mined lattice parameters of the low-symmetry phase [a_{hex} = 4.164 (2) Å, c_{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 *R*3*m*, 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 $\boldsymbol{p} = (-\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4})$ 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 $(\boldsymbol{Q}, \boldsymbol{q}) = (\boldsymbol{P}, \boldsymbol{p})^{-1} = (\boldsymbol{P}^{-1}, -\boldsymbol{P}^{-1}\boldsymbol{p})$ is necessary for the calculation of the atomic coordinates of the reference description X'_c. Given the matrix $\boldsymbol{P}$, its inverse $\boldsymbol{P}^{-1}$ can be calculated either directly (*i.e.* applying the algebraic procedure for inversion of a matrix) or using the inverse matrices $\boldsymbol{Q}_1 = \boldsymbol{P}_1^{-1}$ and $\boldsymbol{Q}_2 = \boldsymbol{P}_2^{-1}$ listed in Table 1.5.1.1:

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

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

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

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 4*a* 0, 0, 0 in $Fm\bar{3}m$ are transformed to $0, 0, \frac{1}{4}$, while those of Te are transformed from 4*b* $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ 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, *unique axis b* description of monoclinic space groups, the unique symmetry direction is chosen as **b**; it is normal to **c** and **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.

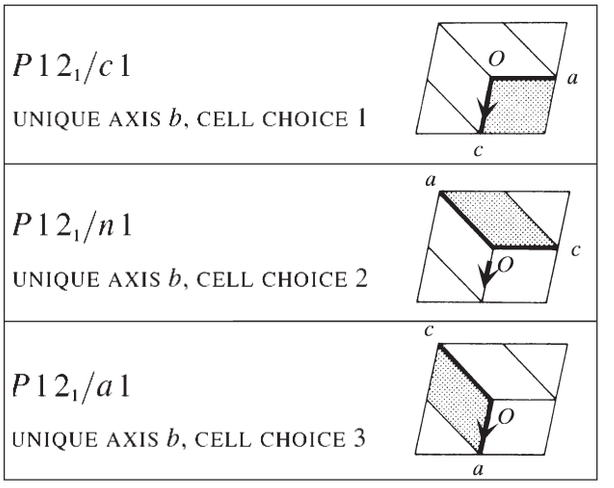

Figure 1.5.3.1
Three possible cell choices for the monoclinic space group $P2_1/c$ (14) with unique axis *b*. Note the corresponding changes in the full Hermann–Mauguin symbols. The glide vector is indicated by an arrow.

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

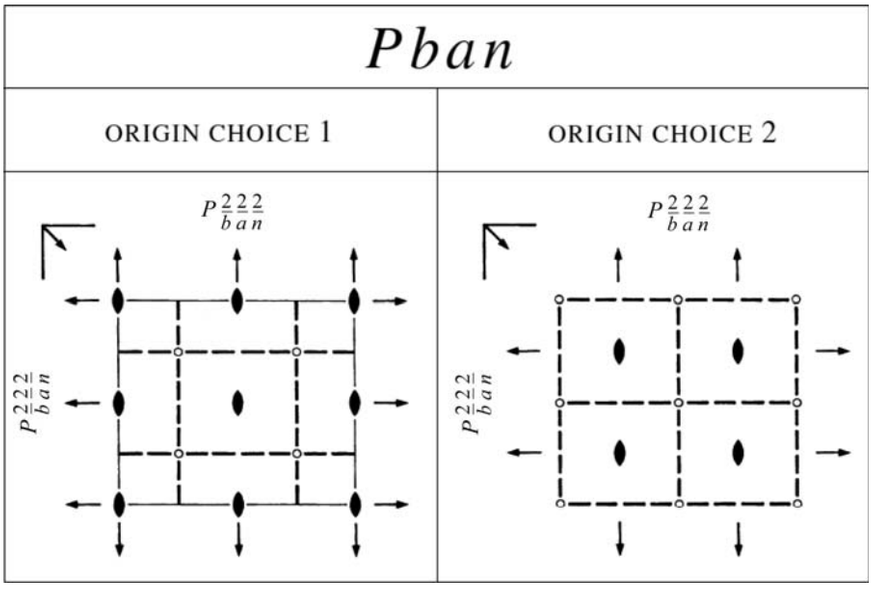

Figure 1.5.3.2
Two possible origin choices for the orthorhombic space group *Pban* (50). Origin choice 1 is on 222, whereas origin choice 2 is on $\bar{1}$.

hexagonal cell ($|\mathbf{a}_{\rm hex}| = |\mathbf{b}_{\rm hex}|$; $\mathbf{c}_{\rm hex} \perp \mathbf{a}_{\rm hex}, \mathbf{b}_{\rm hex}$; $\gamma = 120^\circ$) with a volume three times larger than that of the primitive rhombohedral cell. The second presentation is given with a primitive rhombohedral cell with $a_{\rm rh} = b_{\rm rh} = c_{\rm rh}$ and $\alpha_{\rm rh} = \beta_{\rm rh} = \gamma_{\rm rh}$. The relation between the two types of cell is illustrated in Fig. 1.5.3.3 for the space group *R*3*m* (160). In the hexagonal cell, the coordinates of the special position with site symmetry 3*m* are 0, 0, *z*, whereas in the rhombohedral cell the same special position has coordinates x, x, x. If we refer to the transformations of the primitive rhombohedral cell cited in Table 1.5.1.1, we observe two different centrings with three possible orientations R_1, R_2 and R_3 which are related by $\pm 120^\circ$ to each other. The two kinds of centrings, called *obverse* and *reverse*, are illustrated in Fig. 1.5.1.6. A rotation of 180° around the rhombohedral axis relates the obverse and reverse descriptions of the rhombohedral lattice. The obverse triple *R* cells have lattice points at $0, 0, 0$; $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$; $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$, whereas the reverse *R* cells have lattice points at $0, 0, 0$; $\frac{1}{3}, \frac{2}{3}, \frac{1}{3}$; $\frac{2}{3}, \frac{1}{3}, \frac{2}{3}$. The triple hexagonal cell R_1 of the obverse setting (*i.e.* $\mathbf{a}_{\rm hex} = \mathbf{a}_{\rm rh} - \mathbf{b}_{\rm rh}$, $\mathbf{b}_{\rm hex} = \mathbf{b}_{\rm rh} - \mathbf{c}_{\rm rh}$, $\mathbf{c}_{\rm hex} = \mathbf{a}_{\rm rh} + \mathbf{b}_{\rm rh} + \mathbf{b}_{\rm rh}$) has been used in the description of the rhombohedral space groups in this volume (*cf.* Table 1.5.1.1 and Fig. 1.5.3.3).

The hexagonal lattice can be referred to a centred rhombohedral cell, called the *D* cell (*cf.* Table 1.5.1.1). The centring points of this cell are $0, 0, 0$, $\frac{1}{3}, \frac{1}{3}, \frac{1}{3}$ and $\frac{2}{3}, \frac{2}{3}, \frac{2}{3}$. However, the *D* cell is rarely used in crystallography.

1.5.3.2. Examples

1.5.3.2.1. Transformations between different settings of $P2_1/c$

In the space-group tables of this volume, the monoclinic space group $P2_1/c$ (14) is described in six different settings: for each of the 'unique axis *b*' and 'unique axis *c*' settings there are three descriptions specified by different cell choices (*cf.* Section 2.1.3.15). The different settings are identified by the appropriate full Hermann–Mauguin symbols. The basis transformations $(\boldsymbol{P}, \boldsymbol{p})$ between the different settings are completely specified by the linear part of the transformation, the 3×3 matrix $\boldsymbol{P}$ [*cf.* equation (1.5.1.4)], as all settings of $P2_1/c$ refer to the same origin, *i.e.* $\boldsymbol{p} = \boldsymbol{o}$. The transformation matrices $\boldsymbol{P}$ necessary for switching between the different descriptions of $P2_1/c$ can either be read off directly or constructed from the transformation-matrix data listed in Table 1.5.1.1.

(*A*) *Transformation from $P12_1/c1$ (unique axis b, cell choice 1) to $P112_1/a$ (unique axis c, cell choice 1)*. The change of the direction of the screw axis 2_1 indicates that the unique direction **b**

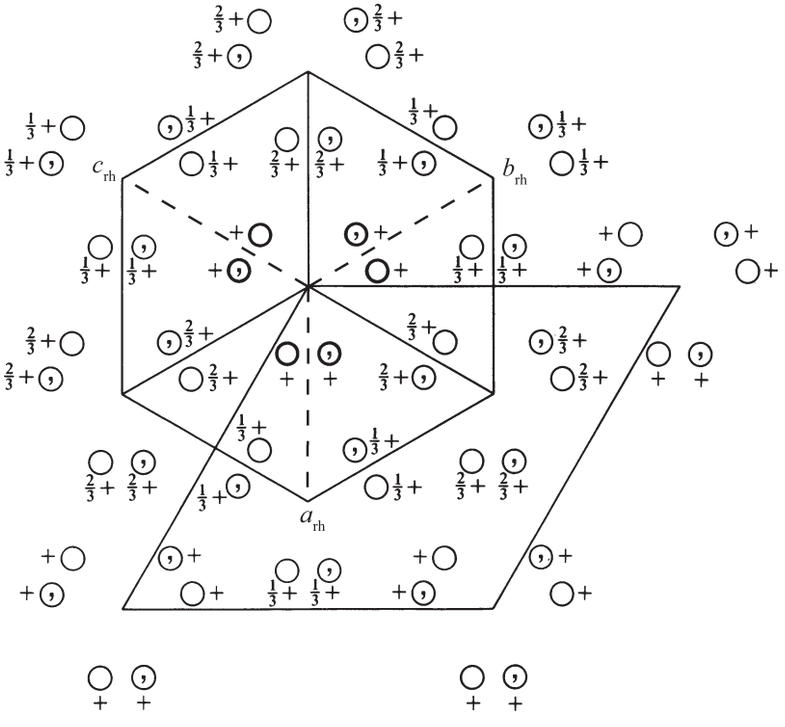

Figure 1.5.3.3
General-position diagram of the space group *R*3*m* (160) showing the relation between the hexagonal and rhombohedral axes in the obverse setting: $\mathbf{a}_{\rm rh} = \frac{1}{3}(2\mathbf{a}_{\rm hex} + \mathbf{b}_{\rm hex} + \mathbf{c}_{\rm hex})$, $\mathbf{b}_{\rm rh} = \frac{1}{3}(-\mathbf{a}_{\rm hex} + \mathbf{b}_{\rm hex} + \mathbf{c}_{\rm hex})$, $\mathbf{c}_{\rm rh} = \frac{1}{3}(-\mathbf{a}_{\rm hex} - 2\mathbf{b}_{\rm hex} + \mathbf{c}_{\rm hex})$.

references