Choice of basis vectors for conventional unit cells revisited

Yoyo Hinuma, Atsushi Togo, Hiroyuki Hayashi, Isao Tanaka

Abstract

Band diagrams often pass through special \( \mathbf{k} \)-vector points with “irrational” fractional coordinates such as some Brillouin zone vertices and centers of edges. Use of “standard” primitive cells as defined by Setyawan and Curtarolo [Comp. Mater. Sci. 49, 299] is convenient for band diagram and effective mass calculations because the definitions and coordinates of special \( \mathbf{k} \)-vector points including “irrational” fractional points are provided, but their basis vectors are taken differently and/or special \( \mathbf{k} \)-vector point definitions differ from the crystallographic convention in many cases. On the other hand, the Bilbao Crystallographic Server [Bulg. Chem. Commun. 43, 183] defines special \( \mathbf{k} \)-vector points based on crystallographic convention; however, symbols for “irrational” special \( \mathbf{k} \)-vector points are not defined. Obviously there is a need for a crystallographic convention-friendly scheme to describe such “irrational” special \( \mathbf{k} \)-vector points. Therefore, we derived a procedure to uniquely choose basis vectors for all space groups from the crystal symmetry, basis vector lengths, and interaxial angles, and implemented this algorithm in the spglib code [http://spglib.sourceforge.net/]. This paper outlines an algorithm that is relatively straightforward to implement in software to bridge between crystallographic conventional cells and “standard” primitive cells by retaking basis vectors. The procedure is expected to ease systematic electronic and phonon band calculations.

1. Introduction

An algorithm for efficient and systematic generation of electronic and phonon band diagrams would be useful not only in detailed investigation of certain compounds but also in combinatorial or “high-throughput” calculations [1,2]. Band diagrams and effective carrier masses are typically obtained by sampling \( \mathbf{k} \)-points along a path spanning the first Brillouin zone (BZ). Although the shape of a BZ is independent on how the basis vectors are chosen, the fractional coordinates of vertices and centers of edges and faces, hereafter denoted as special \( \mathbf{k} \)-vector points, are not. Therefore, rules to determine basis vectors that give the same special \( \mathbf{k} \)-vector point coordinates for a given form of a BZ would be useful. The choice of basis vectors, definitions of special \( \mathbf{k} \)-vector points, and suggested band diagram paths are provided in detail for “standard” primitive cells as defined by Setyawan and Curtarolo [3]. However, the “standard” cell differs from the crystallographic conventional cell in many cases, and for this reason we use the term “standard” with quotation marks in this article when referring to Setyawan and Curtarolo’s definition. Consequently, there is demand for a simple procedure, preferably using transformation matrices for retaking basis vectors, to convert a crystallographic conventional cell into a “standard” cell. We note that the AFLOW code [4] can automatically generate “standard” cells; however, details of the algorithm to derive a “standard” cell is not disclosed.

The objective of this article is to review how the conventional and “standard” definitions are different and to outline an algorithm to convert a crystallographic conventional unit cell of the standard setting into a “standard” primitive cell. This algorithm is comprehensive and relatively easy to implement in software. Section 2 provides a summary of definitions and notations used in this paper. Section 3 introduces the crystallographic convention on basis vector choice. Section 4 outlines the dif-
ferences between crystallographic and “standard” conventional cells for each Bravais lattice and gives procedures and transformation matrices to convert the former to the latter. Section 2 outlines how “standard” primitive basis vectors are expressed in Cartesian coordinates. The definitions are based on Setyawan and Curtarolo [3] but re-written in a form more convenient for implementation in software. Section 3 shows criteria that determine the topology of the BZ. Section 4 brings up the necessity of handling special k-vector points with “irrational” coordinates and discusses issues arising in comparing special k-vector point symbols between those in the Bilbao Crystallographic Server [4, 5, 6] and Setyawan and Curtarolo [3]. Section 5 is a summary of this paper.

2. Symbols and terminologies

Definitions of symbols are summarized in Table 1 Symbols for basis vectors are written in this article as \( a_1, a_2, \) and \( a_3 \) in line with the Fifth edition of the International Tables of Crystallography A (ITA) [1] and the Third edition of the International Tables of Crystallography B (ITB) [2]. The “standard” conventional and primitive cells are defined according to Setyawan and Curtarolo [3]. In essence, reciprocal space basis vectors of “standard” primitive cells penetrate the center of Bragg planes belonging to the first BZ and direct space basis vector lengths are chosen as \( a' < b' < c' \) when there is ambiguity. Primes are added for “standard” cells and the subscript P indicates a primitive cell. All direct space basis vectors are column vectors and reciprocal space basis vectors are row vectors. The direct and reciprocal space basis vectors are related by \( a_i^* \cdot a_j = \delta_{ij}, \ a_k^* \cdot a_j = \delta_{kj}, \ a_{P,i} \cdot a_{P,j} = \delta_{ij} \) \((i, j \in \{1, 2, 3\})\) using the Kronecker delta symbol \( \delta_{ij} \). Lengths of basis vectors and interaxial angles are collectively referred to as lattice constants.

The symbols of the Bravais lattices and the sections where topics are discussed in this article with respect to each Bravais lattice are summarized in Table 2.

A change of basis matrix \( M \) relates a choice of basis vectors to another choice of basis vectors. \( M \) is a \( 3 \times 3 \) matrix and is used as

\[
(a_1', a_2', a_3') = (a_1, a_2, a_3)M.
\]

A transformation matrix, \( P \), transforms a conventional unit cell to one of the primitive cells by

\[
(a_{P,1}', a_{P,2}', a_{P,3}') = (a_1', a_2', a_3')P.
\]

With the exception of rhombohedral cells, the change of basis \( M \) conserves the number of atoms in the unit cell, \( n_a \), because \( \det(M) = 1 \). On the other hand, \( \det(P) = 1 \) for cells without centring, \( \det(P) = 1/2 \) for base- and body-centred cells and \( \det(P) = 1/4 \) for face-centred cells. The number of atoms in the primitive cell is \( n_a \det(P) \).

The unit cell is a parallelepiped determined by the basis vectors \( a_1, a_2, a_3 \). A point in the unit cell \( x \) is represented by a column vector of fractional values with respect to basis vector lengths:

\[
x^T = (x_1, x_2, x_3) \quad \text{where} \quad 0 \leq x_i < 1. \quad (3)
\]

The position of an atom at a point \( x \) in the unit cell is given by

\[
X = \sum_i x_i a_i = (a_1, a_2, a_3)x. \quad (4)
\]

\( X \) is invariant with change of basis. However, as

\[
(a_1, a_2, a_3)x = (a_1', a_2', a_3')M^{-1}x, \quad (5)
\]

the vector representation of the atom varies with change of basis \( M \) according to

\[
x' = M^{-1}x + t, \quad (6)
\]

where \( t \) is the lattice translation vector necessary to fulfill the condition (3) so that the point is in the new unit cell.

Irrational special k-vector points are defined as special k-vector points that always have irrational fractional coordinates irrespective of basis vector lengths except in virtual crystals. Some vertices of the BZ are located at irrational special k-vector points in body-centred tetragonal, face-, body-, and base-centred orthorhombic, rhombohedral, monoclinic, base-centred monoclinic, and triclinic Bravais lattices.

3. Convention on basis vector choice

There is a crystallographic convention on which specific choice of basis vectors should be used out of an infinite number of choices, and this is outlined in the ITA [2] and ITB [3]. Here, the Bravais lattice is determined, symmetry operations are identified, and then the origin is decided. A total of 530 choices, distinguished by Hermann-Mauguin and Hall symbols [3, 4], of 230 space group types are listed in the ITA and ITB. Multiple choices are
Table 1: List of symbols used in this study.

| Definition | Basis vectors | Basis vector lengths | Interaxial angles |
|------------|---------------|----------------------|-------------------|
| Crystallographic conventional cell | \( \{a_1, a_2, a_3\} \) | \( \{a, b, c\} \) | \( \{\alpha, \beta, \gamma\} \) |
| Reciprocal crystallographic conventional cell | \( \{a_1^*, a_2^*, a_3^*\} \) | \( \{k_a, k_b, k_c\} \) | \( \{k_a^*, k_b^*, k_c^*\} \) |
| “standard” conventional cell | \( \{a', a', a'\} \) | \( \{a', b', c'\} \) | \( \{\alpha', \beta', \gamma'\} \) |
| Reciprocal “standard” conventional cell | \( \{a_1'^*, a_2'^*, a_3'^*\} \) | \( \{k_{a'}, k_{b'}, k_{c'}\} \) | \( \{k_{a'^*}, k_{b'^*}, k_{c'^*}\} \) |
| “standard” primitive cell | \( \{a_1'^*, a_2'^*, a_3'^*\} \) | \( \{k_{a'^*}, k_{b'^*}, k_{c'^*}\} \) | \( \{k_{a'^*}, k_{b'^*}, k_{c'^*}\} \) |
| Reciprocal “standard” primitive cell | \( \{a_1'^*, a_2'^*, a_3'^*\} \) | \( \{k_{a'^*}, k_{b'^*}, k_{c'^*}\} \) | \( \{k_{a'^*}, k_{b'^*}, k_{c'^*}\} \) |

Table 2: Symbols of the Bravais lattices and sections of this article where they are discussed.

| Crystal system | Centring | Symbol | Sections |
|----------------|----------|--------|---------|
| Triclinic      | Primitive| \( aP \) | \( \{3.3, 4.7, 5.6\} \) |
| Monoclinic     | Primitive| \( mP \) | \( \{3.2, 4.5, 6.1\} \) |
|                | Base-centred| \( mS \) | \( \{3.3, 4.5, 5.24, 6.3\} \) |
| Orthorhombic   | Primitive| \( oP \) | \( \{3.1, 4.3, 6.1\} \) |
|                | Base-centred| \( oS \) | \( \{3.1, 4.3, 5.22, 6.1\} \) |
|                | Body-centred| \( oI \) | \( \{3.1, 4.3, 5.23, 6.1\} \) |
|                | Face-centred| \( oF \) | \( \{3.1, 4.3, 5.24, 6.3\} \) |
| Tetragonal     | Primitive| \( tP \) | \( \{3.4, 4.1, 5.6\} \) |
|                | Body-centred| \( tI \) | \( \{3.4, 4.1, 5.2, 6.3\} \) |
| Hexagonal      | Primitive| \( hP \) | \( \{3.4, 4.1, 6.1\} \) |
| Rhombohedral   | *        | \( hR \) | \( \{3.4, 4.1, 6.4\} \) |
| Cubic          | Primitive| \( cP \) | \( \{3.4, 4.1, 6.1\} \) |
|                | Body-centred| \( cI \) | \( \{3.4, 4.1, 5.2, 6.3\} \) |
|                | Face-centred| \( cF \) | \( \{3.4, 4.1, 5.24, 6.4\} \) |

*Primitive or triple hexagonal.

provided for many space group types. For instance, space group type \( Pn\bar{m}2 \) (No. 34) can be \( Pn\bar{m}n \) or \( P2\bar{m}n \) depending on how the basis vectors are chosen, and space group type \( P4/nnc \) (No. 130) has two choices with different origins. In general, changing the basis may change the centring in base-centred cells but does not in body- or face-centred cells; one exception is that body-centred monoclinic cells can be converted into base-centred cells by using a different choice. The standard choice for monoclinic cells always has unique axis \( b \) and \( \beta > 90^\circ \) and base-centred cells are always \( C \)-centred. Base-centred orthorhombic cells are \( C \)-centred with the exception of four space group numbers 38 to 41; the conventional setting of these four space group types is \( A \)-centred such that the point group is \( m\bar{m}2 \) and the proper two-fold rotation axis is along the \( c \)-axis. The triple hexagonal unit cell for rhombohedral Bravais lattices could be obverse or reverse; the current version of the International Tables takes the obverse setting as the standard setting although the reverse setting was the standard until 1952 [7].

The ITA by itself does not uniquely define the crystallographic conventional cell in a number of situations. For instance, the order of basis vector lengths is not specified, which becomes problematic in many monoclinic and orthorhombic space group types. One standardization algorithm to uniquely determine the conventional cell is proposed by Parthé et al. [10]. They require the cell to be right-handed and have the following constraints: the Niggli reduced cell is used for triclinic structures, “best” cell with unique axis \( b \) and \( \beta > 90^\circ \) [11] is used for monoclinic structures, that is, the
cell where $a$ and $c$ are as short as possible while conforming to the standard space group symbol, $a \leq b$ or $a \leq b \leq c$ for orthorhombic structures, and obverse triple hexagonal cell for rhombohedral structures. Additionally, origin 2 is used for centrosymmetric structures. The space group type with the smallest index for the relevant screw axis is taken. For instance, one can choose to define space group number 80 as $I4_3$ but, as this space group type can also be defined as $I4_1$, the former is not accepted as a choice of the space group type and the latter is adopted because the screw axis index is smaller. Parthé et al. [10] provides further rules to reduce the values of internal coordinates that we will not discuss in this paper. The above procedure unambiguously defines the basis vectors of the crystallographic conventional cell but the internal coordinates are not necessarily determined.

One example is CsCl with space group type $Pn3m$ as mentioned in Parthé and Gelato [12]. Wyckoff positions 1a and 1b, which both have the same site symmetry $m3m$, must be occupied by Cs or Cl, but the above requirement does not determine whether Cs should occupy 1a or 1b sites. This ambiguity still remains after the standardization procedure of Parthé et al. [10]. However, the band diagram is not affected by the choice of origin since this is a physical property in reciprocal space that is invariant under translation in direct space. The conventional cells employed in this work conform to the conventional coordinate system in Table 2.1.2.1 of the ITA [3]. The basis vectors cannot be uniquely defined from Table 2.1.2.1 in many space group types, and therefore the following additional rules are imposed. We take the first choice that appears in Table A1.4.2.7 of the ITB [8] as the standard choice. This means that origin 1 is always used and the space group type with the smallest index for the relevant screw axis is automatically taken. All other choices in a particular space group type can be converted into the first choice by change of basis and/or translation of the origin. Table 9.3.7.1 of the ITA provides definitions of conventional cells based on lattice constants; however, the resulting space group choice is not necessarily the first one in Table A1.4.2.7 of the ITB [8], therefore the definition in Table 9.3.7.1 of the ITA is not adopted. Parthé et al. [10] instead takes the symmetry center at the origin, that is, adopt origin choice 2, for centrosymmetric structures. Origin choice 2 is never the first choice that appears in Table A1.4.2.7 of the ITB [8]. Parthé et al. [10] also requires that “orthorhombic structures where the space group symbols do not prescribe a particular labelling of any of the three unit-cell axes have to be described with a unit cell where $a < b < c$; however, this condition is inappropriate in some orthorhombic space group types as discussed below. Conventional cells are defined as above in the spglib code [13] versions 1.7.3 and higher.

### 3.1. Orthorhombic lattices

Some space group types have ambiguity in how to take basis vectors. An obvious example is space group type $P222$ (No. 16) where the six permutations of $a, b, c$ do not change the space group type.

The conditions to resolve ambiguity in basis vector lengths of orthorhombic space groups, with or without centring, other than $Pbca$ (No. 61) and $Ibca$ (No. 73) are $a < b$, and if necessary, additionally $b < c$. For example, only the former is necessary in $Pcc2$ (No. 27) and both is necessary in $Fmmm$ (No. 69). The imposed condition for $Pbca$ and $Ibca$ is to make $a$ the shortest. Two choices for $Pbca$ exist: $Pbca$ (adopted choice) and $Pcab$. If $Pbca$ is $a < b < c$ then $Pcab$ is $a < c < b$, and if $Pcab$ is $a < b < c$ then $Pbca$ is $a < c < b$. Therefore, $a < b < c$ cannot be enforced if $Pbca$ is to be used as the adopted choice. Similar logic applies to $Ibca$ (No. 73). The point groups that are allowed for an orthorhombic lattice are $222$, $mm2$, and $mmm$. As the proper two-fold rotation axis is taken along the $c$-axis in the point group $mm2$, $Amn2$, $Abm2$, $Ama2$, and $Aba2$ (numbers 38 to 41) become $A$-centred.

### 3.2. Monoclinic lattices

The definition according to Parthé and Gelato [11] is adopted and is summarized as follows. The $b$-axis is taken as the unique axis and $\beta > 90^\circ$, and the basis vectors corresponding to $a$ and $c$ are taken as short as possible. Base centring, if it exists, is always $C$-centred. The condition $a < c$ is imposed if the $c$-glide symmetry element identifiable by the “$c$” in the Hermann-Mauguin symbol is absent.

### 3.3. Triclinic lattices

The crystallographic conventional cell for a triclinic system is the Niggli reduced cell that can be robustly obtained using the algorithm by Křivý and Gruber [14] and its modified version that addresses numerical errors arising in finite precision floating
point algebra by Grosse-Kunstleve et al. [15] Parthé et al. [16] also employs the Niggli-reduced cell.

3.4. Cubic, tetragonal, hexagonal, and rhombohedral lattices

For cubic, tetragonal, and hexagonal lattices, the usual conditions are adopted when choosing basis vectors in this article, that are,

\[ a = b = c \quad \text{and} \quad \alpha = \beta = \gamma = 90^\circ \] for cubic,
\[ a = b \quad \text{and} \quad \alpha = \beta = \gamma = 90^\circ \] for tetragonal,
\[ a = b, \alpha = \beta = 90^\circ \quad \text{and} \quad \gamma = 120^\circ \] for hexagonal,

respectively. For primitive rhombohedral cells, the condition is
\[ a = b = c \quad \text{and} \quad \alpha = \beta = \gamma. \]

However, the conventional rhombohedral cell is defined on a hexagonal lattice. The obverse setting of the conventional rhombohedral cell can be recovered from the primitive rhombohedral cell using the transformation matrix \( M^{-1} \) of Eq. (7) shown in Sec. 4.2.

4. Deriving basis vectors of the “standard” cell

The crystallographic conventional unit cell as defined in Secs. 4.1 to 4.3 is chosen as the starting point except in triclinic cells as discussed in section 4.4. Computer programs typically represent basis vectors in Cartesian coordinates and store internal coordinates of atoms using fractional coordinates or Cartesian coordinates. In this case, converting between fractional and Cartesian coordinates is easily done by a linear transformation such as Eq. (1).

Standardization of basis vectors is carried out by choosing different basis vectors, and the positions of atoms are invariant in Cartesian coordinates during retaking of basis vectors. The volume of the unit cell is kept constant with the exception of rhombohedral cells.

We will not discuss cases when the basis vectors cannot be uniquely defined. This can happen in virtually designed crystals; one example is an orthorhombic cell with space group type \( I222 \) and \( a = b = c \). The basis vectors cannot be uniquely defined unless \( a, b, \) and \( c \) are all different from each other in this case.

The first step of the outlined algorithm is identification of the Bravais lattice, which can be deduced easily from the space group number. The cell is triclinic if the space group number is 1 or 2, monoclinic if 3 to 15, orthorhombic if 16 to 74, tetragonal if 75 to 142, hexagonal or rhombohedral if 143 to 194, and cubic otherwise. The first character of the Hermann-Mauguin symbol gives the centring (\( P, A, C, I, F, \) or \( R \)) and distinguishes hexagonal and rhombohedral cells for space group numbers 143 to 194.

4.1. \( cP, cF, cI, tP, tI, \) and \( hP \)

The crystallographic and “standard” conventional cells are the same for these Bravais lattices; therefore, the change of basis matrix \( M \) is the identity matrix.

4.2. \( hR \)

The rhombohedral crystallographic conventional cell is obverse triple hexagonal while the “standard” conventional cell is primitive rhombohedral [3]. The change of basis matrix and the inverse are

\[
M = \begin{pmatrix}
\frac{2}{3} & \frac{1}{3} & \frac{1}{3} \\
\frac{1}{3} & \frac{2}{3} & \frac{1}{3} \\
\frac{1}{3} & \frac{1}{3} & \frac{2}{3}
\end{pmatrix},
M^{-1} = \begin{pmatrix}
1 & 0 & 1 \\
1 & 1 & 1 \\
0 & 1 & 1
\end{pmatrix},
\]

respectively. The determinant of \( M \) is 1/3, which means that the “standard” conventional cell volume is one-third of the crystallographic conventional cell. One simple procedure to remove duplicate atoms in the “standard” cell is to apply Eq. (6) and remove duplicate atoms.

4.3. \( oP, oF, \) and \( oI \)

The order of basis vector lengths is not always \( a < b < c \) in a non-base centred crystallographic conventional cell whereas the order in a “standard” conventional cell is always \( a' < b' < c' \) [3]. The change of basis matrix \( M \) and the inverse are given in Table 3.

4.4. \( oS \)

A base-centred orthorhombic crystallographic conventional cell is generally \( C \)-centred but some space group types with point group type \( mm2 \), namely space group types \( Amm2, Abm2, Ama2, \) and \( Aba2 \) (38 to 41) are \( A \)-centred. The order of basis vector lengths is not unique in some space group types. In contrast, a “standard” conventional cell is always \( C \)-centred and \( a' < b' \) regardless of symmetry [3]. The change of basis matrix \( M \) and the inverse are given in Table 3.
Table 3: Change of basis matrix $M$ for non-base centred orthorhombic cells.

| Condition | $M$ | $M^{-1}$ |
|-----------|-----|----------|
| $a < b < c$ | $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ | $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ |
| $a < c < b$ | $\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ | $\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ |
| $b < a < c$ | $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ | $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ |
| $b < c < a$ | $\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$ |
| $c < a < b$ | $\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$ |
| $c < b < a$ | $\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$ | $\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$ |

4.5. $mP$

As outlined in Parthé and Gelato [11], a crystallographic conventional cell has unique axis $b$ and $\beta > 90^\circ$. The additional constraint of $a < c$ is always imposed on space group types without c-glide symmetry. The order of $a$ and $c$ is not always the same when there is c-glide symmetry because this symmetry element distinguishes $\mathbf{a}_1$ and $\mathbf{a}_3$. On the other hand, a “standard” conventional cell has unique axis $a$, lattice constants $b' \leq c'$, and $\alpha' < 90^\circ$ [3]. The change of basis matrix $M$ and the inverse are given in Table 3.

4.6. $mS$

A crystallographic conventional cell is $C$-centred with unique axis $b$ and $\beta > 90^\circ$, which is required in a “best” cell as defined by Parthé and Gelato [11]. In contrast, a “standard” conventional cell is $C$-centred with unique axis $a$ and $\alpha' < 90^\circ$ [3]. We believe the condition $b' \leq c'$ in the original paper by Setyawan and Curtarolo cannot be enforced because the basis vector length of $\mathbf{a}_3'$ in the plane with centring is not necessarily shorter than the basis vector length of $\mathbf{a}_2'$ without centring. The three basis vectors are distinguished by symmetry; one of the basis vectors comprising the plane with centring forms a right angle with the unique axis while the other does not. The change of basis matrix and its inverse are

$$M = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad M^{-1} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{8}$$

The reason why only one change of basis matrix is sufficient is provided in Appendix A.

4.7. $aP$

The crystallographic conventional triclinic cell is the Niggli reduced cell [10, 14, 15] that is determined with direct space lattice constants. The order of basis vector lengths are $a < b < c$, and $\alpha, \beta,$
and γ are all smaller than (Type I) or larger than (Type II) 90°. On the other hand, the “standard” conventional cell is defined based on reciprocal basis vectors. The requirement that reciprocal basis vectors must penetrate centers of faces of the first BZ means that the reciprocal “standard” conventional cell must be a Niggli reduced cell in reciprocal space with axes relabeled. In other words, the set of basis vector lengths of the reciprocal “standard” conventional cell must match that of the Niggli reduced cell in reciprocal space. Moreover, the interaxial angles of the reciprocal “standard” conventional cell, \( k_\alpha, k_\beta, \) and \( k_\gamma, \) must be either all larger than or smaller than 90° and \( k_\gamma \) is always the one closest to 90° [3].

The conversion from crystallographic to “standard” cells is done in the following three steps. First, the Niggli reduced cell in reciprocal space is obtained and its reciprocal basis vectors, that is, basis vectors in direct space, are used as \( \mathbf{a}_1, \mathbf{a}_2, \) and \( \mathbf{a}_3 \) instead of the basis vectors of the crystallographic conventional cell. Next, basis vectors are relabeled such that \( k_\gamma \) is closest to 90° by using a change of basis matrix \( \mathbf{M}_1 \) that transforms to an intermediate form: \( (\mathbf{a}_1', \mathbf{a}_2', \mathbf{a}_3') = (\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3) \mathbf{M}_1. \)

Finally, another change of basis matrix \( \mathbf{M}_2 \) is used as \( \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3' \) = \( \mathbf{a}_1', \mathbf{a}_2', \mathbf{a}_3' \)\( \mathbf{M}_2 \) to invert basis vectors as necessary such that \( k_\alpha, k_\beta, \) and \( k_\gamma \) become all larger than or smaller than 90°. In other words,

\[
(\mathbf{a}_1', \mathbf{a}_2', \mathbf{a}_3') = (\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3) \mathbf{M}_1 \mathbf{M}_2. \tag{9}
\]

The change of basis matrix for the second step, \( \mathbf{M}_1, \) is given in Table 6. The change of basis matrix for the third step, \( \mathbf{M}_2, \) depends on the interaxial angles of the reciprocal unit cell of the intermediate form \( k_\alpha', k_\beta', \) and \( k_\gamma' \) and is given in Table 7.

| Condition | \( \mathbf{M}_1 \) | \( \mathbf{M}_1^{-1} \) |
|-----------|------------------|------------------|
| \( k_\alpha' \) closest to 90° | \( \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \) | \( \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \) |
| \( k_\beta' \) closest to 90° | \( \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \) | \( \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \) |
| \( k_\gamma' \) closest to 90° | \( \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \) | \( \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \) |

Table 6: Change of basis matrix \( \mathbf{M}_1 \) for triclinic cells.

| Condition | \( \mathbf{M}_2 = \mathbf{M}_2^{-1} \) |
|-----------|----------------------------------|
| \( k_\alpha'' < 90°, k_\beta'' < 90°, k_\gamma'' < 90° \) | \( \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \) |
| \( k_\alpha'' > 90°, k_\beta'' > 90°, k_\gamma'' > 90° \) | \( \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \) |
| \( k_\beta'' < 90°, k_\beta'' > 90°, k_\gamma'' > 90° \) | \( \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \) |
| \( k_\gamma'' < 90°, k_\beta'' < 90°, k_\gamma'' < 90° \) | \( \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \) |
| \( k_\alpha'' > 90°, k_\beta'' > 90°, k_\gamma'' > 90° \) | \( \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \) |
| \( k_\beta'' < 90°, k_\beta'' < 90°, k_\gamma'' < 90° \) | \( \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \) |
| \( k_\gamma'' > 90°, k_\beta'' > 90°, k_\gamma'' > 90° \) | \( \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \) |
| \( k_\alpha'' > 90°, k_\beta'' < 90°, k_\gamma'' > 90° \) | \( \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \) |

Table 7: Change of basis matrix \( \mathbf{M}_2 \) for triclinic cells.

5. "Standard" basis vectors in Cartesian coordinates

“Standard” basis vectors can be given in Cartesian coordinates once the “standard” lattice constants are obtained. Representation of points in a unit cell as given in Eq. 8 is invariant against rigid rotation of the corresponding crystal. The following are how “standard” basis vectors, both conventional and primitive, are represented in Cartesian coordinates according to the definition by Setyawan and Curtarolo [3].

A representation in Cartesian coordinates of the “standard” conventional cell, excluding hexagonal (hP) and rhombohedral (hR) cells, is

\[
\mathbf{a}_1^T = (a', 0, 0),
\]
\[
\mathbf{a}_2^T = (b' \cos \gamma', b' \sin \gamma', 0),
\]
\[
\mathbf{a}_3^T = (c'_x, c'_y, c'_z),
\]
where
\[ c'_x = c' \cos \beta, \]
\[ c'_y = c' \frac{(\cos \alpha' - \cos \beta' \cos \gamma')}{\sin \gamma'}, \]
\[ c'_z = c' \sqrt{\sin^2 \gamma' - \cos^2 \alpha' - \cos^2 \beta' + 2 \cos \alpha' \cos \beta' \cos \gamma'}. \]

For hexagonal cells, the representation is
\[ a'_1 = \left( \frac{a'}{2}, -\frac{\sqrt{3}a'}{2}, 0 \right), \]
\[ a'_2 = \left( \frac{a'}{2}, \frac{\sqrt{3}a'}{2}, 0 \right), \]
\[ a'_3 = (0, 0, c'), \]

and for rhombohedral cells,
\[ a'_1 = \left( a' \cos \frac{a'}{2}, -a' \sin \frac{a'}{2}, 0 \right), \]
\[ a'_2 = \left( a' \cos \frac{a'}{2}, a' \sin \frac{a'}{2}, 0 \right), \]
\[ a'_3 = \left( a' \cos \frac{a'}{2}, 0, a' \sqrt{1 - \cos^2 \frac{a'}{2}} \right). \]

This means that only three cases are necessary in a code to output the “standard” conventional basis vectors in Cartesian coordinates, and there is no need to provide individual cases for all 14 Bravais lattices. Reduction of cases is available for the “standard” primitive cell as outlined in the following section.

5.2. "Standard" primitive cell

The transformation matrix \( \mathbf{P} \) converting “standard” conventional to “standard” primitive cells is defined as
\[ (a'_{p1}, a'_{p2}, a'_{p3}) = (a'_1, a'_2, a'_3) \mathbf{P}. \]

The “standard” primitive cell is the same as the “standard” conventional system for Bravais lattices without centring, and therefore \( \mathbf{P} \) is the identity matrix.

5.2.1. \( mS \)

For monoclinic base-centred lattices (\( mS \), note the definition is different from \( oS' \)),
\[ a'_{p1} = \left( \frac{a'}{2}, \frac{b'}{2}, 0 \right), \]
\[ a'_{p2} = \left( \frac{a'}{2}, -\frac{b'}{2}, 0 \right), \]
\[ a'_{p3} = (0, c', \cos \alpha', c' \sin \alpha'), \]
\[ \mathbf{P} = \begin{pmatrix} \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & 0 & 0 \\ 0 & 1 & 1 \end{pmatrix}, \quad \mathbf{P}^{-1} = \begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \]

5.2.2. \( oS \)

For orthorhombic base-centred lattices (\( oS \), note the definition is different from \( mS \)),
\[ a'_{p1} = \left( \frac{a'}{2}, -\frac{b'}{2}, 0 \right), \]
\[ a'_{p2} = \left( \frac{a'}{2}, \frac{b'}{2}, 0 \right), \]
\[ a'_{p3} = (0, 0, c'), \]
\[ \mathbf{P} = \begin{pmatrix} \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & 0 & 0 \\ 0 & 1 & 1 \end{pmatrix}, \quad \mathbf{P}^{-1} = \begin{pmatrix} 1 & 0 & 1 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \]

5.2.3. \( oI, tI, \) and \( cI \)

For body-centred lattices (\( oI, tI, cI \)),
\[ a'_{p1} = \left( -\frac{a'}{2}, -\frac{b'}{2}, \frac{c'}{2} \right), \]
\[ a'_{p2} = \left( \frac{a'}{2}, -\frac{b'}{2}, \frac{c'}{2} \right), \]
\[ a'_{p3} = \left( \frac{a'}{2}, \frac{b'}{2}, -\frac{c'}{2} \right), \]
\[ \mathbf{P} = \begin{pmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix}, \quad \mathbf{P}^{-1} = \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}. \]

5.2.4. \( oF \) and \( cF \)

For face-centred lattices (\( oF, cF \)),
\[ a'_{p1} = \left( 0, \frac{b'}{2}, \frac{c'}{2} \right), \]
\[ a'_{p2} = \left( \frac{a'}{2}, 0, \frac{c'}{2} \right), \]
\[ a'_{p3} = \left( \frac{a'}{2}, \frac{b'}{2}, 0 \right), \]
\[ P = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}, \quad P^{-1} = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}. \] 

(13)

6. Lattice constant dependence on BZ topology

The topology of the BZ depends on the lattice constants in some Bravais lattices. The conditions that decide the topology, using crystallographic conventional [6] and “standard” [3] conventional lattice constants, are outlined below. Special cases for “virtual” crystals are omitted.

6.1. \( cP, \, cF, \, cI, \, tP, \, oP, \, oI, \, oS, \, hP, \, mP \)

There is only one topology for each Bravais lattice.

6.2. \( tI \)

There are two topologies for the body-centred tetragonal lattice as given in Table 8.

6.3. \( oF \)

There are two topologies for the face-centred orthorhombic lattice.

The condition for the crystallographic conventional cell depends on the order of basis vector lengths and is rather involved. The “standard” conventional cell relabels the crystallographic conventional basis vectors such that \( a' < b' < c' \), and the condition for each topology can be written easily using “standard” conventional basis vector lengths as given in Table 9. Then the condition for the crystallographic conventional cell is obtained using that for the “standard” conventional cell and Table 4.

6.4. \( hR \)

There are two topologies for the rhombohedral lattice as given in Table 10.

6.5. \( mS \)

There are three topologies for the base-centred monoclinic lattice as given in Table 11. The crystallographic conventional cell is \( C \)-centred with unique axis \( b \) and \( \beta > 90^\circ \), while a “standard” conventional cell is \( C \)-centred with unique axis \( a \) and \( \alpha' < 90^\circ \). The quantity \( k'_{\gamma} \) that appears in the conditions can be expressed using “standard” conventional lattice constants as

\[
\cos k'_{\gamma} = \frac{a'^2 - b'^2 \sin^2 \alpha'}{a'^2 + b'^2 \sin^2 \alpha'}. \]

The reasoning behind how the conditions are determined is provided in Appendix B.

6.6. \( aP \)

The reciprocal “standard” conventional cell for a triclinic lattice is a Niggli reduced cell in reciprocal space where the axes are relabeled such that the interaxial angles are either all larger (all-obtuse) than or all smaller (all-acute) than 90° and \( k'_{\gamma} \) is the closest to 90°. Nevertheless there is only one topology of the BZ, that is, the truncated octahedron. The proof of this is given in Appendix C. There is a distinct difference between the all-obtuse and all-acute reciprocal “standard” conventional cells regarding the orientation of reciprocal basis vectors in the BZ.

All reciprocal basis vectors penetrate hexagonal faces in an all-obtuse reciprocal “standard” conventional cells. Our investigation of BZs of all-acute triclinic structures using the Materials Project database [12] shows discrepancies from the claims that Setyawan and Curtarolo [3] make. Setyawan and Curtarolo writes that the BZ is a truncated octahedron and the faces of the BZ where “standard” reciprocal basis vectors \( \mathbf{a}^*_1 \), \( \mathbf{a}^*_2 \), and \( \mathbf{a}^*_3 \) penetrate are hexagonal, hexagonal, and quadrilateral (parallelogram), respectively. We find that \( \mathbf{a}^*_1 \) penetrates a parallelogram face and \( \mathbf{a}^*_2 \) and \( \mathbf{a}^*_3 \) penetrate hexagonal faces in the structure of \( \alpha \mathrm{Ge}\alpha \mathrm{S}\alpha \mathrm{Se} \), \( k'_1 = 0.221 \, \text{Å}^{-1}, \, k'_2 = 0.229 \, \text{Å}^{-1}, \, k'_3 = 0.105 \, \text{Å}^{-1}, \, k'_4 = 80.80^\circ, \, k'_5 = 79.36^\circ, \, k'_6 = 83.58^\circ \). On the other hand, \( \mathbf{a}^*_2 \) penetrates a parallelogram face and \( \mathbf{a}^*_1 \) and \( \mathbf{a}^*_3 \) penetrate hexagonal faces in the structure of \( \mathrm{H}_5\mathrm{O}_5\mathrm{CuSe} \), \( k'_1 = 0.184 \, \text{Å}^{-1}, \, k'_2 = 0.207 \, \text{Å}^{-1}, \, k'_3 = 0.141 \, \text{Å}^{-1}, \, k'_4 = 71.00^\circ, \, k'_5 = 75.21^\circ, \, k'_6 = 77.19^\circ \), while \( \mathbf{a}^*_1 \) penetrates a parallelogram face and \( \mathbf{a}^*_2 \) and \( \mathbf{a}^*_3 \) penetrate hexagonal faces in the structure of \( \mathrm{B}_2\mathrm{O}_3\mathrm{Rb}_2 \), \( k'_1 = 0.095 \, \text{Å}^{-1}, \, k'_2 = 0.102 \, \text{Å}^{-1}, \, k'_3 = 0.156 \, \text{Å}^{-1}, \, k'_4 = 78.58^\circ, \, k'_5 = 76.56^\circ, \, k'_6 = 88.15^\circ \). In short, always one of \( \{\mathbf{a}^*_1, \mathbf{a}^*_2, \mathbf{a}^*_3\} \) penetrates a parallelogram face and two penetrates hexagonal faces when the “standard” cell is all-acute, but which one penetrates a parallelogram depends on the lattice constants. In light of this complexity, it is recommended to use the parallelepiped of reciprocal basis vectors [4] [6] to describe band diagrams of triclinic structures unless there is a very strong reason not to do so.
Table 8: BZ topology of a body-centred tetragonal lattice.

| Crystallography | “Standard” | Topology          |
|-----------------|------------|-------------------|
| \(c > a\)       | \(c' > a'\) | Truncated octahedron |
| \(c < a\)       | \(c' < a'\) | Elongated dodecahedron |

Table 9: BZ topology of a face-centred orthorhombic lattice.

| Crystallography | “Standard” | Topology          |
|-----------------|------------|-------------------|
| See the text in Sec. 6.3 | \(\frac{1}{2} < \frac{a}{c} + \frac{1}{2}\) | Truncated octahedron |
| See the text in Sec. 6.3 | \(\frac{1}{2} > \frac{a}{c} + \frac{1}{2}\) | Elongated dodecahedron |

7. Issues regarding special \(k\)-vector point definition

The philosophy behind labeling of reciprocal space is very different between the database on the Bilbao Crystallographic Server [4, 5, 6] and Setyawan and Curtarolo [3]. In short, the Bilbao Crystallographic Server defines and uses a set of labels for each type of representation domain, which is described afterwards, and BZ topology. However, fractional coordinates of irrational special \(k\)-vector points are not provided. On the other hand, Setyawan and Curtarolo provides a set of special \(k\)-vector point symbols, including irrational special \(k\)-vector points, for every BZ topology in each Bravais lattice. The drawbacks are that their “standard” conventional basis vectors are different from the crystallographic conventional basis vectors in many cases and that their definitions are not based on the representation domain.

A number of concepts have to be introduced before looking into how labels of reciprocal space are defined in the Bilbao Crystallographic Server [4, 5, 6]. The reciprocal lattice is represented using basis vectors in reciprocal space, \(\{a_1^*, a_2^*, a_3^*\}\). The reciprocal space group, which is defined as a semidirect product of the point group and the translational group of the reciprocal lattice, is isomorphic with the symmorphic space group. This means that discussion on a reciprocal space group type can be carried out using the corresponding symmorphic space group type in direct space. As a result, concepts defined in direct space, for instance Wyckoff positions and the asymmetric unit that are defined in the ITA [2], can be applied to the reciprocal space group. A representation domain, which is a simply connected parts of the BZ that contains exactly one reciprocal space vector (\(k\)-vector) of each orbit of \(k\), is assigned to each reciprocal space group type. The definitions of all 73 representation domain types are available on the Bilbao Crystallographic Server. Orbits of \(k\) in reciprocal space can be categorized into symmetry-equivalent \(k\) vectors that correspond to point orbits, or Wyckoff positions, of the relevant direct space symmorphic space group [4].

Labels of reciprocal space for every representation domain type are defined in the Bilbao Crystallographic Server [4, 5, 6] using Wyckoff positions of the corresponding direct space symmorphic space group type. Wyckoff positions can have zero, one, two, or three independent coordinate variables; therefore, labels are defined for special \(k\) vector points, lines (line segments, in practice), planes, or general positions (GP), respectively. The number of labels per Wyckoff position is not necessarily one. For instance, coordinates of Wyckoff position 1a (point symmetry mm2) of space group type \(Pmm2\) (No. 25) can be written as \((0, 0, z)\) using coordinates based on the ITA description. Labels defined for this Wyckoff position in the Bilbao Crystallographic Server are \(\Gamma(GM)\) \((z = 0)\), \(Z\) \((z = 1/2)\), \(A(LD)\) \((0 < z < 1/2)\), and \(LE\) \((-1/2 < z < 0)\) [4, 5, 6]. The names of labels depend on the BZ topology in body-centred tetragonal, face-centred orthorhombic, and rhombohedral Bravais lattices and the relation between basis vector lengths in base-, body-, and face-centred orthorhombic Bravais lattices. The topology of the BZ and relative orientation of basis vectors are not explicitly considered in monoclinic, base-centred monoclinic, and triclinic Bravais lattices, and therefore only one set of labels are defined per representation domain.

Band diagrams are drawn along a path in recipro-
Table 10: BZ topology of a rhombohedral lattice.

| Crystallography | “standard” | Topology          |
|-----------------|-------------|-------------------|
| $\sqrt{3}a < \sqrt{2}c$ | $\alpha' < 90^\circ$ | Truncated octahedron |
| $\sqrt{3}a > \sqrt{2}c$ | $\alpha' > 90^\circ$ | Rhombic dodecahedron |

Table 11: BZ topology of a monoclinic lattice.

| Crystallography | “standard” | Topology          |
|-----------------|-------------|-------------------|
| $b < a \sin \beta$ | $k'_{\Gamma} > 90^\circ$ | Truncated octahedron |
| \[
\begin{aligned}
&b > a \sin \beta, \\
&- \frac{a \cos \beta}{c} + \frac{a^2 \sin^2 \beta}{b^2} < 1
\end{aligned}
\]
| $k'_{\Gamma} < 90^\circ$, | Elongated dodecahedron |
| \[
\begin{aligned}
&b > a \sin \beta, \\
&- \frac{a \cos \beta}{c} + \frac{a^2 \sin^2 \beta}{b^2} > 1
\end{aligned}
\]
| $k'_{\Gamma} < 90^\circ$, | Elongated dodecahedron |
| \[
\begin{aligned}
&b > a \sin \beta, \\
&- \frac{a \cos \beta}{c} + \frac{a^2 \sin^2 \beta}{b^2} < 1
\end{aligned}
\]
| $k'_{\Gamma} > 90^\circ$, | Elongated dodecahedron |
| \[
\begin{aligned}
&b > a \sin \beta, \\
&- \frac{a \cos \beta}{c} + \frac{a^2 \sin^2 \beta}{b^2} > 1
\end{aligned}
\]
| $k'_{\Gamma} < 90^\circ$, | Elongated dodecahedron |

The path is typically along line segments connecting special $k$-vector points on the BZ surface as well as line segments connecting the $\Gamma$ point and special $k$-vector points. As a result, symbols of special $k$-vector points on the BZ surface are the only relevant labels of interest besides the $\Gamma$ point in band diagram calculations. In addition to labels, information is also necessary on fractional coordinates of special $k$-vector points where the band diagram path bends.

The fractional coordinates of centers of faces are always rational in a “standard” cell because the $k$-vector of a face center has the form

\[
\left( \frac{p}{2}a_{P_1}^*, \frac{q}{2}a_{P_2}^*, \frac{r}{2}a_{P_3}^* \right) \text{ where } p, q, r \in \{-1, 0, 1\}.
\]

In contrast, some BZ vertices, and therefore center of edges, are irrational special $k$-vector points in a number of Bravais lattices (see the definition of irrational special $k$-vector points at the end of Section 2). Table 12 shows the distribution of Bravais lattices and BZ types among the 58,055 crystal structures in the Materials Project database (obtained May 25, 2015). We find that crystals with irrational BZ vertices account for 59.8% of the structures in this database. Still 46.6% remains even if we choose to not consider triclinic cells.

One might argue that forcing usage of the first BZ is not always a good idea when drawing a band diagram because line segments connecting special $k$-vector points are not necessarily on high symmetry lines and, therefore, band paths should span the asymmetric unit that is uniquely defined for each representative domain. However, taking this viewpoint does not mean that defining symbols and identifying fractional coordinates of irrational special $k$-vector points is unnecessary. For example, consider space group type I4 (No. 79) with $c/a < 1$ (elongated dodecahedron BZ). The definitions of labels in the Bilbao Crystallographic Server and coordinates according to the ITA description is used in this paragraph. Line segment $\Lambda(LD)$ consists of points with coordinates $(0, 0, z)$ where $0 < z \leq ld_0$. The picture of the BZ on the Bilbao Crystallographic Server shows that line segment $\Lambda(LD)$ starts at the $\Gamma$ ($GM$) point and ends at point $Z$, and points with coordinates $(0, 0, z)$ with $ld_0 \leq z \leq 1/2$ form line segment $V A_1$ that connects points $Z$ and $M_0$. The quantity $ld_0$ is very important. Line segments $\Lambda(LD)$ and $V A_1$ together form a straight line segment in reciprocal space and come in touch at point $Z$ at coordinate $(0, 0, ld_0)$.

However, the two line segments differ significantly in character because line segment $\Lambda(LD)$ connects the $\Gamma$ ($GM$) point and point $Z$ at the surface of the BZ while line segment $V A_1$ is entirely on a BZ edge. The quantity $ld_0$ and the definitions of points $Z$ and $M_0$ as well as line segment $V A_1$ are not provided in tables on the Bilbao Crystallographic Server. Although we can deduce using Setyawan and Curtarolo that

\[
ld_0 = \frac{1 + c^2}{4a^2},
\]

unfortunately, cumbersome conversion of basis vec-
tors and coordinates are necessary between the Bilbao Crystallographic Server and Setyawan and Curtarolo. The coordinates of special k-vector points in crystallographic conventional cells may be derived from those of “standard” primitive cells using transformation matrices. Namely, if “standard” primitive basis vectors are related to those of crystallographic conventional cells through

\[(a_p^1, a_p^2, a_p^3) = (a'_1, a'_2, a'_3)P = (a_1, a_2, a_3)MP,\]

the basis vectors of the reciprocal crystallographic conventional cell are related to those of the reciprocal “standard” primitive cell by

\[\begin{pmatrix}
a^1_s \\
a^2_s \\
a^3_s
\end{pmatrix} = MP \begin{pmatrix}
a^*_p^1 \\
a^*_p^2 \\
a^*_p^3
\end{pmatrix}.\]

Naively mixing symbols in the Bilbao Crystallographic Server and those in Setyawan and Curtarolo is out of the question. Existing symbols attributed to the same special k-vector point may or may not differ based on the two definitions; therefore, the definition must be clearly stated when describing results. The symbol for the same point differ for example in space group type R3m (No. 160) with \(\sqrt{3}a < \sqrt{2}c\) (rhombohedron BZ). Here, point \(T\) in the Bilbao Crystallographic Server corresponds to point \(Z\) in Setyawan and Curtarolo, and the label \(P\) is used to indicate a line segment in the former whereas \(P\) is a BZ edge center in the latter. Existence of multiple crystallographic and “standard” primitive cells are related to those of crystallographic conventional cells are identical. Basis vector lengths satisfy \(a < b < c\) in VOBr (basis vector lengths: \(a = 3.473\ \text{Å}, b = 3.854\ \text{Å}, c = 9.050\ \text{Å}\) hence crystallographic and “standard” conventional cells are the same and the special k-vector point symbols are the same in the two definitions. In contrast, in CdCu_2O_2 (basis vector lengths: \(a = 4.002\ \text{Å}, b = 9.889\ \text{Å}, c = 3.680\ \text{Å}\)) basis vectors are re-taken in the “standard” conventional cell such that \(a' < b' < c'\), therefore the same special k-vector point symbol specifies different points in the BZ.

In summary, the following two issues need to be addressed when performing band diagram calculations. First, a unique choice of basis vectors must be determined for band diagram calculations. The change of basis matrix need to be readily available if the choice of basis vectors to be used in band diagram calculations is different from the crystallographic convention. Second, a suggested path together with definitions and fractional coordinates of special k-vector points on the path should be predetermined for each representation domain type and BZ topology. Time-reversal symmetry, in which band positions at \(k\) becomes the same as at \(-k\), significantly reduces the number of representative domain types that have to be considered. Time-reversal symmetry forces inversion symmetry to exist in the representative domain type of the BZ regardless of whether the original representative domain type has inversion symmetry or not. A list of symmorphic space group types with inversion symmetry is given in Table 13. In other words, if there is time-reversal symmetry the suggested band diagram paths in reciprocal space need to be considered only for representative domain types corresponding to the 24 space group types instead of all 73 representative domain types.

8. Summary

An algorithm to obtain “standard” primitive cells for efficient and systematic band diagram calculations is derived. First, a crystallographic conventional cell based on the definition outlined in this work is obtained, for example, by using the spglib code versions 1.7.3 and higher. Next, atom positions are obtained in Cartesian coordinates and basis vectors are re-taken as necessary to derive the “standard” conventional cell. Finally, the atom positions are converted to fractional coordinates and the basis vectors of the “standard” primitive cell are determined in Cartesian coordinates. Band diagrams often pass through special k-vector points with irrational coordinates, and we find that there is a need for a crystallographic convention-friendly scheme to describe such irrational special k-vector points.

ACKNOWLEDGMENTS

This work was supported by Scientific Research on Innovative Areas “Nano Informatics” (Grant...
Appendix A. Derivation of $M$ for $mS$

We provide simple proof that one change of basis matrix suffices for all base-centred monoclinic cells. The reciprocal primitive basis vectors of a base-centred monoclinic lattice can be taken in Cartesian coordinates as

$$ a'''_1 = (p, q, 0), $$
$$ a'''_2 = (-p, q, 0), $$
$$ a'''_3 = (0, -(r + nq), s) $$

using four positive variables $p$, $q$, $r$, and $s$ and an integer $n$. The restriction that this reciprocal cell is primitive determines $p$, $q$, and $s$. The quantity $r$ can be unambiguously defined such that $r < q$, and the cell is “standard”, or $a'''_1 = a'''_2$, when $n = 0$. The direct space basis vectors of the corresponding primitive cell can be expressed as

$$ (a'''_1, a'''_2, a'''_3) = \frac{1}{2} \begin{pmatrix} \frac{1}{p} & -\frac{1}{p} & 0 \\ \frac{1}{q} & \frac{1}{q} & 0 \\ \frac{1}{r + nq} & \frac{1}{r + nq} & \frac{2}{n} \end{pmatrix}. $$

The basis vector lengths and interaxial angles of the corresponding conventional cell with basis vectors $(a''_1, a''_2, a''_3)$ are

$$ a'' = \frac{1}{p}, $$
$$ b'' = \frac{\sqrt{(r + nq)^2 + s^2}}{qs}, $$
$$ c'' = \frac{1}{s}, $$

and

$$ \cos \alpha'' = \frac{(r + nq)}{\sqrt{(r + nq)^2 + s^2}}, $$
$$ \beta'' = 90^\circ, $$
$$ \gamma'' = 90^\circ. $$

The set of basis vector lengths is invariant when the change of basis matrix

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

is used to transform this $a$-axis, $C$-centred cell to a $b$-axis unique, $C$-centred cell with basis vectors $(a''_1', a''_2', a''_3')$ through $(a''_1', a''_2', a''_3') = (a''_1, a''_2, a''_3) M$. The basis vectors are minimized in a crystallographic conventional cell, therefore $n = 0$. This is exactly the condition for a “standard” conventional cell.

Appendix B. BZ topology of $mS$

We present the reasoning behind how conditions to determine the topology of the BZ of base-centred monoclinic cells are determined. This section uses the shorthand notation $b'_i = a'''_i$ and discussion is based on “standard” primitive cells.

The reason why the shape of the first BZ of base-centred monoclinic cells can be categorized into three types is discussed. Cases where inequality relations become exact equalities are not considered. We rely on the fact that the possible shapes of Voronoi cells are limited \cite{17} and the following lemma:

Take two reciprocal “standard” primitive basis vectors $b'_i$ and $b'_j$, where $i, j \in \{1, 2, 3\}$ and $i \neq j$. The two-dimensional (2D) BZ in the plane where $b'_i$ and $b'_j$ lies is a hexagon and must:

a) if $b'_i \cdot b'_j > 0$, the points

$$ \frac{b'_i}{2}, \frac{b'_j}{2}, \frac{b'_i - b'_j}{2}, $$

and these negatives exist on centers of different sides of the 2DBZ, or
b) if $b'_i \cdot b'_j < 0$, the points

$$ \frac{b'_i}{2}, \frac{b'_j}{2}, \frac{b'_i + b'_j}{2}, $$

and these negatives exist on centers of different sides of the 2DBZ.

As $b'_i \cdot b'_j = b'_2 \cdot b'_3 < 0$ by definition,

$$ \frac{b'_i}{2}, \frac{b'_2}{2}, \frac{b'_3}{2}, \frac{b'_i + b'_j}{2}, \frac{b'_i + b'_j}{2}, $$

and these negatives automatically become centers of faces. This means that the BZ must have 10 or more faces, which forces the BZ to be either an elongated dodecahedron (faces are four hexagons and eight parallelepipeds), a rhombic dodecahedron (faces are 12 parallelepipeds), or a truncated octahedron (faces are eight hexagons and six parallelepipeds).
1) If \( b'_1 \cdot b'_2 < 0 \), or \( k'_\gamma > 90^\circ \), then \( \frac{b'_1 - b'_2}{2} \) and its negative will be centers of faces. This is geometrically possible only when the BZ is a truncated octahedron and \( \frac{b'_1 + b'_2}{2} \) and these negatives are at the center of hexagonal faces. \( \frac{b'_1 + b'_2}{2} \) and its negative are also on a hexagonal face.

2) If \( b'_1 \cdot b'_2 > 0 \), or \( k'_\gamma < 90^\circ \), there are two cases. One is when \( \frac{b'_1 + b'_2}{2} \) is not on a face and the BZ is an elongated dodecahedron, and the remaining case is when \( \frac{b'_1 + b'_2}{2} \) is on a face and the BZ is a truncated octahedron.

Appendix C. BZ topology of \( aP \)

We show that the BZ must be a truncated octahedron if there is no pair of basis vectors that are perpendicular to each other. According to Horváth [17], the five topologies that a BZ can take is the parallelepiped, hexagonal prism, rhombic dodecahedron, elongated dodecahedron, and truncated octahedron. The concept of a “zone” is introduced, where any edge \( e \) of a Brillouin zone determines a zone of faces in which each face has two sides equal and parallel to the given edge \( e \). The number of the opposite pairs of relevant faces corresponding to a given zone is two or three, and if it is two then the corresponding faces are orthogonal to each other [1]. This means that a pair of basis vectors of the Brillouin zone must be perpendicular to each other if the number of pairs of faces in a zone is two. In a triclinic cell, basis vectors are generally not perpendicular to each other and therefore all zones should consist of three pairs of faces. Edges that are shared by hexagons in an elongated dodecahedron constitute a zone of two pairs of hexagons, thus the BZ of a triclinic cell cannot be an elongated dodecahedron. The rhombic dodecahedron is a special case of the elongated dodecahedron where the length of edges shared by hexagons is 0, and at least one rectangular cross-section where the centers of edges are penetrated by basis vectors always exist. Therefore, the rhombic dodecahedron also cannot be a BZ of a triclinic cell. In summary, the BZ of a triclinic cell must be a truncated dodecahedron.

References

[1] S. Curtarolo, G. L. W. Hart, M. B. Nardelli, N. Mingo, S. Sanvito, O. Levy, The high-throughput highway to computational materials design, Nat Mater 12 (3) (2013) 191–201, 10.1038/nmat3568.
[2] G. Hautier, A. Miglio, G. Ceder, G.-M. Rignanese, X. Gonze, Identification and design principles of low hole effective mass p-type transparent conducting oxides, Nat Commun 4. doi:10.1038/ncomms3292.
[3] W. Setyawan, S. Curtarolo, High-throughput electronic band structure calculations: Challenges and tools, Computational Materials Science 49 (2) (2010) 209–312. doi:http://dx.doi.org/10.1016/j.commatsci.2010.05.010
[4] M. I. Arroyo, D. Orohenga, G. de la Flor, E. S. Tasci, J. M. Perez-Mato, H. Wondratschek, Brillouin-zone database on the bilbao crystallographic server, Acta Crystallographica Section A 70 (2) (2014) 126–137. doi:10.1107/S000188851304911X.
[5] B. C. Server, The bilbao crystallographic server http://www.cryst.ehu.es/.
[6] A. P. Cracknell, B. L. Davies, S. C. Miller, W. F. Love, Kronecker product tables, Vol. 1, General introduction and tables of irreducible representations of space groups., IFI/Plenum, New York, 1979.
[7] I. U. o. Crystallography, International Tables of Crystallography A, 5th Edition, Kluwer Academic Publishers, Dordrecht, the Netherlands, 2002.
[8] I. U. o. Crystallography, International Tables of Crystallography B, 3rd Edition, Kluwer Academic Publishers, Dordrecht, the Netherlands, 2008.
[9] S. Hall, Space-group notation with an explicit origin, Acta Crystallographica Section A 37 (4) (1981) 517–525. doi:10.1107/S056773948101228.
[10] E. Parthé, K. Cenzual, R. E. Gladyshevskii, Standardization of crystal structure data as an aid to the classification of crystal structure types, Journal of Alloys and Compounds 197 (2) (1993) 291–301.
[11] E. Parthé, L. M. Gelato, The ‘best’ unit cell for monoclinic structures consistent with \( b \) axis unique and cell choice 1 of international tables for crystallography (1980), Acta Crystallographica Section A 41 (2) (1985) 142–151. doi:10.1107/S0567779485000289.
[12] E. Parthé, L. M. Gelato, The standardization of inorganic crystal-structure data, Acta Crystallographica Section A 40 (3) (1984) 169–183. doi:10.1107/S0567779483000416.
[13] A. Togo, Spglib, http://spglib.sourceforge.net/.
[14] I. Krivý, B. Gruber, A unified algorithm for determining the reduced (niggli) cell, Acta Crystallographica Section A 32 (2) (1976) 297–298. doi:10.1107/S0567779476000366.
[15] R. W. Grosse-Kunstleve, N. K. Sauter, P. D. Adams, Numerically stable algorithms for the computation of reduced unit cells, Acta Crystallographica Section A 60 (1) (2004) 1–6. doi:10.1107/S056777940400016X.
[16] The materials project https://www.materialsproject.org/.
[17] A. G. Horváth, On dirichlet-voronoi cell part i. classical problems, Periodica Polytechnica Mechanical Engineering 39 (1) (1995) 25–42.
Table 12: Breakdown of 58,055 crystals in the Materials Project by Bravais lattice and BZ topology. Symbols denoted with an asterisk (*) indicate Bravais lattices where some BZ vertices are irrational special k-vector points. BZ topologies are TO: truncated octahedron, ED: elongated dodecahedron, and RD: rhombic dodecahedron. All-obtuse and all-acute cells are distinguished for triclinic cells. “Other” in base-centred monoclinic and triclinic cells indicate that an reciprocal interaxial angle which should be larger or smaller than 90° is very close to 90° and therefore the cell cannot be categorized into any case.

| Crystal system | Centring | Symbol | Topology | Count | Ratio |
|----------------|----------|--------|----------|-------|-------|
| Triclinic      | Primitive| $aP*$  | All      | 7646  | 13.2% |
|                |          |        | (All-obtuse) | 3831 | 6.6% |
|                |          |        | (All-acute) | 3797 | 6.5% |
|                |          |        | (Other) | 18 | 0.0% |
| Monoclinic     | Primitive| $mP*$  | All      | 8858  | 15.3% |
|                | Base-centred| $mS*$ | All      | 6919  | 11.9% |
|                |          |        | $b < a \sin \beta$ TO | 4973 | 8.6% |
|                |          |        | $b > a \sin \beta$ ED | 1288 | 2.2% |
|                |          |        | $b > a \sin \beta$ TO | 641 | 1.1% |
|                |          |        | Other | 17 | 0.0% |
| Orthorhombic   | Primitive| $oP$   | All      | 7572  | 13.0% |
|                | Base-centred| $oS*$ | All      | 2731  | 4.7% |
|                | Face-centred| $oF*$ | All      | 476   | 0.8% |
|                |          |        | ED | 338 | 0.6% |
|                |          |        | TO | 138 | 0.2% |
|                | Body-centred| $oI*$ | All      | 1080  | 1.9% |
| Tetragonal     | Primitive| $tP$   | All      | 2696  | 4.6% |
|                | Body-centred| $tI*$ | All      | 3544  | 6.1% |
|                |          |        | ED | 826 | 1.4% |
|                |          |        | TO | 2718 | 4.7% |
| Hexagonal      | Primitive| $hP$   | All      | 5496  | 9.5% |
| Rhombohedral   | Primitive| $hR*$  | All      | 3435  | 5.9% |
|                |          |        | TO | 2861 | 4.9% |
|                |          |        | RD | 574 | 1.0% |
| Cubic          | Primitive| $cP$   | All      | 2096  | 3.6% |
|                | Face-centred| $cF$ | All      | 4775  | 8.2% |
|                | Body-centred| $cI$ | All      | 731   | 1.3% |
Table 13: List of symmorphic space group types with inversion symmetry. Brackets indicate the space group number.

| Crystal system | Centring      | Symbol | Space group type |
|----------------|---------------|--------|------------------|
| Triclinic      | Primitive     | aP     | P1 (2)           |
| Monoclinic     | Primitive     | mP     | P2/m (10)        |
|                | Base-centred  | mS     | C2/m (12)        |
| Orthorhombic   | Primitive     | oP     | Pmmn (47)        |
|                | Base-centred  | oS     | Cmmm (65)        |
|                | Body-centred  | oI     | Immm (71)        |
|                | Face-centred  | oF     | Fmmn (69)        |
|                |               |        | Tetragonal       |
|                | Primitive     | tP     | P4/m (83), P4/mmm (123) |
|                | Body-centred  | tI     | I4/m (87), I4/mmm (139) |
|                |               |        | Hexagonal        |
|                | Primitive     | hP     | P3 (147), P31m (162), P3m1 (164), P6/m (175), P6/mmm (191) |
|                |               |        | Rhombohedral     |
|                | *             | hR     | R3 (148), R3m (166) |
|                | Primitive     | cP     | Pm3 (200), Pm3m (221) |
|                | Body-centred  | cI     | Im3 (204), Im3m (229) |
|                | Face-centred  | cF     | Fm3 (202), Fm3m (225) |

* Primitive or triple hexagonal.