. The number k is finite and the relation $i = \prod_{j=1}^k i_j$ holds, *i.e.* the total index [i] is the product of the indices i_j .

In a similar way, one can express the transformation matrix $(\boldsymbol{P}, \boldsymbol{p})$ for the symmetry reduction $\mathcal{G} \longrightarrow \mathcal{H}$ as a product of the transformation matrices $(\boldsymbol{P}, \boldsymbol{p})_j$ characterizing each of the intermediate steps $\mathcal{Z}_{j-1} > \mathcal{Z}_j$: $(\boldsymbol{P}, \boldsymbol{p}) = (\boldsymbol{P}, \boldsymbol{p})_1 (\boldsymbol{P}, \boldsymbol{p})_2 \cdots (\boldsymbol{P}, \boldsymbol{p})_k$ (here the matrices $(\boldsymbol{P}, \boldsymbol{p})_j$ relate the bases of \mathcal{Z}_{j-1} and \mathcal{Z}_j , *i.e.* $(\mathbf{a}, \mathbf{b}, \mathbf{c})_j = (\mathbf{a}, \mathbf{b}, \mathbf{c})_{j-1} \boldsymbol{P}_j$).

1.5.3 Generation of Space Groups

A set of generators of a group is a subset of the group elements which by proper combination permits the generation of all elements of the group. Different sets of generators are possible.

In International Tables for Crystallography, Vol. A (referred to as ITA in the following), the generators and the generating procedure have been chosen such as to make the entries in the blocks of General position and Symmetry operations as transparent as possible. Given the set of h generators $G_1, G_2, \ldots, G_p, \ldots G_h$, any space-group operation W is generated by the following algorithm, starting with the identity and the translations as right-most factors:

$$\mathsf{W} = \mathsf{G}_{h}^{k_{h}} \cdot \mathsf{G}_{h-1}^{k_{h-1}} \dots \cdot \mathsf{G}_{p}^{k_{p}} \dots \cdot \mathsf{G}_{3}^{k_{3}} \cdot \mathsf{G}_{2}^{k_{2}} \cdot \mathsf{G}_{1}.$$
(1.5.28)

Here, the exponents k_p are positive or negative integers, including zero.

The space-group generator G_1 is the identity (zero translation). It is chosen first and assures that the general position of \mathcal{G} starts with the coordinate triplet x, y, z. The following generators G_2 , G_3 , G_4 are the translations corresponding to the three basis vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}$ and G_5, G_6 are the generators for the centring translations, if present. The rest of the generators G_7, G_8, \ldots give all those symmetry operations of the space group \mathcal{G} which are not pure translations. They have been chosen such that their exponents can assume only the values 0,1 and 2. Space groups of the same crystal class are generated in the same way. In *ITA*, the generators are designated by the numbers in front of the corresponding general-position co-ordinate triplets.

The coordinate triplets of the *General position* are obtained by single-sided, (*i.e* left-sided) multiplication of the matrices representing the generators until no new matrices are found. Resulting matrices that differ only by a lattice translation are considered as equal, and the translations parts are chosen such so that the symmetry operations lie within the unit cell.

The generating procedure used in *ITA* highlights important subgroups of space groups as much as possible. For example, once the translation subgroup $\mathcal{T}_{\mathcal{G}}$ of a space group \mathcal{G} is generated, the process of generation follows step-wise procedure via a chain of normal and maximal subgroups

$$\mathcal{G} \triangleright \mathcal{H}_1 \triangleright \mathcal{H}_2 \triangleright \cdots \triangleright \mathcal{T}_{\mathcal{G}}, \tag{1.5.29}$$

with indices $|\mathcal{H}_i : \mathcal{H}_{i+1}|$ equal to 2 or 3. In other words, each new (non-translational) generator generates a minimal *translationengleiche* or *t*-supergroup \mathcal{H}_i of \mathcal{H}_{i+1} of index 2 or 3.

Chapter 2

Exercises

2.1 Matrix calculus in crystallography (brief revision)

- Exercise 2.1.1. Matrix transposition
 - 1. Construct the transposed matrix of the (3×1) row matrix $\mathbf{A} = \begin{pmatrix} 1 & 3 & 4 \end{pmatrix}$.
 - 2. Determine which of the following matrices are symmetric and which are skew-symmetric (a, b)

$$A = \begin{pmatrix} 3 & 0 \\ 0 & 2 \end{pmatrix}; B = \begin{pmatrix} 3 & 4 \\ -4 & 1 \end{pmatrix}; C = \begin{pmatrix} 2 & -1 \\ -1 & 1 \end{pmatrix}; D = \begin{pmatrix} 0 & 2 \\ -2 & 0 \end{pmatrix}; E = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix};$$
$$F = \begin{pmatrix} 2 \end{pmatrix}; G = \begin{pmatrix} 0 & 1 & -2 \\ -1 & 0 & 3 \\ 2 & -3 & 0 \end{pmatrix}; H = \begin{pmatrix} 3 & 2 \\ 2 & 1 \\ 1 & 0 \end{pmatrix}; J = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}.$$

- Exercise 2.1.2. Matrix addition and subtraction
 - 1. Find 3*A*-2*B*, where $\boldsymbol{A} = \begin{pmatrix} 1 & 2 \\ 3 & 0 \end{pmatrix}$ and $\boldsymbol{B} = \begin{pmatrix} 1 & 3 \\ 0 & -4 \end{pmatrix}$.
 - 2. Show that the sum of any matrix and its transposed is a symmetric matrix, *i.e.* $(\mathbf{A} + \mathbf{A}^T)^T = \mathbf{A} + \mathbf{A}^T$.
 - 3. Show that the difference of any matrix and its transposed is a skew-symmetric matrix, *i.e.* $(\mathbf{A} \mathbf{A}^T)^T = -(\mathbf{A} \mathbf{A}^T).$
- Exercise 2.1.3. Matrix multiplication
 - 1. Find the products AB and BA if they exists, where $A = \begin{pmatrix} 1 & 2 \\ 3 & -4 \end{pmatrix}$ and $B = \begin{pmatrix} 3 & -2 & 2 \\ 1 & 0 & -1 \end{pmatrix}$.
 - 2. Find the matrix products AB and BA of the row vector $A = \begin{pmatrix} 1 & 2 & 3 \end{pmatrix}$ and the column vector $B = \begin{pmatrix} -2 \\ 4 \\ 1 \end{pmatrix}$.

3. Prove that
$$\boldsymbol{A}(\boldsymbol{B}\boldsymbol{C}) = (\boldsymbol{A}\boldsymbol{B})\boldsymbol{C}$$
 where $\boldsymbol{A} = \begin{pmatrix} 1 & 2 \\ -1 & 3 \end{pmatrix}, \boldsymbol{B} = \begin{pmatrix} 1 & 0 & -1 \\ 2 & 1 & 0 \end{pmatrix}$ and $\boldsymbol{C} = \begin{pmatrix} 1 & -1 \\ 3 & 2 \\ 2 & 1 \end{pmatrix}$.

• Exercise 2.1.4. Trace and determinant of a matrix

1. Find the values of the traces and the determinants of \boldsymbol{A} and \boldsymbol{B} where

$$\boldsymbol{A} = \begin{pmatrix} 1 & 2 \\ -1 & 3 \end{pmatrix} \text{ and } \boldsymbol{B} = \begin{pmatrix} 0 & 4 & 2 \\ 4 & -2 & -1 \\ 5 & 1 & 3 \end{pmatrix}.$$

2. Show that $det(\boldsymbol{A}\boldsymbol{B}) = det(\boldsymbol{A})det(\boldsymbol{B})$ where $\boldsymbol{A} = \begin{pmatrix} 3 & 2 \\ 5 & 1 \end{pmatrix}$ and $\boldsymbol{B} = \begin{pmatrix} 1 & 6 \\ 2 & 9 \end{pmatrix}.$
3. Show that $det(\boldsymbol{A}) = det(\boldsymbol{A}^T)$ where $\boldsymbol{A} = \begin{pmatrix} 1 & 1 & 3 \\ 2 & 2 & 2 \\ 3 & 2 & 3 \end{pmatrix}.$

• Exercise 2.1.5. Inverse of a matrix

1. Show that the matrix
$$\boldsymbol{B} = 1/3 \begin{pmatrix} 11 & -9 & 1 \\ -7 & 9 & -2 \\ 2 & -3 & 1 \end{pmatrix}$$
 is the inverse of $\boldsymbol{A} = \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 5 \\ 1 & 5 & 12 \end{pmatrix}$.
2. Determine the inverses of the matrices $\boldsymbol{A} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$; $\boldsymbol{B} = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$; $\boldsymbol{C} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$; $\boldsymbol{D} = \begin{pmatrix} 1 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$; $\boldsymbol{E} = \begin{pmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{pmatrix}$ and $\boldsymbol{F} = \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}$.
3. Given that $\boldsymbol{A} = \begin{pmatrix} 1 & 2 & 0 \\ -1 & 0 & 3 \\ 2 & -1 & 0 \end{pmatrix}$ determine \boldsymbol{A}^{-1} .

2.2 Group theory in crystallography (basic concepts)

- Exercise 2.2.1. With binary composition defined to be addition:
 - (a) Does the set of positive integers $\{p\}$ form a group?
 - (b) Do the positive integers $\{p\}$, including zero (0) form a group?
 - (c) Do the positive $\{p\}$ and the negative $\{-p\}$ integers, including zero, form a group?
- Exercise 2.2.2. Cyclic groups:
 - (a) Show that cyclic groups are Abelian.
 - (b) Show that for a finite cyclic group the existence of the inverse of each element is guaranteed.
 - (c) Show that $w = exp(-2\pi i/n)$ generates a cyclic group of index n, when binary composition is defined as multiplication of complex numbers.
- Exercise 2.2.3. There are two groups of order four that are not isomorphic and so have different multiplication tables.
 - (a) Derive the multiplication tables of these two groups. (*Hint*: First derive the multiplication table of the cyclic group of order 4. How many elements are equal to their inverses? Try to construct further groups in which a different number of elements are equal to their inverses.)
 - (b) Arrange the elements of these two groups into classes of conjugate elements.

- (c) Identify their subgroups.
- Exercise 2.2.4. Symmetry group of the pentacene molecule



Consider the model of the molecule of the organic semiconductor pentacene $(C_{22}H_{14})$:

- 1. Determine all symmetry operations and their matrix and the short-hand (x, y) presentation;
- 2. Draw up the general-position and the symmetry-elements stereographic-projection diagrams;
- 3. Find a set of generators;
- 4. Construct the multiplication table of the group of the pentacene molecule;
- 5. Distribute the elements of the group into classes of conjugate elements.
- Exercise 2.2.5. Symmetry group of the square



Consider the symmetry group of the square:

- 1. Determine all symmetry operations and their matrix and the short-hand (x, y) presentation;
- 2. Draw up the general-position and the symmetry-elements stereographic-projection diagrams;
- 3. Find a set of generators;
- 4. Construct the multiplication table of the group of the square;
- 5. Distribute the elements of the group into classes of conjugate elements.
- Exercise 2.2.6. Symmetry group of the equilateral triangle

Consider the symmetry group of the equilateral triangle:

- 1. Determine all symmetry operations and their matrix and the short-hand (x, y) presentation;
- 2. Draw up the general-position and the symmetry-elements stereographic-projection diagrams;
- 3. Find a set of generators;
- 4. Construct the multiplication table of the group of the equilateral triangle;
- 5. Distribute the elements of the group into classes of conjugate elements.
- Exercise 2.2.7. Consider the symmetry group of the square 4mm, cf. Exercise 2.2.5.
 - 1. Which are the possible orders of the subgroups of 4mm?
 - 2. With the help of the stereographic projections of 4mm derive all subgroups of indices [2] and [4] of 4mm.



- 3. Determine the subgroups of 4mm and construct the complete subgroup graph of point group 4mm, see *Remarks*.
- 4. Which of these subgroups are conjugate (symmetrically equivalent) in 4mm and which are normal subgroups?

Remarks

In a subgroup diagram each, subgroup is located at a level which is determined by its index (the original group with index [1] on top, subgroups of index [2] next lower level, etc.). Each of these groups is connected with its maximal subgroups by straight lines.

• Exercise 2.2.8. Consider the symmetry group of the equilateral triangle 3m and its stereographic projections, *cf.* Exercise 2.2.6.



1. Determine the subgroups of 3m;



- 2. Distribute the subgroups into classes of conjugate subgroups;
- 3. Construct the graph of maximal subgroups of 3m.
- Exercise 2.2.9. Consider $\mathcal{H} \triangleleft \mathcal{G}$ and the coset decomposition $\mathcal{G} : \mathcal{H}$. Show that the set of cosets $\{g_i\mathcal{H}, i = 1, \ldots, |\mathcal{G} : \mathcal{H}|\}$ satisfy the group axioms with *sets product* as a binary operation.
- Exercise 2.2.10. Consider the subgroup $\mathcal{2} = \{1, 2\}$ of 4mm.
 - 1. Write down the left and right coset decomposition of the group 4mm with respect to the subgroup 2.
 - 2. Are the right and the left coset decompositions equal or different? Why?
 - 3. Show that the cosets of the decomposition of 4mm with respect to 2 satisfy the group axioms and the set of cosets forms a factor group.
 - 4. Construct the multiplication table of the factor group.
 - 5. Indicate a crystallographic point group isomorphic to the factor group.
- Exercise 2.2.11. Consider the subgroup $3 = \{1, 3^+, 3^-\}$ of 3m.
 - 1. Show that the cosets of the decomposition of 3m with respect to 3 satisfy the group axioms and the set of cosets forms a factor group.
 - 2. Construct the multiplication table of the factor group.
 - 3. Indicate a crystallographic point group isomorphic to the factor group.
- Exercise 2.2.12. Show that $\mathcal{H} \triangleleft \mathcal{G}$ holds always for $|\mathcal{G} : \mathcal{H}| = 2$, *i. e.* subgroups of index 2 are always normal subgroups.
- Exercise 2.2.13. Consider the symmetry group of the square 4mm (cf. Exercise 2.2.5) and the point group 422 that is isomorphic to it. Determine the general and special Wyckoff positions for the two groups.
- Exercise 2.2.14. Consider the general and the special Wyckoff positions of the symmetry group of the square 4mm (cf. Exercise 2.2.13) and those of its subgroup mm2 (cf. Exercise 2.2.7). Determine the splitting schemes of the Wyckoff positions for the pair 4mm > mm2.
- Exercise 2.2.15. Consider the group 4mm and its subgroups of index 4 (*cf.* Exercise 2.2.7). Determine their normalizers in 4mm. Distribute the subgroups of 4mm of index 4 into conjugacy classes with the help of their normalizers in 4mm.
- Exercise 2.2.16. Show that the sets of symmetry operations of the point groups $\overline{6}$ and 3/m are identical.
- Exercise 2.2.17. Show that the rotational symmetries of a crystal pattern with translational symmetry are limited to 1-fold, 2-fold, 3-fold, 4-fold, and 6-fold.

- Exercise 2.2.18. Consider the following 10 figures of the symmetry elements and the general positions of the plane point groups.
 - 1. Determine the order of the point groups and arrange them vertically by descending pointgroup orders (*i.e.* the point group of highest order at the top, and that of lowest order at the bottom).
 - 2. Determine the complete group-subgroup graph for all plane point groups.
 - 3. Consider the plane point group 2mm. Determine its maximal subgroups, its minimal supergroups and the corresponding indices.



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2.2. GROUP THEORY IN CRYSTALLOGRAPHY (BASIC CONCEPTS)

• Exercise 2.2.19. Point groups isomorphic to 4mm Consider the following three pairs of stereographic projections. Each of them correspond to a crystallographic point group isomorphic to 4mm:



- 1. Determine the point groups isomorphic to 4mm by indicating their symbols, symmetry operations and possible sets of generators;
- 2. Construct the corresponding multiplication tables;
- 3. For each of the isomorphic point groups indicate the one-to-one correspondence with the symmetry operations of 4mm;
- 4. Distribute the elements of the point groups isomorphic to 4mm into classes of conjugate elements.
- Exercise 2.2.20. Explain the terms composition series and solvable groups. Write down the composition series for the point groups 4/mmm, $m\overline{3}m$ and 6/mmm. Generate the symmetry operations of the groups 4/mmm and $\overline{3}m$ following their composition series.
- Exercise 2.2.21. Determine the symmetry elements and the corresponding point groups for each of the following models of molecules:



• Exercise 2.2.22. Symmetry elements of the cube, the octahedron, the tetrahedron and the hexagonal prism

Consider the following bodies: a cube, an octahedron, a tetrahedron and a hexagonal prism. For each of the four bodies:

- 1. Determine and draw the symmetry elements and the natural coordinate system.
- 2. List the determined symmetry elements and the corresponding point groups (crystal classes).
- 3. Determine the set of symmetry operations whose combinations (products) can generate the full point group (*i.e.* the so-called *generators*).
- 4. Consider the set of symmetry operations, and construct the subset excluding the operations of the second kind (*i.e.* reflections, rotoinversions, *etc.*). Does this subset form a group, and if 'yes', which?





2.3 Matrix-column presentation of symmetry operations

• Exercise 2.3.1. Referred to an 'orthorhombic' coordinate system ($a \neq b \neq c$; $\alpha = \beta = \gamma = 90$) two symmetry operations are represented by the following matrix-column pairs: (W_1, w_1) =

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \overline{1} \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \text{ and } (\boldsymbol{W}_2, \boldsymbol{w}_2) = \left(\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \overline{1} \end{pmatrix}, \begin{pmatrix} 1/2 \\ 0 \\ 1/2 \end{pmatrix} \right).$$

- 1. Determine the images X_i of a point $X = \begin{pmatrix} 0.7 \\ 0.31 \\ 0.95 \end{pmatrix}$ under the action of the symmetry operations.
- 2. Can you guess what is the 'geometric nature' of $(\boldsymbol{W}_1, \boldsymbol{w}_1)$ and $(\boldsymbol{W}_2, \boldsymbol{w}_2)$?
- 3. Determine the determinant and the trace of \boldsymbol{W}_1 .
- 4. Determine the sets of fixed points of $(\boldsymbol{W}_1, \boldsymbol{w}_1)$ and $(\boldsymbol{W}_2, \boldsymbol{w}_2)$.
- Exercise 2.3.2. Applying the procedure for the geometric interpretation of matrix-column pairs of symmetry operations characterize the following matrix-column pairs (W, w) taking into account that they refer to a cubic basis:
 - (1) $y + \frac{1}{4}, \bar{x} + \frac{1}{4}, z + \frac{3}{4}$
 - (2) $\bar{z} + \frac{1}{2}, x + \frac{1}{2}, y$
 - (3) $\bar{y} + 3/4, \bar{x} + 1/4, z + 1/4$
- Exercise 2.3.3. The General position of a space group is listed as: (1) x, y, z (2) $\bar{x}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$ (3) $\bar{x}, \bar{y}, \bar{z}$ (4) $x, \bar{y} + \frac{1}{2}, z + \frac{1}{2}$.
 - 1. Construct the matrix-column pairs of these 'coordinate triplets'. Write down the corresponding (4×4) matrix representation.
 - 2. Characterize geometrically the matrices if they refer to a monoclinic basis with unique axis b (type of operation, glide (screw) component, fixed points, nature and location of the symmetry element).
 - 3. Use the program SYMMETRY OPERATIONS for the geometric interpretation of the matrix-column pairs of the symmetry operations.
- Exercise 2.3.4. Consider the following coordinate triplets: (1) x, y, z (2) $\bar{x} + \frac{1}{2}, \bar{y}, z + \frac{1}{2}$ (3) $\bar{x}, \bar{y}, \bar{z}$ (4) $x + \frac{1}{2}, y, \bar{z} + \frac{1}{2}$.
 - 1. Construct the matrix-column pairs of these 'coordinate triplets'. Write down the corresponding (4×4) matrix representation.
 - 2. Characterize geometrically the matrices if they refer to a monoclinic basis with unique axis c (type of operation, glide (screw) component, fixed points, nature and location of the symmetry element).
- Exercise 2.3.5. Consider the matrix-column pairs of the two symmetry operations $(\boldsymbol{W}_1, \boldsymbol{w}_1) = \begin{pmatrix} \begin{pmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$ and $(\boldsymbol{W}_2, \boldsymbol{w}_2) = \begin{pmatrix} \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}, \begin{pmatrix} 1/2 \\ 0 \\ 1/2 \end{pmatrix} \end{pmatrix}$.

- 1. Determine and compare the matrix-column pairs of the combined symmetry operations: $(\boldsymbol{W}, \boldsymbol{w}) = (\boldsymbol{W}_1, \boldsymbol{w}_1)(\boldsymbol{W}_2, \boldsymbol{w}_2)$ and $(\boldsymbol{W}, \boldsymbol{w})' = (\boldsymbol{W}_2, \boldsymbol{w}_2)(\boldsymbol{W}_1, \boldsymbol{w}_1)$.
- 2. Determine the inverse symmetry operations $(\boldsymbol{W}_1, \boldsymbol{w}_1)^{-1}$ and $(\boldsymbol{W}_2, \boldsymbol{w}_2)^{-1}$.
- 3. Determine the inverse symmetry operation $(\boldsymbol{W}, \boldsymbol{w})^{-1}$ if $(\boldsymbol{W}, \boldsymbol{w}) = (\boldsymbol{W}_1, \boldsymbol{w}_1)(\boldsymbol{W}_2, \boldsymbol{w}_2)$.
- 4. Characterize geometrically the symmetry operations $(\boldsymbol{W}_1, \boldsymbol{w}_1)$ and $(\boldsymbol{W}_2, \boldsymbol{w}_2)$ and their products $(\boldsymbol{W}, \boldsymbol{w})$ and $(\boldsymbol{W}, \boldsymbol{w})'$ if they refer to a tetragonal basis (type of operation, glide (screw) component, fixed points, nature and location of the symmetry element).

• Exercise 2.3.6. Consider the matrix-column pairs $(\boldsymbol{A}, \boldsymbol{a}) = \begin{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & \overline{1} \end{pmatrix}, \begin{pmatrix} 1/2 \\ 1/2 \\ 1/2 \end{pmatrix}$ and $(\boldsymbol{B}, \boldsymbol{b}) =$

- $\left(\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}\right).$
 - 1. What are the matrix-column pairs resulting from: (A, a)(B, b) = (C, c) and (B, b)(A, a) = (D, d).
 - 2. Determine $(A, a)^{-1}$, $(B, b)^{-1}$, $(C, c)^{-1}$ and $(D, d)^{-1}$. What is $(B, b)^{-1}(A, a)^{-1}$?
 - 3. Characterize geometrically the symmetry operations (\mathbf{A}, \mathbf{a}) and (\mathbf{B}, \mathbf{b}) and their products (\mathbf{C}, \mathbf{c}) and (\mathbf{D}, \mathbf{d}) if they refer to a cubic basis (type of operation, direction of the rotation (or rotoinversion) axis, sense of rotation, glide (screw) component, fixed points, nature and location of the geometric element).

2.4 Metric Tensors. Simple crystallographic calculations: Distances and angles

- Exercise 2.4.1. Metric tensors (Fundamental matrices)
 - (a) Write down the explicit expressions for the metric tensors G of the conventional bases of the seven crystal systems using the general expressions for their lattice parameters.
 - (b) Which are the conditions for the elements of the metric tensor G if the lattice L is invariant under a six-fold rotation 6⁺ described by the matrix x - y, x, z. Hint: The metric tensor G of a lattice L is invariant under a symmetry operation W of L:

Hint: The metric tensor G of a lattice L is invariant under a symmetry operation W of L $W^T G W = G$

- (c) Derive the metric tensors for the conventional bases of the seven crystal systems using their invariance with respect to the symmetry operations of the holohedries of their lattices.
- Exercise 2.4.2. A body-centred cubic lattice (cI) has as its conventional basis the basis $(\mathbf{a}_P, \mathbf{b}_P, \mathbf{c}_P)$ of a primitive cubic lattice, but the lattice also contains the centring vector $1/2(\mathbf{a}_P + \mathbf{b}_P + \mathbf{c}_P)$ which points to the centre of the conventional cell.



Calculate the coefficients of the metric tensor for the body-centred cubic lattice:

- 1. for the conventional basis $\mathbf{a}_P, \mathbf{b}_P, \mathbf{c}_P$;
- 2. for the primitive basis: $\mathbf{a}_I = 1/2(-\mathbf{a}_P + \mathbf{b}_P + \mathbf{c}_P)$, $\mathbf{b}_I = 1/2(\mathbf{a}_P \mathbf{b}_P + \mathbf{c}_P)$, $\mathbf{c}_I = 1/2(\mathbf{a}_P + \mathbf{b}_P \mathbf{c}_P)$;
- 3. determine the lattice parameters of the primitive cell if $a_P = 4$ Å.
- Exercise 2.4.3. A face-centred cubic lattice (cF) has as its conventional basis the basis $(\mathbf{a}_P, \mathbf{b}_P, \mathbf{c}_P)$ of a primitive cubic lattice, but the lattice also contains the centring vectors $1/2(\mathbf{b}_P + \mathbf{c}_P)$, $1/2(\mathbf{a}_P + \mathbf{c}_P)$, $1/2(\mathbf{a}_P + \mathbf{b}_P)$ which point to the centres of the faces of the conventional cell.



Calculate the coefficients of the metric tensor for the face-centred cubic lattice:

- 1. for the conventional basis $\mathbf{a}_P, \mathbf{b}_P, \mathbf{c}_P$;
- 2. for the primitive basis: $\mathbf{a}_F = 1/2(\mathbf{b}_P + \mathbf{c}_P)$, $\mathbf{b}_F = 1/2(\mathbf{a}_P + \mathbf{c}_P)$, $\mathbf{c}_F = 1/2(\mathbf{a}_P + \mathbf{b}_P)$;
- 3. determine the lattice parameters of the primitive cell if $a_P = 4$ Å.
- Exercise 2.4.4. Consider a monoclinic *F*-cell with the parameters $a = 6\text{\AA}$, $b = 7\text{\AA}$, $c = 8\text{\AA}$ and $\beta = 110^{\circ}$. Show that a monoclinic *C*-cell with obtuse angle represents the same lattice. What are the lattice parameters of the *C*-cell? What is the relation between the volumes of the two cells?
- Exercise 2.4.5. For a crystal with lattice parameters $a = 3\text{\AA}$, $b = 4\text{\AA}$, $c = 6\text{\AA}$ $\alpha = 90^{\circ}$, $\beta = 120^{\circ}$, $\gamma = 90^{\circ}$ (*i.e* a monoclinic crystal), calculate
 - 1. the length of the main body diagonal;
 - 2. the volume of the unit cell.
- Exercise 2.4.6. Consider a crystal with basis vectors (a, b, c) and lattice parameters (5Å, 7Å, 3Å, 90°, 90°, 90°. As a result of a phase transition, the basis vectors (a', b', c') of the low-symmetry phase change to a' = a b, b' = a + b, c' = 3c.

Calculate the lattice parameters of the lower symmetry phase. What is the volume of the lower unit cell? And the crystal system?

- Exercise 2.4.7. For a crystal with lattice parameters $a = 2\text{\AA}$, $b = 2\text{\AA}$, $c = 3\text{\AA}$, $\alpha = 90^{\circ}$, $\beta = 90^{\circ}$, $\gamma = 90^{\circ}$, calculate the distance between two atoms with coordinates (1/3, 1/3, 1/4) and (1/3, 1/2, 3/4). *Hint*: The distance between any two points in a crystal equals the length of the vector connecting those two points.
- Exercise 2.4.8. In a cubic crystal with lattice parameter a, an oxygen atom is present at the position (0,0,0); this atom is bonded to two titanium atoms, located at the positions (1/2, 1/2, 0) and (1/2, 0, 1/2). Compute the angle between the two bonds.

Hint: The angle between the two bonds corresponds to the angle between the two direction vectors parallel to the bonds.

• Exercise 2.4.9. Consider a monoclinic crystal with lattice parameter $a = 4\text{\AA}$, $b = 6\text{\AA}$, $c = 5\text{\AA}$, $\beta = 120^{\circ}$. What is the angle between the [101] and [$\overline{2}01$] directions?

2.5 Space-group symmetry data

- Exercise 2.5.1.
 - (a) Consider the General position data given in ITA for the space group Cmm2 (No. 35):
 - 1. Characterize geometrically the matrix-column pairs listed under *General position* of the space group *Cmm*². Compare the results with the data listed under *Symmetry operations*.
 - 2. Consider the diagram of the symmetry elements of Cmm2. Try to determine the matrixcolumn pairs of the symmetry operations whose symmetry elements are indicated on the unit-cell diagram.
 - 3. Compare your results with the results of the program SYMMETRY OPERATIONS for the geometric interpretation of the matrix-column pairs of the symmetry operations considered in this exercise.
 - (b) The same for the space group P4mm (No.99).

Attachments: Copies of the ITA pages with the space-group data of Cmm2, No. 35.

Copies of the ITA pages with the space-group data of P4mm, No. 99.

- Exercise 2.5.2. Consider the special Wyckoff positions of the the space group P4mm (No. 99)
 - 1. Determine the site-symmetry groups of Wyckoff positions 1a and 1b. Compare the results with the listed data of P4mm in ITA.
 - 2. The coordinate triplets (x, 1/2, z) and (1/2, x, z), belong to Wyckoff position 4f. Compare their site-symmetry groups.
 - 3. Compare your results with the output of the program WYCKPOS for the space group P4mm.
 - 4. Use the option *Non-conventional settings* of the program WYCKPOS to determine the coordinate triplets of the Wyckoff positions of the space group P4mm referred to a non-conventional setting with the four-fold rotation axes parallel to **a** axis.

Attachments: Copies of the ITA pages with the space-group data of P4mm, No. 99.

- Exercise 2.5.3. Consider the Wyckoff-position data given in *ITA* for the space group $P4_2/mbc$ (No. 135):
 - 1. Determine the site-symmetry groups of the following *Wyckoff positions*: 4(a); 4(c); 4(d); 8(g). Construct the corresponding oriented site-symmetry symbols and compare them with those listed in *ITA*. Compare your results with the results listed by the program WYCKPOS.

2.5. SPACE-GROUP SYMMETRY DATA

- 2. Characterize geometrically the isometries (3), (8), (12), (15) and (16) as listed under *General Position*. Compare the results with the corresponding geometric descriptions listed under *Symmetry operations* in *ITA*.
- 3. Compare the calculated geometric descriptions of the isometries by the program SYMMETRY OPERATIONS

Attachments: Copies of the ITA pages with the space-group data of $P4_2/mbc$, No. 135.

- Exercise 2.5.4. The following matrix-column pairs $(\boldsymbol{W}, \boldsymbol{w})$ are determined with respect to a basis $(\mathbf{a}, \mathbf{b}, \mathbf{c})$: (1) x, y, z (2) $\bar{x}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$ (3) $\bar{x}, \bar{y}, \bar{z}$ (4) $x, \bar{y} + \frac{1}{2}, z + \frac{1}{2}$.
 - Determine the corresponding matrix-column pairs (W', w') with respect to the basis $(\mathbf{a}', \mathbf{b}', \mathbf{c}') = (\mathbf{a}, \mathbf{b}, \mathbf{c})P$, with $P = \mathbf{c}, \mathbf{a}, \mathbf{b}$.
 - The coordinates of a point $X = \begin{pmatrix} 0.70\\ 0.31\\ 0.95 \end{pmatrix}$ are determined with respect to the basis (**a**,**b**,**c**). What would be the coordinates X' referred to the basis (**a**', **b**', **c**')?
- Exercise 2.5.5. Consider the symmetry operation $\{2_{001}|0, v, 0\}$ where 2_{001} represents a two-fold rotation around a rotation axis parallel to **c**. What origin shift should be applied so that the symmetry operation is represented by $\{2_{001}|0, 0, 0\}$, *i.e.* its geometric element goes through the origin?
- Exercise 2.5.6. ITA -conventional settings of space groups: monoclinic settings
 - 1. Consider the space group $P2_1/c$ (No. 14). Show that the relation between the (i) General and (ii) Special position data of $P112_1/a$ (setting unique axis c) can be obtained from the data $P12_1/c1$ (setting unique axis b) applying the transformation $(\mathbf{a}', \mathbf{b}', \mathbf{c}')_c = (\mathbf{a}, \mathbf{b}, \mathbf{c})_b \mathbf{P}$, with $\mathbf{P} = \mathbf{c}, \mathbf{a}, \mathbf{b}$.
 - 2. Show that the data of the *Reflection conditions* block of $P112_1/a$ (setting *unique axis c*) can be obtained from the data $P12_1/c1$ (setting *unique axis b*) applying the same transformation, *i.e.* P = c, a, b.

Hint: Under a coordinate transformation specified by a matrix \boldsymbol{P} , the indices of reflection conditions (Miller indices) transform according to $(h' k' l') = (h k l) \boldsymbol{P}$.

3. Use the retrieval tools GENPOS (generators and general positions) and WYCKPOS (Wyckoff positions for accessing *ITA* data. Get the data on general and special positions in different settings either by specifying transformation matrices to new bases, or by selecting one of the 530 settings of the monoclinic and orthorhombic groups listed in *ITA* (*cf.* Table 4.3.2.1).

Attachments Copies of the *ITA* pages with the space-group data of $P2_1/c$ (No. 14).

- Exercise 2.5.7. ITA -conventional settings of space groups: different origins
 - 1. Consider the space group Pmmn (No. 59). Show that the relation between the (i) *General* and (ii) *Special position* data of Pmmn (origin choice 1) can be obtained from the data Pmmn (origin choice 2) applying the origin shift p=(1/4, 1/4, 0).
 - 2. How are the data of the *Reflection conditions* block of *Pmmn* (origin choice 1) can be obtained from the corresponding data of *Pmmn* (origin choice 2)? Why?

Attachments: Copies of the ITA pages with the space-group data of Pmmn (No. 59).

• Exercise 2.5.8. ITA and Non-conventional settings of space groups

Apart from the translation generators, the space group $Im\bar{3}m$ (No. 229) can be generated by the following five generators (\bar{x}, \bar{y}, z) , (\bar{x}, y, \bar{z}) , (z, x, y), (y, x, \bar{z}) and $(\bar{x}, \bar{y}, \bar{z})$, where the matrix-column presentations of the generators are given with respect to the conventional *I*-centred basis.

- 1. Define a transformation matrix from the conventional to a primitive basis;
- 2. What are the matrix-column pairs of the generators with respect to the primitive basis?
- 3. Consider the lattice points inside and at the border of the conventional unit cell: what are the coordinates of these points with respect to the chosen primitive basis?
- Exercise 2.5.9. Structure descriptions for different space-group settings (Wondratschek, 2002)
 - (a) In R. W. G. Wyckoff, *Crystal structures*, vol. II, Ch. VIII, one finds the important mineral zircon $ZrSiO_4$ and a description of its crystal structure. Many rare-earth phosphates, arsenates, and vanadates belong to the same structure type.

Structural data: Space group $I4_1/amd = D_{4h}^{19}$, No. 141; lattice constants a = 6.60 Å; c = 5.88 Å.

The origin choice is not stated explicitly. However, Wyckoff's *Crystal Structures* started to appear in 1948, when there was one conventional origin only (the later ORIGIN CHOICE 1, *i. e.* **Origin** at $\bar{4}m^2$).

$$\begin{array}{lll} Zr:&(a) & 0,0,0; \ 0,\frac{1}{2},\frac{1}{4}; \ \frac{1}{2},0,\frac{3}{4}; \ \frac{1}{2},\frac{1}{2},\frac{1}{2};\\ Si:&(b) & 0,0,\frac{1}{2}; \ 0,\frac{1}{2},\frac{3}{4}; \ \frac{1}{2},0,\frac{1}{4}; \ \frac{1}{2},\frac{1}{2},0;\\ O:&(h) & (0,u,v; \ 0,\bar{u},v; \ u,0,\bar{v}; \ \bar{u},0,\bar{v}; \ 0,\frac{1}{2}+u,\frac{1}{4}-v; \ 0,\frac{1}{2}-u,\frac{1}{4}-v;\\ & \bar{u},\frac{1}{2},v+\frac{1}{4}; \ u,\frac{1}{2},v+\frac{1}{4};) \ \left[\text{and the same with } (\frac{1}{2},\frac{1}{2},\frac{1}{2})+\right]. \end{array}$$

The parameters u and v are listed with u = 0.20 and v = 0.34.

(b) In the *Structure Reports*, vol. **22**, (1958), p. 314 one finds:

'a = 6.6164(5) Å, c = 6.0150(5) Å' 'Atomic parameters. Origin at center (2/m) at $0, \frac{1}{4}, \frac{1}{8}$ from $\overline{4}m2$.' 'Oxygen: (0, y, z) with y = 0.067, z = 0.198.'

Compare the two structure descriptions and check if they belong to the same structure type.

Hint: In order to compare the different data, one possibility would be to transform the structure data of Wyckoff's book to 'origin at center 2/m' description of the structure, *i. e.* to ORIGIN CHOICE 2 description where the relation between the two origins is given by the shift vector \boldsymbol{p} , $O(2)=O(1)+\boldsymbol{p}$ with $\boldsymbol{p}=0, \frac{1}{4}, \frac{1}{8}$.

Questions

- (i) What are the new coordinates of the Zr atoms?
- (ii) What are the new coordinates of the Si atoms ?
- (iii) What are the new coordinates of the O atom at 0, u, v?
- (iv) What are the new coordinates of the other O atoms?

2.5. SPACE-GROUP SYMMETRY DATA

For a physical problem it is advantageous to refer the crystal structure onto a primitive cell with origin in 2/m. The choice of the new basis is

 $a' = a; b' = b; c' = \frac{1}{2}(a + b + c).$

Questions

- (v) What are the new coordinates of the first Zr atom ?
- (vi) What are the new coordinates of the first Si atom ?
- (vii) What are the new coordinates of the O atom originally at 0, u, v?
- (viii) What are the lattice parameters of the primitive unit cell?
- Exercise 2.5.10. The non-translation generators of the space group Pccn are the symmetry operations $\{2_{100}|1/2, 1/2, 0\}, \{2_{010}|1/2, 1/2, 0\}$ and $\{\overline{1}|1/2, 1/2, 1/2\}$. Determine the coordinate triplets of the general positions of Pccn. Characterize geometrically the symmetry operations that are represented by these coordinate triplets. What are the special Wyckoff positions of Pccn? What are the matrix-column pairs of the symmetry operations of Pccn with respect to a new origin O' such that OO' = (1/4, 1/4, 1/4).
- Exercise 2.5.11. Determine the orientation and location of the three mutually perpendicular 2-fold rotation axes in the space groups P222, P222₁, P2₁2₁2 y P2₁2₁2₁.
- Exercise 2.5.12. $P12_1/n1$ is one of the non-conventional settings of the space group $P12_1/c1$. What is the orientation of the axes of the non-conventional setting with respect to the conventional ones?. Write down the transformation matrix that transforms the indices $(h_2k_2l_2)$, relative to the space group $P12_1/n1$, to the indices $(h_1k_1l_1)$ referred to the space group $P12_1/c1$?
- Exercise 2.5.13. Consider the following coordinate triplets of the general position of a space group \mathcal{G} :

$$\begin{array}{ll} (x,y,z) & (x,-y,1/2+z) \\ (1/2+x,1/2+y,z) & (1/2+x,1/2-y,1/2+z) \end{array}$$

- 1. What is the Hermann-Mauguin symbol of the space group?
- 2. Determine the special Wyckoff positions of the group.
- Exercise 2.5.14. Space-group description

The coordinate triplets of the general position of a space group \mathcal{G} are given as follows in the *International Tables for Crystallography*, Vol. A:

- - Construct the matrix-column pairs of the symmetry operations of the space group \mathcal{G} that correspond to these coordinate triplets;
 - Characterize geometrically the symmetry operations represented by the matrix-column pairs if they refer to a monoclinic basis (type and order of the symmetry operation, location, screw and glide vectors, etc.)
 - Write down the Hermann-Mauguin symbol of the space group \mathcal{G} . Calculate the integral (due to the lattice), zonal (due to glide planes) and serial (due to screw axes) systematic absences.
 - Consider the point A with coordinates (0.127, 0.261, 0.76). Write down the coordinates of the set of points in the unit cell of \mathcal{G} symmetrically equivalent to A. Is it a *general-position* point?

- Consider the point B with coordinates (3/2, 0.77, -1/4). Determine the site-symmetry group of B and write down the set of points in the unit cell of \mathcal{G} symmetrically equivalent to B.
- How are transformed
 - (i) the coordinates of points A and B;
 - (ii) the matrix-column pairs of the symmetry operation of \mathcal{G} ;

under the change of the basis $\mathbf{a'=c}$, $\mathbf{b'=a}$, $\mathbf{c'=b}$. Write down the Hermann-Mauguin symbol of \mathcal{G} with respect to the 'primed' setting $\mathbf{a',b',c'}$.

- Determine the symmetry restrictions on the atomic anisotropy temperature factors $\beta_{ij}, i, j = 1, 2, 3$ for the site *B*. (Under the symmetry operations of the site-symmetry group, the matrix $||\beta_{ij}||, i, j = 1, 2, 3$ of the coefficients of the atomic anisotropy temperature factors transforms as a symmetrized tensor of rank 2.)
- (optional): Draw the general-position diagram and the symmetry-element diagram of \mathcal{G} in projection (\mathbf{a}, \mathbf{c}) .
- Exercise 2.5.15. Space-group symmetry: crystal-physics properties
 - (i) Complete the data for each of the space groups given in the following table

Space group	Crystal system	Point group	Laue class	Pyroelectricity (*)
P222				
$P2_1/a$				
Fmm2				
$I42_{1}2$				
$P\bar{4}c2$				
R3m				
$P\bar{3}c1$				
P23				

(*) Indicate in the column if the space-group symmetry allows pyroelectricity; specify the direction of the polarization in the cases of possible pyroelectric effect.

- (ii) Indicate and prove for which of the space groups given in the table the piezoelectric effect is forbidden.
- (iii) Which of the space groups given in the table are polar?

2.6 Group-subgroup relations of space groups

- Exercise 2.6.1. Translation engleiche subgroups of P4mm
 - (a) Construct the diagram of the t-subgroups of P4mm using the 'analogy' with the subgroup diagram of the group 4mm, cf. Exercise 2.2.7. Give the standard Hermann-Mauguin symbols of the t-subgroups of P4mm.
 - (b) With the help of the program SUBGROUPGRAPH obtain the graph of the *t*-subgroups of P4mm (No. 99). Explain the difference between the *contracted* and *complete* graphs of the *t*-subgroups of P4mm (No. 99).
 - (c) Explain why the t-subgroup graphs of all 8 space groups from No. 99 (P4mm) to No. 106 $(P4_2bc)$ show the same 'topology' (*i. e.* the same type of 'family tree'), only the corresponding subgroup entries differ.

- Exercise 2.6.2. Study the group-subgroup relations between the groups $\mathcal{G} = P4_12_12$, No. 92, and $\mathcal{H} = P2_1$, No. 4 using the program SUBGROUPGRAPH. Consider the cases with specified (*e.g.* [i] = 4) and unspecified index of the group-subgroup pair.
- Exercise 2.6.3. Domain-structure analysis

Determine the type and number of domain states in structural phase transitions specified by:

- 1. High-symmetry phase: P2/mLow-symmetry phase: P1 with small unit-cell deformation;
- 2. High-symmetry phase: P2/mLow-symmetry phase: P1 with duplication of the unit cell;
- 3. High-symmetry phase: *P4mm* Low-symmetry phase: *P2* of index 8;
- High-symmetry phase: P42bc
 Low-symmetry phase: P21 of index 8.
- Exercise 2.6.4. Phase transitions in BaTiO₃

The crystal structure of BaTiO₃ is of perovskite type. Above 120C BaTiO₃ has the ideal paraelectric cubic structure (space group $Pm\bar{3}m$) shown in Figure 2.1. Below 120C BaTiO₃ assumes three structures with slightly deformed unit cells, all three being ferroelectric with different directions of the axis of spontaneous polarisation (polar axis). The three ferroelectric polymorphs differ in the direction of displacement of the Ti-atoms from the centres of the octahedra (and the accompanying lattice distortion):

- (a) No displacement: cubic structure
- (b) Displacement parallel to a cube edge: < 100 >, symmetry group P4mm;
- (c) Displacement parallel to face diagonal of the cube: < 110 >, symmetry group Amm2;
- (d) Displacement parallel to a body diagonal of the cube: < 111 >, symmetry group R3m.



Figure 2.1: (1) Perovskite structure (undistorted); (2) Distorted perovskite structure: Ti displacements and lattice distortion parallel to a cube edge, and the related dipole generation in $BaTiO_3$

Questions

- (i) Which subgroup indices do the three space groups of the ferroelectric polymorphs display with respect to the cubic group $Pm\bar{3}m$?
- (ii) How many orientation states of the twin domains occur for each polymorph? Which mutual orientation do the domains exhibit for case (b)?

• Exercise 2.6.5. SrTiO₃ has the cubic perovskite structure, space group $Pm\bar{3}m$. Upon cooling below 105K, the coordination octahedra are mutually rotated and the space group is reduced to I4/mcm; c is doubled and the unit cell is increased by the factor of four. Can we expect twinned crystals of the low symmetry form? If so, how many kinds of domains?

Determine the number and type of domains of the low-symmetry form of $SrTiO_3$ using the computer tools of the Bilbao Crystallographic server.

- Exercise 2.6.6. Study the splittings of the Wyckoff positions for the group-subgroup pair P4mm (No. 99)> Cm (No. 4) of index 4 by the program WYCKSPLIT.
- Exercise 2.6.7. Consider the group-supergroup pair $\mathcal{H} < \mathcal{G}$ with $\mathcal{H} = P222$, No. 16, and the supergroup $\mathcal{G} = P422$, No. 89, of index [i] = 2. Using the program MINSUP determine all supergroups P422 of P222 of index [i] = 2. How does the result depend on the normalizer of the supergroup and/or that of the subgroup.

2.7 Symmetry relations between crystal structures

Structure data for the exercises: ExercisesData-Beijing2022.txt

- Exercise 2.7.1. Structure descriptions for different space-group settings (Wondratschek, 2002) Do the calculations of the Problem 2.5.9 applying the corresponding tools of the Bilbao Crystallographic server (the text of the problem is repeated below).
 - (a) In R. W. G. Wyckoff, *Crystal structures*, vol. II, Ch. VIII, one finds the important mineral zircon $ZrSiO_4$ and a description of its crystal structure. Many rare-earth phosphates, arsenates, and vanadates belong to the same structure type.

Structural data: Space group $I4_1/amd = D_{4h}^{19}$, No. 141; lattice constants a = 6.60 Å; c = 5.88 Å.

The origin choice is not stated explicitly. However, Wyckoff's *Crystal Structures* started to appear in 1948, when there was one conventional origin only (the later ORIGIN CHOICE 1, *i. e.* **Origin** at $\bar{4}m^2$).

 $\begin{array}{lll} Zr:&(a)&0,0,0;\ 0,\frac{1}{2},\frac{1}{4};\ \frac{1}{2},0,\frac{3}{4};\ \frac{1}{2},\frac{1}{2},\frac{1}{2};\\ Si:&(b)&0,0,\frac{1}{2};\ 0,\frac{1}{2},\frac{3}{4};\ \frac{1}{2},0,\frac{1}{4};\ \frac{1}{2},\frac{1}{2},0;\\ O:&(h)&(0,u,v;\ 0,\bar{u},v;\ u,0,\bar{v};\ \bar{u},0,\bar{v};\ 0,\frac{1}{2}+u,\frac{1}{4}-v;\ 0,\frac{1}{2}-u,\frac{1}{4}-v;\\ & \bar{u},\frac{1}{2},v+\frac{1}{4};\ u,\frac{1}{2},v+\frac{1}{4};)\ [\text{ and the same with }(\frac{1}{2},\frac{1}{2},\frac{1}{2})+]. \end{array}$

The parameters u and v are listed with u = 0.20 and v = 0.34.

(b) In the *Structure Reports*, vol. **22**, (1958), p. 314 one finds:

'a = 6.6164(5) Å, c = 6.0150(5) Å' 'Atomic parameters. Origin at center (2/m) at $0, \frac{1}{4}, \frac{1}{8}$ from $\overline{4}m2$.' 'Oxygen: (0, y, z) with y = 0.067, z = 0.198.'

Compare the two structure descriptions and check if they belong to the same structure type. Which of the structure tools of the Bilbao Crystallographic Server could help you to solve the problem?

Hint: In order to compare the different data, the parameters of Wyckoff's book are to be transformed to 'origin at center 2/m', *i. e.* ORIGIN CHOICE 2.

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- Exercise 2.7.2. Equivalent structure descriptions
 - (a) CsCl is cubic, space group $Pm\bar{3}m$, with the following co-ordinates

Atom	Wyckoff	Coordinate	triplets	
	position	x	y	z
Cl	1a	0.0	0.0	0.0
\mathbf{Cs}	1b	0.5	0.5	0.5

How many equivalent sets of co-ordinates can be used to describe the structure? What are their co-ordinates?

Hint: The number of different equivalent descriptions of CsCl is equal to the index of its space group $Pm\bar{3}m(\mathbf{a}, \mathbf{b}, \mathbf{c})$ in the Euclidean normalizer $Im\bar{3}m(\mathbf{a}, \mathbf{b}, \mathbf{c})$, *i.e.* [i] = 2. The two different descriptions are generated by the coset representatives of the decomposition of the normalizer with respect to the space group.

(b) $P(C_6C_5)_4$ [MoNCl₄] is tetragonal, space group P4/n, with the following co-ordinates:

Atom	Wyckoff	Coordinate	triplets		
	position	x	y	z	
Р	2b	0.25	0.75	0	
Mo	2c	0.25	0.25	0.121	(II and C2 to C6 amitted)
Ν	2c	0.25	0.25	-0.093	(H and C3 to C6 omitted)
C1	8g	0.362	0.760	0.141	
C2	8g	0.437	0.836	0.117	
Cl	8g	0.400	0.347	0.191	

How many equivalent sets of co-ordinates can be used to describe the structure? What are their co-ordinates?

Hint: The number of different equivalent descriptions of $P(C_6C_5)_4[MoNCl_4]$ is equal to the index of its space group P4/n in the Euclidean normalizer. The different descriptions are generated by the coset representatives of the decomposition of the normalizer with respect to the space group. In the special case of $P(C_6C_5)_4[MoNCl_4]$ such equivalent descriptions can be generated, for example, by the translations t(0, 0, 1/2) and t(1/2, 1/2, 0), and by a reflection through a mirror plane at (x, x, z) represented by the coordinate triplet (y, x, z).

• Exercise 2.7.3. Isoconfigurational structure types (Koch & , Fischer, 2002)

Do the following three structures belong to the same structure type? Try to find analogous coordinate descriptions for all three crystal structures.

1.	KAsF_6	(ICSD: 59	413)		
	Unit C	ell 7.3	48(1) 7.348	(1) 7.274(8)	8) 90. 90. 120
	Space g	group R-3	3h		
	Atom	Wyckoff	Coordinate	triplets	
		position	x	y	z
	K	3b	0.33333	0.66667	0.166667
	As	3a	0	0	0
	\mathbf{F}	18f	0.1292(2)	0.2165(2)	0.1381(2)

2. BaIrF₆ (ICSD: 803188)

	Unit Ce Space g	ell 7.39 group R-3	$965(1) ext{ 7.396} \ ext{Bh}$	55(1) 7,282	6(1) 90. 90. 120
	Atom	Wyckoff	Coordinate	triplets	
		position	x	y	z
	Ba	3b	0.33333	0.6666	0.166666
	Ir	3a	0	0	0
	\mathbf{F}	18f	0.0729(2)	0.2325(2)	0.1640(2)
3.	BaSnFe	, (ICSD: 33	3788)		
	Unit Ce	ell 7.4	279(2) 7.427	79(2) 7.418	(2) 90. 90. 120
	Space g	roup R-3	Bh		
	Atom	Wyckoff	Coordinate	triplets	
		position	x	y	<i>z</i>
	Ba	3a	0	0	0
	Sn	3b	0	0	0.5
	\mathbf{F}	18f	0.2586(3)	0.8262(3)	0.0047(3)

Hint: Consider the Euclidean normalizer of symmetry group $R\overline{3}$ (hex) of KAsF₆. The number of different equivalent descriptions of KAsF₆ is equal to the index of its space group in the Euclidean normalizer. The different descriptions are generated by the coset representatives of the decomposition of the normalizer with respect to the space group. In the special case of KAsF₆ such equivalent descriptions can be generated, for example, by the translation t(0, 0, 1/2), by a reflection through a mirror plane at (x, -x, z) represented by the coordinate triplet (-y, -x, z), etc.

• Exercise 2.7.4. Crystal structure descriptions

In Inorganic Crystal Structure Database can be found several structure data sets of ϵ -Fe₂O₃, all of them of symmetry $Pna2_1$ (No.33). Compare the two structure descriptions listed in the *Exercise Data* file and check if they belong to the same structure type.

• Exercise 2.7.5. Cristobalite phase transitions

At low temperatures, the space-group symmetry of cristobalite is given by the space group is $P4_{1}2_{1}2$ (92) with lattice parameters a = 4.9586Å, c = 6.9074Å. The four silicon atoms are located in Wyckoff position 4(a)..2 with the coordinates x, x, 0; -x, -x, 1/2; 1/2 - x, 1/2 + x, 1/4; 1/2 + x, 1/2 - x, 3/4, x = 0.3028. During the phase transition, the tetragonal structure is transformed into a cubic one with space group $Fd\bar{3}m(227)$, a = 7.147A. It is listed in the space-group tables with two different origins.

- 1. If Origin choice 2 setting is used (with point symmetry $\bar{3}m$ at the origin), then the silicon atoms occupy the position 8(a) $\bar{4}3m$ with the coordinates 1/8, 1/8, 1/8, 7/8, 3/8, 3/8 and those related by the face - centring translations. Describe the structural distortion from the cubic to the tetragonal phase by the determination of (i) the displacements if the Si atoms in relative and absolute units, and (ii) the lattice distortion accompanying the transition.
- 2. Repeat the calculations for the characterization of the phase transition using the *Origin-choice* 1 description of the high-symmetry phase (*cf. Exercise Data* file for the structure data).
- Exercise 2.7.6. Ferroelastic phase transitions

2.7. SYMMETRY RELATIONS BETWEEN CRYSTAL STRUCTURES

- (a) Lead phosphate $Pb_3(PO_4)_2$ shows a phase transition from a paraelastic high-temperature phase with symmetry $R\bar{3}m$ (No.166) to a ferroelastic phase of symmetry C2/c (No.15). Using the structure data given in the *ExerciseData* file and the tools of the *Bilbao Crystallographic Server*:
 - (a) characterize the symmetry reduction between the high- and low-symmetry phases (index and transformation matrix);
 - (b) describe the structural distortion from the rhombohedral to the monoclinic phase by the evaluation of the lattice strain and the atomic displacements accompanying the phase transition.
- (b) Lead phosphate-vanadate $Pb_3(PVO_4)_2$ shows a phase transition from a paraelastic hightemperature phase with symmetry $R\bar{3}m$ (No.166) to a ferroelastic phase of symmetry $P2_1/c$ (No.14). Using the structure data given in the *ExerciseData* file and the tools of the *Bilbao Crystallographic Server* describe the structural distortion from the rhombohedral to the monoclinic phase by the evaluation of the lattice strain and the atomic displacements accompanying the phase transition.
- Exercise 2.7.7. Order-disorder phase transitions in CuAu alloy
 - (i) A high-temperature form where Au and Cu are distributed statistically over the sites of an fcc packing: *i.e.* symmetry $Fm\bar{3}m$, Wyckoff position $4a \ m\bar{3}m \ 0, 0, 0$ and a lattice parameter $a_c = 3.83 \text{\AA}$;
 - (ii) A low temperature phase where Au and Cu are ordered in layers perpendicular to one of the four-fold axes of $Fm\bar{3}m$: the positions 0,0,0 and 1/2,1/2,0 are occupied by Cu, and 1/2,0,1/2 and 0,1/2,1/2 by Au. The symmetry is reduced to P4/mmm, with lattice parameters $a_t = 2.86\text{\AA}$, $c_t = a_c$.
 - (a) characterize the symmetry reduction between the high- and low-symmetry phases (index and transformation matrix);
 - (b) describe the structural distortion from the rhombohedral to the monoclinic phase by the evaluation of the lattice strain and the atomic displacements accompanying the phase transition.
- Exercise 2.7.8. CoU hettotype of the β -brass structure

Show that the crystal structure of CoU maybe interpreted as a slightly distorted CsCl (or β -brass, CuZn)-type structure. Using the structural data in the *Exercise Data* file, characterize the structural relationship between the CoU structure and CsCl structure.

- Exercise 2.7.9. (Müller, 2008): Crystal-structure relationships
 - 1. HT-quartz and LT-quartz

Upon heating above 573 °C the LT-quartz transforms to its HT form. Set up the corresponding Bärnighausen tree that describes the symmetry relations between the two quartz forms. Which additional degree of freedom are present in the lower symmetry form?

The crystal data of LT-quartz are:

Unit C	ell: 4.	91 4.91	5.41 9	0. 90. 120
Space g	group: P	3_221		
Atom	Wyckoff	Coordinate	triplet	s
	position	x	y	z
Si	3a	0.470	0	$\frac{1}{6}$
Ο	6c	0.414	0.268	0.286

	THC OL	/			
	Unit C	ell: 5	5 5.4	6 90. 9	90. 120.
	Space §	group: P	$6_2 22$		
	Atom	Wyckoff	Coordinate	triplets	5
		position	x	y	z
	Si	3c	0.5	0	0.5
	Ο	6j	0.416	0.208	0.66666
2.	$\overline{\alpha}$ -AlPO	D_A			
		- T			
	The cry	ystal data o	of α -AlPO ₄ :		
	The cry Unit C	ystal data o ell: 4.9	of α -AlPO ₄ : 94 4.94	10.95	90. 90. 120
	The cry Unit C Space g	ystal data o ell: 4.9 group: <i>P</i> :	of α -AlPO ₄ : 94 4.94 $\beta_1 21$	10.95	90. 90. 120
	$\frac{\text{The cry}}{\text{Unit C}}$ $\frac{\text{Space g}}{\text{Atom}}$	ystal data o ell: 4.9 group: P3 Wyckoff	$\begin{array}{c} \text{of } \alpha \text{-AlPO}_4: \\ 04 & 4.94 \\ 03_121 \\ \hline \text{Coordinate} \end{array}$	10.95 triplets	90. 90. 120 s
	The cry Unit C Space g Atom	ystal data o ell: 4.9 group: <i>P</i> Wyckoff position	$\begin{array}{c} \text{of } \alpha \text{-AlPO}_4: \\ 94 & 4.94 \\ 3_1 21 \\ \hline \text{Coordinate} \\ x \end{array}$	$\frac{10.95}{\text{triplets}}$	90. 90. 120
	$\frac{\text{The cry}}{\text{Space g}}$ $\frac{\text{Space g}}{\text{Atom}}$ $\frac{\text{Al}}{\text{Al}}$	ystal data o ell: 4.9 group: P Wyckoff position 3a	$ \begin{array}{c} \text{of } \alpha \text{-AlPO}_4: \\ 04 & 4.94 \\ 3_121 \\ \hline \text{Coordinate} \\ x \\ \hline 0.466 \\ \end{array} $	$\frac{10.95}{\text{triplets}}$	90. 90. 120 s z 0.33333
	$\frac{\text{The cry}}{\text{Unit C}}$ $\frac{\text{Space g}}{\text{Atom}}$ $\frac{\text{Al}}{\text{P}}$	ystal data o ell: 4.9 group: P: Wyckoff position 3a 3b	$\begin{array}{c} \text{of } \alpha \text{-AlPO}_4: \\ 94 & 4.94 \\ 3_1 21 \\ \hline \text{Coordinate} \\ x \\ \hline 0.466 \\ 0.467 \end{array}$	$ \begin{array}{c} 10.95 \\ \hline triplets \\ y \\ 0 \\ 0 \end{array} $	90. 90. 120 s z 0.33333 $\frac{5}{6}$
	The cry Unit C Space g Atom Al P O1	ystal data o ell: 4.9 group: P ? Wyckoff position 3a 3b 6c	$ \begin{array}{c} & \text{of } \alpha \text{-AlPO}_4: \\ \hline 94 & 4.94 \\ \hline 3_1 21 \\ \hline \text{Coordinate} \\ \hline x \\ \hline 0.466 \\ 0.467 \\ 0.417 \\ \end{array} $	$ \begin{array}{c} 10.95 \\ \hline triplets \\ \hline y \\ \hline 0 \\ \hline 0 \\ \hline 0.292 \\ \end{array} $	90. 90. 120 z 0.33333 $\frac{5}{6}$ 0.398

What is the symmetry relation of α -AlPO₄ to quartz?

• Exercise 2.7.10. Hettotypes of the fluorite structure (Hahn & Wondratschek, 1984)

The structure of α -XOF (X=La, Y, and Pu) can be derived from that of cubic CaF₂ (fluorite structure) by splitting the fluorine positions into two: one for oxygen and one for fluorine, and by shifting the metal positions along c. By these changes the space-group symmetry is reduced.

The conventional basis \mathbf{a}' , \mathbf{b}' , \mathbf{c}' of α -XOF is $\mathbf{a}' = \frac{1}{2}(\mathbf{a} - \mathbf{b})$, $\mathbf{b}' = \frac{1}{2}(\mathbf{a} + \mathbf{b})$, $\mathbf{c}' = \mathbf{c}$ where $\mathbf{a}, \mathbf{b}, \mathbf{c}$ is the basis of CaF₂. Moreover, the conventional origin of α -XOF is shifted by $\mathbf{p} = \frac{1}{4}, 0, \frac{1}{4}$ relative to that of α -XOF (symmetry group P4/nmm (129)).

The coordinates of CaF_2 are:

Ca $4a \ m\bar{3}m$ 0,0,0 $\frac{1}{2}, \frac{1}{2}, 0$ $\frac{1}{2}, 0\frac{1}{2}$ 0, $\frac{1}{2}, \frac{1}{2}$ F $8c \ \bar{4}3m$ $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{3}{4}, \frac{3}{4}$

Questions

- (i) Display the relation between the old $(\mathbf{a}, \mathbf{b}, \mathbf{c})$ and the new $(\mathbf{a}', \mathbf{b}', \mathbf{c}')$ unit cell by means of a drawing.
- (ii) Which is the crystal system of the new unit cell? Which is its centring type? (The lattice of CaF₂ is *F*-centred cubic (*fcc*), a = b = c, $\alpha = \beta = \gamma$.)
- (iii) Construct the transformation matrix P describing the change of the basis.
- (iv) What is the volume of the new unit cell compared to that of the old one?
- (v) What are the coordinates of the atoms of the CaF₂ structure referred to the new coordinate system?
- (vi) Can the structure of α -LaOF be considered as a *hettotype* (derivative structure) of the *aristo-type* (basic) structure of CaF₂ ? (structure data of α -LaOF in *Exercise Data* file)

2.7. SYMMETRY RELATIONS BETWEEN CRYSTAL STRUCTURES

• Exercise 2.7.11. Structural pseudosymmetry of Pb₂MgWO₆

Analyse the structural pseudosymmetry of Pb_2MgWO_6 using the program PSEUDO, *cf.* structure data in *Exercise Data* file: (i) Try to determine the maximal possible preudosymmetry stepwise, *i.e. climbing* via the minimal supergroups (applying Option 1 of the program); (ii) Apply Option 3 of PSEUDO (Pseudosymmetry search for a specific supergroup given by a transformation matrix (\mathbf{P}, \mathbf{p})) to confirm the flagged maximal pseudosymmetry in (i).

• **Exercise** 2.7.12. Structural pseudosymmetry of a $C222_1$ structure

Using the program PSEUDO, Option1, analyse the structural pseudosymmetry of a hypothetical $C222_1$ (No. 20) structure stepwise, *i.e. climbing* via the minimal supergroups (*cf.* structure data in *Exercise Data* file). Compare the results if different minimal-supergroup paths are followed.

• Exercise 2.7.13. Apparently complex phase Ga-II of Ga under pressure

Analyse the structural pseudosymmetry of the orthorhombic phase Ga-II of Ga under pressure using the program **PSEUDO** (structure data in *Exercise Data* file).

Hint: As a first step check the structural pseudosymmetry with respect to an isomorphic supergroup of index 13 (can you guess why?), specified by the transformation matrix: **a**,**b**,13**c**, Option 3.

• Exercise 2.7.14. Tetragonal phase of GeF₂

The compound GeF₂, of symmetry $P2_12_12_1$ (No. 19) (*cf.* structure data in *Exercise Data* file), is reported to have at high temperatures an unknown tetragonal phase, with the primitive unit cell volume being essentially maintained. Using PSEUDO, with the option 2, which allows to check supergroups with a fixed k-index (multiplication of the primitive unit cell), postulate a probable space group or groups and a starting structural model for this high-temperature phase.

• Exercise 2.7.15. Non-polar phases of NaSb₃F₁₀

The compound NaSb₃F₁₀ whose room-temperatute phase is polar, space group $P6_3$, has been predicted to be ferroelectric (*cf.* structure data in *Exercise Data* file). The symmetries $P6_322$ and $P6_3/mmc$ had been proposed for two successive non-polar phases at high temperature. Applying the pseudosymmetry approach confirm the predictions for the non-polar phases of NaSb₃F₁₀. Show that apart from $P6_322$ phase, there are two more appropriate candidates for the intermediate phases between the polar phase $P6_3$ and the non-polar one of maximal symmetry, $P6_3/mmc$.

• Exercise 2.7.16. Structural pseudosymmetry of Nd₄GeO₈

The compound Nd₄GeO₈ is reported to have polar $Pmc2_1$ symmetry (*Doklady Akademii Nauk* SSSR (1978) **241**, 353-356) (*cf.* structure data in *Exercise Data* file).

- (i) Using PSEUDO (Option 1), show that this structure can be considered a small distortion of a *Cmcm* structure.
- (ii) Using SUBGROUPGRAPH show the graph of maximal subgroups connecting the two symmetries.
- (iii) Using again PSEUDO (Option 3) obtain the atomic displacements relating the two structures.
- Exercise 2.7.17. Overlooked symmetry of Ca₂Ge₇O₁₆

According to a structural model for $Ca_2Ge_7O_{16}$ published in *Doklady Akademii Nauk SSSR* (1979) **245**, 110-113, the symmetry group of the compound is *Pba2*.

Despite the 4/mmm Laue symmetry of the diffraction diagram the authors of this publication were unable to find an appropriate tetragonal structural model, and refined the compound in *Pba2* symmetry.

Using PSEUDO, demonstrate that this structure differs from a tetragonal one with space group $P\bar{4}b2$, by atomic displacements which are practically negligible or within experimental accuracy, so that in fact this structure file should be considered incorrect, being a case of *overlooked symmetry*. The pseudosymmetry of the structure was reported in (*Acta Cryst.* B (2002) **58**, 921) and the compound has been recently confirmed to have $P\bar{4}b2$ symmetry by a new study of the structure (*Acta Cryst.* C (2007) **63**, i47).

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