

# The crystallographic chameleon: when space groups change skin

**Massimo Nespolo and Mois I. Aroyo**

*Acta Cryst.* (2016). **A72**, 523–538



**IUCr Journals**

CRYSTALLOGRAPHY JOURNALS ONLINE

Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site or institutional repository provided that this cover page is retained. Republication of this article or its storage in electronic databases other than as specified above is not permitted without prior permission in writing from the IUCr.

For further information see <http://journals.iucr.org/services/authorrights.html>

# The crystallographic chameleon: when space groups change skin

 Massimo Nespolo<sup>a\*</sup> and Moïse I. Aroyo<sup>b</sup>

<sup>a</sup>Université de Lorraine, CRM2, UMR 7036, Vandoeuvre-lès-Nancy 54500, and CNRS, CRM2, UMR 7036 Vandoeuvre-lès-Nancy 54506, France, and <sup>b</sup>Física de la Materia Condensada, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apartado 644, Bilbao, 48080, Spain. \*Correspondence e-mail: massimo.nespolo@crm2.uhp-nancy.fr

Received 5 April 2016

Accepted 8 June 2016

 Edited by H. Schenk, University of Amsterdam,  
 The Netherlands

**Keywords:** space groups; axial setting;  
 Hermann–Mauguin symbols.

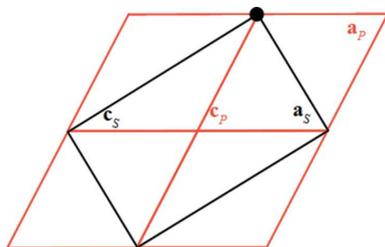
Volume *A* of *International Tables for Crystallography* is the reference for space-group information. However, the content is not exhaustive because for many space groups a variety of settings may be chosen but not all of them are described in detail or even fully listed. The use of alternative settings may seem an unnecessary complication when the purpose is just to describe a crystal structure; however, these are of the utmost importance for a number of tasks, such as the investigation of structure relations between polymorphs or derivative structures, the study of pseudo-symmetry and its potential consequences, and the analysis of the common substructure of twins. The aim of the article is twofold: (i) to present a guide to expressing the symmetry operations, the Hermann–Mauguin symbols and the Wyckoff positions of a space group in an alternative setting, and (ii) to point to alternative settings of space groups of possible practical applications and not listed in Volume *A* of *International Tables for Crystallography*.

## 1. Introduction

Space groups are uniquely identified by their Hermann–Mauguin symbols, the parameters of the conventional cell and the choice of the origin. The infinite number of possible space groups is then reduced to a finite number of isomorphism types leaving aside the cell parameters, arriving thus at the well known number of 230 crystallographic space-group types, or 219 affine space-group types if no distinction is made between enantiomorphic group types, in the three-dimensional space. The corresponding Hermann–Mauguin symbols appear in the headline of the space-group diagrams in Volume *A* of *International Tables for Crystallography* (2002) (hereafter referred to as ITA) and should be familiar to any crystallographer. They describe the so-called *standard settings* of space groups. However, these *standard* Hermann–Mauguin symbols represent only a subset of the possible Hermann–Mauguin symbols; the whole set is actually much larger because space groups may occur in alternative settings, corresponding to a different choice of the basis vectors. The adoption of an alternative setting may be useful in a number of cases:

(i) In the study of phase transitions between polymorphs showing a group–subgroup relation, when the axial setting inherited from the parent structure may correspond to an alternative setting of the daughter structure.

(ii) In the analysis of the relations between hettotypes and their aristotype (Megaw, 1973), or derivative structures and their basic structure (Buerger, 1947), where a common axial setting, or an axial setting directly related to the higher-



symmetry structure, may correspond to an alternative setting of the lower-symmetry phase.

(iii) In the presence of a high degree of structural pseudo-symmetry, which may be hidden by adopting a standard setting.

(iv) In the case of twins, when the lattice common to the twinned individuals (domains), built on the twin element and the direct lattice element quasi-perpendicular to it, requires a space-group description corresponding to a non-standard setting.

(v) In the case of metric specialization, when the symmetry of the lattice is higher than the structural symmetry.

Alternative settings may correspond to unusual Hermann–Mauguin symbols, like  $B2_1/e$ ,  $R12/c$  or  $P41c$ . Some of these are presented in ITA4,<sup>1</sup> others appear in the list of subgroups in Volume A1 of *International Tables for Crystallography* (2010); some are not listed at all. We present a detailed analysis of these alternative settings and of the axial transformations from and to the corresponding standard settings. From a terminological viewpoint we make a distinction between *unconventional* and *non-standard* settings, depending on whether or not the metric of the alternative unit cell still corresponds to the same crystal family.

## 2. Conventional cells

Any finite polyhedron representing a translational unit can be taken as a representative of an infinite lattice, *i.e.* as a unit cell. To establish a unique correspondence between the infinite lattice and the finite unit cell representing it, the concept of *conventional* cell is commonly adopted in crystallography, which satisfies the three conditions (ITA2): (i) its basis vectors define a right-handed axial setting; (ii) its edges are along symmetry directions of the lattice; (iii) it is the smallest cell compatible with the above conditions.

These criteria are sufficient to uniquely establish a relation with the lattice when the latter possesses at least three symmetry directions, *i.e.* from the orthorhombic symmetry upwards. In a monoclinic lattice, the unique symmetry direction leaves a degree of freedom for the choice of the axes in the plane normal to that direction. These two axes are then chosen coincident with the two shortest lattice vectors perpendicular to the unique axis and the angle between them is taken as non-acute. Accordingly, the conventional cell can be either primitive, *S*-centred or *I*-centred<sup>2</sup> (Mighell, 2003). This leaves open the possibility of a large number of unconventional settings for the monoclinic space groups. In a triclinic lattice, the absence of symmetry directions makes the concept of conventional cell undefined; the reduced cell (ITA9) is normally used instead.

<sup>1</sup> For the sake of brevity, the different parts of the ITA will be quoted below as ITAX, where 'X' represents the number of the part.

<sup>2</sup> We remind the reader that the expression '*L*-centred lattice' (where *L* stands for any type of centring) is a shortcut for 'lattice whose conventional cell is *L*-centred'. The lattice itself, being infinite, is neither primitive nor centred. See the detailed discussion in Kettle & Norrby (1993).

## 3. Symmetry elements

The definition and detailed discussion of the term *symmetry element* can be found in the reports of the *Ad-Hoc Committee on the Nomenclature of Symmetry* (de Wolff *et al.*, 1989, 1992) with addenda (Flack *et al.*, 2000). In short, a symmetry element is defined through two concepts, *i.e.* as the combination of a *geometric element* with the set of symmetry operations having this geometric element in common (the so-called *element set*). For most of the symmetry operations, the geometric element is defined as the set of points in space that is fixed by the reduced symmetry operation (*i.e.* the operation obtained by removing its intrinsic translation). Next, one chooses the so-called *defining operation*, which in general may be any symmetry operation from the element set that suffices to identify the symmetry element. In most cases the simplest symmetry operation from the element set is chosen as the defining operation, where 'simplest' means with the smallest (possibly zero) intrinsic translation part. The defining operation specifies the name and the symbol (alphanumeric and graphical) of the symmetry element. For reflections and glide reflections the element set includes the defining operation and all its *coplanar equivalents*, *i.e.* glide reflections through the same reflection plane but with glide vectors differing by a lattice-translation vector. For rotations and screw rotations of angle  $2\pi/k$  the element sets include the defining operation, its 1st ... ( $k - 1$ )-th powers and all their *coaxial equivalents*, *i.e.* rotations and screw rotations whose screw vectors differ from that of the defining operation by lattice-translation vectors.

Consider, for example, the symmetry operation described by the coordinate triplet  $x + \frac{1}{2}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$  of *Cmcm* (No. 63) [*general position* ( $\frac{1}{2}, \frac{1}{2}, 0$ ) block]. This is an *n*-glide reflection through the plane  $x, y, \frac{1}{4}$ . However, the corresponding symmetry element is a mirror plane because among the glide reflections of the element set of the plane  $x, y, \frac{1}{4}$  one also finds the reflection  $x, y, \bar{z} + \frac{1}{2}$  [symmetry operation (6) of the *general position* (0, 0, 0) block] which has a zero intrinsic translation part.

It is important to note that according to the recommendations of the same *Ad-Hoc Committee* (de Wolff *et al.*, 1992) the characters appearing after the symbol of the conventional cell in the (short or full) Hermann–Mauguin symbol of a space group, which originally were meant to represent generating *symmetry operations*, should be interpreted as *symmetry elements*. The introduction of the *e*-glide notation in the standard Hermann–Mauguin symbols of five *oC* space groups was a direct consequence of this decision. In general, the *e*-glide planes are symmetry elements characterized by the existence of two glide reflections through the same plane with perpendicular glide vectors and with the additional requirement that at least one glide vector is along a crystal axis. The *e*-glide planes can occur only in centred cells and the two perpendicular glide vectors are related by a centring translation.

For example, in *Aea2* (No. 41) the *b*-glide reflection  $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, z$  coexists with the *c*-glide reflection  $\bar{x} + \frac{1}{2}, y, z + \frac{1}{2}$ . The geometric element is the plane  $\frac{1}{4}x, y, z$  and its element set

consists of glide reflections with glide vectors of the type  $(u + \frac{1}{2})\mathbf{b} + v\mathbf{c} + \frac{1}{2}m(\mathbf{b} + \mathbf{c})$ , where  $u, v, m$  are integers. Among them, one finds a  $b$ -glide reflection with a glide vector  $\frac{1}{2}\mathbf{b}$  related to  $\frac{1}{2}\mathbf{c}$  by the centring translation; a  $b$ -glide reflection and a  $c$ -glide reflection share the same plane as a geometric element: the corresponding symmetry element is an  $e$ -glide plane.

#### 4. Short, full and extended Hermann–Mauguin symbols

There are different kinds of Hermann–Mauguin symbols of a space group. One distinguishes short, full and extended Hermann–Mauguin symbols. The three types of symbols represent different levels of information content with respect to the symmetry elements and the related symmetry operations of the space group. The short and full Hermann–Mauguin symbols only display information about a chosen set of generators for a space group from which all elements of a space group can in principle be deduced. Both the short and the full Hermann–Mauguin symbols consist of two parts: (i) a letter indicating the centring type of the conventional cell and (ii) a set of characters indicating symmetry elements of the space group parallel or perpendicular to the symmetry directions of the lattice of the space group. In general, the symbols of the symmetry elements shown in the Hermann–Mauguin symbols are selected according to the so-called priority rule which requires that rotation axes are chosen over screw axes of the same rotational order, when these coexist along the same symmetry direction, and mirror planes are chosen in the sequence  $m > e > a, b, c > n$  (where  $>$  means ‘has priority over’). A few exceptions occur when these rules would not allow differentiating space-group types bringing the same type of symmetry elements but differently positioned in space, for example  $I222$  (No. 23) and  $I2_12_12_1$  (No. 24), where the rotation axes cross in a point for the former but not for the latter. Short and full Hermann–Mauguin symbols coincide for most space groups with the exception of the monoclinic space groups (the full symbol explicitly states the symmetry direction: for example,  $Pc$  short symbol *versus*  $P1c1$  full symbol), the space groups of the holohedries (with the exception of  $P\bar{1}$ ) and of the geometric crystal class  $m\bar{3}$  (for example,  $Pa\bar{3}$  short symbol *versus*  $P2_1/a\bar{3}$  full symbol). Short symbols give a reduced set of symmetry elements about the symmetry directions of the lattice, where reduced means that some of the symmetry elements along certain symmetry directions may not be explicitly shown. In the orthorhombic or higher crystal systems when a symmetry axis of order two and a normal to a symmetry plane are parallel, in the full symbols, the symmetry axes and symmetry planes normal to them for each symmetry direction are listed while in the short symbols, only the symmetry-plane symbols are shown. For example, the full and short symbols of space-group type No. 55 are, respectively,  $P2_1/b2_1/a2/m$  and  $Pbam$ . This reduced set of symmetry elements shown in the short Hermann–Mauguin symbols however is not limited to the elements corresponding to the generators of the space group; for example, in orthorhombic merohedral space groups the operations corresponding to the

symmetry elements about two of the three symmetry directions of the lattice are generators, the third is obtained as the product (composition) of these two.

In the extended Hermann–Mauguin symbols, the symmetry of the space group is listed in a rather complete fashion and provides information not only on the chosen set of space-group generators but also on the additional symmetry operations in most of the cases obtained by the compositions of the generating symmetry operations with lattice translations. These symbols are constructed following the same rules as the short symbols but give the corresponding full list of symmetry operations, including the different symmetry operation of the same nature (rotation or screw rotations of the same order, mirror or glide reflections) that may occur about geometric elements in parallel orientation (*cf.* ITA4 and Table 4.3.2.1 of ITA). The result is a symbol composed of one (when the extended symbol coincides with the short one), two or four lines depending on the crystal system and the type of unit cell. The following discussion is limited to the short and full Hermann–Mauguin symbols and, in fact, the extended Hermann–Mauguin symbols are scarcely used in crystallographic practice. However, they are the direct counterpart of the symmetry-element diagrams, where the full set of parallel symmetry elements is visible. For example, the diagram of  $C12/m1$  (No. 12) clearly shows the presence of screw axes and  $a$ -glide planes, which appear only in the extended symbols. A look at these symbols gives an immediate answer to the question, often posed by newcomers in the field, why a group  $C2/a$  ‘does not exist’. The extended symbols are also given in Table 1 and it must be emphasized that, in the forthcoming sixth edition of ITA, the characters of the extended Hermann–Mauguin symbols represent symmetry *operations*, rather than *elements*. This is the reason why the  $e$  glide does occur in short and full Hermann–Mauguin symbols but not in extended symbols.

#### 5. Coordinate system transformations

Consider a coordinate system defined by a basis  $(\mathbf{a}, \mathbf{b}, \mathbf{c})$  and an origin  $O$ . Referred to this coordinate system, the symmetry operation is described by a matrix–column pair often written as  $(\mathbf{W}, \mathbf{w})$ . The coordinates  $\tilde{\mathbf{x}}$  of the image point  $\tilde{X}$  obtained by the action of  $(\mathbf{W}, \mathbf{w})$  on the point  $X$  with coordinates  $\mathbf{x}$  are given by

$$\tilde{\mathbf{x}} = \mathbf{W}\mathbf{x} + \mathbf{w}. \quad (1)$$

A transformation between two coordinate systems defined by their bases  $(\mathbf{a}, \mathbf{b}, \mathbf{c})$  and  $(\mathbf{a}', \mathbf{b}', \mathbf{c}')$  and origins  $O$  and  $O'$ , respectively, consists of two parts:

(i) A  $(3 \times 3)$  matrix  $\mathbf{P}$  which relates the ‘new’ basis  $(\mathbf{a}', \mathbf{b}', \mathbf{c}')$  to the ‘old’ basis  $(\mathbf{a}, \mathbf{b}, \mathbf{c})$  according to

$$(\mathbf{a}', \mathbf{b}', \mathbf{c}') = (\mathbf{a}, \mathbf{b}, \mathbf{c})\mathbf{P}. \quad (2)$$

The matrix  $\mathbf{P}$  is often referred to as the linear part of the coordinate transformation and it describes a change of direction and/or length of the basis vectors.

Table 1

Setting-independent short Hermann–Mauguin (H–M) symbols and extended Hermann–Mauguin symbols for the 13 types of monoclinic space groups.

The former are obtained by indicating the conventional cell as *P* or *S*; if a glide plane is present in the Hermann–Mauguin symbol, it is indicated as *g*. The eight monoclinic space-group types characterized by either a glide plane or a centred cell can each be described by three cell choices: accordingly, three lines are given for the extended symbols, corresponding to the cell choices 1, 2 and 3, as defined in ITA4. The table is divided into two vertical halves, under the headings ‘Hermann–Mauguin symbols for conventional cells’ and ‘Hermann–Mauguin symbols for multiple cells’, which is inspired by the corresponding division for tetragonal groups in ITA4. The first half reproduces what is already present in ITA4. The second half adopts a non-conventional cell with a volume doubled with respect to that of the corresponding conventional cell. This information is not present in ITA4 and leads to an increase in the number of settings, as shown in the corresponding column, where the value in parentheses corresponds to the cases presented in ITA. The minimal number of settings increases from 3 to 6, the maximal number from 18 to 21.

Setting-independent		H–M symbols for conventional cells						H–M symbols for multiple cells							
No. symbol	No. of settings	<i>abc</i>	<i>c̄ba</i>	<i>abc</i>	<i>bāc</i>	<i>abc</i>	<i>ācb</i>	<i>abc</i>	<i>c̄ba</i>	<i>abc</i>	<i>bāc</i>	<i>abc</i>	<i>ācb</i>		
3	<i>P</i> 2	6 (3)	<i>P</i> 121	<i>P</i> 121	<i>P</i> 112	<i>P</i> 112	<i>P</i> 211	<i>P</i> 211	<i>B</i> 121	<i>B</i> 121	<i>C</i> 112	<i>C</i> 112	<i>A</i> 211	<i>A</i> 211	
4	<i>P</i> 2 <sub>1</sub>	6 (3)	<i>P</i> 12 <sub>1</sub>	<i>P</i> 12 <sub>1</sub>	<i>P</i> 112 <sub>1</sub>	<i>P</i> 112 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 11	<i>P</i> 2 <sub>1</sub> 11	<i>B</i> 12 <sub>1</sub>	<i>B</i> 12 <sub>1</sub>	<i>C</i> 112 <sub>1</sub>	<i>C</i> 112 <sub>1</sub>	<i>A</i> 2 <sub>1</sub> 11	<i>A</i> 2 <sub>1</sub> 11	
5	<i>S</i> 2	9 (3) Cell choice 1	<i>C</i> 121	<i>A</i> 121	<i>A</i> 112	<i>B</i> 112	<i>B</i> 211	<i>C</i> 211	<i>F</i> 121	<i>F</i> 121	<i>F</i> 112	<i>F</i> 112	<i>F</i> 211	<i>F</i> 211	
			2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>
		Cell choice 2	<i>A</i> 121	<i>C</i> 121	<i>B</i> 112	<i>A</i> 112	<i>C</i> 211	<i>B</i> 211	<i>F</i> 121	<i>F</i> 121	<i>F</i> 112	<i>F</i> 112	<i>F</i> 211	<i>F</i> 211	
		2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	
	Cell choice 3	<i>I</i> 121	<i>I</i> 121	<i>I</i> 112	<i>I</i> 112	<i>I</i> 211	<i>I</i> 211	<i>F</i> 121	<i>F</i> 121	<i>F</i> 112	<i>F</i> 112	<i>F</i> 211	<i>F</i> 211		
		2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	2 <sub>1</sub>	
6	<i>P</i> <i>m</i>	6 (3)	<i>P</i> 1 <i>m</i> 1	<i>P</i> 1 <i>m</i> 1	<i>P</i> 11 <i>m</i>	<i>P</i> 11 <i>m</i>	<i>P</i> <i>m</i> 11	<i>P</i> <i>m</i> 11	<i>B</i> 1 <i>m</i> 1	<i>B</i> 1 <i>m</i> 1	<i>B</i> 11 <i>m</i>	<i>B</i> 11 <i>m</i>	<i>B</i> <i>m</i> 11	<i>B</i> <i>m</i> 11	
									<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	
7	<i>P</i> <i>g</i>	15 (9)	<i>P</i> 1 <i>c</i> 1	<i>P</i> 1 <i>a</i> 1	<i>P</i> 11 <i>a</i>	<i>P</i> 11 <i>b</i>	<i>P</i> <i>b</i> 11	<i>P</i> <i>c</i> 11	<i>B</i> 1 <i>d</i> 1	<i>B</i> 1 <i>d</i> 1	<i>C</i> 11 <i>d</i>	<i>C</i> 11 <i>d</i>	<i>A</i> <i>d</i> 11	<i>A</i> <i>d</i> 11	
			<i>P</i> 1 <i>n</i> 1	<i>P</i> 1 <i>n</i> 1	<i>P</i> 11 <i>n</i>	<i>P</i> 11 <i>n</i>	<i>P</i> <i>n</i> 11	<i>P</i> <i>n</i> 11	<i>B</i> 1 <i>a</i> 1	<i>B</i> 1 <i>a</i> 1	<i>C</i> 11 <i>a</i>	<i>C</i> 11 <i>a</i>	<i>A</i> <i>b</i> 11	<i>A</i> <i>b</i> 11	
									<i>c</i>	<i>c</i>	<i>b</i>	<i>b</i>	<i>c</i>	<i>c</i>	
			<i>P</i> 1 <i>a</i> 1	<i>P</i> 1 <i>c</i> 1	<i>P</i> 11 <i>b</i>	<i>P</i> 11 <i>a</i>	<i>P</i> <i>c</i> 11	<i>P</i> <i>b</i> 11	<i>B</i> 1 <i>d</i> 1	<i>B</i> 1 <i>d</i> 1	<i>C</i> 11 <i>d</i>	<i>C</i> 11 <i>d</i>	<i>A</i> <i>d</i> 11	<i>A</i> <i>d</i> 11	
8	<i>S</i> <i>m</i>	12 (9) Cell choice 1	<i>C</i> 1 <i>m</i> 1	<i>A</i> 1 <i>m</i> 1	<i>A</i> 11 <i>m</i>	<i>B</i> 11 <i>m</i>	<i>B</i> <i>m</i> 11	<i>C</i> <i>m</i> 11	<i>F</i> 1 <i>m</i> 1	<i>F</i> 1 <i>m</i> 1	<i>F</i> 11 <i>m</i>	<i>F</i> 11 <i>m</i>	<i>F</i> <i>m</i> 11	<i>F</i> <i>m</i> 11	
			<i>a</i>	<i>c</i>	<i>b</i>	<i>a</i>	<i>c</i>	<i>b</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	
									<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	
								<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>		
	Cell choice 2	<i>A</i> 1 <i>m</i> 1	<i>C</i> 1 <i>m</i> 1	<i>B</i> 11 <i>m</i>	<i>A</i> 11 <i>m</i>	<i>C</i> <i>m</i> 11	<i>B</i> <i>m</i> 11	<i>F</i> 1 <i>m</i> 1	<i>F</i> 1 <i>m</i> 1	<i>F</i> 11 <i>m</i>	<i>F</i> 11 <i>m</i>	<i>F</i> <i>m</i> 11	<i>F</i> <i>m</i> 11		
		<i>c</i>	<i>a</i>	<i>a</i>	<i>b</i>	<i>b</i>	<i>c</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>		
								<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>		
								<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>		
	Cell choice 3	<i>I</i> 1 <i>m</i> 1	<i>I</i> 1 <i>m</i> 1	<i>I</i> 11 <i>m</i>	<i>I</i> 11 <i>m</i>	<i>I</i> <i>m</i> 11	<i>I</i> <i>m</i> 11	<i>F</i> 1 <i>m</i> 1	<i>F</i> 1 <i>m</i> 1	<i>F</i> 11 <i>m</i>	<i>F</i> 11 <i>m</i>	<i>F</i> <i>m</i> 11	<i>F</i> <i>m</i> 11		
		<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>		
								<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>		
								<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>		
9	<i>S</i> <i>g</i>	12 (9) Cell choice 1	<i>C</i> 1 <i>c</i> 1	<i>A</i> 1 <i>a</i> 1	<i>A</i> 11 <i>a</i>	<i>B</i> 11 <i>b</i>	<i>B</i> <i>b</i> 11	<i>C</i> <i>c</i> 11	<i>F</i> 1 <i>d</i> 1	<i>F</i> 1 <i>d</i> 1	<i>F</i> 11 <i>d</i>	<i>F</i> 11 <i>d</i>	<i>F</i> <i>d</i> 11	<i>F</i> <i>d</i> 11	
			<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	
		Cell choice 2	<i>A</i> 1 <i>n</i> 1	<i>C</i> 1 <i>n</i> 1	<i>B</i> 11 <i>n</i>	<i>A</i> 11 <i>n</i>	<i>C</i> <i>n</i> 11	<i>B</i> <i>n</i> 11	<i>F</i> 1 <i>d</i> 1	<i>F</i> 1 <i>d</i> 1	<i>F</i> 11 <i>d</i>	<i>F</i> 11 <i>d</i>	<i>F</i> <i>d</i> 11	<i>F</i> <i>d</i> 11	
		<i>a</i>	<i>c</i>	<i>b</i>	<i>a</i>	<i>c</i>	<i>b</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>		
	Cell choice 3	<i>I</i> 1 <i>a</i> 1	<i>I</i> 1 <i>c</i> 1	<i>I</i> 11 <i>b</i>	<i>I</i> 11 <i>a</i>	<i>I</i> <i>c</i> 11	<i>I</i> <i>b</i> 11	<i>F</i> 1 <i>d</i> 1	<i>F</i> 1 <i>d</i> 1	<i>F</i> 11 <i>d</i>	<i>F</i> 11 <i>d</i>	<i>F</i> <i>d</i> 11	<i>F</i> <i>d</i> 11		
		<i>c</i>	<i>a</i>	<i>a</i>	<i>b</i>	<i>b</i>	<i>c</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>		
10	<i>P</i> 2/ <i>m</i>	6 (3)	<i>P</i> 12/ <i>m</i> 1	<i>P</i> 12/ <i>m</i> 1	<i>P</i> 112/ <i>m</i>	<i>P</i> 112/ <i>m</i>	<i>P</i> 2/ <i>m</i> 11	<i>P</i> 2/ <i>m</i> 11	<i>B</i> 12/ <i>m</i> 1	<i>B</i> 12/ <i>m</i> 1	<i>C</i> 112/ <i>m</i>	<i>C</i> 112/ <i>m</i>	<i>A</i> 2/ <i>m</i> 11	<i>A</i> 2/ <i>m</i> 11	
									2/ <i>n</i>	2/ <i>n</i>	2/ <i>n</i>	2/ <i>n</i>	2/ <i>n</i>	2/ <i>n</i>	
11	<i>P</i> 2 <sub>1</sub> / <i>m</i>	6 (3)	<i>P</i> 12 <sub>1</sub> / <i>m</i> 1	<i>P</i> 12 <sub>1</sub> / <i>m</i> 1	<i>P</i> 112 <sub>1</sub> / <i>m</i>	<i>P</i> 112 <sub>1</sub> / <i>m</i>	<i>P</i> 2 <sub>1</sub> / <i>m</i> 11	<i>P</i> 2 <sub>1</sub> / <i>m</i> 11	<i>B</i> 12 <sub>1</sub> / <i>m</i> 1	<i>B</i> 12 <sub>1</sub> / <i>m</i> 1	<i>C</i> 112 <sub>1</sub> / <i>m</i>	<i>C</i> 112 <sub>1</sub> / <i>m</i>	<i>A</i> 2 <sub>1</sub> / <i>m</i> 11	<i>A</i> 2 <sub>1</sub> / <i>m</i> 11	
									2 <sub>1</sub> / <i>n</i>	2 <sub>1</sub> / <i>n</i>	2 <sub>1</sub> / <i>n</i>	2 <sub>1</sub> / <i>n</i>	2 <sub>1</sub> / <i>n</i>	2 <sub>1</sub> / <i>n</i>	
12	<i>S</i> 2/ <i>m</i>	9 (6) Cell choice 1	<i>C</i> 12/ <i>m</i> 1	<i>A</i> 12/ <i>m</i> 1	<i>A</i> 112/ <i>m</i>	<i>B</i> 112/ <i>m</i>	<i>B</i> 2/ <i>m</i> 11	<i>C</i> 2/ <i>m</i> 11	<i>F</i> 12/ <i>m</i> 1	<i>F</i> 12/ <i>m</i> 1	<i>F</i> 112/ <i>m</i>	<i>F</i> 112/ <i>m</i>	<i>F</i> 2/ <i>m</i> 11	<i>F</i> 2/ <i>m</i> 11	
			2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>c</i>	2 <sub>1</sub> / <i>b</i>	2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>c</i>	2 <sub>1</sub> / <i>b</i>	2/ <i>n</i>	2/ <i>n</i>	2/ <i>n</i>	2/ <i>n</i>	2/ <i>n</i>	2/ <i>n</i>	
									2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>a</i>	
									2 <sub>1</sub> / <i>c</i>	2 <sub>1</sub> / <i>c</i>	2 <sub>1</sub> / <i>c</i>	2 <sub>1</sub> / <i>c</i>	2 <sub>1</sub> / <i>c</i>		
	Cell choice 2	<i>A</i> 12/ <i>m</i> 1	<i>C</i> 12/ <i>m</i> 1	<i>B</i> 112/ <i>m</i>	<i>A</i> 112/ <i>m</i>	<i>C</i> 2/ <i>m</i> 11	<i>B</i> 2/ <i>m</i> 11	<i>F</i> 12/ <i>m</i> 1	<i>F</i> 12/ <i>m</i> 1	<i>F</i> 112/ <i>m</i>	<i>F</i> 112/ <i>m</i>	<i>F</i> 2/ <i>m</i> 11	<i>F</i> 2/ <i>m</i> 11		
		2 <sub>1</sub> / <i>c</i>	2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>b</i>	2 <sub>1</sub> / <i>b</i>	2 <sub>1</sub> / <i>c</i>	2/ <i>n</i>	2/ <i>n</i>	2/ <i>n</i>	2/ <i>n</i>	2/ <i>n</i>	2/ <i>n</i>		
								2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>a</i>		
								2 <sub>1</sub> / <i>c</i>	2 <sub>1</sub> / <i>c</i>	2 <sub>1</sub> / <i>c</i>	2 <sub>1</sub> / <i>c</i>	2 <sub>1</sub> / <i>c</i>	2 <sub>1</sub> / <i>c</i>		
	Cell choice 3	<i>I</i> 12/ <i>m</i> 1	<i>I</i> 12/ <i>m</i> 1	<i>I</i> 2/ <i>m</i> 11	<i>I</i> 2/ <i>m</i> 11	<i>I</i> 2/ <i>m</i> 11	<i>I</i> 2/ <i>m</i> 11	<i>F</i> 12/ <i>m</i> 1	<i>F</i> 12/ <i>m</i> 1	<i>F</i> 112/ <i>m</i>	<i>F</i> 112/ <i>m</i>	<i>F</i> 2/ <i>m</i> 11	<i>F</i> 2/ <i>m</i> 11		
		2 <sub>1</sub> / <i>n</i>	2 <sub>1</sub> / <i>n</i>	2 <sub>1</sub> / <i>n</i>	2 <sub>1</sub> / <i>n</i>	2 <sub>1</sub> / <i>n</i>	2 <sub>1</sub> / <i>n</i>	2/ <i>n</i>	2/ <i>n</i>	2/ <i>n</i>	2/ <i>n</i>	2/ <i>n</i>	2/ <i>n</i>		
								2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>a</i>	2 <sub>1</sub> / <i>a</i>		
								2 <sub>1</sub> / <i>c</i>	2 <sub>1</sub> / <i>c</i>	2 <sub>1</sub> / <i>c</i>	2 <sub>1</sub> / <i>c</i>	2 <sub>1</sub> / <i>c</i>	2 <sub>1</sub> / <i>c</i>		

Table 1 (continued)

Setting-independent No. symbol	No. of settings		H–M symbols for conventional cells						H–M symbols for multiple cells							
			<i>abc</i>	<i>c̄ba</i>	<i>abc</i>	<i>bāc</i>	<i>abc</i>	<i>ācb</i>	<i>abc</i>	<i>c̄ba</i>	<i>abc</i>	<i>bāc</i>	<i>abc</i>	<i>ācb</i>		
13	P2/g	15 (9)	Cell choice 1	<i>P12/c1</i>	<i>P12/a1</i>	<i>P112/a</i>	<i>P112/b</i>	<i>P2/b11</i>	<i>P2/c11</i>	<i>B12/d1</i>	<i>B12/d1</i>	<i>C112/d</i>	<i>C112/d</i>	<i>A2/d11</i>	<i>A2/d11</i>	
			Cell choice 2	<i>P12/n1</i>	<i>P12/n1</i>	<i>P112/n</i>	<i>P112/n</i>	<i>P2/n11</i>	<i>P2/n11</i>	<i>B12/a1</i>	<i>B12/a1</i>	<i>C112/a</i>	<i>C112/a</i>	<i>A2/b11</i>	<i>A2/b11</i>	
		Cell choice 3	<i>P12/a1</i>	<i>P12/c1</i>	<i>P112/b</i>	<i>P112/a</i>	<i>P2/c11</i>	<i>P2/b11</i>	<i>B12/d1</i>	<i>B12/d1</i>	<i>C112/d</i>	<i>C112/d</i>	<i>A2/d11</i>	<i>A2/d11</i>		
14	P2 <sub>1</sub> /g	15 (9)	Cell choice 1	<i>P12<sub>1</sub>/c1</i>	<i>P12<sub>1</sub>/a1</i>	<i>P112<sub>1</sub>/a</i>	<i>P112<sub>1</sub>/b</i>	<i>P2<sub>1</sub>/b11</i>	<i>P2<sub>1</sub>/c11</i>	<i>B12<sub>1</sub>/d1</i>	<i>B12<sub>1</sub>/d1</i>	<i>C112<sub>1</sub>/d</i>	<i>C112<sub>1</sub>/d</i>	<i>A2<sub>1</sub>/d11</i>	<i>A2<sub>1</sub>/d11</i>	
			Cell choice 2	<i>P12<sub>1</sub>/n1</i>	<i>P12<sub>1</sub>/n1</i>	<i>P112<sub>1</sub>/n</i>	<i>P112<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n11</i>	<i>P2<sub>1</sub>/n11</i>	<i>B12<sub>1</sub>/a1</i>	<i>B12<sub>1</sub>/a1</i>	<i>C112<sub>1</sub>/a</i>	<i>C112<sub>1</sub>/a</i>	<i>A2<sub>1</sub>/b11</i>	<i>A2<sub>1</sub>/b11</i>	
			Cell choice 3	<i>P12<sub>1</sub>/a1</i>	<i>P12<sub>1</sub>/c1</i>	<i>P112<sub>1</sub>/b</i>	<i>P112<sub>1</sub>/a</i>	<i>P2<sub>1</sub>/c11</i>	<i>P2<sub>1</sub>/b11</i>	<i>B12<sub>1</sub>/d1</i>	<i>B12<sub>1</sub>/d1</i>	<i>C112<sub>1</sub>/d</i>	<i>C112<sub>1</sub>/d</i>	<i>A2<sub>1</sub>/d11</i>	<i>A2<sub>1</sub>/d11</i>	
15	S2/g	21 (18)	Cell choice 1	<i>C12/c1</i>	<i>A12/a1</i>	<i>A112/a</i>	<i>B112/b</i>	<i>B2/b11</i>	<i>C2/c11</i>	<i>F12/d1</i>	<i>F12/d1</i>	<i>F112/d</i>	<i>F112/d</i>	<i>F2/d11</i>	<i>F2/d11</i>	
				<i>2<sub>1</sub>/n</i>	<i>2<sub>1</sub>/n</i>	<i>2<sub>1</sub>/n</i>	<i>2<sub>1</sub>/n</i>	<i>2<sub>1</sub>/n</i>	<i>2<sub>1</sub>/n</i>	<i>2<sub>1</sub>/n</i>	<i>2<sub>1</sub>/d</i>	<i>2<sub>1</sub>/d</i>	<i>2<sub>1</sub>/d</i>	<i>2<sub>1</sub>/d</i>	<i>2<sub>1</sub>/d</i>	<i>2<sub>1</sub>/d</i>
			Cell choice 2	<i>A12/a<sub>n</sub>1</i>	<i>C12/n1</i>	<i>B112/n</i>	<i>A112/n</i>	<i>C2/n11</i>	<i>B2/n11</i>	<i>F12/d1</i>	<i>F12/d1</i>	<i>F112/d</i>	<i>F112/d</i>	<i>F2/d11</i>	<i>F2/d11</i>	<i>F2/d11</i>
		<i>2<sub>1</sub>/a</i>	<i>2<sub>1</sub>/c</i>	<i>2<sub>1</sub>/b</i>	<i>2<sub>1</sub>/a</i>	<i>2<sub>1</sub>/c</i>	<i>2<sub>1</sub>/b</i>	<i>2<sub>1</sub>/d</i>	<i>2<sub>1</sub>/d</i>	<i>2<sub>1</sub>/d</i>	<i>2<sub>1</sub>/d</i>	<i>2<sub>1</sub>/d</i>	<i>2<sub>1</sub>/d</i>	<i>2<sub>1</sub>/d</i>		
		Cell choice 3	<i>I12/a1</i>	<i>I12/c1</i>	<i>I112/b</i>	<i>I112/a</i>	<i>I2/c11</i>	<i>I2/b11</i>	<i>F12/d1</i>	<i>F12/d1</i>	<i>F112/d</i>	<i>F112/d</i>	<i>F2/d11</i>	<i>F2/d11</i>		
			<i>2<sub>1</sub>/c</i>	<i>2<sub>1</sub>/a</i>	<i>2<sub>1</sub>/a</i>	<i>2<sub>1</sub>/b</i>	<i>2<sub>1</sub>/b</i>	<i>2<sub>1</sub>/c</i>	<i>2<sub>1</sub>/d</i>	<i>2<sub>1</sub>/d</i>	<i>2<sub>1</sub>/d</i>	<i>2<sub>1</sub>/d</i>	<i>2<sub>1</sub>/d</i>	<i>2<sub>1</sub>/d</i>		

(ii) A (3 × 1) column matrix containing the components of the shift vector  $\mathbf{p} = (p_1\mathbf{a} + p_2\mathbf{b} + p_3\mathbf{c})$  where  $(p_1, p_2, p_3)$  are the coordinates of the ‘new’ origin  $O'$  in the ‘old’ coordinate system.

The column of coordinates  $\mathbf{x}'$  of the point  $X$  with respect to the new coordinate system is given by

$$\mathbf{x}' = (\mathbf{P}, \mathbf{p})^{-1}\mathbf{x} = \mathbf{P}^{-1}\mathbf{x} - \mathbf{P}^{-1}\mathbf{p} = \mathbf{P}^{-1}(\mathbf{x} - \mathbf{p}). \quad (3)$$

Also, the matrix–column pairs of the symmetry operations are transformed 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

$$(\mathbf{W}', \mathbf{w}') = (\mathbf{P}, \mathbf{p})^{-1}(\mathbf{W}, \mathbf{w})(\mathbf{P}, \mathbf{p}). \quad (4)$$

The relation between  $(\mathbf{W}, \mathbf{w})$  and  $(\mathbf{W}', \mathbf{w}')$  can be derived using relations of the types (1) and (3) between the primed and unprimed coordinates  $\mathbf{x}$  and  $\mathbf{x}'$  of point  $X$ , and  $\tilde{\mathbf{x}}$  and  $\tilde{\mathbf{x}}'$  of its image point  $\tilde{X}$ . On the one hand,  $\tilde{\mathbf{x}}' = (\mathbf{W}', \mathbf{w}')\mathbf{x}'$  while on the other,  $\tilde{\mathbf{x}}' = (\mathbf{P}, \mathbf{p})^{-1}\tilde{\mathbf{x}} = (\mathbf{P}, \mathbf{p})^{-1}(\mathbf{W}, \mathbf{w})\mathbf{x} = (\mathbf{P}, \mathbf{p})^{-1}(\mathbf{W}, \mathbf{w})(\mathbf{P}, \mathbf{p})\mathbf{x}'$ . The comparison of the two results yields equation (4).

The result (4) shows how the matrix–column representation of a symmetry operation changes from one setting of a space group to another; once the alternative setting is specified by a transformation matrix–column pair  $(\mathbf{P}, \mathbf{p})$ , the whole set of symmetry operations can be transformed to the new setting. The Hermann–Mauguin symbol of the space group in the alternative setting is then constructed following the same rules adopted for the standard setting.

As an example, consider a symmetry break from  $Fddd$  (No. 70, origin choice 2) to  $Cc$   $b$ -unique setting (No. 9), and characterized by the transformation  $\mathbf{a}, \mathbf{b}, -\mathbf{a}/2 + \mathbf{c}/2$  (a short expression for  $\mathbf{a}' = \mathbf{a}, \mathbf{b}' = \mathbf{b}, \mathbf{c}' = -\mathbf{a}/2 + \mathbf{c}/2$ ) between the bases  $(\mathbf{a}, \mathbf{b}, \mathbf{c})$  of  $Fddd$  and  $(\mathbf{a}', \mathbf{b}', \mathbf{c}')$  of  $Cc$  [cf. equation (2)]. For some applications, e.g. twin analysis or structural phase tran-

sitions, it could be of interest to identify the subset of symmetry operations of  $Fddd$  that forms the specific subgroup  $Cc$ , or in other words to express the symmetry operations of the standard setting of  $Cc$  in the basis of  $Fddd$ . The inverse transformation,  $\mathbf{a}', \mathbf{b}', \mathbf{a}' + 2\mathbf{c}'$ , restores the original axial setting and can be directly used in equation (4) to express the symmetry operations of  $Cc$  in the setting of the parent  $Fddd$  phase. In particular, the transformation of the generating translations of  $Cc$  results in an  $F$ -centred description of the lattice (whose conventional cell is  $C$ -centred). Further, the  $c$ -glide reflection  $(x, y, z \rightarrow x, \bar{y}, z + \frac{1}{2})$  becomes a  $d$  glide  $(x, y, z \rightarrow x - \frac{1}{4}, \bar{y}, z + \frac{1}{4})$  and the Hermann–Mauguin symbol for this alternative setting of  $Cc$  is  $Fd$  in the  $b$ -unique setting ( $F1d1$ ), as could be expected from the parent structure.

## 6. Alternative settings of space groups

As already indicated, the specific settings of space groups that coincide with the conventional space-group descriptions found in ITA will be referred to as *standard* settings (the term *default* settings is also used). 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 on  $\bar{1}$ ) for the centrosymmetric groups listed with respect to two origins in ITA. The space-group settings different from the standard one will be referred to as *alternative settings*.

Any alternative setting can be conveniently described by the matrix–column pair  $(\mathbf{P}, \mathbf{p})$  in equations (2), (3) and (4) which specifies the relationship between the coordinate systems of the alternative and the standard space-group setting, where the unprimed and primed vectors refer to the standard and alternative basis, respectively. The coordinates of the alternative-setting origin  $O'$  with respect to the standard origin  $O$  are given by the coefficients of the origin shift  $\mathbf{p}$ .

In general, there is an infinite number of possible space-group descriptions, but the alternative settings in which we are interested are limited to alternative bases of the same lattice with unit-cell descriptions that are different from the standard one. The condition can be expressed formally as  $\det(\mathbf{P}) = f'/f$  where  $\det(\mathbf{P})$  is the determinant of the transformation matrix in equation (2), and  $f'$  and  $f$  are the so-called unit-cell centring factors of the alternative and standard space-group descriptions, respectively (the centring factor for a primitive unit cell is equal to 1, for  $I$ ,  $A$ ,  $B$  or  $C$  unit cells it is 2, for an  $R$  unit cell in hexagonal axes it is 3 and for an  $F$  unit cell it is 4). The choice of the transformation matrices may lead to unit-cell parameters whose relationships are not limited to the original crystal family; if a metric specialization occurs in the standard setting, the alternative setting corresponds to a higher crystal family. For example, consider the transformation  $\mathbf{a}' = \mathbf{a} + \mathbf{c}$ ,  $\mathbf{b}' = \mathbf{b}$ ,  $\mathbf{c}' = -\mathbf{a} + \mathbf{c}$ , which applied to a primitive unit-cell description of a monoclinic lattice (unique symmetry direction along  $\mathbf{b}$ ) leads to a  $B$ -centred description of the same lattice: the determinant of the transformation matrix  $\mathbf{P}$  in equation (2) is 2, which means that the unit cell in the alternative setting has a double volume but also a doubled centring factor, the latter coming precisely from the  $B$ -centring vector. The cell parameters of the alternative  $B$  cell still satisfy the metric requirements of the monoclinic crystal family (unique symmetry direction along  $\mathbf{b}$ ), but in the presence of metric specialization may actually satisfy the metric requirements of a higher crystal family, as in the examples discussed in §6.2.2.

The assignment of a Hermann–Mauguin symbol to a space group in an alternative setting is another way of characterization. Given the matrix–column pair  $(\mathbf{P}, \mathbf{p})$  of the transformation, the symmetry operations of a space group can always be expressed with respect to the alternative choice of the basis vectors, but only for some choices do we get a Hermann–Mauguin symbol which (i) is different from the standard one; (ii) can be obtained with the construction rules of conventional Hermann–Mauguin symbols and can be used for the identification of the space-group type. In the following, the alternative Hermann–Mauguin symbol is termed *accurate* when it correctly describes the alternative setting of the space group; in most cases this simply corresponds to the condition that the alternative symbol is compatible with the equivalence of symmetry directions required by the corresponding holohedry. The transformations generated by the mappings of the space-group normalizers (ITA15: see also Koch & Fischer, 2006; Nespolo, 2015) can serve as examples of changes of the basis vectors which do not affect the Hermann–Mauguin symbols of the space groups. Our discussion of alternative space-group settings will focus on basis transformations which do result in modifications of the standard Hermann–Mauguin symbols.

In the following, we differentiate alternative space-group settings of two general types:

(i) Alternative-setting descriptions whose unit-cell parameters are compatible with the crystal family of the standard space-group description (hereafter referred to as *unconventional settings*). Unconventional settings can always be

described by accurate Hermann–Mauguin symbols and can be chosen for all space groups but the cubic ones; for the latter, with just one exception (*cf.* §6.1.6), any permutation of the axes does not affect the Hermann–Mauguin symbol, and any other alternative choice of the basis vectors would result in a non-cubic metric, *i.e.* to a lower crystal family. More than 500 unconventional settings of space groups are presented in ITA4, Table 4.3.2.1, but the list is still incomplete: for example, in the monoclinic family, settings corresponding to unit cells with double volume are absent; in the hexagonal family settings corresponding to the  $D$  unit cell are missing; and the  $Pb\bar{3}$  setting of  $Pa\bar{3}$  is not given.

(ii) Alternative-setting descriptions whose unit-cell parameters are compatible with crystal families different from that of the standard space-group description (hereafter referred to as *non-standard settings*):

(a) Alternative settings compatible with crystal families higher than that of the standard space-group description: in general, such alternative descriptions are applied when the lattice parameters of the standard setting show some metric specialization compatible with a higher crystal family.

(b) Alternative settings compatible with crystal families lower than that of the standard space-group description. In general, a lower crystal family description is possible for any space group but the triclinic ones, which correspond to the lowest crystal family. The corresponding non-standard Hermann–Mauguin symbols, constructed following the general rules, may not, however, describe correctly such alternative settings because of the fewer number of symmetry directions in the lower crystal family. For example, in an orthorhombic lattice there are only three symmetry directions instead of five for a tetragonal lattice; this does not allow an orthorhombic description of tetragonal space groups belonging to geometric crystal classes  $422$ ,  $4mm$ ,  $\bar{4}2m$  ( $\bar{4}m2$ ) and  $4/mmm$ . Indeed, a space group of type  $P4$  (No. 75) can be described in an orthorhombic setting as  $P114$ , the  $[001]$  direction coming first in the tetragonal setting symbol but last in the orthorhombic one:  $P114$  is therefore an accurate non-standard symbol for  $P4$ . In contrast, an orthorhombic Hermann–Mauguin symbol assigned to the four group types belonging to the  $\bar{4}2mP$  arithmetic crystal class, namely  $P\bar{4}2m$ ,  $P\bar{4}2c$ ,  $P\bar{4}2_1m$ ,  $P\bar{4}2_1c$  (No. 111 to No. 114), would not uniquely identify the space-group type unless properly modified. In fact,  $P22\bar{4}$  could correspond to either  $P\bar{4}2m$  or  $P\bar{4}2c$ ,  $P2_12_1\bar{4}$  to either  $P\bar{4}2_1m$  or  $P\bar{4}2_1c$ ,  $Cmm\bar{4}$  to either  $P\bar{4}2m$  or  $P\bar{4}2_1m$ , and  $Ccc\bar{4}$  to either  $P\bar{4}2c$  or  $P\bar{4}2_1c$ .

Obviously, the correct description of alternative space-group settings compatible with lower crystal families requires the introduction of appropriately modified Hermann–Mauguin symbols (see, for example, the modified Hermann–Mauguin symbols of polar space-group normalizers listed in ITA15). However, such a subject goes beyond the scope of this article and will be treated elsewhere.

Müller (2013) has presented some concrete guidelines for the choice of unconventional settings, with a number of examples and practical hints. Our derivation has a wider scope and is not restricted to alternative settings compatible with the

same crystal family but can be considered an extension and generalization of the results presented there.

## 6.1. Unconventional settings of space groups

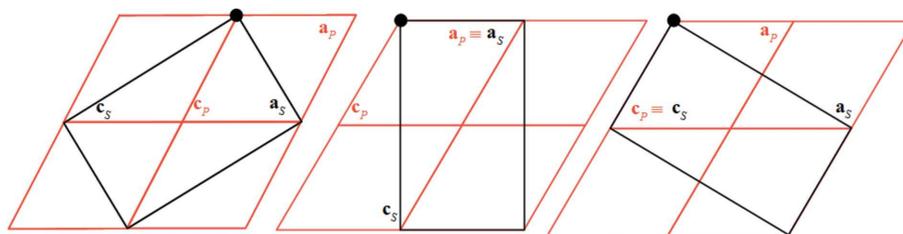
**6.1.1. Triclinic space groups.** Only two types of triclinic space groups exist whose standard Hermann–Mauguin symbols are  $P1$  (No. 1) and  $P\bar{1}$  (No. 2). Because there is no symmetry direction in a triclinic lattice, the reduced cell (ITA9) is usually taken as standard. In the case of nearly metric specialization, the use of an unconventional centred cell may allow the metric pseudo-symmetry to be emphasized. However, also in the absence of metric specialization a centred cell can be useful when comparing the structure of polymorphs, or in the study of modular structures built by the polysynthetic repetition of the same module (Ferraris *et al.*, 2008). For example, anorthite,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ , end-member of the plagioclase solid solution and one of the main rock-forming minerals, crystallizes in three triclinic holohedral polymorphs. At ambient pressure and temperature, a  $P\bar{1}$  phase is stable, which transforms to two different  $\bar{1}1$  phases, one with the same cell parameters, setting aside the thermal expansion, at high temperature, and one with a doubled  $c$  parameter at high pressure (Christy & Angel, 1995). Plagioclases with intermediate composition between albite ( $\text{NaAlSi}_3\text{O}_8$ ) and anorthite also show average structures corresponding to a triclinic holohedral space group in a setting  $C\bar{1}$  (Wenk *et al.*, 1980), which also corresponds to the true structure of an Mn-bearing anorthite (Matsui & Kimata, 1997). Clearly, the space group of any of these structures can be described by a reduced cell and would have the same Hermann–Mauguin symbol  $P\bar{1}$ , but this would conceal the structural relations among the various polymorphs.

Another example comes from modular structures. Micas occur in a large number of polytypes obtained by stacking along the  $c$  axis a layer with symmetry  $c2/m11$  [No. 18 following Volume *E* of *International Tables for Crystallography*, or  $C12/m(1)$  according to the notation of layer groups after Dornberger-Schiff (1959)], with an almost orthohexagonal cell in the (001) plane. The cell parameters resulting from the stacking of these layers are  $a \simeq 5.3$ ,  $b \simeq 9.2$ ,  $c \simeq 10N \text{ \AA}$ , where  $N$  is the number of layers in the period of the polytype, which also determines the monoclinic angle (Nespolo *et al.*, 1998). The most frequent polytypes are short-period polytypes with monoclinic or trigonal symmetry; rarer long-period polytypes do however exist and most of these are triclinic. The choice of a primitive unit cell to describe the structure of these polytypes would hide the stacking mode of layers, which is instead explicitly revealed by adopting an unconventional setting which keeps the length of the  $a$  and  $b$  axes of the building layer. For example, the two long-period polytypes discovered by Kogure & Nespolo (1999) crystallize in

a space group of type  $C1$ , where the use of a non-conventional  $C$ -centred cell for a triclinic space group is justified precisely by the need to preserve the pseudo-orthohexagonal cell in the plane of the layer.

**6.1.2. Monoclinic space groups.** Thirteen types of monoclinic space groups exist, whose Hermann–Mauguin symbols depend on the setting chosen. First, the settings of the monoclinic space-group types depend on whether the unique symmetry direction (called the *unique axis*) is taken as  $a$ ,  $b$  or  $c$ . Then, following ITA, each of the eight monoclinic space-group types characterized by either a glide plane or a centred cell can be described in three cell choices. Finally, the two axes in the plane normal to the unique symmetry direction can be interchanged, leading to a total of up to 18 settings, *cf.* Table 4.3.2.1 of ITA. Yet, this ‘monoclinic monster’, as it has been called (Th. Hahn, personal communication), does not exhaust the whole set of possible unconventional settings. Rarer and apparently awkward Hermann–Mauguin symbols of monoclinic space groups do also occur and make sense, especially in the case of metric pseudo-symmetry, although not many investigators are aware of them, partly because they are not listed in ITA4.

Aside from the specific setting adopted, the 13 types of monoclinic space groups can be generally indicated with a conventional cell  $P$  or  $S$ ; if a glide plane is present in the Hermann–Mauguin symbol, it can be indicated as  $g$ . The resulting setting-independent symbols for the monoclinic space-group types are shown in the first column of Table 1. For each choice of the unique axis and for each cell choice, two cell types can be taken, conventional or multiple (with doubled volume). The Hermann–Mauguin symbols for conventional cells are given in Table 4.3.2.1 of ITA; those for multiple cells correspond to unconventional settings and are not shown in ITA (some of them appear in Volume *A1* of *International Tables for Crystallography*, 2010). By considering the multiple cells, the number of possible settings for monoclinic space-group types increases to 21. Some unusual settings appear, like  $B2/d$ ,  $B_{21}/d$ ,  $B2/e$ ,  $B_{21}/e$  or  $F2/d$  and the corresponding subgroups. To understand how these settings are obtained, let us consider the example of No. 7 in Table 1, whose setting-independent symbol is  $Pg$ ; it can be realized as  $Pc$ ,  $Pn$  or  $Pa$  in cell choice 1, 2 and 3, respectively. Fig. 1 shows the three possible choices of a  $B$ -centred cell (the figure is drawn for the special case when  $a = c$ , which leads to an orthorhombic  $B$  cell



**Figure 1**

The three possible choices of an  $S$ -centred cell (black) obtained from a primitive cell (red). The figure is drawn for the special case of a metric specialization  $a = c$ , which leads to an  $oB$  cell. The black dot indicates the origin common to the two cells.

used in the discussion of §6.2.2, but the axial transformations are independent of any metric specialization), corresponding to transformations  $\mathbf{a} + \mathbf{c}$ ,  $\mathbf{b}$ ,  $-\mathbf{a} + \mathbf{c}$ ;  $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{a} + 2\mathbf{c}$ ; and  $2\mathbf{a} + \mathbf{c}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$ , respectively. By applying equation (4) to the  $(\mathbf{W}, \mathbf{w})$  matrix–column pair representation of the  $c$ -glide reflection (cell choice 1 of  $Pg$ , *i.e.*  $P1c1$ ), where  $\mathbf{P}$  is one of the matrices corresponding to the three transformations above, and no shift of the origin (*i.e.*  $\mathbf{p} = \mathbf{0}$ ), the result is a glide reflection with  $(a + c)/4$  glide component for the first two cases and a  $c$ -glide reflection for the third; when adding the  $B$ -centring vector one gets a glide reflection with  $3(a + c)/4$  glide component for the first two cases and an  $a$ -glide reflection for the third. Taken together, the results are a  $d$ -glide reflection for the first two cases and a double glide reflection for the third, whose symmetry element is an  $e$ -glide plane. The unconventional settings are thus expressed by the Hermann–Mauguin symbols  $B1d1$  for the first two cases and  $B1e1$  for the third. If then we start from another cell choice of  $Pg$  (*i.e.*  $P1n1$  or  $P1a1$ ), we have to compute the corresponding transformation matrices, which are obtained as follows. Given the transformation matrix  $\mathbf{P}_1$  relating the basis of cell choice 1,  $(\mathbf{a}, \mathbf{b}, \mathbf{c})_1$ , and the basis of the  $B$ -centred description,  $(\mathbf{a}, \mathbf{b}, \mathbf{c})_B$ ,

$$(\mathbf{a}, \mathbf{b}, \mathbf{c})_B = (\mathbf{a}, \mathbf{b}, \mathbf{c})_1 \mathbf{P}_1,$$

and the transformation matrices  $\mathbf{M}_i$  between the bases of the different cell-choice descriptions,

$$(\mathbf{a}, \mathbf{b}, \mathbf{c})_i = (\mathbf{a}, \mathbf{b}, \mathbf{c})_1 \mathbf{M}_i, \quad i = 1, 2, 3,$$

then the matrices  $\mathbf{P}_i$  defined as

$$(\mathbf{a}, \mathbf{b}, \mathbf{c})_B = (\mathbf{a}, \mathbf{b}, \mathbf{c})_i \mathbf{P}_i$$

are obtained from

$$(\mathbf{a}, \mathbf{b}, \mathbf{c})_B = (\mathbf{a}, \mathbf{b}, \mathbf{c})_1 \mathbf{P}_1 = (\mathbf{a}, \mathbf{b}, \mathbf{c})_i \mathbf{M}_i \mathbf{P}_1,$$

*i.e.*  $\mathbf{P}_i = \mathbf{M}_i \mathbf{P}_1$ .

Here, the matrices  $\mathbf{M}_i$  are taken following the choice of ITA (Table 5.1.3.1): *i.e.*  $\mathbf{M}_1$  is the identity matrix for cell choice 1 ( $Pg = P1c1$ ),

$$\mathbf{M}_2 = \begin{pmatrix} \bar{1} & 0 & 1 \\ 0 & 1 & 0 \\ \bar{1} & 0 & 0 \end{pmatrix}$$

for cell choice 2 ( $Pg = P1n1$ ) and

$$\mathbf{M}_3 = \begin{pmatrix} 0 & 0 & \bar{1} \\ 0 & 1 & 0 \\ 1 & 0 & \bar{1} \end{pmatrix}$$

for cell choice 3 ( $Pg = P1a1$ ). The resulting unconventional Hermann–Mauguin symbols for cell choices 2 and 3 are the same as for cell choice 1, the only difference being the sequence in which the unconventional settings are obtained ( $B1d1$ ,  $B1d1$ ,  $B1e1$  for cell choice 1;  $B1e1$ ,  $B1d1$ ,  $B1d1$  for cell choice 2;  $B1d1$ ,  $B1e1$ ,  $B1d1$  for cell choice 3). Finally, the permutations of the axes in the (010) plane do not affect the symbol, the glide components being either diagonal ( $d$ -glide plane) or along both axes ( $e$ -glide plane), whereas the permutations of the axes outside the (010) plane change the

setting from  $b$ -unique to  $c$ -unique and  $a$ -unique, leading to unconventional symbols  $C11d$ ,  $C11e$ ,  $Ad11$  and  $Ae11$ .

The usefulness of these unconventional settings may seem questionable at first sight. As an example of application, we may quote the elbow twins in cassiterite and rutile (Nespolo & Souvignier, 2015), where the maximal subgroup of the crystal space group compatible with the twin lattice is of type  $B2_1/e$  (unconventional setting of No. 13) with a monoclinic angle of  $91.41^\circ$ , which in the standard  $P2_1/n$  setting (unique axis  $b$ , cell choice 2) becomes  $100.83^\circ$  (other cell choices correspond to an even larger angle), making the orthorhombic pseudo-symmetry of the twin lattice undetected.

**6.1.3. Orthorhombic space groups.** In an orthorhombic space-group type a priority labelling of the basis vectors cannot be decided on the basis of the symmetry; as a consequence, the 59 orthorhombic space-group types can have up to six settings depending on the six possible permutations of the basis vectors:  $\mathbf{a}, \mathbf{b}, \mathbf{c}$ ;  $\mathbf{b}, \mathbf{a}, \bar{\mathbf{c}}$ ;  $\mathbf{c}, \mathbf{a}, \mathbf{b}$ ;  $\bar{\mathbf{c}}, \mathbf{b}, \mathbf{a}$ ;  $\mathbf{b}, \mathbf{c}, \mathbf{a}$ ;  $\mathbf{a}, \bar{\mathbf{c}}, \mathbf{b}$  (*cf.* ITA4). The standard description of the anti-hemihedral space groups<sup>3</sup> in ITA corresponds to the  $mm2$  setting, rather than  $m2m$  or  $2mm$ ; for groups with an  $S$ -centred cell, the  $C$ -centred description is preferred or, when this is not compatible with the  $mm2$  setting of the anti-hemihedral groups, an  $A$ -centred description is adopted. The  $B$  setting is never taken as the standard setting, but it too appears in ITA4 among the unconventional settings. This list is thus complete for transformations not affecting the volume of the unit cell [determinant of the transformation matrix in equation (2) equals 1].

**6.1.4. Tetragonal space groups.** The 68 tetragonal types of space groups are described with respect to a conventional  $P$  or  $I$  unit cell. An unconventional unit cell with double volume,  $C$  or  $F$ , respectively, can also be adopted. This can be useful in the investigation of phase transitions, for example coming from a  $cF$  structure, where keeping the same axial setting allows one to compare the atomic displacements in the parent and daughter phase. The unconventional Hermann–Mauguin symbols obtained by the adoption of these multiple cells are given in ITA4. Here we illustrate the basic principles of the transformations and analyse a couple of examples.

The axial transformation  $P$  to  $C$  and  $I$  to  $F$  is simply  $\mathbf{a} - \mathbf{b}$ ,  $\mathbf{a} + \mathbf{b}$ ,  $\mathbf{c}$  (or  $\mathbf{a} + \mathbf{b}$ ,  $-\mathbf{a} + \mathbf{b}$ ,  $\mathbf{c}$ ). As a consequence, the secondary and tertiary symmetry directions are exchanged, *i.e.* the directions  $\langle 100 \rangle$  in the  $P$  or  $I$  setting become  $\langle 1\bar{1}0 \rangle$  in the  $C$  or  $F$  setting, and *vice versa*. Further, a centring vector has to be added. The consequences are:

(i) The Bravais type of lattice becomes  $tC$  or  $tF$ .

(ii) Apart from the exchange between the  $\langle 100 \rangle$  and  $\langle 1\bar{1}0 \rangle$  orientations,

(a) no change for the rotation, rotoinversion or screw rotation axes;

(b) no change for  $m$  mirror planes or  $c$ -glide planes;

<sup>3</sup> The geometric crystal class corresponding to a subgroup  $\mathcal{H}$  of index 2 in a holohedral group  $\mathcal{G}$  obtained by removing from  $\mathcal{G}$  the inversion and all the operations that are in the same coset is called *holoaxial hemihedry* or *anti-hemihedry* depending on whether it is a Sohncke group (*i.e.* contains only first-kind isometries: Friedel, 1926) or not.

(c) no change for the  $d$  glides: this occurs in  $I4_1md$ ,  $I4_1cd$  and  $\bar{I}42d$ , which become  $F4_1dm$ ,  $F4_1dc$  and  $F\bar{4}d2$ , as well as in the holohedral supergroups having them as subgroups.

(iii) Glides perpendicular to  $[001]$ :

(a) the  $n$  glide perpendicular to  $[001]$  becomes an  $a$  glide because of the  $\langle 100 \rangle$  and  $\langle \bar{1}\bar{1}0 \rangle$  direction exchange; to this a  $b$  glide is added by the  $C$  centring so that finally it becomes an  $e$  glide; this occurs in  $P4/n$  and  $P4_2/n$ , which become  $C4/e$  and  $C4_2/e$ , as well as in the holohedral supergroups having them as subgroups;

(b) the  $a$  glide perpendicular to  $[001]$  becomes a  $d$  glide and the same occurs for the  $b$  glide at  $\mathbf{c}/4$  from it; this occurs in  $I4_1/a$  which becomes  $F4_1/d$ , as well as in the holohedral supergroups having it as subgroup.

(iv) Glides perpendicular to  $\langle 100 \rangle$ :

(a) the  $b$  glide perpendicular to  $[100]$ , accompanied by the  $a$  glide perpendicular to  $[010]$ , become glide planes with non-standard vector parts  $(\frac{1}{4}, \frac{1}{4}, 0)$  perpendicular to  $\langle \bar{1}\bar{1}0 \rangle$ , for which the symbol  $g_1$  is adopted. This occurs in  $P4bm$  (No. 100),  $P4_2bc$  (No. 106) and  $P\bar{4}b2$  (No. 117), which become  $C4mg_1$ ,  $C4_2cg_1$  and  $C\bar{4}2g_1$ , as well as in the holohedral supergroups having them as subgroups;

(b) the  $n$  glides perpendicular to  $\langle 100 \rangle$  become glide planes with non-standard vector parts  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$  perpendicular to  $\langle \bar{1}\bar{1}0 \rangle$ , for which the symbol  $g_2$  is adopted. This occurs in  $P4_2nm$  (No. 102),  $P4nc$  (No. 104) and  $P4n2$  (No. 118), which become  $C4_2mg_2$ ,  $C4cg_2$  and  $C\bar{4}2g_2$ , as well as in the holohedral supergroups having them as subgroups.

It is to be noted that the  $g$  glide never occurs in a standard Hermann–Mauguin symbol because of its last position in the priority rule; it appears instead in the unconventional  $tC$  symbol, where no glide plane with higher priority is found parallel to it. Also note that  $e$ -glide notation is not applied consistently in the Hermann–Mauguin symbols of the unconventional multiple cell settings of some tetragonal space groups. For example,  $C4/a$  and  $C4_2/a$  are used instead of  $C4/e$  and  $C4_2/e$ ; this will be corrected in the forthcoming sixth edition of ITA.

**6.1.5. Trigonal and hexagonal space groups.** The seven rhombohedral space-group types can be described with respect to either a rhombohedral primitive cell or a hexagonal triple cell, without any change in the Hermann–Mauguin symbol. Both descriptions are shown in the space-group tables of ITA and are considered as conventional. When the hexagonal triple cell is adopted, two possible orientations exist, known as observe and reverse, respectively, which correspond to the hexagonal-to-rhombohedral transformations  $\mathbf{a} - \mathbf{b}$ ,  $\mathbf{b} - \mathbf{c}$ ,  $\mathbf{a} + \mathbf{b} + \mathbf{c}$ ; and  $-\mathbf{a} + \mathbf{b}$ ,  $-\mathbf{b} + \mathbf{c}$ ,  $\mathbf{a} + \mathbf{b} + \mathbf{c}$ , respectively (row permutations lead to three cells, called  $R_1$ ,  $R_2$  and  $R_3$ , in both cases). The observe setting is the standard one whereas the reverse setting is seldom used. However, in isomorphic group–subgroup relations of rhombohedral space groups involving an increase of the hexagonal  $c$  axis, the reversal of the directions of  $\mathbf{a}$  and  $\mathbf{b}$  ( $-\mathbf{a}, -\mathbf{b}$ ,  $pc$ ) can be avoided if a reverse setting is used for one of the space groups – cf. Volume A1 of *International Tables for Crystallography* (2010).

The 45 space-group types with a hexagonal lattice can be described in two different triple cells (cf. §4.3.5.3 and Table 5.1.3.1 of ITA):

(i) A metrically hexagonal cell indicated as  $H$ , having additional nodes at  $(\frac{2}{3}, \frac{1}{3}, 0)$  and  $(\frac{1}{3}, \frac{2}{3}, 0)$ . Three possible orientations exist for the  $hH$  cell with respect to the  $hP$  cell, with axial transformations  $\mathbf{a} - \mathbf{b}$ ,  $\mathbf{a} + 2\mathbf{b}$ ,  $\mathbf{c}$ ;  $2\mathbf{a} + \mathbf{b}$ ,  $-\mathbf{a} + \mathbf{b}$ ,  $\mathbf{c}$ ;  $\mathbf{a} + 2\mathbf{b}$ ,  $-2\mathbf{a} - \mathbf{b}$ ,  $\mathbf{c}$ .

(ii) A metrically rhombohedral cell indicated as  $D$ , having additional nodes at  $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$  and  $(\frac{2}{3}, \frac{2}{3}, \frac{2}{3})$ . There are six possible axial transformations from the conventional  $hP$  cell to the  $hD$  cell:  $\mathbf{a} + \mathbf{c}$ ,  $\mathbf{b} + \mathbf{c}$ ,  $-\mathbf{a} - \mathbf{b} + \mathbf{c}$ ;  $-\mathbf{a} + \mathbf{c}$ ,  $-\mathbf{b} + \mathbf{c}$ ,  $\mathbf{a} + \mathbf{b} + \mathbf{c}$ ; the other four being obtained through cyclic permutations. This description was called ‘hexagonal centring’ by Buerger (1949), and is known as the ‘rhombohedral description of the hexagonal lattice’ in §4.3.5.3 of ITA.

Similarly to what happens in the tetragonal unconventional settings, the secondary directions  $\langle 100 \rangle$  in the  $P$  setting become tertiary directions  $\langle \bar{1}\bar{1}0 \rangle$  in both the  $hH$  and the  $hD$  description, and *vice versa*. However, because the only mirror planes that occur in the short and full Hermann–Mauguin symbols are of the type  $m$  and  $c$ , the only modification of the symbols when adopting the triple  $hH$  or  $hD$  cell, apart from the cell type, is the exchange of the second and third characters. The  $hH$  description of the hexagonal space groups can be found in Table 4.3.2.1 of ITA and is used in the maximal-subgroup tables of space groups in Volume A1 of *International Tables for Crystallography* (2010) as well as in the OD (order-disorder) theory to express the symmetry of the family structure (Nespolo & Đurovič, 2002); due to the lack of practical importance, no data on the  $hD$  description of hexagonal space groups can be found in the literature.

**6.1.6. Cubic space groups.** Because there is no degree of freedom on the lattice parameters for cubic space groups, the only alternative descriptions that satisfy the conditions discussed in §6 are those obtained by the same permutations of the axes that we have seen for orthorhombic groups (§6.1.3). However, in a cubic group the basis vectors are equivalent under the action of the threefold axes (characteristic for any cubic group), so that one is tempted to conclude that any permutation of the axes would not generate an unconventional setting and would therefore not affect the standard Hermann–Mauguin symbol of the group. This is not quite true for  $Pa\bar{3}$  (No. 205). The six permutations of the basis vectors listed in ITA4 for the orthorhombic groups correspond to the transformations  $\mathbf{a}, \mathbf{b}, \mathbf{c}$ ;  $\mathbf{b}, \mathbf{c}, \mathbf{a}$ ;  $\mathbf{c}, \mathbf{a}, \mathbf{b}$ ;  $\mathbf{b}, \mathbf{a}, \bar{\mathbf{c}}$ ;  $\bar{\mathbf{c}}, \mathbf{b}, \mathbf{a}$ ; and  $\mathbf{a}, \bar{\mathbf{c}}, \mathbf{b}$  that occur as linear parts of the Euclidean normalizer operations of all cubic space groups but  $Pa\bar{3}$ . The normalizer of  $Pa\bar{3}$  is only hemihedral, namely of type  $Ia\bar{3}$  (No. 206), and does not contain any operation whose linear part corresponds to the last three transformations. Therefore, these three transformations produce an unconventional setting of  $Pa\bar{3}$ , as becomes evident by the corresponding transformation of the symmetry operations of  $Pa\bar{3}$ , cf. equation (4). The group  $Pa\bar{3}$  presents only one type of glide plane perpendicular to each of the basis vectors, with a glide component along one of the in-plane basis vectors. These are chosen as  $b$  glide perpendicular to  $[100]$ ,  $c$

glide perpendicular to [010] and  $a$  glide perpendicular to [001]; the priority rule uses the last one in the Hermann–Mauguin symbol of the space-group type. The unconventional setting of  $Pa\bar{3}$ , obtained, for example, by the transformation  $\mathbf{b}, \mathbf{a}, \bar{\mathbf{c}}$  is characterized by a  $c$  glide perpendicular to [100],  $a$  glide perpendicular to [010] and  $b$  glide perpendicular to [001]. The strict application of the priority rule would not suggest a modification of the Hermann–Mauguin symbol for the unconventional setting of  $Pa\bar{3}$  and, in fact, such practice can be found in the literature (see, for example, ITA7, or Volume A1 of *International Tables for Crystallography*, 2010). However, our recommendation is to use a different symbol, namely  $Pb\bar{3}$ , for the designation of the unconventional setting of  $Pa\bar{3}$ . The reason is that the use of the same Hermann–Mauguin symbol could disguise the important difference between the sequence of glide planes of the two settings. One can say that the two settings are ‘experimentally’ distinguishable as becomes evident from the zonal reflection conditions which for  $Pa\bar{3}$  are  $0kl: k = 2n, h0l: l = 2n, hk0: h = 2n$ , whereas for  $Pb\bar{3}$  they are  $0kl: l = 2n, h0l: h = 2n, hk0: k = 2n$ ; there is no operation either in  $Pa\bar{3}$  or in its Euclidean normalizer  $Ia\bar{3}$  that maps one set of reflection conditions to the other.

## 6.2. Non-standard settings of space groups: alternative settings with metric specialization

The non-standard settings discussed in the following are limited to the cases of alternative space-group descriptions whose unit-cell parameters are compatible with crystal families higher than the one of the standard space-group description. Obviously, such non-standard descriptions are applicable when the cell parameters exhibit higher metric symmetry which, in fact, occurs more frequently than one might expect (Janner, 2004a,b; Gelder & Janner, 2005). Grimmer & Nespolo (2006) have studied the effects of metric specializations of lattices and collected the results in a path through Bravais types of lattice (Fig. 3 therein); this has been reviewed and extended by Grimmer (2015), who analysed in detail the metric specializations leading to a higher lattice symmetry, and exploited by Nespolo *et al.* (2014) to study the effect of merohedric twinning on the diffraction pattern.

As for all alternative settings, the non-standard descriptions are uniquely defined by the transformation matrix–column pair  $(\mathbf{P}, \mathbf{p})$  which relates the bases of the standard and alternative settings (*cf.* §6). The non-standard settings can also often be characterized by the related non-standard Hermann–Mauguin symbols. In the process of deriving these non-standard symbols, the following three cases have to be considered.

(i) Non-standard settings prompted by metric specialization may lead to non-standard Hermann–Mauguin symbols which are intrinsically incoherent. This happens when symmetry elements of different type would occur along directions which are equivalent in the setting of the higher holohedry. For example, a space group of type  $Pmc2_1$  (No. 26) with a tetragonal specialization should have  $m$  and  $c$  (for  $a = b$ ),  $m$  and  $2_1$  (for  $a = c$ ) or  $c$  and  $2_1$  (for  $b = c$ ) along the same direction if a

tetragonal symbol was adopted. Such a setting cannot be properly described by the Hermann–Mauguin symbolism, unless some modifications in the symbol construction rules are adopted, leading to something like  $P2_1(mc)1$ ,  $Pc(m2_1)1$  or  $Pm(c2_1)1$ , respectively. Alternatively, if a priority rule is adopted to avoid introducing new symbols (for example, by denoting mirror planes and leaving undescribed glide planes or rotation or screw axes in the same position), the non-standard Hermann–Mauguin symbol alone cannot convey the full information about the alternative setting but has to be completed by the indication of the change of axial setting and the shift of the origin with respect to the standard setting. If the non-standard Hermann–Mauguin symbols are used to express group–subgroup relations, then also the set of operations of the supergroup retained in the subgroup could be provided, as is done for example in Volume A1 of *International Tables for Crystallography* (2010).

(ii) As a special case of (i) above, one can consider the case when a symmetry element ends up coexisting with no symmetry or, in the case of a fourfold or sixfold rotation or rotoinversion axis, with a rotation axis of lower order, along directions which are equivalent in the setting of the higher holohedry. A non-standard Hermann–Mauguin symbol can be adopted in this case, which, although not accurate, does satisfy the symbol construction rules. For example, a space group of type  $P4cc$  (No. 103) with metric specialization  $a = b = c$  can be described by a non-standard cubic symbol  $P41c$ . Strictly speaking, this symbol is not accurate because (a) of the three directions that correspond to the first position of the non-standard symbol, only one brings a fourfold axis; (b) of the six directions that correspond to the third position of the non-standard symbol, only two bring a  $c$ -glide plane. The lack of a threefold axis in the second position unambiguously indicates that the group is still tetragonal. These non-standard Hermann–Mauguin symbols are widely used as intermediate symbols in the group–maximal subgroup relations in Volume A1 of *International Tables for Crystallography* (2010), where the symmetry reduction is first performed by keeping the setting of the supergroup and removing the symmetry operations which are absent in the subgroup. The result is then expressed in the setting of the subgroup. For example, the maximal *translationengleiche* group–subgroup relation between a space group of type  $Pm\bar{3}m$  (No. 221) and its subgroup of type  $P4/mmm$  (No. 123), with index 3, is expressed by the non-standard symbol  $P4/m12/m$ , in which the cubic setting is kept but only the symmetry operations of the subgroup are retained. Also, the non-standard symbol  $P222$  is adopted as an intermediate step in the group–maximal subgroup relation from  $P622$  (No. 177) to  $C222$  (No. 21). The hexagonal metric expressed by the cell parameters, combined with the lack of sixfold rotation, unambiguously indicates that the rotation axes occur along only three instead of seven symmetry directions. A further example is that of the primitive cell of a cubic  $I$  or  $F$  cell which is rhombohedral with an interaxial angle of  $109.47^\circ$  and  $60^\circ$ , respectively. In a phase transition from a  $cF$  or  $cI$  space-group type to a rhombohedral space-group type the interaxial angle of the daughter phase

**Table 2**

Tetragonal and cubic settings of the 38 types of orthorhombic space groups possessing an enhanced Euclidean normalizer and the corresponding accurate non-standard Hermann–Mauguin symbol (H–M) (a dashed line means the corresponding combination is not possible).

For groups whose symbol changes with the basis vector permutations (Nos. 20, 21, 25, 27, 32, 34, 35, 37, 42, 43, 44, 45, 49, 50, 55, 56, 58, 59, 65, 66, 67, 68, 72 and 74) only the standard symbol is given because the non-standard Hermann–Mauguin is the same, although the metric specialization differs (for example, the *B222* and *A222* descriptions of No. 21 lead to *P212* exactly like for the *C222* description, although the metric specialization becomes  $a = c$  and  $b = c$ , respectively). For 11 of the 12 groups having a cubic enhanced normalizer, the non-standard Hermann–Mauguin symbol looks like that of an *a*-unique setting of a monoclinic group (in bold in the last column of the table): in these cases, the information about the metric specialization is therefore not immediately evident from the non-standard symbol.

No.	Standard H–M symbols	Tetragonal symbol			Cubic symbol	No.	Standard H–M symbols	Tetragonal symbol			Cubic symbol
		$a = b \neq c$	$a = c \neq b$	$b = c \neq a$	$a = b = c$			$a = b \neq c$	$a = c \neq b$	$b = c \neq a$	$a = b = c$
16	<i>P222</i>	<i>P221</i>	<i>P221</i>	<i>P221</i>	<b><i>P211</i></b>	47	<i>Pmmm</i>	<i>Pmm1</i>	<i>Pmm1</i>	<i>Pmm1</i>	<b><i>Pm11</i></b>
17	<i>P222<sub>1</sub></i>	<i>P2<sub>1</sub>21</i>	---	---	---	48	<i>Pnnn</i>	<i>Pnn1</i>	<i>Pnn1</i>	<i>Pnn1</i>	<b><i>Pn11</i></b>
18	<i>P2<sub>1</sub>2<sub>1</sub>2</i>	<i>P22<sub>1</sub>1</i>	---	---	---	49	<i>Pccm</i>	<i>Pmc1</i>	---	---	---
19	<i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i>	<i>P2<sub>1</sub>2<sub>1</sub>1</i>	<i>P2<sub>1</sub>2<sub>1</sub>1</i>	<i>P2<sub>1</sub>2<sub>1</sub>1</i>	<b><i>P2<sub>1</sub>11</i></b>	50	<i>Pban</i>	<i>Pnb1</i>	---	---	---
20	<i>C222<sub>1</sub></i>	<i>P2<sub>1</sub>12</i>	---	---	---	55	<i>Pbam</i>	<i>Pmb1</i>	---	---	---
21	<i>C222</i>	<i>P212</i>	---	---	---	56	<i>Pccn</i>	<i>Pnc1</i>	---	---	---
22	<i>F222</i>	<i>I212</i>	<i>I212</i>	<i>I212</i>	<b><i>I211</i></b>	58	<i>Pnm</i>	<i>Pmn1</i>	---	---	---
23	<i>I222</i>	<i>I221</i>	<i>I221</i>	<i>I221</i>	<b><i>I211</i></b>	59	<i>Pmnn</i>	<i>Pnm1</i>	---	---	---
24	<i>I2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i>	<i>I2<sub>1</sub>2<sub>1</sub>1</i>	<i>I2<sub>1</sub>2<sub>1</sub>1</i>	<i>I2<sub>1</sub>2<sub>1</sub>1</i>	<i>I2<sub>1</sub>11</i>	61	<i>Pbca</i>	---	---	---	<b><i>Pc11</i></b>
25	<i>Pmm2</i>	<i>P2m1</i>	---	---	---	65	<i>Cmmm</i>	<i>Pm1m</i>	---	---	---
27	<i>Pcc2</i>	<i>P2c1</i>	---	---	---	66	<i>Cccm</i>	<i>Pc1m</i>	---	---	---
32	<i>Pba2</i>	<i>P2b1</i>	---	---	---	67	<i>Cmme</i>	<i>Pn1m</i>	---	---	---
34	<i>Pnn2</i>	<i>P2n1</i>	---	---	---	68	<i>Ccce</i>	<i>Pn1c</i>	---	---	---
35	<i>Cmm2</i>	<i>Pm12</i>	---	---	---	69	<i>Fmmm</i>	<i>Im1m</i>	<i>Im1m</i>	<i>Im1m</i>	<b><i>Fm11</i></b>
37	<i>Ccc2</i>	<i>Pc12</i>	---	---	---	70	<i>Fddd</i>	<i>Id1d</i>	<i>Id1d</i>	<i>Id1d</i>	<b><i>Fd11</i></b>
42	<i>Fmm2</i>	<i>I21m</i>	---	---	---	71	<i>Immm</i>	<i>Imm1</i>	<i>Imm1</i>	<i>Imm1</i>	<b><i>Im11</i></b>
43	<i>Fdd2</i>	<i>I21d</i>	---	---	---	72	<i>Ibam</i>	<i>Imb1</i>	---	---	---
44	<i>Imm2</i>	<i>I2m1</i>	---	---	---	73	<i>Ibca–Icab</i>	---	---	---	<b><i>Ib11</i></b>
45	<i>Iba2</i>	<i>I2b1</i>	---	---	---	74	<i>Imma–Immb</i>	<i>Iam1</i>	---	---	---

departs from those specialized values. It can be useful to keep the original axial setting, even if the cell parameters are no longer compatible with the cubic symmetry, to show more straightforwardly how the atoms have moved across the transition. Accordingly, non-standard Hermann–Mauguin symbols like *F1 $\bar{3}$*  or *I13m* can appear.

(iii) The above discussion shows that non-standard settings compatible with metric specialization can be described correctly by accurate non-standard Hermann–Mauguin symbols if symmetry elements of the same type occur along directions that are equivalent in the higher holohedry. This is the case when the space-group type has an enhanced Euclidean normalizer for the given metric specialization. For example, a space group of type *Pcc2* (No. 27) with metric specialization  $a = b$  can be described with a non-standard accurate symbol *P2c1*: the only twofold axis along **c** occurs in the first position (unique tetragonal axis); the two *c*-glide planes are perpendicular to the basis vectors in the (001) plane, which correspond to the second position, whereas there is no symmetry along the diagonal directions, which correspond to the third position; the symbol ‘1’ in the third position indicates the absence of symmetry elements along the diagonal directions.

An enhanced Euclidean normalizer never occurs for space groups in the higher crystal systems (cubic, hexagonal, trigonal or tetragonal), nor for 21 of the 59 types of orthorhombic space groups. In the case of triclinic groups, the only symmetry elements are inversion centres, which do not specify a direction; a metric specialization never affects the Hermann–Mauguin symbol of triclinic groups. Finally, an enhanced

Euclidean normalizer occurs in 38 of the 59 orthorhombic and in the monoclinic space-group types; in the following we concentrate in particular on these types of groups because their non-standard setting compatible with metric specialization can be fully described by an accurate non-standard Hermann–Mauguin symbol.

**6.2.1. Orthorhombic space-group types with enhanced Euclidean normalizer.** Table 2 gives the accurate non-standard Hermann–Mauguin symbols of the 38 types of orthorhombic space groups having at least one type of enhanced Euclidean normalizer: the metric specialization identifies uniquely the setting (tetragonal or cubic). For example, a space group of type *Imma* (No. 74) possesses an enhanced tetragonal Euclidean normalizer if  $a = b$  because, besides having the same type of symmetry elements (*m*) along the [100] and [010] directions, which become equivalent in a tetragonal setting, the glide component along **a** at  $z = 0$  is accompanied by another glide along **b** at  $z = \frac{1}{4}$  generated by the *I*-centring vector. In the axial setting of its minimal tetragonal supergroup of index 2, namely *I4<sub>1</sub>/amd* (No. 141), the non-standard Hermann–Mauguin symbol of *Imma* can be expressed as *Iam1*, or *I2/a2/m1* for the full symbol, as it appears, for example, in Volume *A1* of *International Tables for Crystallography* (2010). A further example is given by the space group of type *Pccm* (No. 49), with metric specialization  $a = b$  indicating a tetragonal lattice. The existence of a tetragonal enhanced normalizer points to the possibility of describing correctly the alternative tetragonal setting of *Pccm* by a non-standard Hermann–Mauguin symbol. With respect to tetragonal basis vectors, the non-standard Hermann–Mauguin symbol becomes *Pmc1* (or

$P2/m2/c1$  for the full symbol), because the two  $c$ -glide planes perpendicular to  $[100]$  and  $[010]$  directions occupy the second position in the tetragonal symbol, the  $m$  perpendicular to  $[001]$  the first position, and no symmetry element is present parallel or normal to the third tetragonal direction.

**6.2.2. Monoclinic space groups with enhanced Euclidean normalizers.** Because in a monoclinic group there is only one symmetry direction, we discuss the various possibilities of metric specialization in terms of a generalized setting-independent symbol where the presence of symmetry elements about that direction is simply indicated as 'x'. Thus,  $Px$  represents  $P2, P2_1, Pm, Pg, P2/m, P2_1/m, P2/g$  or  $P2_1/g$ , and  $Sx$  represents  $S2, Sm, Sg, S2/m$  or  $S2/g$  (here, 'g' stands for a glide-plane symbol, cf. §6.1.2).

An orthorhombic specialization of a  $Px$  group corresponding to  $a = c$  (Fig. 1) or  $2 \cos \beta = -c/a$  ( $b$ -unique setting) results in a cell of type  $oB$ . Accordingly, in the orthorhombic setting an accurate non-standard Hermann–Mauguin symbol  $B1x1$  can be adopted, without a change of position for the unique axis with respect to the monoclinic symbol. The same applies to  $P11x$  for  $a = b$  or  $2 \cos \gamma = -b/a$ , the accurate non-standard Hermann–Mauguin symbol becoming  $C11x$ , and to  $Px11$  for  $b = c$  or  $2 \cos \alpha = -c/b$ , where the accurate non-standard Hermann–Mauguin symbol becomes  $Ax11$ . The presence of a centring vector in the plane perpendicular to the unique axis clearly indicates that the unit cell chosen is not conventional. For example, the lattice of  $C_{19}H_{33}LiN_3Ti$ , reported by Armstrong *et al.* (1993) in the standard setting  $P2_1/c$  (No. 14) with cell parameters  $a = 13.390$  (3),  $b = 25.604$  (6),  $c = 13.390$  (3) Å,  $\beta = 112.39$  (3)°, is actually orthorhombic within one standard uncertainty (s.u.), as suggested by  $a = c$ ; a non-standard setting  $B12_1/d1$  can thus be adopted (transformation  $\mathbf{a} + \mathbf{c}, \mathbf{b}, -\mathbf{a} + \mathbf{c}$ ), with  $a = 14.900$  (15),  $b = 25.604$  (6),  $c = 22.252$  (4) Å. More subtle cases occur when the metric specialization appears only for a cell choice which is not commonly considered. A typical example is that of cafetite,  $Ca[Ti_2O_5](H_2O)$  (Krivovichev *et al.*, 2003), reported in  $P2_1/n$ ,  $a = 4.9436$  (15),  $b = 12.109$  (4),  $c = 15.911$  (5) Å,  $\beta = 98.937$  (5)°, which does not seem to present any metric specialization. This however appears when adopting a  $P2_1/c$  setting (transformation  $\mathbf{c}, \mathbf{b}, -\mathbf{a} - \mathbf{c}$ ), in which  $a = 15.911$  (5),  $b = 12.109$  (4),  $c = 15.911$  (5) Å,  $\beta = 162.13$  (14)°. The very obtuse monoclinic angle makes this cell choice unlikely; yet, the  $a = c$  specialization indicates that the lattice is actually orthorhombic. The non-standard orthorhombic setting is again  $B12_1/d1$  (transformation  $\mathbf{a}, \mathbf{b}, \mathbf{a} + 2\mathbf{c}$  from  $P2_1/n$ , or  $\mathbf{a} + \mathbf{c}, \mathbf{b}, -\mathbf{a} + \mathbf{c}$  from  $P2_1/c$ ) with  $a = 4.9436$  (15),  $b = 12.109$  (4),  $c = 31.436$  (10) Å.

The other cases of monoclinic groups with enhanced Euclidean normalizers are immediately obtained in the same way, with the help of the tables of Euclidean normalizers in ITA15. Hereafter, for  $Sx$  groups, the basis-vector lengths in the plane perpendicular to the unique axis, within and outside the  $S$ -centred plane, are indicated as  $p_{in}$  and  $p_{out}$ , respectively.

(i)  $Px$  or  $Sx$  groups with the symmetry-unrestricted angle accidentally equal to  $90^\circ$  have a metrically orthorhombic cell and the Hermann–Mauguin symbol is the same as the oriented

symbol of the group without metric specialization (e.g.  $P1x1$  or  $S11x$ ).

(ii)  $Px$  groups with the symmetry-unrestricted angle accidentally equal to  $90^\circ$  and basis vectors of the same length in the plane normal to the unique axis have a metrically tetragonal lattice and the non-standard Hermann–Mauguin symbols become  $Px11$ .

(iii)  $Sx$  groups with the symmetry-unrestricted angle accidentally equal to  $135^\circ$  and basis vectors in the plane normal to the unique axis making an axial ratio  $p_{in}/p_{out} = 2^{1/2}$  have a metrically tetragonal lattice with  $tF$  unit cell (transformation  $\mathbf{a}, \mathbf{b}, \mathbf{a} + 2\mathbf{c}$ ), which can be transformed to  $tI$  so that the non-standard Hermann–Mauguin symbols become  $Ix11$ .

(iv)  $Px$  groups with the symmetry-unrestricted angle accidentally equal to  $120^\circ$  and basis vectors of the same length in the plane normal to the unique axis have a metrically hexagonal lattice and the non-standard Hermann–Mauguin symbols become  $Px11$ .

(v)  $Sx$  groups having the cosine of the symmetry-unrestricted angle equal to  $-p_{out}/p_{in}$  or to  $-p_{in}/2p_{out}$  have a metrically orthorhombic lattice with unit cell of type  $oI$ : the non-standard Hermann–Mauguin symbol is  $Ix$  ( $I11x, Ix11$  or  $I1x1$  for  $A11x, Bx11$  and  $C1x1$ , respectively).

## 7. Wyckoff positions in alternative settings

The space-group tables in ITA list the Wyckoff positions for the standard settings of all types of space groups, as well as for the three cell choices of standard monoclinic  $b$ -unique and  $c$ -unique settings. The transformation of the coordinate triplets of each Wyckoff position under coordinate transformation ( $\mathbf{P}, \mathbf{p}$ ) is given by equation (3). The multiplicity of each Wyckoff position is multiplied by the determinant of the transformation matrix  $\mathbf{P}$ , which gives the increase of the volume of the unit cell: a larger unit cell involves additional centring points and a corresponding increase in the multiplicity of the Wyckoff position.

For example, the unconventional  $F12/d1$  setting of  $C2/c$  (No. 15) can be obtained by the same transformation seen in §5 for the  $Cc$ -to- $Fd$  transformation, namely  $\mathbf{a}', \mathbf{b}', \mathbf{c}' = \mathbf{a}, \mathbf{b}, \mathbf{a} + 2\mathbf{c}$ . Accordingly, the multiplicity of each Wyckoff position in  $C2/c$  doubles when expressed in  $F12/d1$ . The coordinates are transformed by the inverse mapping,  $x', y', z' = x - z/2, y, z/2$ . The translation vectors  $(\frac{1}{2}\frac{1}{2}0)$ ,  $(101)$  and  $(\frac{1}{2}\frac{1}{2}1)$  in the standard setting become  $(\frac{1}{2}\frac{1}{2}0)$ ,  $(\frac{1}{2}0\frac{1}{2})$ ,  $(0\frac{1}{2}\frac{1}{2})$  in the unconventional setting, showing the presence of  $F$ -centring vectors in the latter. Position  $4a$  (site-symmetry group 1), which corresponds to coordinates  $(000)$ ,  $(00\frac{1}{2})$  in the standard setting, transforms to  $(000)$ ,  $(\frac{1}{4}0\frac{1}{4})$  in the unconventional setting; to these the  $F$ -centring vectors have to be added, leading to an unconventional  $F12/d1$  setting in which the position is finally expressed as  $8a$ .

For the transformation of structural data (such as lattice parameters and atomic positions) to alternative space-group settings, it is necessary to know the specific transformation matrix–column pairs that relate the alternative settings to the standard one, which, in the general case, cannot be determined

Table 3

Comparison of the fractional coordinates of high- and low-temperature phases of lead phosphate.

The former is presented twice, first in its conventional rhombohedral setting of the  $R\bar{3}m$  space group (left), then in the  $mC$  setting corresponding to the  $C2/c$  space group of the low-temperature phase (middle). The comparison with the low-temperature phase (right) shows that the fractional coordinates of the two polymorphs are very close when expressed in the same setting.

Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> high-temperature phase					Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> low-temperature phase							
Description in $R\bar{3}m$					Description in $C2/c$							
Atom	Wyckoff	<i>x</i>	<i>y</i>	<i>z</i>	Atom	Wyckoff	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Pb1	3 <i>a</i>	0	0	0	Pb1	4 <i>e</i>	0	0.25	0.25	0	0.291	0.25
Pb2	6 <i>c</i>	0	0	0.2126	Pb2	8 <i>f</i>	0.318901	0.25	0.3563	0.317	0.309	0.352
P1	6 <i>c</i>	0	0	0.4021	P1	8 <i>f</i>	0.603151	0.25	0.451051	0.599	0.241	0.447
O1	6 <i>c</i>	0	0	0.329	O1	8 <i>f</i>	0.493501	0.25	0.451051	0.491	0.222	0.447
O2	18 <i>h</i>	0.181	−0.181	0.096	O2	8 <i>f</i>	0.644001	0.25	0.617001	0.642	0.280	0.612
					(O3	8 <i>f</i>	0.644001	0.0215	0.388500)	0.643	0.030	0.392
					(O4	8 <i>f</i>	0.644001	0.4785	0.388500)	0.634	0.464	0.374

uniquely from the corresponding alternative Hermann–Mauguin symbols. Two representative examples have been worked out by Müller (2013).

(i) In the space-group type  $P222_1$  (No. 17), the Wyckoff positions  $2a$  ( $x, 0, 0$ ) and  $2b$  ( $0, y, \frac{1}{4}$ ) are on rotation axes. The axial transformations **c, a, b** and **c, b, a** both lead to  $P2_122$ . Depending on which of the two transformations is adopted, the positions  $2a$  and  $2c$  in the alternative setting may correspond to  $(0, y, 0)$  and  $(\frac{1}{4}, 0, z)$  or  $(0, 0, z)$  and  $(\frac{1}{4}, y, 0)$ ; without giving explicitly the relation with the standard setting one cannot be aware which of the two possibilities is realized in practice.

(ii) A cyclic permutation of the axes does not modify the Hermann–Mauguin symbol of the space-group type  $Ibca$  (No. 73) but exchanges cyclically the positions  $8c, 8d$  and  $8e$  (**b, c, a**:  $c \rightarrow e$ ;  $d \rightarrow c$ ;  $e \rightarrow d$ ; **c, a, b**:  $c \rightarrow d$ ;  $d \rightarrow e$ ;  $e \rightarrow c$ ).

## 8. Discussion

Alternative (unconventional or non-standard) settings of space groups are described through Hermann–Mauguin symbols which allow a complete identification of the space-group symmetry in the case of accurate symbols, *i.e.* symbols compatible with the equivalence of symmetry directions required by the corresponding holohedry. In the case of the other, non-accurate symbols, in order to fully retrieve the space-group symmetry the alternative Hermann–Mauguin symbols have to be accompanied by additional data, *e.g.* the axial transformation with respect to the standard setting or an origin shift. This is precisely what is done in Volume A1 of *International Tables for Crystallography* (2010), where these alternative symbols are used as intermediate steps in the group–subgroup relations.

We have put special emphasis on alternative settings leading to accurate symbols, *i.e.* unconventional settings of space groups (§6.1) and non-standard settings of space groups having an enhanced Euclidean normalizer for the given metric specialization (§6.2). The number of possible non-standard settings of space-group types without an enhanced Euclidean normalizer (for the chosen metric specialization) is much larger and in general does not correspond to accurate symbols.

As an example of the latter case we draw the reader's attention to the rhombohedral specialization of a monoclinic  $Sx$  group. This is possible when the monoclinic unique axis is along the secondary symmetry direction of the rhombohedral lattice, while no symmetry operation occurs along the primary direction. The Hermann–Mauguin monoclinic symbol assigned to this non-standard setting is  $R1x$ . Monoclinic space groups do not have rhombohedral enhanced Euclidean normalizers; accordingly, the non-standard symbol is not accurate because in a rhombohedral lattice there are three symmetry directions in the plane normal to the threefold axis; the lack of a threefold axis in the first position however makes the symbol unambiguous. An example is the structure of  $Sr_3(Ru_{0.336}, Pt_{0.664})CuO_6$  reported by Friese *et al.* (2003) in the non-standard setting  $R12/c$  with respect to rhombohedral axes. The structural symmetry is still monoclinic but the monoclinic setting  $C2/c$  (No. 15) with cell parameters  $a = 9.294$  (11),  $b = 9.595$  (11),  $c = 6.679$  (10) Å,  $\beta = 92.63$  (9)° does not easily reveal the metric rhombohedral symmetry, which instead becomes evident when applying the axial transformation **(a + b)/2, c, (a – b)/2**, leading to the cell parameters  $a = b = c = 6.679$  (10) Å,  $\alpha = \beta = \gamma = 91.83$  (9)°, from which a further pseudo-cubic metric symmetry is also evident. Another example occurs in  $(\eta^8\text{-cyclooctatetraenyl})[\text{hydrotris(pyrazolyl)borato}]\text{-titan(III)}$  (Herbst-Irmer & Sheldrick, 1998), which crystallizes in a space group of type  $Cm$  with  $a = 10.220$  (2),  $b = 11.083$  (3),  $c = 7.538$  (3) Å,  $\beta = 96.85$  (3)°; the lattice is actually rhombohedral with  $a = b = c = 7.538$  (1) Å,  $\alpha = \beta = \gamma = 94.64$  (2)° – the same transformation as above: **(a + b)/2, c, (a – b)/2** – and a non-standard setting  $R1m$  better describes the symmetry of the crystal. Not surprisingly, the above example shows extensive twinning by metric merohedry (Nespolo & Ferraris, 2000); these twins have been discussed by Nespolo & Ferraris (2004).

Alternative settings do have definite advantages not only in dealing with modular structures, twins, pseudo-symmetric structures and structures characterized by higher metric symmetry, as we have discussed above, but also when comparing polymorphs or derivative structures whose space groups are in a group–subgroup relation. In this case, the transition path from the high-symmetry structure, whose

Table 4

Comparison of the fractional coordinates of  $\alpha$ - and  $\beta$ -cordierite.

The latter is presented twice, first in its conventional  $oC$  setting of the  $Cmcc$  space group, then in the  $hP$  non-standard setting  $Pmcc$ . With respect to the published coordinates, those of symmetry-equivalent atoms nearest to corresponding atoms of the  $\alpha$ -cordierite structure in  $P6/mcc$  have been selected. The fractional coordinates of the two polymorphs when expressed in the same setting are very close. (M is the octahedral site, occupied mainly by Mg, Fe. T stands for tetrahedral sites.)

$\beta$ -Cordierite					$\alpha$ -Cordierite in $P6/mcc$				
Description in $Ccm$					Description in $Pmcc$				
Atom	Wyckoff	$x$	$y$	$z$	Atom	Wyckoff	$x$	$y$	$z$
M	8g	0.339	0	0.25	M	4c	1/3	2/3	0.25
Si(T <sub>1</sub> 6)	4b	0	0.5	0.25	T <sub>1</sub>	6f	0.5	0.5	0.25
Al(T <sub>1</sub> 1)	8k	0.25	0.25	0.252	4k		0	0	0.252
Al(T <sub>2</sub> 6)	8l	0.0527	0.299	0	4l		0.3517	0.2463	0
Si(T <sub>2</sub> 1)	8l	0.1889	0.074	0	4l		-0.2629	0.1149	0
Si(T <sub>2</sub> 3)	8l	0.1314	-0.236	0	4l		0.1046	0.3674	0
O <sub>1</sub> 6	16m	0.068	-0.405	0.352	8m		0.4730	0.3370	0.148
O <sub>1</sub> 3	16m	-0.178	-0.308	0.357	8m		0.1300	0.4860	0.143
O <sub>1</sub> 1	16m	0.241	-0.096	0.362	8m		-0.3370	0.1450	0.138
O <sub>2</sub> 6	8l	0.047	-0.227	0	4l		0.1800	0.2740	0
O <sub>2</sub> 1	8l	0.114	0.18	0	4l		-0.2940	-0.0660	0
O <sub>2</sub> 3	8l	0.148	-0.083	0	4l		-0.0650	0.2310	0

symmetry is described by the supergroup  $\mathcal{G}$ , to the lower-symmetry structure, corresponding to a subgroup  $\mathcal{H} < \mathcal{G}$ , can be divided into two steps:

(i) *A change of the axial setting from  $\mathcal{G}$  to  $\mathcal{H}$* : the basis vectors change to comply with the axial setting of  $\mathcal{H}$  but with metric specialization imposed by the higher symmetry of  $\mathcal{G}$ , which corresponds to the so-called *parent-clamping approximation* (Janovec & Přívratská, 2013); the atomic coordinates and the matrix representation of the symmetry operations of  $\mathcal{G}$  change accordingly, but the symmetry is still unchanged.

(ii) *Desymmetrization of  $\mathcal{G}$  to  $\mathcal{H}$* : the metric specialization inherited from  $\mathcal{G}$  is removed and the cell parameters constrained by the symmetry of the supergroup in the previous step are free to match those of the subgroup; a subset of the symmetry operations of  $\mathcal{G}$  is lost; Wyckoff positions of  $\mathcal{G}$  have their site symmetry reduced to a subgroup and/or split to two or more positions independent in  $\mathcal{H}$  (Wondratschek, 1993); as a consequence, some of the atoms (those with one or more free parameters in their fractional coordinates in  $\mathcal{H}$ ) can move away from the positions they had in the supergroup.

The first step results in cell parameters apparently contradictory with respect to the Hermann–Mauguin symbol of the supergroup  $\mathcal{G}$ , but the metric specialization reflects the higher symmetry. For example:

(i) The primitive cell of a  $b$ -unique monoclinic crystal with an  $mC$  conventional cell appears triclinic because of the three non-right interaxial angles, but the identical parameters along the  $a$  and  $b$  axes reflect the actual monoclinic symmetry.

(ii) The rhombohedral description of  $cF$  or  $cI$  groups, with the corresponding interaxial angle of  $60^\circ$  or  $109.47^\circ$ .

(iii) The  $tI$  description of  $cF$  groups, with the  $c/a$  ratio of  $2^{1/2}$ .

The advantage of adopting an intermediate description resulting in a non-standard Hermann–Mauguin symbol is clearly demonstrated by an example where the relation between polymorphs is hidden if the standard settings are adopted for both polymorphs, whereas it becomes evident when the high-symmetry phase is described in a non-standard

setting which keeps the same axial setting as the low-symmetry phase. Table 3 shows in its left part the fractional coordinates of lead phosphate, which crystallizes at high temperature in  $R\bar{3}m$  with cell parameters  $a = 5.56$  (2),  $c = 20.39$  (5) Å (Ng & Calvo, 1975) but at low temperature in  $C2/c$  with cell parameters  $a = 13.8$  (1),  $b = 5.69$  (1),  $c = 9.42$  (1) Å,  $\beta = 102.3$  (1)° (Guimaraes, 1979). The change of setting from  $\mathcal{G} = R\bar{3}m$  to  $\mathcal{H} = C2/c$  in the middle part of the table simply expresses the fractional coordinates of the high-temperature phase in the setting of the low-temperature phase, without any symmetry reduction (parent-clamping approximation). Oxygen atoms labelled O2, O3 and O4 are still equivalent at this stage, but the fractional coordinates of all of them are explicitly given to allow comparison with those of the low-temperature phase, which are given in the right part of the table. Moving from the middle to the right part of the table, only the symmetry operations of  $\mathcal{H}$  have been kept. The corresponding fractional coordinates in the two polymorphs expressed in the monoclinic setting are very close: the maximum distance between corresponding atoms is about 0.34 Å (for Pb2), computed with the *COMPSTRU* routine at the Bilbao Crystallographic Server [see de la Flor *et al.* (2016) and Aroyo *et al.* (2006), respectively].

In structural studies the opposite procedure can be adopted too, *i.e.* describing the lower-symmetry phase in a non-standard setting corresponding to a higher crystal family. In this case, the non-standard Hermann–Mauguin symbol can always be constructed, because the number of symmetry directions increases, although the symbol is not, in general, accurate. This case can be illustrated by the example of cordierite,  $(Mg, Fe)_2Al_3(Si_5AlO_{18})$ , a cyclosilicate found typically in contact or regional metamorphism of argillaceous rocks. At high temperature it crystallizes in a space group of type  $P6/mcc$  (No. 192): it is called  $\alpha$ -cordierite, or *indialite* when it occurs as a mineral in nature, and is isostructural with beryl. At low temperature, it is stable in a space group of type  $Ccm$  (No. 66), with an almost orthorhombic cell: it is called

$\beta$ -cordierite and is the common form in nature. The phase transition is of first order and involves an intermediate modulated structure (Putnis, 1980), although near equilibrium it takes place through a nucleation and growth process (Kitamura & Hiroi, 1982). The structure of the two polymorphs differs in the Si/Al distribution (ordered in  $\beta$ -cordierite, disordered in  $\alpha$ -cordierite), whereas the atomic displacements are rather small. This structural similarity is however hidden by the  $hP$ -to- $oC$  transformation. By keeping the same axial setting, the close similarity becomes evident; this can be obtained by describing  $\beta$ -cordierite in the high-symmetry setting, as discussed in §5. Here we make reference to the synthetic structures reported by Schwartz *et al.* (1994), with cell parameters  $a = b = 9.7815$  (2),  $c = 9.3537$  (3) Å for  $\alpha$ -cordierite, and  $a = 17.047$  (1),  $b = 9.7315$  (8),  $c = 9.3463$  (6) Å for  $\beta$ -cordierite. The  $ab$  ratio for the latter is  $(3.07)^{1/2}$  so that the lattice is only pseudo-hexagonal. Indeed, the axial transformation from  $oC$  to  $hP$ ,  $\mathbf{a}_h = -\frac{1}{2}(\mathbf{a}_o + \mathbf{b}_o)$ ,  $\mathbf{b}_h = \frac{1}{2}(\mathbf{a}_o - \mathbf{b}_o)$ ,  $\mathbf{c}_h = \mathbf{c}_o$ , gives cell parameters  $a = b = 9.8146$ ,  $c = 9.3463$  Å,  $\gamma = 120.56^\circ$ , slightly diverging from a hexagonal metric. The [001] direction moves from third position in the orthorhombic to first position in the hexagonal setting; the [100] and [010] orthorhombic directions correspond to one each of the  $\langle 100 \rangle$  and  $\langle \bar{1}10 \rangle$  directions in the hexagonal setting, respectively. Accordingly, the non-standard, not accurate Hermann–Mauguin symbol of  $Cccm$  in the hexagonal setting is  $Pmcc$ .

In Table 4 the experimental coordinates of the two polymorphs are compared by the opposite procedure used for the case of lead phosphate. The left part of the table shows the fractional coordinates of  $\beta$ -cordierite in  $Cccm$ , the middle part the same coordinates (or those of equivalent atoms) expressed in the  $Pmcc$  hexagonal setting obtained by applying the transformation  $(x, y, z) \rightarrow (-x - y, x - y, z)$ : at this stage, no symmetry augmentation is applied, the fractional coordinates are simply rewritten in the setting of the supergroup. Finally, the right part of the table gives the experimental coordinates of  $\alpha$ -cordierite in  $P6/mcc$ . The Wyckoff letters of the positions in the non-standard  $Pmcc$  setting of  $Cccm$  remain the same as in the orthorhombic setting but the multiplicity is halved. Sites are labelled as in the original publication. Some of the atomic positions that are independent in  $Pmcc$  become symmetry equivalent in  $P6/mcc$  (Wyckoff positions merge according to the following scheme:  $2b + 4k$  in  $Pmcc$  result in  $6f$  in  $P6/mcc$ ; three  $4l$  positions in  $Pmcc$  give  $12l$  in  $P6/mcc$ ; three  $8m$  positions in  $Pmcc$  give  $24m$  in  $P6/mcc$ : see Table 4) and the coordinate triplet closest to the atomic coordinates of  $\alpha$ -cordierite is shown first. The corresponding fractional coordinates in the two polymorphs expressed in the hexagonal setting are also in this case very close: the maximum distance between corresponding atoms is about 0.43 Å (for O<sub>2</sub>).

### Acknowledgements

This research was partly conducted during a stay of the first author as invited professor at the Kyoto University (June–August 2015) and as Short-Term Invited Fellow of the High-Energy Accelerator Research Organization (KEK), Tsukuba

(February–March 2016). We thank Dr Howard Flack (University of Geneva) for pointing out the case of  $Pb\bar{3}$ . Critical remarks by Professor Ulrich Müller (Phillips Universität Marburg, Germany) and by an anonymous reviewer are gratefully acknowledged.

### References

- Armstrong, D. R., Herbst-Irmer, R., Kuhn, A., Moncrieff, D., Paver, M. A., Russell, C. A., Stalke, D., Steiner, A. & Wright, D. S. (1993). *Angew. Chem. Int. Ed. Engl.* **32**, 1774–1776.
- Aroyo, M. I., Perez-Mato, J. M., Capillas, C., Kroumova, E., Ivantchev, S., Madariaga, G., Kirov, A. & Wondratschek, H. (2006). *Z. Kristallogr.* **221**, 15–27.
- Buerger, M. J. (1947). *J. Chem. Phys.* **15**, 1–16.
- Buerger, M. J. (1949). *X-ray Crystallography*. New York: Wiley.
- Christy, A. G. & Angel, R. J. (1995). *Phys. Chem. Miner.* **22**, 129–135.
- Dornberger-Schiff, K. (1959). *Acta Cryst.* **12**, 173.
- Ferraris, G., Makovicky, E. & Merlino, S. (2008). *Crystallography of Modular Materials*. Oxford: IUCr/Oxford University Press.
- Flack, H. D., Wondratschek, H., Hahn, T. & Abrahams, S. C. (2000). *Acta Cryst.* **A56**, 96–98.
- Flor, G. de la, Orobengoa, D., Tasci, E., Perez-Mato, J. M. & Aroyo, M. I. (2016). *J. Appl. Cryst.* **49**, 653–664.
- Friedel, G. (1926). *Leçons de Cristallographie*. Paris: Berger-Levrault.
- Friese, K., Kienle, L., Duppel, V., Luo, H. & Lin, C. (2003). *Acta Cryst.* **B59**, 182–189.
- Gelder, R. de & Janner, A. (2005). *Acta Cryst.* **B61**, 287–295.
- Grimmer, H. (2015). *Acta Cryst.* **A71**, 143–149.
- Grimmer, H. & Nespolo, M. (2006). *Z. Kristallogr.* **221**, 28–50.
- Guimaraes, D. M. C. (1979). *Acta Cryst.* **A35**, 108–114.
- Herbst-Irmer, R. & Sheldrick, G. M. (1998). *Acta Cryst.* **B54**, 443–449.
- International Tables for Crystallography* (2002). Vol. A, *Space-group Symmetry*, edited by Th. Hahn, 5th ed. Dordrecht: Kluwer Academic Publishers.
- International Tables for Crystallography* (2010). Vol. A1, *Symmetry Relations between Space Groups*, edited by H. Wondratschek & U. Müller, 2nd ed. Chichester: John Wiley and Sons.
- International Tables for Crystallography* (2010). Vol. E, *Subperiodic Groups*, edited by V. Kopský & D. B. Litvin, 2nd ed. Chichester: John Wiley and Sons.
- Janner, A. (2004a). *Acta Cryst.* **A60**, 198–200.
- Janner, A. (2004b). *Acta Cryst.* **A60**, 611–620.
- Janovec, V. & Přivratská, J. (2013). *Domain structures. International Tables for Crystallography*, Vol. D, 2nd ed., edited by A. Authier, ch. 3.4. Dordrecht: Kluwer Academic Publishers.
- Kettle, S. F. A. & Norrby, L. S. (1993). *J. Chem. Educ.* **70**, 959–963.
- Kitamura, M. & Hiroi, Y. (1982). *Contrib. Miner. Petrol.* **80**, 110–116.
- Koch, E. & Fischer, W. (2006). *Z. Kristallogr.* **221**, 1–14.
- Kogure, T. & Nespolo, M. (1999). *Acta Cryst.* **B55**, 507–516.
- Krivovichev, S. V., Yakovenchuk, V. N., Burns, P. C., Pakhomovsky, Y. A. & Menshikov, Yu. P. (2003). *Am. Mineral.* **88**, 424–429.
- Matsui, T. & Kimata, M. (1997). *Eur. J. Miner.* **9**, 333–344.
- Megaw, H. D. (1973). *Crystal Structures: a Working Approach*. Philadelphia: Saunders Co.
- Mighell, A. D. (2003). *Acta Cryst.* **B59**, 300–302.
- Müller, U. (2013). *Symmetry Relationships between Crystal Structures. Applications of Crystallographic Group Theory in Crystal Chemistry*. Oxford: IUCr/Oxford University Press.
- Nespolo, M. (2015). *J. Appl. Cryst.* **48**, 1985–1997.
- Nespolo, M. & Đurovič, S. (2002). *Rev. Mineral. Geochem.* **46**, 155–279.
- Nespolo, M. & Ferraris, G. (2000). *Z. Kristallogr.* **215**, 77–81.
- Nespolo, M. & Ferraris, G. (2004). *Acta Cryst.* **A60**, 89–95.
- Nespolo, M., Ferraris, G. & Souvignier, B. (2014). *Acta Cryst.* **A70**, 106–125.

- Nespolo, M. & Souvignier, B. (2015). *J. Mineral. Petrol. Sci.* **110**, 157–165.
- Nespolo, M., Takeda, H. & Ferraris, G. (1998). *Acta Cryst.* **A54**, 348–356.
- Ng, H. N. & Calvo, C. (1975). *Can. J. Phys.* **53**, 42–51.
- Putnis, A. (1980). *Contrib. Mineral. Petrol.* **74**, 135–141.
- Schwartz, K. B., Leong, D. B. & McConville, R. L. (1994). *Phys. Chem. Miner.* **20**, 563–574.
- Wenk, H.-R., Joswig, W., Tagai, T., Korekawa, M. & Smith, B. K. (1980). *Am. Mineral.* **65**, 81–95.
- Wolff, P. M. de, Billiet, Y., Donnay, J. D. H., Fischer, W., Galiulin, R. B., Glazer, A. M., Hahn, T., Senechal, M., Shoemaker, D. P., Wondratschek, H., Wilson, A. J. C. & Abrahams, S. C. (1992). *Acta Cryst.* **A48**, 727–732.
- Wolff, P. M. de, Billiet, Y., Donnay, J. D. H., Fischer, W., Galiulin, R. B., Glazer, A. M., Senechal, M., Shoemaker, D. P., Wondratschek, H., Hahn, Th., Wilson, A. J. C. & Abrahams, S. C. (1989). *Acta Cryst.* **A45**, 494–499.
- Wondratschek, H. (1993). *Mineral. Petrol.* **48**, 87–96.