

1. INTRODUCTION TO SPACE-GROUP SYMMETRY

translation vector and the transformation behaviour of the translation is considered. The corresponding translation is then described by (\mathbf{I}, \mathbf{v}) , *i.e.* $\mathbf{W} = \mathbf{I}$, $\mathbf{w} = \mathbf{v}$. Equation (1.5.2.13) shows that the translation and thus the translation vector are not changed under an origin shift, $(\mathbf{P}, \mathbf{p}) = (\mathbf{I}, \mathbf{p})$, because $(\mathbf{I}, \mathbf{v})' = (\mathbf{I}, \mathbf{v})$ holds. For the same reason, under a general coordinate transformation the origin shift has no effect on the vector coefficients, *cf.* equation (1.5.2.16).

1.5.2.5. Example: paraelectric-to-ferroelectric phase transition of GeTe

Coordinate transformations are essential in the study of structural relationships between crystal structures. Consider as an example two phases **A** (*basic* or *parent* structure) and **B** (*derivative* structure) of the same compound. Let the space group \mathcal{H} of **B** be a proper subgroup of the space group \mathcal{G} of **A**, $\mathcal{H} \subset \mathcal{G}$. The relationship between the two structures is characterized by a global distortion that, in general, can be decomposed into a homogeneous strain describing the distortion of the lattice of **B** relative to that of **A** and an atomic displacement field representing the displacements of the atoms of **B** from their positions in **A**. In order to facilitate the comparison of the two structures, first the coordinate system of structure **A** is transformed by an appropriate transformation (\mathbf{P}, \mathbf{p}) to that of structure **B**. This new description of **A** will be called the *reference description* of structure **A** relative to structure **B**. Now, the metric tensors \mathbf{G}_A of the reference description of **A** and \mathbf{G}_B are of the same type and are distinguished only by the values of their parameters. The adaptation of structure **A** to structure **B** can be performed in two further steps. In the first step the parameter values of \mathbf{G}_A are adapted to those of \mathbf{G}_B by an affine transformation which determines the metric deformation (spontaneous strain) of structure **B** relative to structure **A**. The result is a hypothetical structure which still differs from structure **B** by atomic displacements. In the second step these displacements are balanced out by shifting the individual atoms to those of structure **B**. In other words, if $\mathbf{a}, \mathbf{b}, \mathbf{c}$ represents the basis of the parent phase, then its image under the transformation $(\mathbf{a}', \mathbf{b}', \mathbf{c}') = (\mathbf{a}, \mathbf{b}, \mathbf{c})\mathbf{P}$ should be similar to the basis of the derivative phase $\mathbf{a}_H, \mathbf{b}_H, \mathbf{c}_H$. The difference between $\mathbf{a}', \mathbf{b}', \mathbf{c}'$ and $\mathbf{a}_H, \mathbf{b}_H, \mathbf{c}_H$ determines the metric deformation (spontaneous strain) accompanying the transition between the two phases. Similarly, the differences between the images X' of the atomic positions X of the basic structure under the transformation (\mathbf{P}, \mathbf{p}) and the atomic positions X_H of the derivative structure give the atomic displacements that occur during the phase transition.

As an example we will consider the structural phase transition of GeTe, which is of displacive type, *i.e.* the phase transition is accomplished through small atomic displacements. The room-temperature ferroelectric phase belongs to the rhombohedral space group $R3m$ (160). At about 720 K a structural phase transition takes place to a high-symmetry paraelectric cubic phase of the NaCl type. The following descriptions of the two phases of GeTe are taken from the ICSD:

(a) Wiedemeier & Siemers (1989), ICSD No. 56037. The symmetry of the high-temperature phase is described by the space group $Fm\bar{3}m$ (225) with cell parameters $a_c = 6.009 \text{ \AA}$ and atomic coordinates listed as

$$\begin{aligned} \text{Ge: } & 4a \ 0, 0, 0 \\ \text{Te: } & 4b \ \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \end{aligned}$$

(b) Chattopadhyay *et al.* (1987), ICSD No. 56038. The structure is described with respect to the hexagonal-axes setting of

$R3m$ (160) (*cf.* Section 1.5.3.1) with cell parameters $a_{\text{hex}} = 4.164$ (2) \AA , $c_{\text{hex}} = 10.69$ (4) \AA . The coordinates of the atoms in the asymmetric unit are given as

$$\text{Ge: } 3a \ 0, 0, 0.2376$$

$$\text{Te: } 3a \ 0, 0, 0.7624$$

The relation between the basis $\mathbf{a}_c, \mathbf{b}_c, \mathbf{c}_c$ of the F -centred cubic lattice and the basis $\mathbf{a}'_c, \mathbf{b}'_c, \mathbf{c}'_c$ of the reference description can be obtained by inspection. The \mathbf{c}'_c axis of the reference hexagonal basis must be one of the cubic threefold axes, say [111]. The axes \mathbf{a}'_c and \mathbf{b}'_c must be lattice vectors of the F -centred lattice, perpendicular to the rhombohedral axis. They must have equal length, form an angle of 120° , and together with \mathbf{c}'_c define a right-handed basis. For example, the vectors $\mathbf{a}'_c = \frac{1}{2}(-\mathbf{a}_c + \mathbf{b}_c)$, $\mathbf{b}'_c = \frac{1}{2}(-\mathbf{b}_c + \mathbf{c}_c)$ fulfil these conditions.

The transformation matrix \mathbf{P} between the bases $\mathbf{a}_c, \mathbf{b}_c, \mathbf{c}_c$ and $\mathbf{a}'_c, \mathbf{b}'_c, \mathbf{c}'_c$ can also be derived from the data listed in Table 1.5.1.1 in two steps:

(i) A cubic F cell can be considered as a primitive rhombohedral cell with $a_p = a_c \frac{1}{2} \sqrt{2}$ and $\alpha = 60^\circ$. The relation between the two cells is described by the transformation matrix \mathbf{P}_1 (*cf.* Table 1.5.1.1 and Fig. 1.5.1.4):

$$(\mathbf{a}_p, \mathbf{b}_p, \mathbf{c}_p) = (\mathbf{a}_c, \mathbf{b}_c, \mathbf{c}_c)\mathbf{P}_1 = (\mathbf{a}_c, \mathbf{b}_c, \mathbf{c}_c) \begin{pmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}. \quad (1.5.2.18)$$

(ii) The transformation matrix \mathbf{P}_2 between the rhombohedral primitive cell and the triple hexagonal cell (obverse setting) of the reference description is read from Table 1.5.1.1 (*cf.* Fig. 1.5.1.6):

$$(\mathbf{a}'_c, \mathbf{b}'_c, \mathbf{c}'_c) = (\mathbf{a}_p, \mathbf{b}_p, \mathbf{c}_p)\mathbf{P}_2 = (\mathbf{a}_p, \mathbf{b}_p, \mathbf{c}_p) \begin{pmatrix} 1 & 0 & 1 \\ \bar{1} & 1 & 1 \\ 0 & \bar{1} & 1 \end{pmatrix}. \quad (1.5.2.19)$$

Combining equations (1.5.2.18) and (1.5.2.19) gives the orientational relationship between the F -centred cubic cell and the rhombohedrally centred hexagonal cell $(\mathbf{a}'_c, \mathbf{b}'_c, \mathbf{c}'_c) = (\mathbf{a}_c, \mathbf{b}_c, \mathbf{c}_c)\mathbf{P}$, where

$$\mathbf{P} = \mathbf{P}_1\mathbf{P}_2 = \begin{pmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 1 \\ \bar{1} & 1 & 1 \\ 0 & \bar{1} & 1 \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & 0 & 1 \\ \frac{1}{2} & -\frac{1}{2} & 1 \\ 0 & \frac{1}{2} & 1 \end{pmatrix}. \quad (1.5.2.20)$$

Formally, the lattice parameters of the reference unit cell can be extracted from the metric tensor \mathbf{G}'_c obtained from the metric tensor \mathbf{G}_c transformed by \mathbf{P} , *cf.* equation (1.5.2.4):

$$\begin{aligned} \mathbf{G}'_c &= \mathbf{P}^T \mathbf{G}_c \mathbf{P} \\ &= \begin{pmatrix} -\frac{1}{2} & \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} & \frac{1}{2} \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} a_c^2 & 0 & 0 \\ 0 & a_c^2 & 0 \\ 0 & 0 & a_c^2 \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & 0 & 1 \\ \frac{1}{2} & -\frac{1}{2} & 1 \\ 0 & \frac{1}{2} & 1 \end{pmatrix} \\ &= a_c^2 \begin{pmatrix} \frac{1}{2} & -\frac{1}{4} & 0 \\ -\frac{1}{4} & \frac{1}{2} & 0 \\ 0 & 0 & 3 \end{pmatrix}, \end{aligned} \quad (1.5.2.21)$$

which gives $a'_c = a_c \frac{1}{2} \sqrt{2} = 4.249 \text{ \AA}$ and $c'_c = a_c \sqrt{3} = 10.408 \text{ \AA}$. The comparison of these values with the experimentally deter-

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mined lattice parameters of the low-symmetry phase [$a_{\text{hex}} = 4.164$ (2) Å, $c_{\text{hex}} = 10.69$ (4) Å (Chattopadhyay *et al.*, 1987)] determines the lattice deformation accompanying the displacive phase transition, which basically consists of expanding the cubic unit cell along the [111] direction. (In fact, the elongation along [111] is accompanied by a contraction in the ab plane that leads to an overall volume reduction of about 1.3%.)

Owing to the polar character of $R3m$, the symmetry conditions following from the group–subgroup relation $Fm\bar{3}m > R3m$ [cf. equation (1.5.2.11)] are not sufficient to determine the origin shift of the transformation between the high- and the low-symmetry space groups. The origin shift of $\mathbf{p} = (-\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4})$ in this specific case is chosen in such a way that the relative displacements of Ge and Te are equal in size but in opposite direction along [111].

The inverse transformation matrix–column pair $(\mathbf{Q}, \mathbf{q}) = (\mathbf{P}, \mathbf{p})^{-1} = (\mathbf{P}^{-1}, -\mathbf{P}^{-1}\mathbf{p})$ is necessary for the calculation of the atomic coordinates of the reference description X'_c . Given the matrix \mathbf{P} , its inverse \mathbf{P}^{-1} can be calculated either directly (*i.e.* applying the algebraic procedure for inversion of a matrix) or using the inverse matrices $\mathbf{Q}_1 = \mathbf{P}_1^{-1}$ and $\mathbf{Q}_2 = \mathbf{P}_2^{-1}$ listed in Table 1.5.1.1:

$$\begin{aligned} \mathbf{Q} = \mathbf{P}^{-1} &= (\mathbf{P}_1\mathbf{P}_2)^{-1} = \mathbf{P}_2^{-1}\mathbf{P}_1^{-1} \\ &= \begin{pmatrix} \frac{2}{3} & -\frac{1}{3} & -\frac{1}{3} \\ \frac{1}{3} & \frac{1}{3} & -\frac{2}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{pmatrix} \begin{pmatrix} \bar{1} & 1 & 1 \\ 1 & \bar{1} & 1 \\ 1 & 1 & \bar{1} \end{pmatrix} = \begin{pmatrix} -\frac{4}{3} & \frac{2}{3} & \frac{2}{3} \\ -\frac{2}{3} & -\frac{2}{3} & \frac{4}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{pmatrix}. \end{aligned} \quad (1.5.2.22)$$

(Note the change in the order of multiplication of the matrices \mathbf{P}_1^{-1} and \mathbf{P}_2^{-1} in \mathbf{Q} .) The corresponding origin shift \mathbf{q} is given by

$$\mathbf{q} = -\mathbf{P}^{-1}\mathbf{p} = -\begin{pmatrix} -\frac{4}{3} & \frac{2}{3} & \frac{2}{3} \\ -\frac{2}{3} & -\frac{2}{3} & \frac{4}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{pmatrix} \begin{pmatrix} -\frac{1}{4} \\ -\frac{1}{4} \\ -\frac{1}{4} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \frac{1}{4} \end{pmatrix}. \quad (1.5.2.23)$$

The atomic positions of the reference description become

$$\begin{pmatrix} x'_c \\ y'_c \\ z'_c \end{pmatrix} = \begin{pmatrix} -\frac{4}{3} & \frac{2}{3} & \frac{2}{3} \\ -\frac{2}{3} & -\frac{2}{3} & \frac{4}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{pmatrix} \begin{pmatrix} x_c \\ y_c \\ z_c \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ \frac{1}{4} \end{pmatrix}.$$

The coordinates of the representative Ge atom occupying position $4a \ 0, 0, 0$ in $Fm\bar{3}m$ are transformed to $0, 0, \frac{1}{4}$, while those of Te are transformed from $4b \ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ in $Fm\bar{3}m$ to $0, 0, \frac{3}{4}$. The comparison of these values with the experimentally determined atomic coordinates of Ge $0, 0, 0.2376$ and Te $0, 0, 0.7624$ reveals the corresponding atomic displacements associated with the displacive phase transition. The low-symmetry phase is a result of relative atomic displacements of the Ge and Te atoms along the polar (rhombohedral) [111] direction, giving rise to non-zero polarization along the same direction, *i.e.* the phase transition is a *paraelectric-to-ferroelectric* one.

1.5.3. Transformations between different space-group descriptions

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1.5.3.1. Space groups with more than one description in this volume

In the description of the space-group symbols presented in Section 1.4.1, we have already seen that in the conventional,

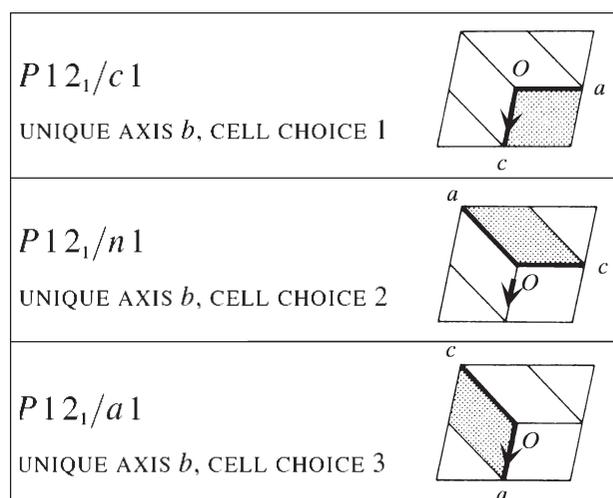


Figure 1.5.3.1

Three possible cell choices for the monoclinic space group $P2_1/c$ (14) with unique axis b . Note the corresponding changes in the full Hermann–Mauguin symbols. The glide vector is indicated by an arrow.

unique axis b description of monoclinic space groups, the unique symmetry direction is chosen as \mathbf{b} ; it is normal to \mathbf{c} and \mathbf{a} , which form the angle β . However, it is often the case that this standard direction is not the most appropriate choice and that another choice would be more convenient. An example of this would be when following a phase transition from an orthorhombic parent phase to a monoclinic phase. Here, it would often be preferable to keep the same orientation of the axes even if the resulting monoclinic setting is not standard.

In some of the space groups, and especially in the monoclinic ones, the space-group tables of Chapter 2.3 provide a selection of possible alternative settings. For example, in space group $P2_1/c$, two possible orientations of the unit-cell axes are provided, namely with unique axis b and c . This is reflected in the corresponding full Hermann–Mauguin symbols by the explicit specification of the unique-axis position (dummy indices ‘1’ indicate ‘empty’ symmetry directions), and by the corresponding change in the direction of the glide plane: $P12_1/c1$ or $P112_1/a$ (*cf.* Section 1.4.1 for a detailed treatment of Hermann–Mauguin symbols of space groups).

It is not just the unique monoclinic axis that can be varied: the choice of the other axes can vary as well. There are cases where the selection of the conventional setting leads to an inconvenient monoclinic angle that deviates greatly from 90° . If another cell choice minimizes the deviation from 90° , it is preferred. Fig. 1.5.3.1 illustrates three cell choices for the monoclinic axis b setting of $P2_1/c$.

In centrosymmetric space groups the origin of the unit cell is located at an inversion centre (‘origin choice 2’). If, however, another point has higher site symmetry \mathcal{S} , a second diagram is displayed with the origin at a point with site symmetry \mathcal{S} (‘origin choice 1’). Fig. 1.5.3.2 illustrates the space group $Pban$ with two possible origins. The origin of the first choice is located on a point with site symmetry 222 , whereas the origin for the second choice is located on an inversion centre. Among the 230 space groups, this volume lists 24 centrosymmetric space groups with an additional alternative origin.

Finally, the seven rhombohedral space-group types (*i.e.* space groups with a rhombohedral lattice) also have alternative descriptions included in the space-group tables of this volume. The rhombohedral lattice is first presented with an R -centred