

5.2. TRANSFORMATIONS OF SYMMETRY OPERATIONS

The orthogonality of the basis vectors \mathbf{a} , \mathbf{b} , \mathbf{c} of direct space and the basis vectors \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* of reciprocal space,

$$\begin{pmatrix} \mathbf{a}^* \\ \mathbf{b}^* \\ \mathbf{c}^* \end{pmatrix} (\mathbf{a}, \mathbf{b}, \mathbf{c}) = \begin{pmatrix} \mathbf{a}^* \cdot \mathbf{a} & \mathbf{a}^* \cdot \mathbf{b} & \mathbf{a}^* \cdot \mathbf{c} \\ \mathbf{b}^* \cdot \mathbf{a} & \mathbf{b}^* \cdot \mathbf{b} & \mathbf{b}^* \cdot \mathbf{c} \\ \mathbf{c}^* \cdot \mathbf{a} & \mathbf{c}^* \cdot \mathbf{b} & \mathbf{c}^* \cdot \mathbf{c} \end{pmatrix} = \mathbf{I},$$

is invariant under a general (affine) transformation. Since both sets of basis vectors are transformed, \mathbf{a}^* is always perpendicular to the plane defined by \mathbf{b} and \mathbf{c} and \mathbf{a}'^* perpendicular to \mathbf{b}' and \mathbf{c}' etc.

5.2.2.1. Position vector

The position vector \mathbf{r} in direct space,

$$\mathbf{r} = (\mathbf{a}, \mathbf{b}, \mathbf{c}) \begin{pmatrix} x \\ y \\ z \end{pmatrix} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c},$$

is invariant if the origin of the coordinate system is not changed in the transformation (see example in Section 5.1.3).

5.2.2.2. Modulus of position vector

The modulus r of the position vector \mathbf{r} gives the distance of the point x, y, z from the origin. Its square is obtained by the scalar product

$$\begin{aligned} \mathbf{r}^t \cdot \mathbf{r} = r^2 &= (x, y, z) \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix} (\mathbf{a}, \mathbf{b}, \mathbf{c}) \begin{pmatrix} x \\ y \\ z \end{pmatrix} \\ &= (x, y, z) \mathbf{G} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \\ &= x^2 a^2 + y^2 b^2 + z^2 c^2 + 2yzbc \cos \alpha \\ &\quad + 2xzac \cos \beta + 2xyab \cos \gamma, \end{aligned}$$

with \mathbf{r}^t the transposed representation of \mathbf{r} ; a, b, c the moduli of the basis vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}$ (lattice parameters); \mathbf{G} the metric matrix of direct space; and α, β, γ the angles of the unit cell.

The same considerations apply to the vector \mathbf{r}^* in reciprocal space and its modulus r^* . Here, \mathbf{G}^* is applied. Note that \mathbf{r}^* and r^* are independent of the choice of the origin in direct space.

5.2.2.3. Metric matrix

The metric matrix \mathbf{G} of the unit cell in the direct lattice

$$\mathbf{G} = \begin{pmatrix} \mathbf{a} \cdot \mathbf{a} & \mathbf{a} \cdot \mathbf{b} & \mathbf{a} \cdot \mathbf{c} \\ \mathbf{b} \cdot \mathbf{a} & \mathbf{b} \cdot \mathbf{b} & \mathbf{b} \cdot \mathbf{c} \\ \mathbf{c} \cdot \mathbf{a} & \mathbf{c} \cdot \mathbf{b} & \mathbf{c} \cdot \mathbf{c} \end{pmatrix} = \begin{pmatrix} aa & ab \cos \gamma & ac \cos \beta \\ ba \cos \gamma & bb & bc \cos \alpha \\ ca \cos \beta & cb \cos \alpha & cc \end{pmatrix}$$

changes under a linear transformation, but \mathbf{G} is invariant under a symmetry operation of the lattice. The volume of the unit cell V is obtained by

$$V^2 = \det(\mathbf{G}).$$

The same considerations apply to the metric matrix \mathbf{G}^* of the unit cell in the reciprocal lattice and the volume V^* of the reciprocal-lattice unit cell. Thus, there are two invariants under an affine transformation, the product

$$VV^* = 1$$

and the product

$$\mathbf{G}\mathbf{G}^* = \mathbf{I}.$$

5.2.2.4. Scalar product

The scalar product

$$\mathbf{r}^* \cdot \mathbf{r} = hx + ky + lz$$

of the vector \mathbf{r}^* in reciprocal space with the vector \mathbf{r} in direct space is invariant under a linear transformation but not under a shift of origin in direct space.

A vector \mathbf{r} in direct space can also be represented as a product of augmented matrices:

$$\mathbf{r} = (\mathbf{a}, \mathbf{b}, \mathbf{c}, 0) \begin{pmatrix} x \\ y \\ z \\ 1 \end{pmatrix} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}.$$

As stated above, the basis vectors are transformed only by the linear part, even in the case of a general affine transformation. Thus, the transformed position vector \mathbf{r}' is obtained by

$$\mathbf{r}' = (\mathbf{a}, \mathbf{b}, \mathbf{c}, 0) \begin{pmatrix} \mathbf{P} & \mathbf{o}^t \\ \mathbf{o} & 1 \end{pmatrix} \begin{pmatrix} \mathbf{Q} & \mathbf{q} \\ \mathbf{o} & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \\ 1 \end{pmatrix}.$$

The shift \mathbf{p} is set to zero. The shift of origin is contained in the matrix \mathbf{Q} only.

Similarly, a vector in reciprocal space can be represented by

$$\mathbf{r}^* = (h, k, l, 1) \begin{pmatrix} \mathbf{a}^* \\ \mathbf{b}^* \\ \mathbf{c}^* \\ 0 \end{pmatrix} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*.$$

The coordinates h, k, l in reciprocal space transform also only linearly. Thus,

$$\mathbf{r}^{*t} = (h, k, l, 1) \begin{pmatrix} \mathbf{P} & \mathbf{o}^t \\ \mathbf{o} & 1 \end{pmatrix} \begin{pmatrix} \mathbf{Q} & \mathbf{q} \\ \mathbf{o} & 1 \end{pmatrix} \begin{pmatrix} \mathbf{a}^* \\ \mathbf{b}^* \\ \mathbf{c}^* \\ 0 \end{pmatrix}.$$

The reader can see immediately that the scalar product $\mathbf{r}^* \cdot \mathbf{r}$ transforms correctly.

5.2.3. Example: low cristobalite and high cristobalite

The positions of the silicon atoms in the low-cristobalite structure (Nieuwenkamp, 1935) are compared with those of the high-cristobalite structure (Wyckoff, 1925; cf. Megaw, 1973). At low temperatures, the space group is $P4_12_12$ (92). The four silicon atoms are located in Wyckoff position $4(a)$..2 with the coordinates $x, x, 0; \bar{x}, \bar{x}, \frac{1}{2}; \frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{4}; \frac{1}{2} + x, \frac{1}{2} - x, \frac{3}{4}; x = 0.300$. During the phase transition, the tetragonal structure is transformed into a cubic one with space group $Fd\bar{3}m$ (227). It is listed in the space-group tables with two different origins. We use 'Origin choice 1' with point symmetry $43m$ at the origin. The silicon atoms occupy the position $8(a)$ $43m$ with the coordinates $0, 0, 0; \frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ and those related by the face-centring translations. In the diamond structure, the carbon atoms occupy the same position.

In order to compare the two structures, the conventional P cell of space group $P4_12_12$ (92) is transformed to an unconventional C cell (cf. Section 4.3.4), which corresponds to the F cell of $Fd\bar{3}m$ (227). The P and the C cells are shown in Fig. 5.2.3.1. The coordinate system $\mathbf{a}', \mathbf{b}', \mathbf{c}'$ with origin O' of the C cell is obtained from that of

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the P cell, origin O , by the linear transformation

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

and the shift

$$\mathbf{p} = \frac{1}{4}\mathbf{a} + \frac{1}{4}\mathbf{b}.$$

The matrices \mathbf{P} , \mathbf{p} and \mathbb{P} are thus given by

$$\mathbf{P} = \begin{pmatrix} 1 & \bar{1} & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \mathbf{p} = \begin{pmatrix} \frac{1}{4} \\ \frac{1}{4} \\ 0 \end{pmatrix}, \quad \mathbb{P} = \begin{pmatrix} 1 & \bar{1} & 0 & \frac{1}{4} \\ 1 & 1 & 0 & \frac{1}{4} \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

From Fig. 5.2.3.1, we derive also the inverse transformation

$$\mathbf{a} = \frac{1}{2}\mathbf{a}' - \frac{1}{2}\mathbf{b}', \quad \mathbf{b} = \frac{1}{2}\mathbf{a}' + \frac{1}{2}\mathbf{b}', \quad \mathbf{c} = \mathbf{c}', \quad \mathbf{q} = -\frac{1}{4}\mathbf{a}'.$$

Thus, the matrices \mathbf{Q} , \mathbf{q} and \mathbb{Q} are

$$\mathbf{Q} = \mathbf{P}^{-1} = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{\bar{1}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \mathbf{q} = -\mathbf{P}^{-1}\mathbf{p} = \begin{pmatrix} \frac{\bar{1}}{4} \\ 0 \\ 0 \end{pmatrix},$$

$$\mathbb{Q} = \mathbb{P}^{-1} = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 & \frac{\bar{1}}{4} \\ \frac{\bar{1}}{2} & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

The coordinates x, y, z of points in the P cell are transformed by \mathbb{Q} :

$$\begin{pmatrix} x' \\ y' \\ z' \\ 1 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 & \frac{\bar{1}}{4} \\ \frac{\bar{1}}{2} & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \\ 1 \end{pmatrix} = \begin{pmatrix} \frac{1}{2}(x+y) - \frac{1}{4} \\ \frac{1}{2}(-x+y) \\ z \\ 1 \end{pmatrix}.$$

The coordinate triplets of the four silicon positions in the P cell are 0.300, 0.300, 0; 0.700, 0.700, $\frac{1}{2}$; 0.200, 0.800, $\frac{1}{4}$; 0.800, 0.200, $\frac{3}{4}$. Four triplets in the C cell are obtained by inserting these values into the equation just derived. The new coordinates are 0.050, 0, 0; 0.450, 0, $\frac{1}{2}$; 0.250, 0.300, $\frac{1}{4}$; 0.250, -0.300 , $\frac{3}{4}$. A set of four further points is obtained by adding the centring translation $\frac{1}{2}, \frac{1}{2}, 0$ to these coordinates.

The indices h, k, l are transformed by the matrix \mathbf{P} :

$$(h', k', l') = (h, k, l) \begin{pmatrix} 1 & \bar{1} & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = (h+k, -h+k, l),$$

i.e. the reflections with the indices h, k, l of the P cell become reflections $h+k, -h+k, l$ of the C cell.

The symmetry operations of space group $P4_12_12$ are listed in the space-group tables for the P cell as follows:

- | | |
|--|--|
| (1) $x, y, z;$ | (2) $\bar{x}, \bar{y}, \frac{1}{2} + z;$ |
| (3) $\frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{4} + z;$ | (4) $\frac{1}{2} + y, \frac{1}{2} - x, \frac{3}{4} + z;$ |
| (5) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{4} - z;$ | (6) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{4} - z;$ |
| (7) $y, x, \bar{z};$ | (8) $\bar{y}, \bar{x}, \frac{1}{2} - z.$ |

The corresponding matrices \mathbb{W} are

$$(1) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}; \quad (2) \begin{pmatrix} \bar{1} & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 1 & \frac{1}{2} \\ 0 & 0 & 0 & 1 \end{pmatrix}; \quad (3) \begin{pmatrix} 0 & \bar{1} & 0 & \frac{1}{2} \\ 1 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & 1 & \frac{1}{4} \\ 0 & 0 & 0 & 1 \end{pmatrix};$$

$$(4) \begin{pmatrix} 0 & 1 & 0 & \frac{1}{2} \\ \bar{1} & 0 & 0 & \frac{1}{2} \\ 0 & 0 & 1 & \frac{3}{4} \\ 0 & 0 & 0 & 1 \end{pmatrix}; \quad (5) \begin{pmatrix} \bar{1} & 0 & 0 & \frac{1}{2} \\ 0 & 1 & 0 & \frac{1}{2} \\ 0 & 0 & \bar{1} & \frac{1}{4} \\ 0 & 0 & 0 & 1 \end{pmatrix}; \quad (6) \begin{pmatrix} 1 & 0 & 0 & \frac{1}{2} \\ 0 & \bar{1} & 0 & \frac{1}{2} \\ 0 & 0 & \bar{1} & \frac{3}{4} \\ 0 & 0 & 0 & 1 \end{pmatrix};$$

$$(7) \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & \bar{1} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}; \quad (8) \begin{pmatrix} 0 & \bar{1} & 0 & 0 \\ \bar{1} & 0 & 0 & 0 \\ 0 & 0 & \bar{1} & \frac{1}{2} \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

These matrices of the P cell are transformed to the matrices \mathbb{W}' of the C cell by

$$\mathbb{W}' = \mathbb{Q}\mathbb{W}\mathbb{P}.$$

For matrix (2), for example, this results in

$$\mathbb{W}' = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 & \frac{\bar{1}}{4} \\ \frac{\bar{1}}{2} & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \bar{1} & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 1 & \frac{1}{2} \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & \bar{1} & 0 & \frac{1}{4} \\ 1 & 1 & 0 & \frac{1}{4} \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$= \begin{pmatrix} \bar{1} & 0 & 0 & \frac{1}{2} \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 1 & \frac{1}{2} \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

The eight transformed matrices \mathbb{W}' , derived in this way, are

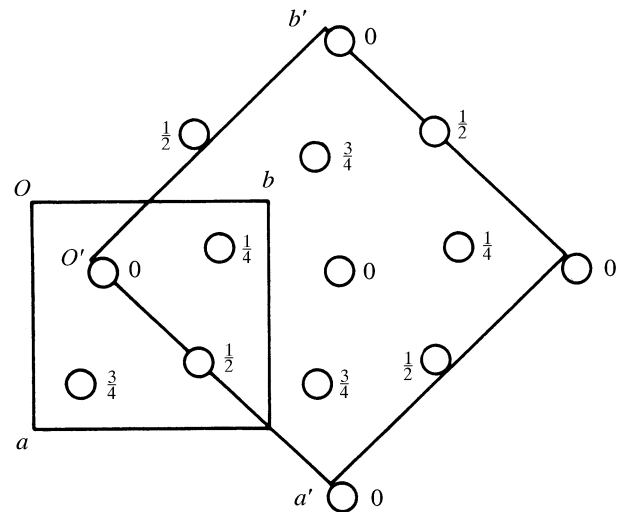


Fig. 5.2.3.1. Positions of silicon atoms in the low-cristobalite structure, projected along $[00\bar{1}]$. Primitive tetragonal cell a, b, c ; C -centred tetragonal cell a', b', c' . Shift of origin from O to O' by the vector $\mathbf{p} = \frac{1}{4}\mathbf{a} + \frac{1}{4}\mathbf{b}$.

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$$\begin{aligned}
 (1) & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}; & (2) & \begin{pmatrix} \bar{1} & 0 & 0 & \frac{1}{2} \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 1 & \frac{1}{2} \\ 0 & 0 & 0 & 1 \end{pmatrix}; & (3) & \begin{pmatrix} 0 & \bar{1} & 0 & \frac{1}{4} \\ 1 & 0 & 0 & \frac{1}{4} \\ 0 & 0 & 1 & \frac{1}{4} \\ 0 & 0 & 0 & 1 \end{pmatrix}; \\
 (4) & \begin{pmatrix} 0 & 1 & 0 & \frac{1}{4} \\ \bar{1} & 0 & 0 & \frac{1}{4} \\ 0 & 0 & 1 & \frac{3}{4} \\ 0 & 0 & 0 & 1 \end{pmatrix}; & (5) & \begin{pmatrix} 0 & 1 & 0 & \frac{1}{4} \\ 1 & 0 & 0 & \frac{1}{4} \\ 0 & 0 & \bar{1} & \frac{1}{4} \\ 0 & 0 & 0 & 1 \end{pmatrix}; & (6) & \begin{pmatrix} 0 & \bar{1} & 0 & \frac{1}{4} \\ \bar{1} & 0 & 0 & \frac{1}{4} \\ 0 & 0 & \bar{1} & \frac{3}{4} \\ 0 & 0 & 0 & 1 \end{pmatrix}; \\
 (7) & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}; & (8) & \begin{pmatrix} \bar{1} & 0 & 0 & \frac{1}{2} \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \bar{1} & \frac{1}{2} \\ 0 & 0 & 0 & 1 \end{pmatrix}.
 \end{aligned}$$

Another set of eight matrices is obtained by adding the C -centring translation $\frac{1}{2}, \frac{1}{2}, 0$ to the w 's.

From these matrices, one obtains the coordinates of the general position in the C cell, for instance from matrix (2)

$$\begin{pmatrix} \tilde{x} \\ \tilde{y} \\ \tilde{z} \\ 1 \end{pmatrix} = \begin{pmatrix} \bar{1} & 0 & 0 & \frac{1}{2} \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 1 & \frac{1}{2} \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \\ 1 \end{pmatrix} = \begin{pmatrix} -x - \frac{1}{2} \\ -y \\ z + \frac{1}{2} \\ 1 \end{pmatrix}.$$

The eight points obtained by the eight matrices \mathbb{W} are

$$\begin{aligned}
 (1) & x, y, z; & (2) & -\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z; \\
 (3) & \frac{1}{4} - y, \frac{1}{4} + x, \frac{1}{4} + z; & (4) & \frac{1}{4} + y, -\frac{1}{4} - x, \frac{3}{4} + z; \\
 (5) & \frac{1}{4} + y, \frac{1}{4} + x, \frac{1}{4} - z; & (6) & \frac{1}{4} - y, -\frac{1}{4} - x, \frac{3}{4} - z; \\
 (7) & x, \bar{y}, \bar{z}; & (8) & -\frac{1}{2} - x, y, \frac{1}{2} - z.
 \end{aligned}$$

The other set of eight points is obtained by adding $\frac{1}{2}, \frac{1}{2}, 0$.

In space group $P4_12_12$, the silicon atoms are in special position $4(a) \dots 2$ with the coordinates $x, x, 0$. Transformed into the C cell, the position becomes

$$\begin{aligned}
 & (0, 0, 0) + \left(\frac{1}{2}, \frac{1}{2}, 0\right) + \\
 & x, 0, 0; \quad \frac{1}{2} - x, 0, \frac{1}{2}; \quad \frac{1}{4}, \frac{1}{4} + x, \frac{1}{4}; \quad \frac{1}{4}, \frac{3}{4} - x, \frac{3}{4}.
 \end{aligned}$$

The parameter $x = 0.300$ of the P cell has changed to $x = 0.050$ in the C cell. For $x = 0$, the special position of the C cell assumes the same coordinate triplets as Wyckoff position $8(a) \bar{4}3m$ in space group $Fd\bar{3}m$ (227), *i.e.* this change of the x parameter reflects the displacement of the silicon atoms in the cubic to tetragonal phase transition.

References

- 5.2**
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