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The 'Best' Unit Cell for Monoclinic Structures Consistent With *b* Axis Unique and Cell Choice 1 of *International Tables for Crystallography* (1983)

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Abstract

Diagrams with the c/a ratio as ordinate and $\cos(180°-\beta)$ as abscissa are given, which allow one to find out how a given monoclinic unit cell can be transformed so that **a** and **c** are the shortest translation vectors compatible with the symmetry of the space group in a setting corresponding to the standard space-group symbol given in *International Tables for Crystallography* [Vol. A. (1983). Dordrecht: Reidel] [denoted as IT(1983)], which means *b* axis unique and cell choice 1 where applicable. The diagrams contain the transformation matrices and indicate whether the origin of the transformed cell has to be shifted in order to obtain a structure description with the Wyckoff positions listed in IT (1983). A 'best' monoclinic unit cell consistent with cell choice 1 is one of the requirements for a standardized description of crystal-structure data according to Parthé & Gelato [*Acta Cryst.* (1984), A**40**, 169-183].

Introduction

This work is a complement to the earlier paper on structure data standardization (Parthé & Gelato, 1984) in so far as a simple test is given, which allows one to decide whether or not a given monoclinic cell is the correct one for the standardization of the atom coordinates.

A standardization procedure may be based on various philosophies such as relying on geometrical relationships, crystal chemical considerations or symmetry. For reasons discussed in our earlier paper we choose symmetry as the basis for our standard. The first step in the standardization of crystal-structure data is the proper choice of a unit cell. We proposed for monoclinic structures the setting that corresponds to the standard space-group symbol with *b* axis unique and cell choice 1 as given in IT (1983) and a unit-cell basis, always with β non-acute, with the following characteristics:

a relabelled Niggli reduced cell* such that *b* is the unique axis and $|\mathbf{a}|<|\mathbf{c}|$ for $P2$, $P2_1$, Pm, $P2/m$, $P2_1/m$;

a cell where **a** and **c** are the shortest translation vectors compatible with the condition of *b* axis unique and cell choice 1 for space groups Pc, $P2/c$, $P2_1/c$, $C2$, Cm, Cc, $C2/m$ and $C2/c$.

The **b**-axis setting of the space group with cell choice 1 as given in IT(1983) corresponds to the only space-group description given in *Internationale Tabellen zur Bestimniung von Kristallstrukturen* (1935) [IT(1935)] and the '2nd setting' in *International Tables*

* This is a Niggli reduced cell [see IT(1983), pp. 737-744] but with interchanged axes where necessary.

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for X-ray Crystallography (1952) [IT(1952)]. In IT(1983) this space-group description is always treated first and its short Hermann–Mauguin symbol, which we use here too, is printed as the standard symbol in bold face type in the heading of all pages treating the different descriptions of a monoclinic space group.

For the standardization of a monoclinic crystal structure it is thus not only necessary to transform to the space-group setting with *b* axis unique and cell choice 1, but also to find the smallest possible basis vectors for this setting. This cell we shall call the 'best' cell for cell choice 1. The particular reasons why we give preference to the best cell consistent with cell choice 1 instead of a fully reduced cell with $c/a \geq 1$ and cell choices different from 1 is discussed below. A study of the literature reveals that many monoclinic crystal structures have been described with a setting corresponding to the standard space-group symbol (*b* axis unique and cell choice 1). The **a** and **c** vectors are, however, not always the smallest possible (and this is true not only of the older literature). There are now computer programs available to perform the unit-cell reduction [XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), *NBS*AIDS*80 (Mighell, Hubbard & Stalick, 1981), the program written by Le Page (1981), *STRUCTURE TIDY* (Gelato & Parthé, 1985)]. There are, however, no simple graphical methods available to see immediately if a given unit cell is the best one or not. A nomogram for monoclinic transformations has been published by Donnay in the first edition of *Crystal Data* (Donnay & Nowacki, 1954). Repeated use of this nomogram leads to a fully reduced cell, but not always to a setting corresponding to the standard space-group symbol with cell choice 1. As will be seen the problem is not without complications because certain cell transformations in certain space groups require a shift of origin in order to describe the transformed structure with the Wyckoff positions as given in IT(1983). It is the purpose of this study to present diagrams that, using as input the c/a ratio and the $\cos(180°-\beta)$ value only, allow us to see whether or not a unit-cell transformation is necessary and whether or not a shift of origin is required for it.

The c/a *versus* $\cos(180°-\beta)$ diagram*

Each monoclinic unit cell with *b* axis unique can be represented by a point in a c/a *versus* $\cos(180°-\beta)$ diagram as shown in Fig. 1. A unit-cell transformation changes the position of the point in the diagram.

Let **a**, **b** and **c** be the basis vectors of a monoclinic structure with *b* axis unique. We assume that the structure is described with the Wyckoff positions as printed in IT(1983) and that the unit-cell volume is the smallest possible. The transformed basis vectors **a**′, **b**′, **c**′ are related to the original ones by the following relations:

$$\begin{aligned} \mathbf{a}' &= p\mathbf{a} + q\mathbf{c} \\ \mathbf{b}' &= t\mathbf{b} \\ \mathbf{c}' &= r\mathbf{a} + s\mathbf{c}. \end{aligned} \tag{1}$$

Since we have assumed that the volume before transformation is the smallest possible and since we make a basis trasformation only, the parameters *p*, *q*, *t*, *r* and *s* must be integers. The condition that the transformation should not change the volume of the unit cell leads to the following relations:

$$(ps - qr)t = 1 \tag{2a}$$

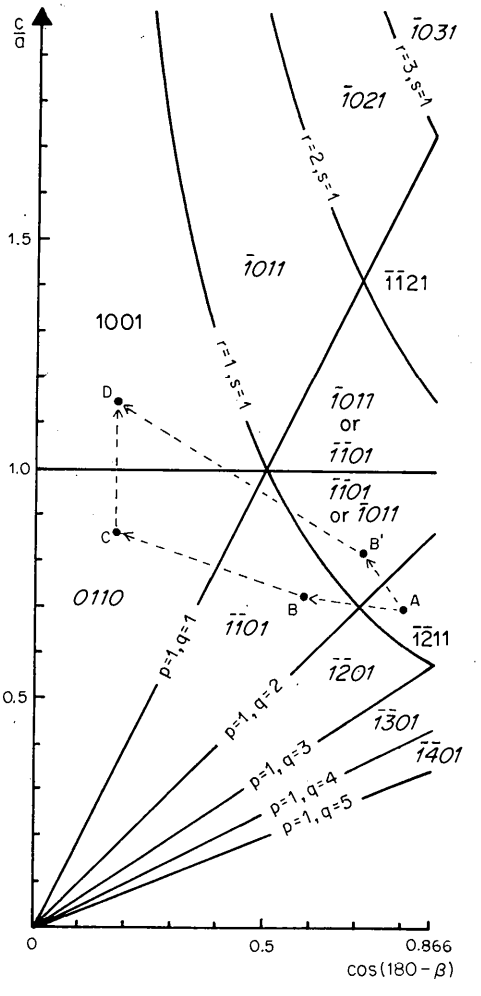

Fig. 1. c/a *versus* $\cos(180°-\beta)$ diagram with inscribed 'first' transformation matrices, obtained from the border line equations. The four-digit matrix elements are in normal type if the **b** vector is unchanged, but in *italics* if **b** changes direction.

* We restrict our considerations to monoclinic cells with *b* axis unique. A transformation should be applied to cells with *c* axis unique in order to obtain a cell with *b* axis unique.

and

$$\cos(\beta'-90°)=\frac{ac}{a'c'}\cos(\beta-90°) \qquad (2b)$$

with

$$a'=[(pa)^2+(qc)^2+2pqac\cos\beta]^{1/2}$$

and

$$c'=[(ra)^2+(sc)^2+2rsac\cos\beta]^{1/2}.$$

Since t can have only the value $+1$ or -1 we have introduced in all figures a shortened form of the transformation matrix. The four digits indicate the matrix elements $p\,q\,r\,s$. They are written in normal type if $t=1$ or in *italics* if $t=-1$.

We note in Fig. 1 that the c/a *versus* $\cos(180°-\beta)$ diagram consists of different fields with different matrix elements inscribed. The border lines between the different fields correspond to cases where a transformed vector is identical in length to an original vector. Expressing this with the cosine rule in a triangle

$$p^2a^2+q^2c^2-2pqac\cos(180°-\beta)=a^2 \qquad (3a)$$

and

$$r^2a^2+s^2c^2-2rsac\cos(180°-\beta)=c^2, \qquad (3b)$$

we obtain the border line equations

$$\frac{c}{a}=\frac{p}{q}\left\{\cos(180°-\beta)\pm\left[\cos^2(180°-\beta)-\frac{p^2-1}{p^2}\right]^{1/2}\right\} \qquad (4a)$$

and

$$\frac{c}{a}=\frac{r}{s}\left\{\cos(180°-\beta)\pm\left[\cos^2(180°-\beta)-\frac{s^2-1}{s^2}\right]^{1/2}\right\}^{-1}. \qquad (4b)$$

The straight lines in Fig. 1 (with the exception of the horizontal line) correspond to solutions of (4*a*) with $p=1$ and the hyperbolae to solutions of (4*b*) with $s=1$. Border lines corresponding to solutions of (4*a*) and (4*b*) with $p=2$ and $s=2$ or higher values occur with $\cos(180°-\beta)\geq 0{\cdot}866$. In order not to overload the right side of the diagram with border lines and since monoclinic structures normally are published with β angles smaller than 150°, an abscissa break-off point of $\cos(180°-\beta)=0{\cdot}866$ was chosen. Also, border lines with $p=1$ and $q>5$ (Fig. 1) or $q>8$ (Figs. 2, 3, 4) have not been drawn.

The simplest approach normally used by crystallographers, for deciding whether a cell can be reduced, consists in a comparison between the projection of one axis, say a, on the second axis, say c, and the length of axis c.

If

$$|\mathbf{a}|\cos(180°-\beta)<\tfrac{1}{2}|\mathbf{c}| \qquad (5a)$$

or

$$|\mathbf{c}|\cos(180°-\beta<\tfrac{1}{2}|\mathbf{a}|, \qquad (5b)$$

a cell reduction (leading to a new smaller $\mathbf{a}'$ or a new smaller $\mathbf{c}'$) is possible. If the inequality sign is replaced by an equal sign, (5*a*) and (5*b*) correspond to (4*a*) and (4*b*) with p, q, r and $s=1$. It is, however, necessary to consider also unit-cell reductions with q and r values greater than 1.

The *pqrs* matrix elements of a 'first' transformation matrix, which transfers the point to a neighbouring field situated towards smaller $\cos(180°-\beta)$ values, correspond to the p, q, r and s values of the two border line equations limiting the field on the left.* In Fig. 1 these first transformation matrices are indicated together with the p, q and r, s values of the border lines.

Note that:

(1) only those matrices are given that lead to cells with smaller $\mathbf{a}'$ or $\mathbf{c}'$ vector, with β' non-acute and with $(ps-qr)t=1$;

(2) from (3*a*) and (3*b*) we see that the products pq and rs must be non-negative [β' being non-acute, $\cos(180°-\beta')$ is positive]. Thus p and q must have the same sign; and so must r and s;

(3) an equivalent matrix exists where p, q, r and s have changed signs; t as well as $|\mathbf{a}'|$, $|\mathbf{c}'|$ and β' are not affected by this sign change. Arbitrarily we choose the matrix where r and s have non-negative values;

(4) the condition $(ps-qr)t=1$ is the reason why the field to the right of the border lines with $p=1$, $q=1$ and $r=1$, $s=1$ is labelled $\bar{1}001$ or $1\bar{1}01$ instead of 1111;

(5) the horizontal line at $c/a=1$, together with the *0110* matrix below that line and to the left of the line with $p=1$ and $q=1$, corresponds to a special transformation that simply ensures that $|\mathbf{a}'|<|\mathbf{c}'|$.

The reduction of the unit cell for space groups $P2$, $P2_1$, Pm, $P2/m$ and $P2_1/m$

As stated in the *Introduction*, for the standard description it is desired to have a cell where b is the unique axis, where $\mathbf{a}$ and $\mathbf{c}$ are the shortest possible translation vectors and where, further, $|\mathbf{a}|<|\mathbf{c}|$. This means the unit cell has to be transformed so that its plot is in the 1001 field. The first transformation matrix inscribed in Fig. 1 is not necessarily the desired matrix since it does not necessarily transform directly to the 1001 field. Thus the procedure has to be repeated by

* The values that characterize the straight lines *underneath* the point will give a *larger a* value, the values characterizing the hyperbola to the *right* give a *larger c* value instead of the desired smaller a and c values.

transforming the unit cell again with the first transformation matrix inscribed in the new field until finally the 1001 field is reached.

The procedure is demonstreated in Fig. 1 with a cell that has a plot in the $\bar{1}\bar{2}11$ field (point A). Three successive transformations lead finally to the 1001 field (from point $A \rightarrow B \rightarrow C \rightarrow D$). Of interest for us is the transformation of the original plot (A) to the plot in the 1001 field (D) in one step. The corresponding matrix can be obtained by matrix multiplication of the three successive transformation matrices according to

$$\begin{matrix} D\leftarrow A & & D\leftarrow C & & C\leftarrow B & & B\leftarrow A \end{matrix}$$

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

In Fig. 2 only one-step-transformation matrices are inscribed, which lead directly to the 1001 field. We note that in Fig. 2 1101 has been written into the field corresponding to the $\bar{1}\bar{2}11$ field of Fig. 1.

In Fig. 2 fields with matrix elements written in normal type and in *italics* (meaning the b axis changes sign) are arranged in checkerboard fashion. Cell transformations using the matrix elements of Fig. 2 lead to best cells that are fully reduced (relabelled Niggli reduced) cells, as discussed in chapter 2.16 of IT(1983). All matrices inscribed in Fig. 2 were tested with a computer program to calculate Niggli reduced unit cells (program *NBS*AIDS*80; Mighell, Hubbard & Stalick, 1981).

The border lines in Fig. 2 are drawn in three different ways, which relate to the shape of the monoclinic mesh after the transformation (new axes $\mathbf{a}'$ and $\mathbf{c}'$) for unit cells having originally their representative point on these lines. Points positioned on long-dashed lines lead after transformation to a rectangular mesh with $\beta' = 90°$. Points on short-dashed lines lead to a mesh where $|\mathbf{a}'| = |\mathbf{c}'|$. Points on solid lines lead to a transformed cell without special features. The letters H or S indicate special points that, after transformation, lead to a hexagonal mesh ($|\mathbf{a}'| = |\mathbf{c}'|$, $\beta' = 120°$) or a square mesh ($|\mathbf{a}'| = |\mathbf{c}'|$, $\beta' = 90°$).

The transformation to the best cell for space groups *Pc*, *P2/c* and *P2₁/c**

We shall at first discuss the cell transformation to a best cell for a structure already described with cell choice 1. Since the transformed structure should allow a description in a setting corresponding to the standard space-group symbol (b axis unique), not all first transformation matrices inscribed in Fig. 1 are permitted for space groups *Pc*, *P2/c* and *P2₁/c*. The constraints on the matrix elements and the necessary origin shifts for monoclinic space groups in the setting with c axis unique have been studied by Billiet (1973) and Sayari & Billiet (1977). The restricting conditions on the matrix elements and the origin shifts for all

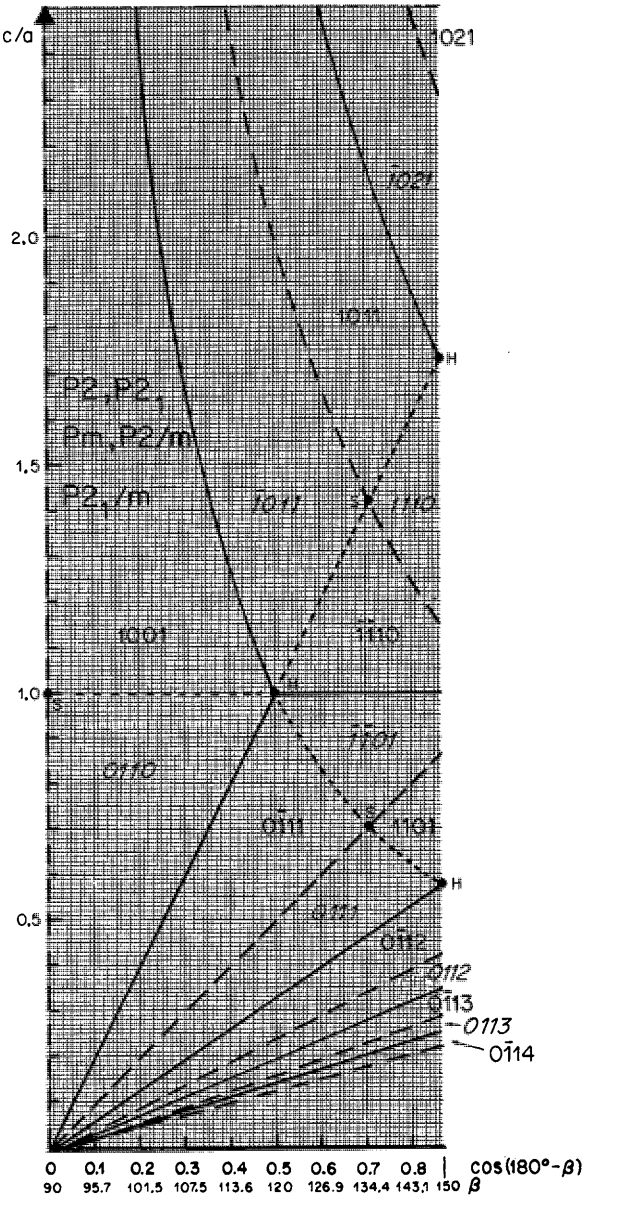

Fig. 2. c/a *versus* $\cos(180° - \beta)$ diagram with inscribed reduction matrices for space groups $P2$, $P2_1$, Pm, $P2/m$ and $P2_1/m$ (b axis unique). The four-digit matrix elements are in normal type if the **b** vector is unchanged, but in *italics* if **b** changes direction. Points on long-dashed border lines lead after transformation to a mesh with $\beta' = 90°$, those on short-dashed lines to a mesh where $|\mathbf{a}'| = |\mathbf{c}'|$. H and S indicate special points that after transformation lead to a hexagonal or a square mesh in the monoclinic plane.

* We shall use throughout most of this paper the standard short space-group symbols, which apply to all three cell choices (always with b axis unique) having three different full symbols. To indicate a particular cell choice we state the standard short space-group symbol and the cell choice number.

Table 1. *Conditions for the matrix elements for a transformation of a monoclinic structure (b axis unique, cell choice 1) and origin shift that ensure that the transformed structure can be described with Wyckoff positions as given in IT(1983) (derived from matrix tables given by Billiet, 1973)*

Space groups	p	q	r	s	Necessary origin shift for transformed atom coordinates
$P2$, $P2_1$, Pm, $P2/m$, $P2_1/m$	—	—	—	—	000
Pc, $P2/c$, $P2_1/c$	odd	—	even	—	000
$C2$, Cm, $C2/m$	—	even	—	odd	000
Cc	odd	even	even	odd	000
	odd	even	odd	odd	$0\frac{1}{4}0$ (or $0\frac{3}{4}0$)
$C2/c$	odd	even	even	odd	000
	odd	even	odd	odd	$\frac{1}{4}\frac{1}{4}0$ (or $\frac{3}{4}\frac{3}{4}0$)

monoclinic space groups with *b*-axis setting, cell choice 1, are summarized in Table 1. We find from Table 1 that for *Pc*, $P2/c$ and $P2_1/c$ with cell choice 1 only matrices with p = odd and r = even are allowed. Thus the glide plane in the transformed structure is a *c* glide and the Wyckoff positions as printed in IT(1983) for *b*-axis setting, cell choice 1, are applicable.

For a demonstration we use a cell that has in Fig. 1 a representative point in the $\bar{1}\bar{2}11$ field (point *A*). As first transformation matrix $\bar{1}\bar{2}11$ cannot be used (r = odd), however $\bar{1}\bar{2}\bar{1}1$ is acceptable. Two successive first transformations, all with p = odd and r = even, lead to the 1001 field as follows:

$$D \leftarrow A \qquad D \leftarrow B' \qquad B' \leftarrow A$$

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

In Fig. 3(*a*) are listed the one-step 1001 field-transformation matrices to be used for *P* space groups with c-glide planes. We note that in comparison to Fig. 2 the 1001 field is much larger because it includes also the form *0110* and $\bar{1}011$ fields.

If the structure was originally described with cell choice 2 or 3, a transformation to cell choice 1 using the diagrams* illustrating different cell choices in IT(1983) should be made before the final transformation to the best cell. For convenience the total transformation matrices (transformation cell choice $2 \rightarrow 1$ or $3 \rightarrow 1$ plus final transformation) necessary to obtain a best cell with cell choice 1 are inscribed in Figs. 3(*b*) and (*c*), respectively. The border lines between the different fields are drawn with full lines or with long dashes. For an explanation see the previous paragraph. All cells obtained by application of the matrices inscribed in Fig. 3 are either fully or half reduced [see chapter 2.16 or IT(1983)]. If the representative point of this best cell is to the left of the line with $p = 1$, $q = 1$ and to the left of the hyperbola with $r = 1$, $s = 1$ (see Fig. 1) the cell is fully reduced, otherwise it is half reduced.*

* These diagrams are only valid for fully, half- or quarter-reduced monoclinic meshes. For other meshes a transformation according to the diagrams leads to cells with an acute monoclinic angle.

The transformation to the best cell for space groups *C2*, *Cm*, *C2/m*, *Cc* and *C2/c*

We shall start again with the transformation to a best cell for a structure already described with cell choice 1. As shown in Table 1, for the transformation of *C*-centred monoclinic cells with cell choice 1, only matrices with q = even and s = odd can be used. For *Cc* and $C2/c$ there exists the extra condition that also p = odd. For the cos $(180° - \beta)$ range chosen only matrices with p = odd occur. Thus the matrices for all five *C*-centred space groups can be presented in one diagram.

The derivation of the matrices is in principle identical to the case discussed above. We consider again as an example the monoclinic cell that in Fig. 1 has a representative point in the $\bar{1}2\bar{1}1$ field. The only transformation matrix that can be used is the $\bar{1}\bar{2}11$, which leads to point *B*. A further reduction of the unit cell is not possible if we want to stay with cell choice 1. Thus the first transformation leads already to the final result, which is a half-reduced cell.

In Fig. 4(*a*) are given the one-step-1001-field-transformation matrices for the *C*-centred space groups. The 1001 field in comparison to Fig. 2 includes here the former *0110* and $0\bar{1}11$ fields.

For structures originally described with cell choices 2 or 3, the total transformation matrices (transformation to cell choice 1 and final transformation to best cell) inscribed in Figs. 4(*b*) or (*c*) have to be used. For the meaning of the different border lines and the distinction between fully and half-reduced monoclinic cells see above.

The transformation of the atom coordinates

To transform atom coordinates the equations given in Table 2 have to be used. Attention has to be paid to whether the four-digit matrix elements in the figures are written in normal type or in *italics*. According to Table 1, for space groups *Cc* and $C2/c$ an origin shift is necessary for certain transformations in order to obtain atom positions that correspond to the Wyck-

* We take the view that it is preferable to have only one cell choice (cell choice 1) for the standardization and consequently only 13 different monoclinic space-group symbols. This decision implies that some standardized cells are half reduced instead of fully reduced. For other reasons to rely on the best cell with cell choice 1 see below.

Table 2. *The transformed atom coordinates for the different kinds of transformation matrices (expressed in Figs.* 2, 3 *and* 4 *in shortened form by their* pqrs *or pqrs matrix elements)*

Column I: For all monoclinic space groups, including *Cc* and *C*2/*c*, but for *Cc* and *C*2/*c* only when the four-digit matrix elements in Fig. 4 are not framed.
Column II: For *Cc* only and only when the four-digit matrix elements in Fig. 4 are framed.
Column III: For *C*2/*c* only and only when the four-digit matrix elements in Fig. 4 are framed.

	I	II	III
pqrs	$x'=+sx \quad -rz$ $y'= \quad +y$ $z'=-qx \quad +pz$	$x'=+sx \quad -rs$ $y'= \quad +y+\frac{1}{4}$ $z'=-qx \quad +pz$	$x'=+sx \quad -rz+\frac{1}{4}$ $y'= \quad +y+\frac{1}{4}$ $z'=-qx \quad +pz$
pqrs	$x'=-sx \quad +rz$ $y'= \quad -y$ $z'=+qx \quad -pz$	$x'=-sx \quad +rz$ $y'= \quad -y+\frac{1}{4}$ $z'=+qx \quad -px$	$x'=-sx \quad +rz+\frac{1}{4}$ $y'= \quad -y+\frac{1}{4}$ $z'=+qx \quad -pz$

off positions given in IT(1983).* The four-digit matrix elements of the transformations that require such an origin shift are framed in Fig. 4. These are the matrices with r = odd when the original structure was already described with cell choice 1 (Fig. 4*a*), the matrices with s = even when the original structure was described with cell choice 2 (Fig. 4*b*) or the matrices with r = even and s = odd when cell choice 3 was used for the description of the original structure (Fig. 4*c*).

Demonstration of the use of the figures and of Table 2

The use of the figures and Table 2 will be demonstrated on three structures, one organic, one inorganic and one of an alloy; in all three examples the structures were described with a setting corresponding to a standard space-group symbol (*b* axis unique, cell choice 1), but the published cell parameters were not those of a best cell. It is shown that the transformation matrices can be determined easily from the figures.

4'-Chloro-2-hydroxy-4-methoxybenzophenone (*Liebich*, 1976)

*C*2/*c*, $a=25{\cdot}04$, $b=3{\cdot}935$, $c=29{\cdot}53$ Å, $\beta=122{\cdot}0°$, $c/a=1{\cdot}179$, $\cos(180°-\beta)=0{\cdot}5299$.
Matrix elements from Fig. 4(*a*): $\boxed{\bar{1}011}$
Best cell: $a'=25{\cdot}04$, $b'=3{\cdot}935$, $c'=26{\cdot}746$ Å, $\beta'=110{\cdot}56°$, $c'/a'=1{\cdot}068$, $\cos(180°-\beta')=0{\cdot}3511$
Matrix elements from Fig. 4(*a*): 1001.

* The origin shifts for certain cell transformations are related, in the case of *Cc*, to the presence of a glide plane at $y=\frac{1}{4}$ with a glide component in the diagonal direction and, in the case of *C*2/*c*, to the occurrence of a symmetry centre at $\frac{1}{4}\frac{1}{4}0$ where the glide plane passing through it has a diagonal glide component (see Billiet, 1973).

As indicated in the right-hand side of Table 2 the transformed atom coordinates have to be shifted by $\frac{1}{4}\frac{1}{4}0$ (or $\frac{3}{4}\frac{3}{4}0$).

$Ca_3(SiO_3OH)_2.2H_2O$, '*Afwillite*' (*Megaw*, 1952)

Cc, $a=16{\cdot}27$, $b=5{\cdot}632$, $c=13{\cdot}23$ Å, $\beta=134°48'$, $c/a=0{\cdot}8132$, $\cos(180°-\beta)=0{\cdot}7046$.
Matrix elements from Fig. 4(*a*): $\boxed{\bar{1}011}$
Best cell: $a'=16{\cdot}27$, $b'=5{\cdot}632$, $c'=11{\cdot}68$ Å, $\beta'=126{\cdot}5°$, $c'/a'=0{\cdot}7178$, $\cos(180°-\beta')=0{\cdot}5949$.
Matrix elements from Fig. 4(*a*): 1001.

As indicated in the middle part of Table 2 the transformed atom coordinates have to be shifted by $0\frac{1}{4}0$ or $0\frac{3}{4}0$).

$AgAuTe_4$, '*sylvanite*' (*Tunell & Pauling*, 1952)

*P*2/*c*, $a=8{\cdot}96$, $b=4{\cdot}49$, $c=14{\cdot}62$ Å, $\beta=145{\cdot}43°$, $c/a=1{\cdot}6317$, $\cos(180°-\beta)=0{\cdot}8234$.
Matrix elements from Fig. 3(*a*): $\bar{1}\bar{1}21$.
Best cell: $a'=8{\cdot}85$, $b'=4{\cdot}49$, $c'=10{\cdot}17$ Å, $\beta'=124{\cdot}30°$, $c'/a'=1{\cdot}1492$, $\cos(180°-\beta')=0{\cdot}5636$.
Matrix elements from Fig. 3(*a*): 1001.

No origin shift is necessary for the transformed atom coordinates.

Numerical test on the possibility of transforming a monoclinic cell described with cell choice 1 to a best cell

A unit cell is not a best cell if its representative point is not in the 1001 field. The equations for the border lines limiting the 1001 fields in Figs. 2, 3(*a*) and 4(*a*) can be obtained from (4*a*) and (4*b*) by inserting the appropriate values for *p*, *q*, *r* and *s* (see corresponding labelled lines and hyperbolae in Fig. 1. For this test we shall ignore the fact that the best cell for space groups without glide planes and with a primitive Bravais lattice is the one where $c/a \geq 1$; thus we shall consider here the boundary lines of the combined 1001 and *0110* fields in Fig. 2. If necessary a simple interchange of the axes would always lead to the best cell. Since *p* and *s* are equal to 1 for the border lines in Fig. 2, 3(*a*) and 4(*a*) we obtain the following inequalities for a cell that can be transformed.

$$\frac{c}{a} \geq \frac{r}{2\cos(180°-\beta)} \quad \text{if} \quad \frac{c}{a} \geq \left(\frac{r}{q}\right)^{1/2}$$

and (6)

$$\frac{c}{a} \leq \frac{2\cos(180°-\beta)}{q} \quad \text{if} \quad \frac{c}{a} \leq \left(\frac{r}{q}\right)^{1/2},$$

where $q=1$, $r=1$ for *P*2, *P*2$_1$, *Pm*, *P*2/*m*, *P*2$_1$/*m*,
$q=1$, $r=2$, for *Pc*, *P*2/*c*, *P*2$_1$/*c*
and $q=2$, $r=1$ for *C*2, *Cm*, *C*2/*m*, *Cc*, *C*2/*c*.

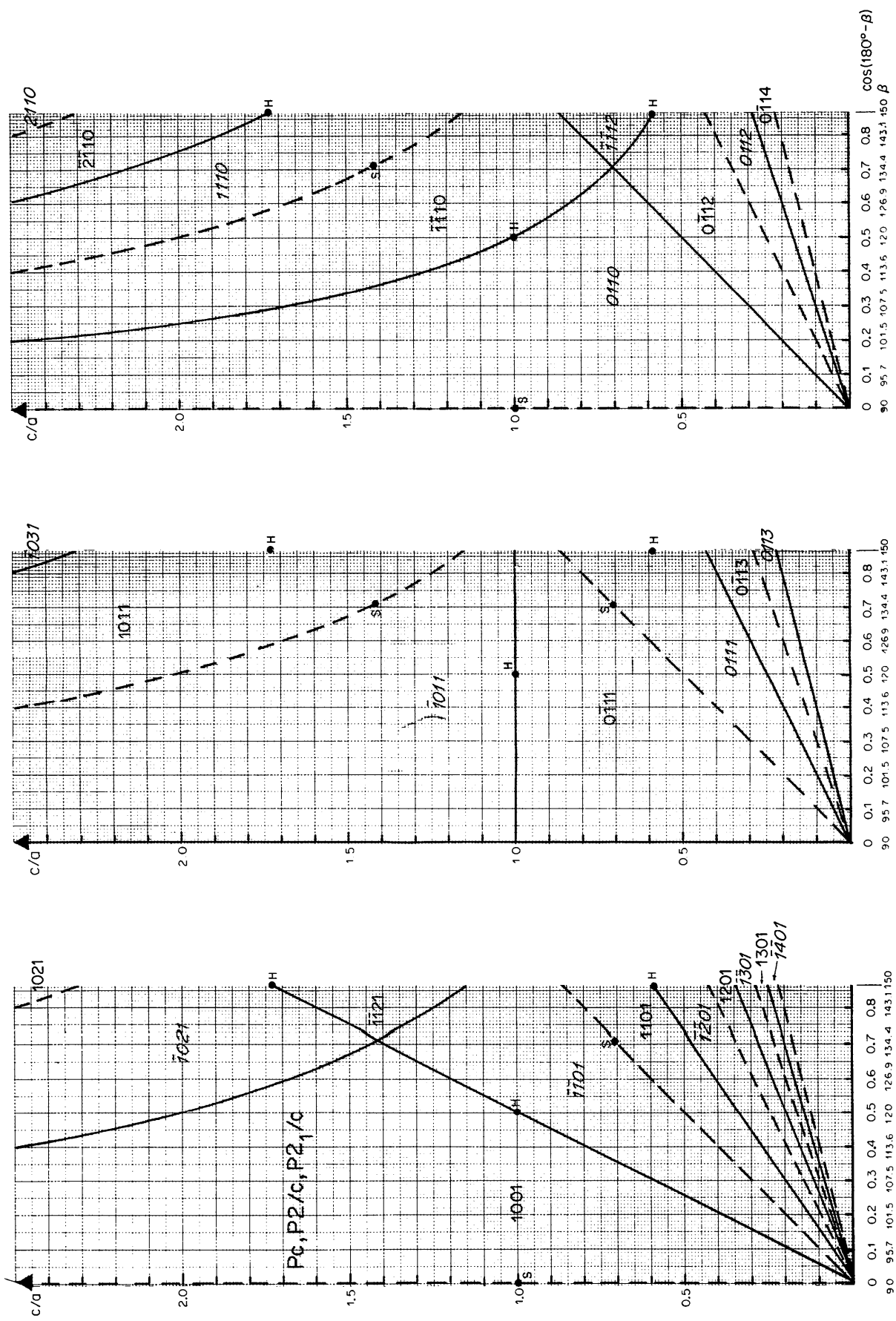

Fig. 3. c/a *versus* $\cos(180°-\beta)$ diagrams with inscribed matrices for transformation to a best cell for space groups Pc, $P2/c$ and $P2_1/c$ (b axis unique). (*a*) Matrices for cell transformation to a best cell for structures already described with cell choice 1. (*b*) Combined transformation matrices (cell choice 2 → cell choice 1 → best cell) for structures originally described with cell choice 2. (*c*) Combined transformation matrices (cell choice 3 → cell choice 1 → best cell) for structures originally described with cell choice 3. The four-digit matrix elements inscribed are in normal type if the **b** vector is unchanged, but in *italics* if **b** changes direction. Points on long-dashed border lines lead after transformation to a mesh with $\beta' = 90°$. *H* and *S* indicate special points that lead to a hexagonal or square mesh in the monoclinic plane.

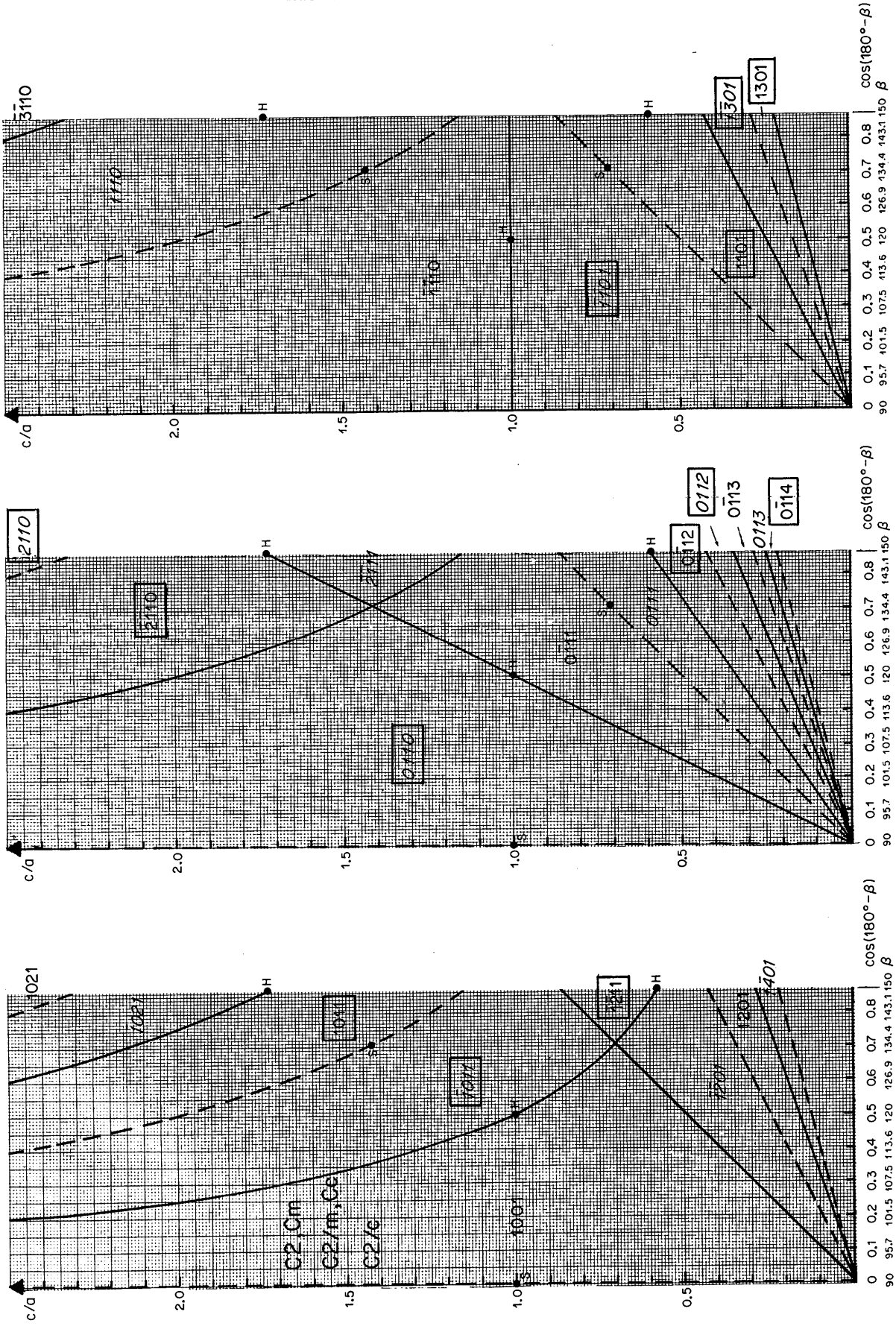

Fig. 4. *c/a versus* cos $(180°-\beta)$ diagrams with inscribed matrices for transformation to a best cell for space groups *C*2, *Cm*, *C*2/*m*, *Cc* and *C*2/*c* (*b* axis unique). (*a*) Matrices for cell transformation to a best cell for structures already described with cell choice 1. (*b*) Combined transformation matrices (cell choice 2 → cell choice 1 → best cell) for structures originally described with cell choice 3. The four-digit matrix elements inscribed are in normal type if the **b** vector is unchanged, but in *italics* if **b** changes direction. They are framed if an origin shift is necessary for space groups *Cc* and *C*2/*c* when transforming the atom coordinates. Points on long-dashed border lines lead after transformation to a mesh with $\beta' = 90°$. *H* and *S* indicate special points that lead to a hexagonal or square mesh in the monoclinic plane.

Equation (6) can be used to find quickly whether a monoclinic unit cell with cell choice 1 can be transformed to a cell with smaller **a** and/or **c** vectors.

We applied this algorithm to the data on monoclinic structures listed in the Cambridge Crystallographic Database, updated version of 1983 (Allen *et al.* 1979). Of the 21 303 monoclinic structures that are described with 70(!) different space-group symbols, 14 798 are in a setting corresponding to a standard space-group symbol (*b* axis unique and cell choice 1 where applicable) and 10% of these (1460 to be exact) have a unit cell that is not the best one, that means that **a** and/or **c** are not the smallest vectors possible for cell choice 1.

The advantages of a best cell with cell choice 1 as compared to a fully reduced cell with cell choices 1, 2 or 3

It has been shown above that the best unit cell consistent with cell choice 1 of IT(1983) is not necessarily fully reduced. It may be only half reduced and β may exceed 120° in some cases. The question arises whether it might not be better to use a fully reduced cell with $c/a \geq 1$, $\beta \leq 120°$ and one of the three different cell choices that are now explicitly given in IT(1983). To explain our preference for the best unit cell consistent with cell choice 1 we want to derive first the fully reduced cells from our results on the best unit cells consistent with cell choice 1.

*P*2, *P*2$_1$, *Pm*, *P*2/*m and P*2$_1$/*m*. The best cells with their representative points in the 1001 field of Fig. 2 are already fully reduced. There is only one cell choice for these space groups.

Pc, *P*2/*c and P*2$_1$/*c*. We need to consider only the best cells that have their representative points in the 1001 field of Fig. 3(*a*). If we superimpose the 1001 field of Fig. 3(*a*) on Fig. 2 we note that the former 1001 field has to be subdivided into three fields. The three matrices inscribed in Fig. 2 lead to fully reduced cells for *Pc*, *P*2/*c* and *P*2$_1$/*c*, all with $c/a \geq 1$ and $\beta \leq 120°$.

1001 field: No transformation is necessary. These cells with cell choice 1 are already fully reduced.

0110 field: Transformation with this matrix leads to a fully reduced cell with cell choice 3. β remains unchanged, but c/a changes to $c/a \geq 1$.

$\bar{1}011$ field: Transformation with this matrix leads from a half-reduced to a fully reduced cell with cell choice 2 and $c/a \geq 1$. The new β and $|\mathbf{a}|$ or $|\mathbf{c}|$ are smaller than before.

*C*2, *Cm*, *C*2/*m*, *Cc and C*2/*c*,. The procedure to obtain a fully reduced cell with $c/a \geq 1$ is similar to the one discussed above. Superimposition of Fig. 4(*a*) on Fig. 2 allows us to read from Fig. 2 the matrices needed for the transformation.

1001 field: No transformation is necessary. The best cells with cell choice 1 are already fully reduced.

$0\bar{1}11$ fields: Transformation with this matrix leads from a half-reduced cell to a fully reduced cell with cell choice 3 and $c/a \geq 1$. The new β and $|\mathbf{a}|$ or $|\mathbf{c}|$ are smaller than before. For space groups *Cc* and *C*2/*c* this transformation does not require any origin shift.

0110 field: Transformation with this matrix leads to a fully reduced cell with cell choice 2. β remains unchanged, but c/a changes to $c/a \geq 1$. For space groups *Cc* and *C*2/*c* this transformation requires the transformed atom coordinates to be shifted by $0\frac{1}{4}0$ and $0\frac{1}{4}\frac{1}{4}$ respectively in order to obtain atom positions that correspond to the Wyckoff positions given in IT (1983).

In conclusion, we note that for space groups with glide planes and/or nonprimitive Bravais lattices, depending on the c/a and β values of the best cell with cell choice 1, all three different cell choices have to be used if a fully reduced cell with $c/a \geq 1$ is required.*

A standardized unit-cell description based on a fully reduced unit cell with $c/a \geq 1$ would be fully appropriate if a structure is considered by itself. The purpose of a structure data standardization is, however, twofold. Not only should a method be found to describe a structure in a unique way, but it should also be possible to recognize the similarity of slightly different structures with slightly different c/a and β values. Instead of the single 1001 field for the best unit cell with cell choice 1 there are for fully reduced cells three different fields. Two closely related structures with their representative points on different sides of the border line between two fields will have, if they are described with fully reduced cells, unit cells and atom coordinates so different that the recognition of their similarity is not evident. By choosing the best cell consistent with cell choice 1 there are less border lines and less examples will occur where geometrically closely related structures, owing to the particular unit-cell metric, will be described in a way that masks their similarity.

As an example, we compare in Table 3 the lattice parameters and atom coordinates of monoclinic Sc_2FeSi_2, recently determined independently in two different laboratories, described both by the best cell in cell choice 1 and by the fully reduced cell. From the numerical values of the atom coordinates referred

* As a demonstration we give here the fully reduced cells with $c/a \geq 1$ for the three examples discussed above.

Substituted chlorobenzophenone
C 1 2/*c* 1: $a = 25{\cdot}04$, $b = 3{\cdot}935$, $c = 26{\cdot}746$ Å, $\beta = 110{\cdot}56°$ (*C*2/*c*, cell choice 1).

Afwillite
I 1 *a* 1: $a = 11{\cdot}68$, $b = 5{\cdot}632$, $c = 13{\cdot}23$ Å, $\beta = 98{\cdot}7°$ (*Cc*, cell choice 3).

Sylvanite
P 1 2/*n* 1: $a = 8{\cdot}85$, $b = 4{\cdot}49$, $c = 8{\cdot}96$ Å, $\beta = 110{\cdot}36°$ (*P*2/*c*, cell choice 2).

Table 3. *Standardized structural data for* Sc_2FeSi_2 *(space group C2/m) from two independent structure determinations using both a best cell consistent with cell choice* 1 *and a fully reduced cell with* $c/a \geq 1$.

All atoms are in equipoint 4(*i*).

Refs	Best cell consistent with cell choice 1			Fully reduced cell with $c/a \geq 1$			
(*a*)	*C* 1 2/*m* 1 (*C* 2/*m*, cell choice 1) $a = 9{\cdot}916$, $b = 3{\cdot}9912$, $c = 9{\cdot}414$ Å, $\beta = 118{\cdot}15°$			*A* 1 2/*m* 1 (*C* 2/*m*, cell choice 2) $a = 9{\cdot}414$, $b = 3{\cdot}9912$, $c = 9{\cdot}916$ Å, $\beta = 118{\cdot}15°$			
	Atoms in $\pm(x0z)+[\frac{1}{2}\frac{1}{2}0]$			Atoms in $\pm(x0z)+[0\frac{1}{2}\frac{1}{2}]$			
	Sc(1)	−0·0002	0	0·3269	Sc(1)	0·1731	0	0·0002
	Sc(2)	0·1856	0	0·1077	Sc(2)	0·6077	0	0·1856
	Fe	0·2720	0	0·6305	Fe	0·1305	0	0·2720
	Si(1)	0·3567	0	0·4348	Si(1)	0·0652	0	0·6433
	Si(2)	0·4891	0	0·1234	Si(2)	0·3766	0	0·5109
(*b*)*	*C* 1 2/*m* 1 (*C* 2/*m*, cell choice 1) $a = 9{\cdot}938$, $b = 3{\cdot}984$, $c = 9{\cdot}409$ Å, $\beta = 118{\cdot}46°$			*I* 1 2/*m* 1 (*C* 2/*m*, cell choice 3) $a = 9{\cdot}409$, $b = 3{\cdot}984$, $c = 9{\cdot}9082$ Å, $\beta = 118{\cdot}14°$			
	Atoms in $\pm(x0z)+[\frac{1}{2}\frac{1}{2}0]$			Atoms in $\pm(x0z)+[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$			
	Sc(1)	−0·0002	0	0·3275	Sc(1)	0·1723	0	−0·0002
	Sc(2)	0·1859	0	0·1080	Sc(2)	0·5779	0	0·1859
	Fe	0·2715	0	0·6302	Fe	0·1413	0	0·2715
	Si(1)	0·3569	0	0·4350	Si(1)	0·4219	0	0·3569
	Si(2)	0·4893	0	0·1237	Si(2)	0·1344	0	0·5107

References: (*a*) Chabot, Engel & Parthé (1984); (*b*) Kotur & Sikiritsa (1983).

* The atom coordinates for Sc_2FeSi_2 published by Kotur & Sikiritsa (1983) do not apply to the monoclinic unit cell given in their paper, but to the different unit cell published for Sc_2CoSi_2 (*a* and/or *b* are not the smallest values possible). The authors obviously wanted to demonstrate that Sc_2FeSi_2 is isostructural with Sc_2CoSi_2 (Gladyshevskii & Kotur, 1978).

to the best cells it is evident that the two structure determinations gave identical results, whereas a study of the right-hand side of Table 3 would not have convinced us that the two determinations concern the same structure.

Concluding remarks

We suggest that each author before publishing data on a monoclinic structure makes certain by use of the figures that he really has a best cell with the shortest **a** and **c** vectors possible for cell choice 1. In this case it will be much simpler to recognize identical structures by the similarity of their lattice-parameter ratios. It is also hoped that these unit-cell transformations will be considered in the crystallographic database.

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