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A groupoid and graph-theoretical analysis of the biopyribole-palysepiole series

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Abstract: The modular analysis of the biopyriboles-palysepioles polysomatic series recently presented by Nespolo and Bouznari (2017) is extended to take into account the local symmetry of each module and the partial operations mapping pairs of modules, to build the corresponding space groupoids. We show that the presence of pseudo-partial mirror in sepiolite and jimthompsonite leads to 40 (pseudo)-isometries, of which eight are total operations appearing in the space groups of the two structures. Chesterite can be described as a contracted twin in which a transmutation operation maps a portion of the larger module (Z_8) onto the smaller module (Z_5). The graph-theoretical analysis of these minerals confirms the results obtained by the application of the groupoid theory.

Key-words: biopyriboles; contracted twin; graph-theory; labelled quotient graphs; modularity; modular crystal structures; palysepioles; pseudo-symmetry; tropochemical cell-twinning; space groupoids.

1 Introduction

In our recent article (Nespolo and Bouznari, 2017) we have shown that the minerals forming the polysomatic series of biopyriboles (pyroxenes, micas, amphiboles, jimthompsonite, chesterite) and of palysepioles (palygorskite, sepiolite, kalifersite) can all be described in the framework of the tropochemical-cell twinning mechanism (Takéuchi, 1997) as obtained from a single prototype, the phyllosilicates. By extracting rods of various width R_n , where n is the number of octahedra along the **b** direction, and stacking these rods through different structure-building operations, we obtain the skeleton of all the minerals in the two series, to be completed by additional components (atoms or water molecules) at the boundary between rods. We have emphasized the close structural similarity of the various structures by expressing the fractional atomic coordinates of a Z_n module (the zero-periodic module corresponding to the portion of the R_n rod contained in a single unit-cell) of a phyllosilicate in the axial setting of the other minerals containing the same type of Z_n module. The results are extremely close to the experimental fractional atomic coordinates of the respective minerals, even despite differences in the atomic species occupying corresponding coordination polyhedra. In order to compare the fractional atomic coordinates of the different minerals in a common axial setting, we had to choose a non-conventional space group setting for some of the structures, like $A2/m$ instead of $C2/m$ for phlogopite or $I2/m$ instead of $C2/m$ for tremolite. In this article, we analyse the (pseudo)-symmetry of each mineral separately, without the need to change its

41 setting. We refer the reader to Nespolo and Bouznari (2017) for a general introduction to the
 42 biopyribole-palysepiole series, with an extensive literature survey that we do not repeat here for the
 43 sake of brevity.

44 We consider the operations mapping the various modules to build the corresponding space
 45 groupoids (Brandt, 1927) which describe their full symmetry. The procedure has been presented in
 46 our article on pyroxenes (Nespolo and Aroyo, 2016); we refer the reader to that article for details.
 47 Nevertheless, because the subject is probably less familiar to many readers, we summarize below
 48 the general guidelines.

49 The full symmetry of a modular structure is composed of three types of operation:

- 50 1. *local operations*: symmetry operations of the module, which act in the subspace spanned by the
 51 module itself;
- 52 2. *partial operations*: operations mapping different modules; a given partial operation is in general
 53 defined only for the pair of modules to which it applies;
- 54 3. *total (global) operations*: ordinary space-group operations valid in the whole space where the
 55 structure exists.

56 The set of local operations forms a subperiodic group (point, rod, or layer group for a 0-, 1- and
 57 2-periodic object), called the *kernel* of the module. A structure composed by n identical modules is
 58 characterized by n kernels, isomorphic to each other, differing for their orientation and/or position
 59 in space. In the following, we will denote the modules by a capital letter and the corresponding
 60 kernel will bear that letter as a subscript: K_X is the kernel of module X , where $X = A, B, C, \dots$ and so
 61 on.

62 A partial operation mapping two different modules will be noted as h_i , where i is a sequential
 63 number. The target module is constant, let us say A , whereas the source module varies with i . For
 64 example, h_1 maps B to A , h_2 maps C to A , and so on (h_0 is simply the identity, *i.e.* a local operation
 65 of A). The product of two partial operations is not, in general, a mapping of two existing modules,
 66 consistent with the fact that the partial operations of a groupoid do not obey the closure property of
 67 a group. On the other hand, the products $h_i^{-1}h_j$ and $h_j^{-1}h_i$ do map existing modules. For example, h_1^{-1}
 68 maps A to B and h_2^{-1} maps A to C , so that $h_1^{-1}h_2$ maps C to B via A ($C \rightarrow A \rightarrow B$) and $h_2^{-1}h_1$ maps B
 69 to C via A ($B \rightarrow A \rightarrow C$).

70 The product of a local operation and a partial operation is again a partial operation that maps the
 71 same pair of modules for a different but equivalent configuration of the target module A . For
 72 example, the product $K_A h_1$ is the set of all partial operations mappings B to A . By making this result
 73 general, the product $K_A h_i$, where $i = [1, n-1]$, n being the number of modules, is the set of all partial
 74 operations mapping *any* module $X \neq A$ to A ; it does not form a group but a set called the *hull* of A ,
 75 H_A . By adjoining the kernel and the hull of a module A one obtains what Loewy (1927) has called
 76 *Mischgruppe* of that module, a term which has been translated as *hybrid group* (Sadanaga, personal
 77 communication) or *compound group* (Brown, 1987), although it is not a group but a set of
 78 operations:

$$79 \quad M_A = K_A \cup H_A = K_A \cup_i K_A h_i$$

80 We have seen that $h_2^{-1}h_1$ is a partial operation mapping B to C via A and that $K_A h_1$ is the set of all
 81 the partial operations mapping B to A . Then, $h_2^{-1}K_A h_1$ is the set of *all* the partial operations mapping
 82 B to C via A . By making this result general, $h_j^{-1}K_A h_i$ is the set of *all* the partial operations mapping
 83 two different modules via A . If now we take $j = i$, the set becomes $h_i^{-1}K_A h_i$ and contains all the

84 operations mapping a module $X \neq A$ to itself via A . Because the modules are identical but
 85 differently oriented/located in space, $h_i^{-1}K_A h_i$ is the set of the local operations of X , *i.e.* the kernel of
 86 X . Indeed, $h_i^{-1}K_A h_i$ is the conjugation of K_A via h_i , and conjugation is a similarity transformation.
 87 Finally, by applying the partial operation $h_j^{-1} (A \rightarrow X)$ to the hybrid group of A , we obtain:

$$88 \quad h_j^{-1}M_A = h_j^{-1}K_A \cup h_j^{-1}H_A = h_j^{-1}K_A \cup_i h_j^{-1}K_A h_i = h_j^{-1}K_A h_j \cup_{i \neq j} h_j^{-1}K_A h_i = K_X \cup_{i \neq j} h_j^{-1}K_A h_i$$

89 which is the set of all the local operations (*i.e.* the kernel) of X and of the partial operations
 90 mapping any module but X to X (*i.e.* the hull of X). In other words, $h_j^{-1}M_A$ is simply M_X , the hybrid
 91 group of module X . The complete set of all the mappings obtained by making not only i but also j a
 92 running index gives the space groupoid D of the structure:

$$93 \quad D = \cup_{ij} h_j^{-1}K_A h_i$$

94 where the indices i and j run from 0 to $n-1$; h_0 is the identity operation. The structure of the groupoid
 95 can be shown in a tabular form:

$$\begin{array}{l|cccccccc} M_A = & K_A & \cup & K_A h_1 & \cup & K_A h_{i2} & \cup & \cdots & \cup & K_A h_p & \cup & \cdots & \cup & K_A h_n \\ M_B = & h_1^{-1}K_A & & K_B & \cup & h_1^{-1}K_A h_2 & \cup & \cdots & \cup & h_1^{-1}K_A h_p & \cup & \cdots & \cup & h_1^{-1}K_A h_n \\ M_C = & h_2^{-1}K_A & \cup & h_2^{-1}K_A h_1 & & K_C & \cup & \cdots & \cup & h_2^{-1}K_A h_p & \cup & \cdots & \cup & h_2^{-1}K_A h_n \\ \dots & \dots & & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ M_Z = & h_n^{-1}K_A & \cup & h_n^{-1}K_A h_1 & \cup & h_n^{-1}K_A h_2 & \cup & \cdots & \cup & h_n^{-1}K_A h_p & \cup & \cdots & \cup & K_Z \end{array}$$

96 The operations in each hybrid group map the various modules to one and the same target
 97 module. A subset of these operations may however occur in more than one hybrid group, *i.e.* map
 98 some of the modules to more than one target module. If this occurs for *all* target modules, than the
 99 corresponding operations become total (global) operations of the structure. This is true at least for
 100 the identity operation of each module, which becomes the only identity operation of the whole
 101 structure. For a structure composed by n identical modules, the groupoid is composed by n hybrid
 102 groups; each hybrid group is composed by one kernel and $n-1$ hulls; the groupoid is then composed
 103 by n^2 blocks. If the kernel is composed by m local operations, than the groupoid contains mn^2
 104 operations, in general not all distinct, distributed in n^2 blocks.

105 In the following, we present the groupoid analysis of the minerals in the biopyribole-palysepiole
 106 series¹ and show how to obtain their space-group operations from the set of local and partial
 107 operations. Partial operations may be *pseudo-isometries*, *i.e.* operations *approximately* mapping two
 108 modules: we do consider these operations in the groupoid structure, because of the important role of
 109 pseudo-symmetry in structural science (phase transitions, twinning, etc.). This corresponds to
 110 implicitly perform a small idealization of the structure, under which the pseudo-partial operation
 111 can be treated as truly partial operations.

112 The case of pyroxenes has already been analysed by Nespolo and Aroyo (2016) and reinterpreted
 113 in terms of labelled quotient graphs by Eon (2017): we refer the reader to that article for details. The
 114 other minerals of the biopyriboles-palysepioles series are analysed below. Before approaching that

5 1 The structural data used here are the same used also in Nespolo and Bouznari (2017); the references are
 6 quoted in that article.

analysis, however, we need to review briefly some fundamental crystallographic definitions and symbols the reader may not necessarily be familiar with.

2 Elements, operations and symbols

A *symmetry operation* is an isometry (or congruence), *i.e.* a distance-preserving mapping (or transformation) that relates equivalent orientations/positions of an object. Symmetry operations from which the screw or glide component – if any – is removed leave invariant a subspace: a point, a line or a plane. This subspace is called the *geometric element* of the symmetry operation. In a space group, an infinite number of symmetry operations share the same line or plane; they differ for a lattice translation. The set of symmetry operations sharing the same geometric element is called the *element set*. Among the operations of the element set, the one characterised by the shortest positive screw (for rotations) or glide (for reflections) component is called the *defining operation*, because it is used to define the *symmetry element* (de Wolff *et al.* 1989, 1992; Flack *et al.* 2000). In the following analysis, we are going to obtain some operations of the element set beyond the defining operation. It is therefore important that the reader understands the concept and the corresponding symbols used.

The Hermann-Mauguin symbol of glide reflections and screw rotations are $g(p,q,r)_{x,y,z}$ and $n(p,q,r)_{x,y,z}$ respectively, where g stands for glide, n is the order of the rotation ($2\pi/n$), p,q,r are the components of the glide or screw vector and x,y,z are the coordinates of the geometric element. In case of (glide) reflections, special symbols are used for both the symmetry operation and the symmetry elements when p,q,r take values smaller than unity: $g(0,0,0) = m$; $g(\frac{1}{2},0,0) = a$; $g(0,\frac{1}{2},0) = b$; $g(0,0,\frac{1}{2}) = c$; when p,q,r correspond to a half-diagonal or a quarter-diagonal, special symbols n and d are used respectively². The element set is composed by infinite number of (glide) reflections, whose glide component differ by a lattice translation; the one with the shortest positive (possibly zero) translation is the defining operation of the symmetry element. For example, an a -glide plane has as element set the operations $g(\pm\frac{1}{2},0,0)$, $g(\pm\frac{1}{2},\pm 1,0)$, $g(\pm\frac{1}{2},0,\pm 1)$, $g(\pm\frac{1}{2},\pm 1,\pm 1)$, $g(\pm\frac{3}{2},0,0)$, $g(\pm\frac{3}{2},\pm 1,0)$ and so on; of these, $g(\frac{1}{2},0,0) = a$ is the defining operation, which gives the name and the symbol to the symmetry element.

For screw rotations, a special symbol is normally used only for symmetry elements. If p is the screw component (then q and r are related to the location of the geometric element with respect to the origin), the defining operation is the one with the largest n and the smallest positive p ($0 \leq p < n$); the symmetry element is then indicated as n_p ³. For example, among the operations $n(p,0,0)$ sharing the line $x,0,\frac{1}{4}$, there are n possible operations, corresponding to values of p restricted from 0 to $n-1$; if $p = 0$, then the defining operation is a pure rotation and the symmetry element is a rotation axis, although it is shared also by an infinite number of screw rotations $n(n,0,0)$, $n(2n,0,0)$, $n(3n,0,0)$ and so on. If $p > 0$, then the defining operation is a screw rotation, there is no pure rotation in the element set and the symmetry element is therefore called a screw axis. For the sake of brevity, when p takes an integer value, the same shortened notation used for symmetry elements can be used also for operations (Nespolo, 2017). For example, $2_2 x,0,\frac{1}{4}$ and $2_3 x,0,\frac{1}{4}$ is a handy notation for $2(1,0,0)x,0,\frac{1}{4}$ and $2(3/2,0,0)x,0,\frac{1}{4}$. This notation may look unusual, but symbols like 2_r with r not restricted

2 The values of p,q,r that correspond to a half- or quarter-diagonal depend on how the geometric element is oriented with respect to the basis vectors.

3 We need to specify “the largest n ” because rotations of different order may share the same geometric element. For example, about the same line (geometric element) we may have operations 4, $4^2 = 2$, 4^3 and $4^4 = 1$. The largest n , in this example $n = 4$, corresponds to the defining operation and the symmetry element is a fourfold rotation axis.

to 1, are extensively used in the OD theory (Dornberger-Schiff and Grell-Niemann, 1961). In case of partial operations, p is not limited to integer values. For example, a two-fold rotation followed by a $\frac{1}{4}$ translation is not a space-group operation but is a possible partial operation, noted $2(\frac{1}{4}, 0, 0)$ $x, 0, \frac{1}{4}$, or synthetically $2_{\frac{1}{2}} x, 0, \frac{1}{4}$. Some of the partial operations we are going to obtain in the following analysis belong to the element set of a symmetry element but are not the defining operations: the synthetic notation 2_r is used in these cases. When p takes irrational values, however, the shortened notation is no longer advantageous and will not be used.

3 Topological analysis based on the Labelled Quotient Graph (LQG)

The so-called *vector method* uses graph-theoretical techniques to represent and analyse the combinatorial topology of crystal structures. The method has been extensively described in two recent papers of one of the authors (Eon, 2016; 2017) but goes back to the work of Chung *et al.* (1984). As a rough guide to the reader, this section summarizes the main features of the method needed to follow our interpretation of modular structures. The case of diopside, with the characterization of the R_2 rod, will be examined as an illustration of the abstract concepts. In the next sections we will focus on the description of phlogopite, palygorskite, sepiolite and jimthompsonite using the R_2 rod. Only the main components of each structure are taken into account.

A crystal structure can be seen as a net of chemical bonds that is commonly summarized in the form of a graph, where atoms are symbolized by a vertex (or a point) and a bond between two atoms is symbolized by an edge (or a line) joining the corresponding vertices. This graph is called the **bond graph** of the structure. The quotient graph is essentially a restriction of the bond graph of the structure to the unit cell, but it also encodes the bonds to neighbouring unit cells. Whereas the conventional unit cell is best suited to describe the symmetry of the structure, a primitive unit cell is preferable (but not mandatory) to obtain a quotient graph, because the conventional unit cell would provide an extended version of it. **Quotient graphs** built from a primitive unit cell represent the network of interatomic bonds of the set of atoms obtained by applying to each atom in the unit cell the full set of translations of the space group, *i.e.* the $P1$ translationengleiche subgroup (t -subgroup) of the space group G . Any atom in the asymmetric unit generates, under the action of G , a crystallographic orbit (Engel *et al.*, 1984). When the $P1$ t -subgroup is considered instead of the full group G , this orbit is split into a set of suborbits, which in graph theory are called *point-lattices* (Chung *et al.*, 1984). The quotient graph is the graph of chemical bonds in the $P1$ t -subgroup expressed in the primitive unit cell. It provides the necessary information about the existence of bonds between atoms belonging to the different point-lattices but does not specify which atoms in these point-lattices are bonded. This information is retrieved from the **labelled quotient graph (LQG)**, which includes also the information about translationally equivalent atoms,

Given a periodic structure and a reference unit cell, the respective labelled quotient graph can be constructed in two steps. Initially, every atom in the unit cell is represented by an isolated vertex (a point) V_i ($i=1, n$) and all bonds between atoms in the unit cell are represented by an edge (a line segment or an arc) joining the representative vertices, thus giving a finite graph G associated to the combinatorial topology of the unit cell. In a 3-dimensional framework, some atoms in the unit cell must obviously be linked to atoms in neighbouring cells. Suppose that atom V_i in the reference cell, is bonded to atom V'_j in a neighbouring unit cell such that the translation $\{1 \mid pqr\}$ (in the Seitz notation: Glazer *et al.*, 2014) maps atom V_j in the reference unit cell to this atom V'_j . Then we add an edge $V_i V_j$ to our graph G ; this edge is oriented from V_i to V_j and carries the triple label pqr that, in topological graph theory, is called the **voltage** on the edge $V_i V_j$. If the orientation of the edge is

199 inverted to $V_j V_i$ the voltage must be changed to the opposite triple \overline{pqr} , in keeping with the previous
200 definition. The final result is the *labelled quotient graph* G : note that different choices of unit cell
201 and basis vectors for the translation group generally provide different - but equivalent - labelled
202 quotient graphs. The keys for labelled quotient graphs analysed in this work were extracted from the
203 CIF files by using the program package TOPOS (Blatov *et al.*, 2014). The LQG of diopside is shown
204 in Figure 1(a) with relation to a primitive unit cell. For the sake of clarity, the different voltages
205 have been coded as different colours with the same colour code in all shown LQGs.

206 The sum of all voltages along a cycle of the LQG, where all edges have been given the same
207 orientation as the cycle, is called the *net voltage over the cycle*. Any cycle of the LQG can be
208 interpreted as the projection of a path between two translationally equivalent atoms in the crystal
209 structure; the respective net voltage provides the vector of the translation mapping the two
210 extremities of this path. For instance, the two Si_2O_2 4-cycles at the inferior and superior part of the
211 LQG of diopside in Figure 1(a) have net voltage 001; these cycles are the projections on the LQG
212 of the two infinite SiO tetrahedral chains of diopside running along [001].

213 Building blocks in complex crystal structures also have their counterpart in the respective
214 labelled quotient graph. They should appear as labelled subgraphs of the LQG with *rank* equal to
215 the periodicity of the building block, where the *rank* of a labelled subgraph is defined as the rank
216 (the dimension) of the subgroup of \mathbb{Z}^3 (the additive group of triples of integers) generated by the net
217 voltages over all cycles in the subgraph. The edges linking two vertices that belong to different
218 representative subgraphs indicate the linkage type between building blocks. A simplified LQG can
219 be constructed by taking the representative subgraphs as new vertices, thus collapsing every edge
220 inside these subgraphs. In other words, the whole blocks are considered as vertices of the structure
221 instead of their constitutive atoms; the topology associated to block linkage is represented by the
222 simplified LQG. Evidencing building blocks generally requires some manipulations of the LQG
223 such as vertex duplication and edge relabelling. Figure 1(b) shows a modified diopside's LQG that
224 puts into evidence the R_2 rod (the I-beam of pyroxenes). Vertices with the same colour contour
225 belong to, and make the connection between, two adjacent, translationally equivalent rods. From
226 this LQG, one can form i) the LQG drawn in Figure 2(a), representing the topology of an isolated
227 R_2 rod, and ii) the simplified LQG drawn in Figure 2(b), evidencing the linking mode between the
228 rods in the diopside structure. Note first that the LQG of the rod has rank 1: the rod is one-periodic
229 along [001]. The simplified LQG has rank 2 and shows that the linkage of R_2 rods corresponds to a
230 **sql** (square lattice) topology in the (001) plane. Double edges indicate a double linkage between
231 pairs of rods in each direction.

232 Symmetry operations in the crystal structure are associated to automorphisms of the quotient
233 graph (*i.e.* permutations of vertices and edges which are consistent with incidence relationships).
234 Such automorphisms must also be consistent with net voltages over cycles, *i.e.* any closed walk
235 with zero net voltage must map a closed walk with zero net voltage. Conversely, any automorphism
236 of the LQG with such properties represents a possible symmetry of the crystal structure. If it does
237 not correspond to an actual symmetry operation, it can be interpreted as a *pseudo-symmetry*.
238 Dashed blue and purple lines in Figure 1(b) act as reflection lines for the drawing: they determine
239 two mirror-like automorphisms (symmetry operations) of the LQG of the R_2 rod. These
240 automorphisms will be called *exchanges across the line* in order to avoid any anticipation
241 concerning the nature of the derived symmetry operation of the crystal structure. A detailed analysis
242 of the cycles (and net voltage over cycles) permutation shows that they correspond to the 2-fold
243 rotation (associated to the exchange across the blue line) and the c glide reflection (associated to the
244 exchange across the purple line). These observations lead, as it could be expected, to the known

245 $\not\sim_a 12/c1$ rod group.

246 4 Prototype structure: phyllosilicates

247 The prototype structure of phyllosilicates is obtained by stacking a layer L parallel to itself along
 248 the \mathbf{c} direction. The layer itself is obtained by repeating a rod R_n along the \mathbf{b} direction and can be
 249 interpreted as $L = R_\infty$ (Nespolo and Bouznari, 2017). The operations building L from R_n depend on
 250 the choice of the rod width n . One can choose a R_3 rod and an a -glide at $x, \frac{1}{4}, z$, or a R_4 rod and a C
 251 ($\mathbf{a}/2 + \mathbf{b}/2$) translation. The result is obviously the same. We illustrate the procedure in detail for the
 252 case of R_3 .

253 Figure 3 shows the three Z_3 modules A, B and C, which are the zero-periodic counterpart of the
 254 R_3 rods, as well the partial operations h_1 mapping B to A, *i.e.* an a -glide at $x, \frac{1}{4}, z$, and h_2 mapping C
 255 to A, *i.e.* $t(0,0,1)$ translation. The product $h_1^{-1}h_2$ maps C to B via A and is a glide reflection $g(\frac{1}{2},0,1)$
 256 about the plane at $x, \frac{1}{4}, z$. This is one of the infinite operations building the element set that share the
 257 same geometric element; the corresponding defining operation is $g(\frac{1}{2},0,0) = a$, *i.e.* the operation
 258 mapping B to A. The inverse operation $h_2^{-1}h_1$ is $g(\frac{1}{2},0,\bar{1})$ and maps B to C via A.

259 The whole set of operations mapping $A, B, C \leftrightarrow A, B, C$ in all possible combinations contains 4
 260 (operations of the kernel) $\times 3^2 = 36$ operations. These are the operations of the groupoid but are not
 261 all distinct. The rod symmetry of the R_3 rod is $\not\sim_a 12/m1$ (symbols of sub-periodic groups from
 262 Kopský and Litvin, 2010), and is the kernel of the module. The groupoid structure is then
 263 immediately obtained.

$$\begin{aligned} & \not\sim_a 12/m1 \quad \cup \quad \not\sim_a 12/m1 \ a_{x, \frac{1}{4}, z} \quad \cup \quad \not\sim_a 12/m1 \ t(0,0,1) \\ & a_{x, \frac{1}{4}, z}^{-1} \not\sim_a 12/m1 \quad \cup \quad a_{x, \frac{1}{4}, z}^{-1} \not\sim_a 12/m1 \ a_{x, \frac{1}{4}, z} \quad \cup \quad a_{x, \frac{1}{4}, z}^{-1} \not\sim_a 12/m1 \ t(0,0,1) \\ & t^{-1}(0,0,1) \not\sim_a 12/m1 \quad \cup \quad t^{-1}(0,0,1) \not\sim_a 12/m1 \ a_{x, \frac{1}{4}, z} \quad \cup \quad t^{-1}(0,0,1) \not\sim_a 12/m1 \ t(0,0,1) \end{aligned}$$

264 If in the top-left block (kernel of module A) we write out explicitly the symmetry operations of
 265 the kernel with translational component smaller than a full lattice translation, *i.e.* the defining
 266 operations of the symmetry elements plus the identity, the result is the following one.

$$\begin{aligned} M_A \quad & 1, 2 \ \frac{1}{2}, y, \frac{1}{2}; \bar{1} \ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}; m \ x, \frac{1}{2}, z \quad \cup \quad a \ x, \frac{1}{4}, z; \bar{1} \ \frac{1}{4}, \frac{1}{4}, \frac{1}{2}; 2_1 \ \frac{1}{4}, y, \frac{1}{2}; \quad \cup \quad t(0,0,1); 2 \ \frac{1}{2}, y, 0; \bar{1} \ \frac{1}{2}, \frac{1}{2}, 0; g(0,0,1) \\ & \quad \quad \quad t(\frac{1}{2}, \frac{1}{2}, 0) \quad \quad \quad x, \frac{1}{2}, z \\ M_B \quad & a_{x, \frac{1}{4}, z}^{-1}; \bar{1} \ \frac{1}{4}, \frac{1}{4}, \frac{1}{2}; 2_1 \ \frac{1}{4}, y, \frac{1}{2}; \quad \cup \quad 1; 2 \ 0, y, \frac{1}{2}; \bar{1} \ 0, 0, \frac{1}{2}; m \ x, 0, z \quad \cup \quad g(\frac{1}{2}, 0, 1) \ x, \frac{1}{4}, z; \bar{1} \ \frac{1}{4}, \frac{1}{4}, 0; 2_1 \ \frac{1}{4}, y, 0; \\ & \quad \quad \quad t(\frac{1}{2}, \frac{1}{2}, 0) \quad \quad \quad t(\frac{1}{2}, \frac{1}{2}, 1) \\ M_C \quad & t(0,0,\bar{1}); 2 \ \frac{1}{2}, y, 0; \bar{1} \ \frac{1}{2}, \frac{1}{2}, 0; \quad \cup \quad g(\frac{1}{2}, 0, \bar{1}) \ x, \frac{1}{4}, z; \bar{1} \ \frac{1}{4}, \frac{1}{4}, 0; 2_1 \ \frac{1}{4}, y, 0; \quad \cup \quad 1; 2 \ \frac{1}{2}, y, \bar{\frac{1}{2}}; \bar{1} \ \frac{1}{2}, \frac{1}{2}, \bar{\frac{1}{2}}; m \ x, \frac{1}{2}, z \\ & \quad \quad \quad g(0,0,\bar{1}) \ x, \frac{1}{2}, z \quad \quad \quad t(\frac{1}{2}, \frac{1}{2}, 1) \end{aligned}$$

267 If we consider the kernel and the first hull of M_A and M_B , *i.e.* the 2×2 block at the top-left of the
 268 groupoid, we obtain the layer group of the $c2/m11$, No. 18 in volume E of the *International Tables*
 269 *for Crystallography* (Kopský and Litvin, 2010), or $C12/m(1)$ in the OD notation (Dornberger-
 270 Schiff, 1959). Indeed, a full lattice translation along \mathbf{a} is contained in the rod symmetry and a full

lattice translation about **b** is obtained by applying twice the partial operation $2_1 \frac{1}{4}, y, \frac{1}{2}$. The operations that look different in the two hybrid groups are simply related by a unit translation in plane of the layer. For example, $2_{0,y,\frac{1}{2}}$ is obtained by combining $2_{\frac{1}{2},y,\frac{1}{2}}$ and a unit translation along **a**, $\bar{1}_{0,0,\frac{1}{2}}$ from $\bar{1}_{\frac{1}{2},\frac{1}{2},\frac{1}{2}}$ and a unit translation along **a+b**, $m_{x,0,z}$ from $m_{x,\frac{1}{2},z}$ and a unit translation along **b**. The operation $a^{-1}_{x,\frac{1}{4},z}$ in $h_1^{-1}K_A$ is $g(\frac{1}{2}, 0, 0)$. The *a*-glide planes at $x, \frac{3}{4}, z$ and at $x, \frac{1}{4}, z$ do not appear explicitly in this analysis because they are at the boundary of the pair of modules BA but are generated when combining the *a*-glide reflection at $x, \frac{1}{4}, z$ with a full translation along $\pm \mathbf{b}$. These are therefore global operations for the layer.

The operations in the second hull of the first and second hybrid groups, as well as those in the third hybrid group (M_C), map different layers along the stacking direction **c**, by a full translation, a glide reflection with a full translation (noted *g*), an inversion at $z = 0$ or a screw rotation about an axis at $z = 0$. They are again global operations, because they, or their translational equivalent, occur in all hybrid groups. In fact:

- $t(0,0,1)$ in M_A is equivalent to $t(\frac{1}{2}, \frac{1}{2}, 1)$ in M_B through the *C* translation of the layer group, and to $t(0,0,\bar{1})$ of M_C by $2\mathbf{c}$ translation;
- $2_{\frac{1}{2},y,0}$ occurs in both M_A and M_C is equivalent to $2_{0,y,\frac{1}{2}}$ in M_B by a translation $-\mathbf{a}+\mathbf{c}$;
- $\bar{1}_{\frac{1}{2},\frac{1}{2},0}$ occurs in both M_A and M_C is equivalent to $\bar{1}_{0,0,\frac{1}{2}}$ in M_B by a translation $\mathbf{a}+\mathbf{b}-\mathbf{c}$;
- $g(0,0,1)_{x,\frac{1}{2},z}$ in M_A is equivalent to $g(0,0,\bar{1})_{x,\frac{1}{2},z}$ in M_C through the $-2\mathbf{c}$ translation and to $g(\frac{1}{2}, 0, 1)_{x,\frac{1}{4},z}$ of M_B by a translation $-\mathbf{a}/2+\mathbf{b}/2$, *i.e.* the *C* translation of the layer group plus a $-\mathbf{a}$ translation of the rod.

These global operations, added to the layer group and the full lattice translations give as a result the $C12/m1$ space group of phlogopite. Therefore, in this case the groupoid simply degenerates to a group.

Figure 4(a) displays the LQG of phlogopite for the primitive cell defined by $\mathbf{a}' = \frac{1}{2}(\mathbf{a} - \mathbf{b})$, $\mathbf{b}' = \frac{1}{2}(\mathbf{a} + \mathbf{b})$, $\mathbf{c}' = \mathbf{c}$. The central cation in this graph was deleted and some oxygen atoms were split to give the LQG shown in Figure 4(b); apart from the presence of OH groups instead of terminal oxygen vertices, the resulting LQG shows clearly that phlogopite can be built from the R_2 rod of diopside. Whereas a 3-periodic structure is obtained in diopside by linking any rod to four neighbours in two independent directions, a 2-periodic structure is formed in phlogopite by linking each rod to two neighbours along a single direction. Moreover, linkages in diopside involve a double connection of rods between the tetrahedral chain of each rod and the octahedral chain of the other. Linkages in phlogopite occur through homogeneous connections: octahedral to octahedral and tetrahedral to tetrahedral chains. After the R_2 rods have been assembled according to the LQG given in Figure 4(b), the structure has to be stuffed by additional cations in octahedral coordination to yield the phlogopite structure.

To be emphasized that this analysis concerns the stacking of *rods* to build the one-layer polytype. Phyllosilicates, and in particular micas, occur in many different polytypes and the stacking of *layers* again is rationalized in terms of partial operations leading to groupoids. This is however outside the scope of the present article. Interested readers can refer to a review in Nespolo and Đurovič (2002).

5 Structures built on R_5 rods: amphiboles and palygorskite

The R_5 rods, whose rod symmetry (kernel) is $\not p_c 12/m1$, occur in amphiboles and in palygorskite. The partial operation is a *C*-centring translation in both cases; the unit cell having different dimensions, the resulting structure is different, but the symmetry (type of group) is the same. The groupoid is therefore composed by two hybrid groups, each containing a kernel and a hull.

$$\not\sim_c 12/m1 \quad \cup \quad \not\sim_c 12/m1 \, t(\frac{1}{2}, \frac{1}{2}, 0)$$

$$t(\frac{1}{2}, \frac{1}{2}, 0) \not\sim_c 12/m1 \quad \cup \quad t(\frac{1}{2}, \frac{1}{2}, 0) \not\sim_c 12/m1 \, t(\frac{1}{2}, \frac{1}{2}, 0)$$

and, by specifying the operations:

$$\begin{aligned} 1, 2 \, \frac{1}{2}, y, \frac{1}{2}, \bar{1} \, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, m \, x, \frac{1}{2}, z & \quad \cup \quad t(\frac{1}{2}, \frac{1}{2}, 0), 2_1 \, \frac{1}{4}, y, \frac{1}{2}, \bar{1} \, \frac{1}{4}, \frac{1}{4}, \frac{1}{2}, a \, x, \frac{1}{4}, z \\ t(\frac{1}{2}, \frac{1}{2}, 0), 2_{\bar{1}} \, \frac{1}{4}, y, \frac{1}{2}, \bar{1} \, \frac{1}{4}, \frac{1}{4}, \frac{1}{2}, a^{-1} \, x, \frac{1}{4}, z & \quad \cup \quad 1, 2 \, 0, y, \frac{1}{2}, \bar{1} \, 0, 0, \frac{1}{2}, m \, x, 0, z \end{aligned}$$

As in the case of R_3 , all the operations listed, or their translational equivalent, occur in both hybrid groups and are therefore global. Their set-theoretical union, results in the space-group type of the two minerals, which is $C2/m$ in both cases.

Figure 5 displays the LQG of palygorskite, already organized so as to put into evidence the structural role of the R_5 rod and its relation with the R_2 rod of diopside. Indeed, the left and right parts of the R_5 rod form two interlinked R_2 rods to which the central octahedral cation must be added to yield the full R_5 rod. The LQG presents two symmetry operations that can be seen as exchanges across the blue and purple dashed lines and can be associated respectively to the 2-fold rotation and the mirror reflection m of palygorskite. The first reflection leaves each rod invariant while the second one exchanges the two R_2 rods, thus corresponding to an operation of the kernel of the rods and a partial operation, respectively: they are of course global symmetry operations. Hence, the c -glide reflection of the ideal R_2 rod (belonging to the respective kernel) is missing in the symmetry group of this structure. It may be looked at as a *pseudo*-symmetry of the space-groupoid of palygorskite in the extended sense that it corresponds to a symmetry operation defined by the subgraph representing the rod.

6 Structures built on R_8 rods: sepiolite and jimthompsonite

As shown by Nespolo and Bouznari (2017), the Z_8 module, and thus the R_8 rod, can be almost exactly reconstructed by expanding the Z_5 module through the action of a pseudo-partial mirror, slicing the Z_8 module into a Z_5 part and Z_8-Z_5 part. This same relation occurs both along $+\mathbf{b}$ and along $-\mathbf{b}$ so that the R_8 rod can be ideally separated into three R_2 rods, below labelled as A (middle),

B (left) and C (right). The exact (A) and approximate (B, C) rod symmetry (kernel) is $\not\sim_c 12/c1$ and

$\not\sim_c 1c1$ respectively for sepiolite and jimthompsonite. The octahedral cations and oxygen atoms at the boundaries between the rods, *i.e.* approximately on the pseudo-partial mirrors, are the additional components necessary to obtain the R_8 rod from the stacking of R_2 rods. The unit cell of sepiolite contains two Z_8 modules and the unit cell of jimthompsonite four; these are related by one and three partial operations respectively. These, and the corresponding R_8 rods, are labelled sequentially from 1 to 2 and from 1 to 4 respectively; the same numbering scheme is applied to the R_2 components A, B and C. Concretely, the structure of the two title minerals can be obtained in two steps (Figures 6 and 7).

1. build the target R_8 rod by applying the partial operations to R_2 rod A1 to obtain B1 and C1: a partial mirror reflection at $x, 0.421, z$ (sepiolite) or at $x, 0.666065, z$ (jimthompsonite) mapping A1 to B1 and a second partial mirror reflection at $x, 0.579, z$ (sepiolite) or at $x, 0.833935, z$

(jimthompsonite), mapping A1 to C1; complete the R_8 rod with the additional atoms;
 2. build the structure of the two minerals by applying the mapping of different R_8 rods; this leads automatically to the mappings of (A_j, B_j, C_j) R_2 rods in the $j > 1$ R_8 rod to the corresponding (A_1, B_1, C_1) R_2 rods in target R_8 rod.

For sepiolite the operation in step 2 is an n -glide reflection at $\frac{1}{4}, y, z$, whereas for jimthompsonite, there are three operations, namely a b -glide reflection at $\frac{1}{4}, y, z$, an a -glide reflection at $x, y, \frac{1}{4}$, and an inversion at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The two groupoids are therefore composed by $6^2 = 36$ blocks for sepiolite and $12^2 = 144$ blocks for jimthompsonite. This means we have to derive $4 \times 36 = 144$ and $2 \times 144 = 288$ operations respectively, not all of which will turn out to be different; some of the operations obtained in this way will actually be global operations building the space group of the mineral.

The careful reader may remark a slight difference with respect to Nespolo and Bouznari (2017), concerning the position of the first pseudo-partial mirror in sepiolite (the one mapping B1 to A1), whose position was given as $x, 0.4151, z$ there whilst it is $x, 0.421, z$ here. In our previous article, the position of the pseudo-partial mirror was chosen on an octahedral cation, whereas here it is chosen so that the matrix representation of the global operations take a standard expression, with vector components equal to $0, \frac{1}{4}$ or $\frac{1}{2}$ (or integer multiples) of these. The slight difference comes evidently from the fact that these operations are *pseudo*-isometries.

Table 1 presents the groupoid structure of sepiolite. The 144 combinations $h_j^{-1} K_A h_i$ ($i, j = 0, 1, 2$, h_0 = identity), result in 40 operations, listed with a sequence number in Table 2. Finally, Table 3 gives the operations in each kernel and hull by the sequential number defined in Table 2. To be noted that some of the operations obtained in this way are *not* the defining operations of the corresponding symmetry element. For example, the operations No. 33, $2_2 \frac{1}{4}, \frac{1}{4}, z$, which is a shorthand notation for $2 (0, 0, 1) \frac{1}{4}, \frac{1}{4}, z$, is a screw rotation about the direction $\frac{1}{4}, \frac{1}{4}, z$ with screw component corresponding to a full translation along c . The defining operation is $2 \frac{1}{4}, \frac{1}{4}, z$ and does also occur when $2_2 \frac{1}{4}, \frac{1}{4}, z$ is combined with a lattice translation along $-c$, which belongs to the rod symmetry.

The operations that occur in each hybrid group M_X , which are therefore global operations, are shown in bold in Table 3. As expected, these eight operations belong to $Pbcn$, *i.e.* the space-group type of sepiolite. The remaining 32 operations, *i.e.* 80% of the operations relating R_2 modules, are partial or local and do not appear in the space group of the mineral.

Figure 8 displays the LQG of sepiolite evidencing the structural role of two R_8 rods and their relations with the R_2 rod of diopside. Indeed, one can look at each R_8 rod as built from three interlinked R_2 rods stuffed by two octahedral cations at the third and sixth position, starting from the left or from the right of the figure. Alternatively, one can build the R_8 rod by interlinking an R_5 rod with an R_2 rod and stuffing it with an additional octahedral cation in the third ($R_2 + R_5$), or equivalently in the sixth position ($R_5 + R_2$). Figure 9 shows the simplified LQG of sepiolite representing the linkage of the R_8 rods. This LQG is that of the **sql** lattice in a body-centred cell, which indicates that the two R_8 rods are related by a translation in the (001) plane. This centring translation is associated to the permutation $\phi_1 = (a, d)(b, c)$, also exchanging the two rods M1 and M2, which leaves invariant every net voltage over the cycles of the simplified LQG. However, the permutation induced by ϕ_1 in the full LQG of sepiolite realizes an inversion of the [001] direction. This permutation must therefore be associated to the glide reflection $n (\frac{1}{2}, \frac{1}{2}, 0)$. Partial operations between the three R_2 rods forming the R_8 rod can be deduced from those of palygorskite using the ($R_2 + R_5$) or ($R_5 + R_2$) construction. Indeed, the central R_2 rod A of R_8 belongs to the R_5 rod in both interpretations, ($R_2 + R_5$) or ($R_5 + R_2$), and so it can be obtained from any of the other two R_2 rods, B or C, by a partial mirror reflection with mirror plane going through the added octahedral cations. The orientation of the mirror plane can be obtained from a complete analysis of the other two generators of the symmetry group of sepiolite using the two LQGs. It can be seen that the

permutations $\phi_2 = (a,c)(b,d)$ and $\phi_3 = (a,b)(c,d)$, both fixing the two rods M1 and M2, of the simplified LQG are associated to a 2-fold rotation 2_{010} and a c -glide reflection, respectively. This shows that the octahedral chain has its *flat* face parallel to the (001) plane so that the mirrors mapping the A rod to rods B and C are orthogonal to the 010 axis. We also note that rod A, located at the intersection of the two possible R_5 rods is invariant by the c -glide reflection. This rod has thus the full $\sqrt{2}12/c1$ symmetry of the diopside R_2 rod.

Tables 4-6 present the corresponding results for jimthompsonite. The 288 combinations $h_j^{-1}K_A h_i$ ($i,j = 0,1,2$, $h_0 = \text{identity}$), result again in 40 operations. Analogously to the case of sepiolite, an unusual symbol is used for operation No. 21, namely $2_3 0,y,\frac{1}{4}$. This is a screw rotation with screw component $3b/2$ along the $0,y,\frac{1}{4}$ direction. It occurs in all the 12 hybrid groups and is therefore a global operation. The corresponding defining operation of the symmetry element is $2_1 0,y,\frac{1}{4}$, which is obtained from $2_3 0,y,\frac{1}{4}$ by combination with a $-b$ lattice translation.

The operations that occur in each hybrid group M_x , which are therefore global operations, are shown in bold in Table 6. These eight operations belong to $Pbca$, the space-group type of jimthompsonite. As in the case of sepiolite, the remaining 32 operations (80%) are partial or local and do not appear in the space group of the mineral.

Due to the large size of its unit cell, the LQG of jimthompsonite was divided into two figures, each evidencing the presence of two distinct rods R_8 : Figure 10 represents the two rods M1 and M2 while Figure 11 shows the two rods M3 and M4. In this structure, rods R_8 make double, heterogeneous linkages joining the octahedral chain of one rod to the tetrahedral chain of the other rod by sharing pairs of oxygen atoms. Shared pairs of oxygen atoms are indicated by identical letters in the LQG. For example, the two oxygen atoms on each side of letter “a” in rod M1 (Figure 10) should be identified with the two oxygen atoms on each side of letter “a” in rod M4 (Figure 11), each oxygen atom joining a tetrahedral chain to an octahedral one. The simplified LQG, given in Figure 12, represents the complete linkage of these rods throughout the structure; each edge in this graph carries, along with the respective voltage, the letter indicating the corresponding shared oxygen pair. This LQG can be associated to a 2-periodic topology in the (001) plane, which we identify as follows. We first observe that the graph presents an automorphism of order 4, described by the vertex permutation (M1,M2,M3,M4) and by the edge permutation $\phi = (a,d',b,c')(a',d,b',c)$, which leaves the two voltages 100 and 010 invariant and does not possess fixed vertices or edges. Hence, ϕ can be associated to a translation of the 2-periodic net. Because the quotient of the simplified LQG by ϕ , has a single vertex and two edges (loops), it describes a square lattice net (**sql**), but with quadruple unit cell. The basis vectors of the primitive cell of this lattice are given by $\frac{1}{4} \frac{1}{2} 0$ and $\frac{1}{4} -\frac{1}{2} 0$ with reference to the basis vectors of the unit cell of jimthompsonite. However, the automorphism induced by ϕ in the full LQG of jimthompsonite does not act consistently on the net voltages over cycles along 001, so that it cannot correspond to an isometry in Euclidean space. The net effect of this automorphism in this direction is reported by the signs (+, -, -, +) carried by the vertices (M1, M2, M3, M4) of the simplified LQG: As ϕ maps rod M1 to rod M2, it inverts the direction [001] (+ to -), but at the same time, rod M2 is mapped to rod M3 with preservation of the direction [001] (- to -), and so on. The symmetry operation induced by ϕ should therefore be interpreted as an element of the space-groupoid of jimthompsonite. It appears that the operation associated to ϕ^2 can be associated to the translation $t(\frac{1}{2},1,0)$ in the (001) plane and systematically inverts the third direction (+ to -): this operation is thus related to the a -glide reflection. Reconstruction of the whole structure from an idealized R_8 rod is possible by using the information contained in the simplified LQG. First, rods are linked according to a square lattice net in the (001)

plane. Then the symmetry groupoid operation ϕ is applied to get the correct inversion sequence of the rods (following direction [001]) along the main axes of the square lattice net.

7 Chesterite as a contracted twin of jimthompsonite

Chesterite is composed by an alternation along the **b** axis of R_8 and R_5 rods. The unit cell contains four Z_8 and four Z_5 modules; pairs of modules of the same type are related by an A translation, *i.e.* $\mathbf{b}/2 + \mathbf{c}/2$, an a -glide reflection about the plane $x, y, 1/2$, and their combination, *i.e.* an n -glide about the plane $x, y, 1/4$. The kernel is $\mu_c 1c1$ for Z_8 and $\mu_c 1m1$ for Z_5 . The two structure-building operations applied to the two modules produce the space group of chesterite, of type $A2_1ma$; the groupoid degenerates to a group, as in the case of phlogopite, palygorskite and tremolite.

We already know that the Z_8 module can be obtained from the Z_5 module by a pseudo-partial mirror. The coexistence of these two modules makes the structure of chesterite fit Takéuchi's definition of *contracted twin* (Takéuchi, 1997), where the term “twin” has to be understood as “cell-twin”, *i.e.* a modular structure. The concept of contracted twin is schematically presented in Figure 13. A cell-twin is obtained by a polysynthetic repetition of a unit, let it be A , through a partial operation mapping A to A' . A and A' are identical but differently oriented and positioned in the unit cell; the structure is composed by the sequence AA' . Let us indicate as B the unshaded portion of A in Figure 13. A pair of modules B and B' is related by the same partial operation that related the pair A and A' . Because A and B are structurally different, there is no real operation mapping them; however, the same operation mapping A and A' , or B and B' , can be applied to the B part of A to obtain B' ; in other words, from A we obtained A' and contract the result by removing the part of A' which is not contained in B' . In this way, the AB' module is described as a contracted twin of A .

If we adopt this viewpoint, the structure of chesterite (Figure 14) can be schematically idealized as in Figure 15, where A and B represent Z_8 and Z_5 modules respectively. The partial operations mapping pairs of modules are the following.

- $h_1: A2 \rightarrow A1$ and $B2 \rightarrow B1$: A -centring translation: $t(0, 1/2, 1/2)$
- $h_2: A3 \rightarrow A1$ and $B3 \rightarrow B1$: $a\ xy^{1/2}$
- $h_3: A4 \rightarrow A1$ and $B4 \rightarrow B1$: $n\ xy^{1/4}$
- $T_1: A1 \rightarrow B1$: $\bar{1}\ 1/4^2/5^{1/4}$
- $T_2: A2 \rightarrow B1$: $2_1\ 1/4^3/5^z$
- $T_3: A3 \rightarrow B1$: $\bar{1}\ 1/2^2/5^{1/2}$
- $T_4: A4 \rightarrow B1$: $\bar{1}\ 1/2^3/5^{3/4}$

Table 7 gives the fractional atomic coordinate of the B right part of $A1$, the result of the application of T_1 operation, and the corresponding coordinates in $B1$, together with the differences expressed as fractional coordinates and in Å. The average difference is 0.1 Å, which shows the very high degree of pseudo-symmetry. The same result is obtained when considering the other T operations.

The symbol T is used here to follow Sadanaga's definition of *transmutation operation* (Sadanaga, personal communication) as an operation mapping two different modules. In Sadanaga's definition, the transmutation operation is invertible (if T_{AB} maps A to B , then there exist a transmutation operation T_{BA} that maps B to A). We deal here with a non-invertible transmutation operation because T “shrinks” A to B by acting on the corresponding submodule of A ; the hypothetical inverse operation should “expand” B to A by acting also outside the module B . The structure that

we would obtain by considering both the partial operations h and the transmutation operations T is therefore no longer a groupoid but a category (we remind the reader that a groupoid is an invertible category; for details see Spivak, 2014).

The same interpretation can be applied to kalifersite, for which however the quality of the available refinement is too poor to provide any quantitative analysis of the modular structure of this mineral. Kalifersite is composed of two different modules which only partly fit our definition. Nespolo and Bouznari (2017) have described the structure of kalifersite as built by a Z_6 module around the centre on the unit cell, and a Z_3 module around the origin, which however span eight and four tetrahedra respectively, instead of six and two as in the definition of the Z_n modules. The additional tetrahedra can be seen as bridges between the Z_6 and Z_3 modules. Alternatively, the two modules could also be seen as Z_8 and Z_5 with octahedral cations removed from the two boundaries of the modules. By using this description, however, the composition of the two modules in the structure of kalifersite requires an overlap of the tetrahedra on the boundaries, which would break the general scheme common to all the other minerals of the two polysomatic series

8 Discussion

A non-molecular crystal structure can be decomposed in elementary building blocks of variable size. The smallest and universally known block is the coordination polyhedron, which is however not always uniquely defined (Hoppe, 1970). Bigger and more complex building blocks occur in modular structures (Nespolo *et al.*, 2004), which are built by stacking and juxtaposing one (*monoarchetypal structures*) or more (*polyarchetypal structures*) kinds of 0-, 1- or 2-period blocks (bricks, rods, layers) and give rise to large variety of complex structures (Ferraris *et al.*, 2008; Krivovichev, 2017). A general approach to modular structures should not only point out salient common structural features of apparently highly heterogeneous structures, as in the case of the two series of minerals we have analysed, but also display predictive power on the possible stacking modes, occurrence probability of stacking fault, diffraction features. Such a general result has been obtained in the case of OD structures (Dornberger-Schiff and Grell-Niemann, 1961), *i.e.* monoarchetypal modular structures built by the stacking of 2-periodic building blocks (layers), but is far from having reached its final goal in the most general case, despite some general results already present in the literature (see, *e.g.* Sadanaga and Ohsumi, 1979). We have shown that a groupoid and graph-theoretical analysis of modular structures built by 1-periodic building blocks (rods) looks promising as a possible extension and generalization. We plan to develop this approach to other types of modular structures in the near future.

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575 FIGURE CAPTIONS

576 **Figure 1.** (a) Labelled quotient graph of diopside with relation to a primitive unit cell and (b)
577 modification evidencing the R_2 rod. Colour code (common to all figures): octahedral cations in
578 orange, tetrahedral cation in green and oxygen ions in red; oxygen atoms with the same colour
579 contour should be identified. Voltages are given as coloured arrows: blue (100), red (010), black
580 (001).

581 **Figure 2.** (a) Labelled quotient graph of the R_2 rod of diopside and (b) the simplified LQG
582 representing the rod linkages: the grey box stands for the rod.

583 **Figure 3.** The Z_3 modules (the portion of the R_3 rod contained in a single unit cell) of phyllosilicates
584 and the partial operations mapping the various modules. A is the target module; B is mapped by the
585 a -glide reflection about the plane at $x, \frac{1}{4}, z$. A lattice translation along \mathbf{b} applied to the pair of R_3 rods
586 BA produced the $R_\infty = L$ layer of phyllosilicates. The second operation, mapping C to A, is a lattice
587 translation along the \mathbf{c} axis. The product $h_1^{-1}h_2 = g(\frac{1}{2}, 0, 1)$ about the plane at $x, \frac{1}{4}, z$. maps C to B via
588 A: this is one of the operations of the element set of the a -glide plane. (This and the following
589 figures of crystal structures drawn with VESTA: Momma and Izumi, 2011).

590 **Figure 4.** (a) Labelled quotient graph of phlogopite and (b) LQG obtained after deleting the central
591 octahedral atom putting into evidence the R_2 rod of diopside. Hydrogen atoms in violet. Green
592 arrows: 110.

593 **Figure 5.** Labelled quotient graph of palygorskite evidencing the R_5 rod. Water molecules in purple.

594 **Figure 6.** The structure of sepiolite in which the two Z_8 modules are shown, one centred at the
595 middle of the unit cell, the other centred at the origin. The R_8 rods (of which the Z_8 modules are the
596 portion contained in a single unit cell) can be seen as composed by three R_2 rods (A,B,C) related by
597 pseudo-partial mirror reflections, completed by additional atoms on the corresponding planes (blue
598 in the figure).

599 **Figure 7.** The structure of jimthompsonite in which the four Z_8 modules are shown. As in the case
600 of sepiolite, the R_8 rods can be seen as composed by three R_2 rods (A,B,C) related by pseudo-partial
601 mirror reflections, completed by additional atoms on the corresponding planes (blue in the figure).

602 **Figure 8.** Labelled quotient graph of sepiolite evidencing the two R_8 rods M1 (top) and M2
603 (bottom); oxygen atoms with the same colour contour should be identified.

604 **Figure 9.** Simplified LQG of sepiolite emphasizing the linkages between R_8 rods; letters on the
605 edges indicate oxygen atoms shared by the tetrahedral chains in rods M1 and M2, as identified in
606 Figure 8.

607 **Figure 10.** Labelled quotient graph (partial) of jimthompsonite evidencing the two R_8 rods M1 (top)
608 and M2 (bottom).

609 **Figure 11.** Labelled quotient graph (partial) of jimthompsonite evidencing the two R_8 rods M3 (top)
610 and M4 (bottom).

611 **Figure 12.** Simplified LQG of jimthompsonite. Signs (+ or -) over the vertices indicate the
612 orientation of the respective rod; letters on the edges indicate the linkages between octahedral and
613 tetrahedral chains.

614 **Figure 13.** The concept of contracted twin (after Takéuchi, 1997). Left: the module A is mapped to
615 the module A' by a partial operation (here represented by a mirror reflection about a vertical plane
616 drawn in red). The hatched part of the two modules can be removed to transform the result in a pair
617 of modules BB' (centre). If the hatched part is removed only on one side, we obtain a contracted
618 twin, AB' (right, where the hatched part is still visible to emphasize the relation between A' and B')
619 or BA'.

620 **Figure 14.** The structure of chesterite, where the local c -glide plane of the Z_8 module is shown in
621 red and the mirror plane of the Z_5 module is shown in blue.

622 **Figure 15.** A schematic view of the structure of chesterite along the c axis, where the Z_8 and Z_5
623 modules are replaced by larger A and smaller B rectangles. Partial operations map A to A and B to
624 B, whereas transmutation operations map A to B but not B to A. Thin-line rectangle is the unit cell
625 of chesterite.

626 **Table 1.** Space groupoid construction for sepiolite. K_X is the kernel of the X rod R_2 ($X = A1, B1,$
627 $C1, A2, B2, C2$, the partial operations are h_1 ($B1 \rightarrow A1$): $m_{x,0.42215,z}$; h_2 ($C1 \rightarrow A1$): $m_{x,0.5794,z}$; h_3 ($A2$
628 $\rightarrow A1$): $n_{\frac{1}{4},y,z}$; h_4 ($B2 \rightarrow A1$) = $h_1h_3 = 2_1 \frac{1}{4},0.17215,z$; h_5 ($C2 \rightarrow A1$) = $h_2h_3 = 2_1 x,0.3294,z$.

K_{A1}	$K_{A1}h_1: B1 \rightarrow A1$	$K_{A1}h_2: C1 \rightarrow A1$	$K_{A1}h_3: A2 \rightarrow A1$	$K_{A1}h_4: B2 \rightarrow A1$	$K_{A1}h_5: C2 \rightarrow A1$
$h_1^{-1}K_{A1}: A1 \rightarrow B1$	$h_1^{-1}K_{A1}h_1 = K_{B1}$	$h_1^{-1}K_{A1}h_2: C1 \rightarrow B1$	$h_1^{-1}K_{A1}h_3: A2 \rightarrow B1$	$h_1^{-1}K_{A1}h_4: B2 \rightarrow B1$	$h_1^{-1}K_{A1}h_5: C2 \rightarrow B1$
$h_2^{-1}K_{A1}: A1 \rightarrow C1$	$h_2^{-1}K_{A1}h_1: B1 \rightarrow C1$	$h_2^{-1}K_{A1}h_2 = K_{C1}$	$h_2^{-1}K_{A1}h_3: A2 \rightarrow C1$	$h_2^{-1}K_{A1}h_4: B2 \rightarrow C1$	$h_2^{-1}K_{A1}h_5: C2 \rightarrow C1$
$h_3^{-1}K_{A1}: A1 \rightarrow A2$	$h_3^{-1}K_{A1}h_1: B1 \rightarrow A2$	$h_3^{-1}K_{A1}h_2: C1 \rightarrow A2$	$h_3^{-1}K_{A1}h_3 = K_{A2}$	$h_3^{-1}K_{A1}h_4: B2 \rightarrow A2$	$h_3^{-1}K_{A1}h_5: C2 \rightarrow A2$
$h_4^{-1}K_{A1}: A1 \rightarrow B2$	$h_4^{-1}K_{A1}h_1: B1 \rightarrow B2$	$h_4^{-1}K_{A1}h_2: C1 \rightarrow B2$	$h_4^{-1}K_{A1}h_3: A2 \rightarrow B2$	$h_4^{-1}K_{A1}h_4 = K_{B2}$	$h_4^{-1}K_{A1}h_5: C2 \rightarrow B2$
$h_5^{-1}K_{A1}: A1 \rightarrow C2$	$h_5^{-1}K_{A1}h_1: B1 \rightarrow C2$	$h_5^{-1}K_{A1}h_2: C1 \rightarrow C2$	$h_5^{-1}K_{A1}h_3: A2 \rightarrow C2$	$h_5^{-1}K_{A1}h_4: B2 \rightarrow C2$	$h_5^{-1}K_{A1}h_5 = K_{C2}$

629 **Table 2.** The 40 operations appearing in the space groupoid of sepiolite. Fr. is the occurrence
630 frequency of the corresponding operation, *i.e.* the number of hybrid groups in which the operation
631 occurs. Operations No. 1, 8, 13, 16, 21, 28, 33 and 36 in this list occur six times, *i.e.* in each of the
632 hybrid group, and are therefore global operations. These are the coset representatives of the
633 operations of *Pbcn*, the space-group type of sepiolite, as well as the defining operations of the
634 corresponding symmetry elements.

No	Op.	Fr	No	Op.	Fr	No	Op.	Fr	No	Op.	Fr
1	1	6	11	$2_1 x,0.171,\frac{1}{4}$	4	21	$2 \frac{1}{2},y,\frac{1}{2}$	6	31	$2_1 \frac{1}{4},0.171,z$	4
2	$t(0,0.158,0.5)$	4	12	$2_1 x,0.329,\frac{1}{4}$	4	22	$2 (0,0.158,0) \frac{1}{2},y,\frac{1}{2}$	4	32	$2_1 \frac{1}{4},0.329,z$	4
3	$t(0,-0.158,0.5)$	4	13	$2_1 x,\frac{1}{4},\frac{1}{4}$	6	23	$2 (0,0,-0.158,0) \frac{1}{2},y,\frac{1}{2}$	4	33	$2_2 \frac{1}{4},\frac{1}{4},z$	6
4	$t(0,-0.316,0.5)$	2	14	$2_1 x,0.092,\frac{1}{4}$	2	24	$2 (0,-0.316,0) \frac{1}{2},y,\frac{1}{2}$	2	34	$2_2 \frac{1}{4},0.092,z$	2
5	$t(0,0.316,0.5)$	2	15	$2_1 x,0.408,\frac{1}{4}$	2	25	$2 (0,0.316,0) \frac{1}{2},y,\frac{1}{2}$	2	35	$2_2 \frac{1}{4},0.408,z$	2
6	$\bar{1} \frac{1}{2},0.421,\frac{1}{2}$	4	16	$n \frac{1}{4},y,z$	6	26	$m x,0.421,z$	4	36	$n x,y,\frac{1}{4}$	6
7	$\bar{1} \frac{1}{2},0.579,\frac{1}{2}$	4	17	$g(0,0.658,1) \frac{1}{4},y,z$	4	27	$m x,0.579,z$	4	37	$g (\frac{1}{2},0.658,0) x,y,\frac{1}{4}$	4
8	$\bar{1} \frac{1}{2},\frac{1}{2},\frac{1}{2}$	6	18	$g(0,0.342,1) \frac{1}{4},y,z$	4	28	$c x,\frac{1}{2},z$	6	38	$g (\frac{1}{2},0.342,0) x,y,\frac{1}{4}$	4
9	$\bar{1} \frac{1}{2},0.342,\frac{1}{2}$	2	19	$g(0,0.184,\frac{1}{2}) \frac{1}{4},y,z$	2	29	$c x,0.342,z$	2	39	$g (\frac{1}{2},0.184,0) x,y,\frac{1}{4}$	2
10	$\bar{1} \frac{1}{2},0.658,\frac{1}{2}$	2	20	$g(0,0.816,\frac{1}{2}) \frac{1}{4},y,z$	2	30	$c x,0.658,z$	2	40	$g (\frac{1}{2},0.816,0) x,y,\frac{1}{4}$	2

635 **Table 3.** Space groupoid of sepiolite, with the operations synthetically indicated by the sequence
636 number in Table 2. In bold the operations occurring in every hybrid group: these are global
637 operations which build the space group of the mineral.

M_{A1}	1,8,21,28	2,6,22,26	3,7,27,23	13,16,33,36	11,17,31,37	12,18,32,38
M_{B1}	3,6,23,26	1,9,21,29	4,8,24,28	11,18,31,38	14,16,34,36	13,19,33,39
M_{C1}	2,7,22,27	5,8,25,28	1,10,21,30	12,17,32,37	13,20,33,40	15,16,35,36
M_{A2}	13,16,33,36	11,17,31,37	12,18,32,38	1,8,21,28	2,6,22,26	3,7,23,27
M_{B2}	11,18,31,38	14,16,24,36	13,19,33,39	3,6,23,26	1,9,21,29	4,8,24,28
M_{C2}	12,17,32,37	13,20,33,40	15,16,35,36	2,7,22,27	5,8,25,28	1,10,21,30

638 **Table 4.** Space groupoid construction for jimthompsonite. K_X is the kernel of the X rod R_2 ($X = A1$,
639 $B1, C1, A2, B2, C2$, the partial operations are $h_1 (B1 \rightarrow A1): m_{x,0.6662,z}$; $h_2 (C1 \rightarrow A1): m_{x,0.83407,z}$; h_3
640 $(A2 \rightarrow A1): b_{\frac{1}{4},y,z}$; $h_4 (B2 \rightarrow A1) = h_1 h_3 = 2_{1\frac{1}{4},0.4162,z}$; $h_5 (C2 \rightarrow A1) = h_2 h_3 = 2_{1\frac{1}{4},0.58407,z}$; $h_6 (A3 \rightarrow$
641 $A1): a_{x,y,\frac{1}{4}}$; $h_7 (B3 \rightarrow A1) = h_1 h_6 = 2_{1x,0.6662,\frac{1}{4}}$; $h_8 (C3 \rightarrow A1) = h_2 h_6 = 2_{1x,0.83407,\frac{1}{4}}$; $h_9 (A4 \rightarrow A1): \bar{1}_{\frac{1}{2},\frac{1}{2},\frac{1}{2}}$;
642 $h_{10} (B4 \rightarrow A1) = h_1 h_9 = 2 (0,0.3324,0)_{\frac{1}{2},y,0}$; $h_{11} (C4 \rightarrow A1) = h_2 h_9 = 2 (0,0.66814,0)_{\frac{1}{2},y,0}$.

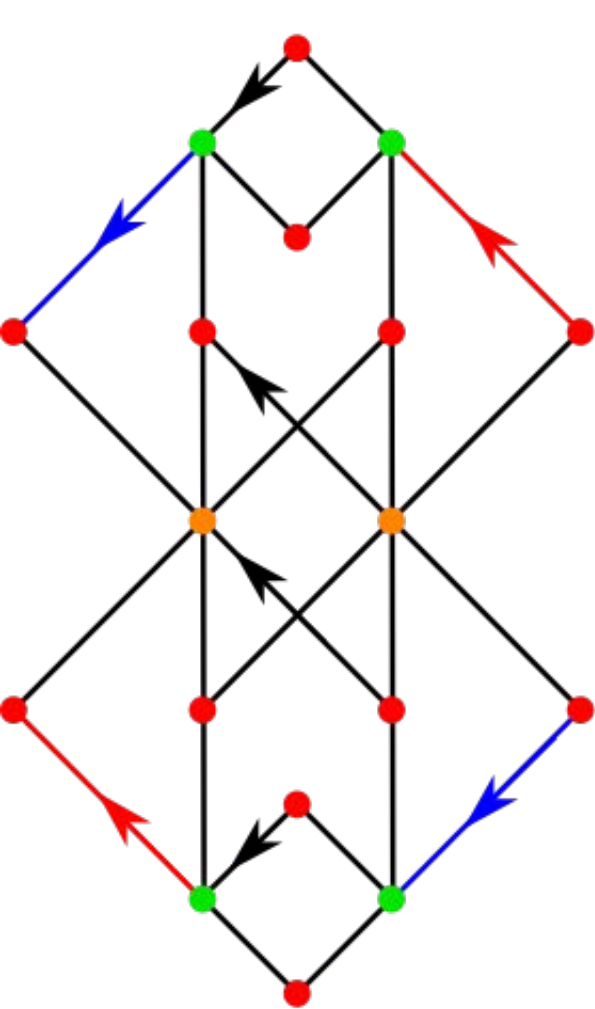
K_{A1}	$K_{A1}h_1$	$K_{A1}h_2$	$K_{A1}h_3$	$K_{A1}h_4$	$K_{A1}h_5$	$K_{A1}h_6$	$K_{A1}h_7$	$K_{A1}h_8$	$K_{A1}h_9$	$K_{A1}h_{10}$	$K_{A1}h_{11}$
$A1 \rightarrow A1$	$B1 \rightarrow A1$	$C1 \rightarrow A1$	$A2 \rightarrow A1$	$B2 \rightarrow A1$	$C2 \rightarrow A1$	$A3 \rightarrow A1$	$B3 \rightarrow A1$	$C3 \rightarrow A1$	$A4 \rightarrow A1$	$B4 \rightarrow A1$	$C4 \rightarrow A1$
$h_1^{-1}K_{A1}$	$h_1^{-1}K_{A1}h_1$	$h_1^{-1}K_{A1}h_2$	$h_1^{-1}K_{A1}h_3$	$h_1^{-1}K_{A1}h_4$	$h_1^{-1}K_{A1}h_5$	$h_1^{-1}K_{A1}h_6$	$h_1^{-1}K_{A1}h_7$	$h_1^{-1}K_{A1}h_8$	$h_1^{-1}K_{A1}h_9$	$h_1^{-1}K_{A1}h_{10}$	$h_1^{-1}K_{A1}h_{11}$
$A1 \rightarrow B1$	$B1 \rightarrow B1$	$C1 \rightarrow B1$	$A2 \rightarrow B1$	$B2 \rightarrow B1$	$C2 \rightarrow B1$	$A3 \rightarrow B1$	$B3 \rightarrow B1$	$C3 \rightarrow B1$	$A4 \rightarrow B1$	$B4 \rightarrow B1$	$C4 \rightarrow B1$
$h_2^{-1}K_{A1}$	$h_2^{-1}K_{A1}h_1$	$h_2^{-1}K_{A1}h_2$	$h_2^{-1}K_{A1}h_3$	$h_2^{-1}K_{A1}h_4$	$h_2^{-1}K_{A1}h_5$	$h_2^{-1}K_{A1}h_6$	$h_2^{-1}K_{A1}h_7$	$h_2^{-1}K_{A1}h_8$	$h_2^{-1}K_{A1}h_9$	$h_2^{-1}K_{A1}h_{10}$	$h_2^{-1}K_{A1}h_{11}$
$A1 \rightarrow C1$	$B1 \rightarrow C1$	$C1 \rightarrow C1$	$A2 \rightarrow C1$	$B2 \rightarrow C1$	$C2 \rightarrow C1$	$A3 \rightarrow C1$	$B3 \rightarrow C1$	$C3 \rightarrow C1$	$A4 \rightarrow C1$	$B4 \rightarrow C1$	$C4 \rightarrow C1$
$h_3^{-1}K_{A1}$	$h_3^{-1}K_{A1}h_1$	$h_3^{-1}K_{A1}h_2$	$h_3^{-1}K_{A1}h_3$	$h_3^{-1}K_{A1}h_4$	$h_3^{-1}K_{A1}h_5$	$h_3^{-1}K_{A1}h_6$	$h_3^{-1}K_{A1}h_7$	$h_3^{-1}K_{A1}h_8$	$h_3^{-1}K_{A1}h_9$	$h_3^{-1}K_{A1}h_{10}$	$h_3^{-1}K_{A1}h_{11}$
$A1 \rightarrow A2$	$B1 \rightarrow A2$	$C1 \rightarrow A2$	$A2 \rightarrow A2$	$B2 \rightarrow A2$	$C2 \rightarrow A2$	$A3 \rightarrow A2$	$B3 \rightarrow A2$	$C3 \rightarrow A2$	$A4 \rightarrow A2$	$B4 \rightarrow A2$	$C4 \rightarrow A2$
$h_4^{-1}K_{A1}$	$h_4^{-1}K_{A1}h_1$	$h_4^{-1}K_{A1}h_2$	$h_4^{-1}K_{A1}h_3$	$h_4^{-1}K_{A1}h_4$	$h_4^{-1}K_{A1}h_5$	$h_4^{-1}K_{A1}h_6$	$h_4^{-1}K_{A1}h_7$	$h_4^{-1}K_{A1}h_8$	$h_4^{-1}K_{A1}h_9$	$h_4^{-1}K_{A1}h_{10}$	$h_4^{-1}K_{A1}h_{11}$
$A1 \rightarrow B2$	$B1 \rightarrow B2$	$C1 \rightarrow B2$	$A2 \rightarrow B2$	$B2 \rightarrow B2$	$C2 \rightarrow B2$	$A3 \rightarrow B2$	$B3 \rightarrow B2$	$C3 \rightarrow B2$	$A4 \rightarrow B2$	$B4 \rightarrow B2$	$C4 \rightarrow B2$
$h_5^{-1}K_{A1}$	$h_5^{-1}K_{A1}h_1$	$h_5^{-1}K_{A1}h_2$	$h_5^{-1}K_{A1}h_3$	$h_5^{-1}K_{A1}h_4$	$h_5^{-1}K_{A1}h_5$	$h_5^{-1}K_{A1}h_6$	$h_5^{-1}K_{A1}h_7$	$h_5^{-1}K_{A1}h_8$	$h_5^{-1}K_{A1}h_9$	$h_5^{-1}K_{A1}h_{10}$	$h_5^{-1}K_{A1}h_{11}$
$A1 \rightarrow C2$	$B1 \rightarrow C2$	$C1 \rightarrow C2$	$A2 \rightarrow C2$	$B2 \rightarrow C2$	$C2 \rightarrow C2$	$A3 \rightarrow C2$	$B3 \rightarrow C2$	$C3 \rightarrow C2$	$A4 \rightarrow C2$	$B4 \rightarrow C2$	$C4 \rightarrow C2$
$h_6^{-1}K_{A1}$	$h_6^{-1}K_{A1}h_1$	$h_6^{-1}K_{A1}h_2$	$h_6^{-1}K_{A1}h_3$	$h_6^{-1}K_{A1}h_4$	$h_6^{-1}K_{A1}h_5$	$h_6^{-1}K_{A1}h_6$	$h_6^{-1}K_{A1}h_7$	$h_6^{-1}K_{A1}h_8$	$h_6^{-1}K_{A1}h_9$	$h_6^{-1}K_{A1}h_{10}$	$h_6^{-1}K_{A1}h_{11}$
$A1 \rightarrow A3$	$B1 \rightarrow A3$	$C1 \rightarrow A3$	$A2 \rightarrow A3$	$B2 \rightarrow A3$	$C2 \rightarrow A3$	$A3 \rightarrow A3$	$B3 \rightarrow A3$	$C3 \rightarrow A3$	$A4 \rightarrow A3$	$B4 \rightarrow A3$	$C4 \rightarrow A3$
$h_7^{-1}K_{A1}$	$h_7^{-1}K_{A1}h_1$	$h_7^{-1}K_{A1}h_2$	$h_7^{-1}K_{A1}h_3$	$h_7^{-1}K_{A1}h_4$	$h_7^{-1}K_{A1}h_5$	$h_7^{-1}K_{A1}h_6$	$h_7^{-1}K_{A1}h_7$	$h_7^{-1}K_{A1}h_8$	$h_7^{-1}K_{A1}h_9$	$h_7^{-1}K_{A1}h_{10}$	$h_7^{-1}K_{A1}h_{11}$
$A1 \rightarrow B3$	$B1 \rightarrow B3$	$C1 \rightarrow B3$	$A2 \rightarrow B3$	$B2 \rightarrow B3$	$C2 \rightarrow B3$	$A3 \rightarrow B3$	$B3 \rightarrow B3$	$C3 \rightarrow B3$	$A4 \rightarrow B3$	$B4 \rightarrow B3$	$C4 \rightarrow B3$
$h_8^{-1}K_{A1}$	$h_8^{-1}K_{A1}h_1$	$h_8^{-1}K_{A1}h_2$	$h_8^{-1}K_{A1}h_3$	$h_8^{-1}K_{A1}h_4$	$h_8^{-1}K_{A1}h_5$	$h_8^{-1}K_{A1}h_6$	$h_8^{-1}K_{A1}h_7$	$h_8^{-1}K_{A1}h_8$	$h_8^{-1}K_{A1}h_9$	$h_8^{-1}K_{A1}h_{10}$	$h_8^{-1}K_{A1}h_{11}$
$A1 \rightarrow C3$	$B1 \rightarrow C3$	$C1 \rightarrow C3$	$A2 \rightarrow C3$	$B2 \rightarrow C3$	$C2 \rightarrow C3$	$A3 \rightarrow C3$	$B3 \rightarrow C3$	$C3 \rightarrow C3$	$A4 \rightarrow C3$	$B4 \rightarrow C3$	$C4 \rightarrow C3$
$h_9^{-1}K_{A1}$	$h_9^{-1}K_{A1}h_1$	$h_9^{-1}K_{A1}h_2$	$h_9^{-1}K_{A1}h_3$	$h_9^{-1}K_{A1}h_4$	$h_9^{-1}K_{A1}h_5$	$h_9^{-1}K_{A1}h_6$	$h_9^{-1}K_{A1}h_7$	$h_9^{-1}K_{A1}h_8$	$h_9^{-1}K_{A1}h_9$	$h_9^{-1}K_{A1}h_{10}$	$h_9^{-1}K_{A1}h_{11}$
$A1 \rightarrow A4$	$B1 \rightarrow A4$	$C1 \rightarrow A4$	$A2 \rightarrow A4$	$B2 \rightarrow A4$	$C2 \rightarrow A4$	$A3 \rightarrow A4$	$B3 \rightarrow A4$	$C3 \rightarrow A4$	$A4 \rightarrow A4$	$B4 \rightarrow A4$	$C4 \rightarrow A4$
$h_{10}^{-1}K_{A1}$	$h_{10}^{-1}K_{A1}h_1$	$h_{10}^{-1}K_{A1}h_2$	$h_{10}^{-1}K_{A1}h_3$	$h_{10}^{-1}K_{A1}h_4$	$h_{10}^{-1}K_{A1}h_5$	$h_{10}^{-1}K_{A1}h_6$	$h_{10}^{-1}K_{A1}h_7$	$h_{10}^{-1}K_{A1}h_8$	$h_{10}^{-1}K_{A1}h_9$	$h_{10}^{-1}K_{A1}h_{10}$	$h_{10}^{-1}K_{A1}h_{11}$
$A1 \rightarrow B4$	$B1 \rightarrow B4$	$C1 \rightarrow B4$	$A2 \rightarrow B4$	$B2 \rightarrow B4$	$C2 \rightarrow B4$	$A3 \rightarrow B4$	$B3 \rightarrow B4$	$C3 \rightarrow B4$	$A4 \rightarrow B4$	$B4 \rightarrow B4$	$C4 \rightarrow B4$
$h_{11}^{-1}K_{A1}$	$h_{11}^{-1}K_{A1}h_1$	$h_{11}^{-1}K_{A1}h_2$	$h_{11}^{-1}K_{A1}h_3$	$h_{11}^{-1}K_{A1}h_4$	$h_{11}^{-1}K_{A1}h_5$	$h_{11}^{-1}K_{A1}h_6$	$h_{11}^{-1}K_{A1}h_7$	$h_{11}^{-1}K_{A1}h_8$	$h_{11}^{-1}K_{A1}h_9$	$h_{11}^{-1}K_{A1}h_{10}$	$h_{11}^{-1}K_{A1}h_{11}$
$A1 \rightarrow C4$	$B1 \rightarrow C4$	$C1 \rightarrow C4$	$A2 \rightarrow C4$	$B2 \rightarrow C4$	$C2 \rightarrow C4$	$A3 \rightarrow C4$	$B3 \rightarrow C4$	$C3 \rightarrow C4$	$A4 \rightarrow C4$	$B4 \rightarrow C4$	$C4 \rightarrow C4$

643 **Table 5.** The 40 operations appearing in the space groupoid of jimthompsonite. Fr. is the occurrence
644 frequency of the corresponding operation, *i.e.* the number of hybrid groups in which the operation
645 occurs. Operations No. 1,6,11,16,21,26,31 and 36 in this list occur six times, *i.e.* in each of the
646 hybrid groups, and are therefore global operations. These are the coset representatives of the
647 operations of *Pbca*, the space-group type of jimthompsonite, as well as the defining operations of
648 the corresponding symmetry elements.

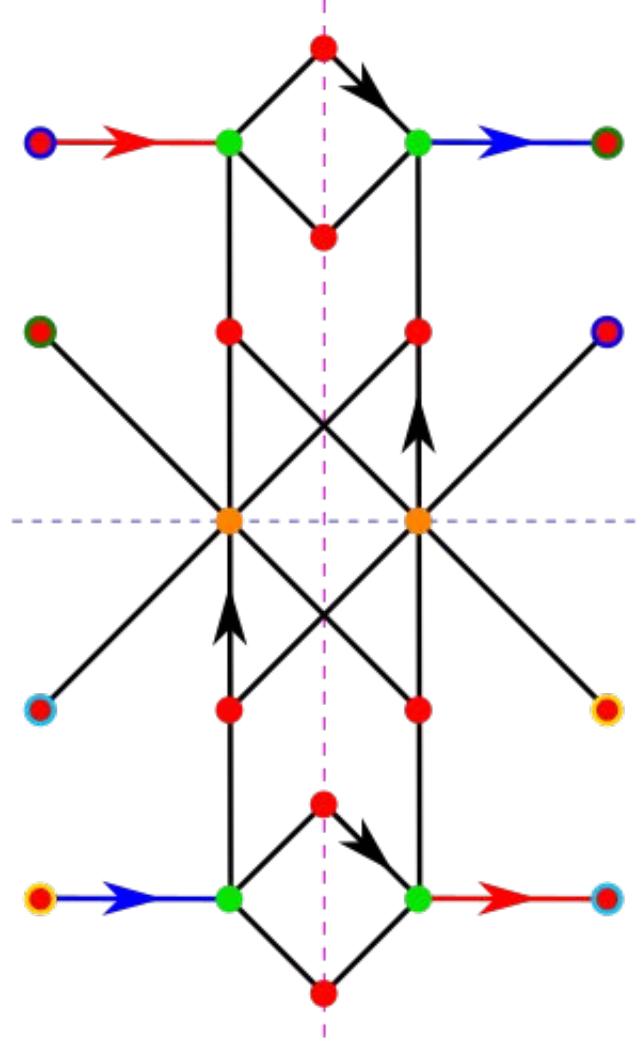
No	Op.	Fr	No	Op.	Fr	No	Op.	Fr	No	Op.	Fr
1	1	12	11	$2_1 x, \frac{3}{4}, \frac{1}{2}$	12	21	$2_3 0, y, \frac{1}{4}$	12	31	$2_1 \frac{1}{4}, \frac{1}{2}, z$	12
2	$t(0, 0.16787, 0.5)$	8	12	$2_1 x, 0.666065, \frac{1}{4}$	8	22	$2(0, 1.33213, 0) 0, y, 0$	8	32	$2 \frac{1}{4}, -0.083935, z$	8
3	$t(0, -0.16787, 0.5)$	8	13	$2_1 x, 0.833935, \frac{1}{4}$	8	23	$2(0, 1.66787, 0) 0, y, 0$	8	33	$2 \frac{1}{4}, 0.083935, z$	8
4	$t(0, -0.33574, 0.5)$	4	14	$2_1 x, 0.58213, 0$	4	24	$2(0, 1.16426, 0) 0, y, \frac{1}{4}$	4	34	$2_1 \frac{1}{4}, -0.16787, z$	4
5	$t(0, 0.33574, 0.5)$	4	15	$2_1 x, 0.91787, 0$	4	25	$2(0, 1.83574, 0) 0, y, \frac{1}{4}$	4	35	$2_1 \frac{1}{4}, 0.16787, z$	4
6	$\bar{1} 0, 0, 0$	12	16	$b \frac{1}{4}, y, z$	12	26	$c x, \frac{3}{4}, z$	12	36	$a x, y, \frac{1}{4}$	12
7	$\bar{1} 0, 0.083935, \frac{1}{4}$	8	17	$g(0, -0.33213, \frac{1}{2}) \frac{1}{4}, y, z$	8	27	$m x, 0.666065, z$	8	37	$g(\frac{1}{2}, 0.16787, 0) x, y, 0$	8
8	$\bar{1} 0, -0.083935, \frac{1}{4}$	8	18	$g(0, -0.66787, \frac{1}{2}) \frac{1}{4}, y, z$	8	28	$m x, 0.8343935, z$	8	38	$g(\frac{1}{2}, -0.16787) x, y, 0$	8
9	$\bar{1} 0, -0.16787, 0$	4	19	$g(0, 0.16426, 0) \frac{1}{4}, y, z$	4	29	$c x, 0.58213, z$	4	39	$g(\frac{1}{2}, -0.33574, 0) x, y, \frac{1}{4}$	4
10	$\bar{1} 0, 0.16787, 0$	4	20	$g(0, 0.83574, 0) \frac{1}{4}, y, z$	4	30	$c x, 0.91787, z$	4	40	$g(\frac{1}{2}, 0.33574, 0) x, y, \frac{1}{4}$	4

649 **Table 6.** Space groupoid of jimthompsonite, with the operations synthetically indicated by the
650 sequence number in Table 5. In bold the operations occurring in every hybrid group: these are
651 global operations which build the space group of the mineral.

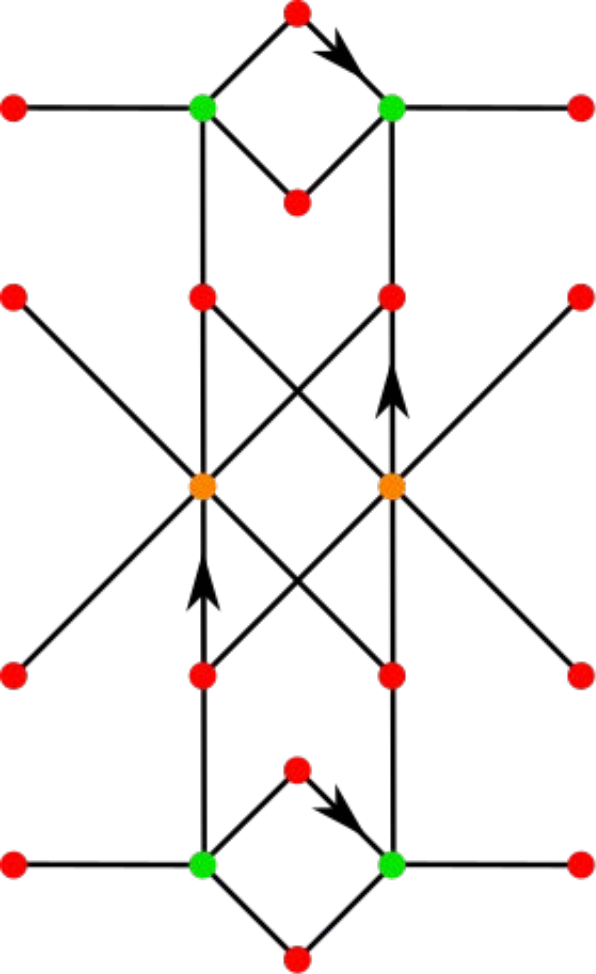
M _{A1}	1,26	2,27	3,28	16,31	17,32	18,33	11,36	12,37	13,38	6,21	7,22	8,23
M _{B1}	3,27	1,29	4,26	18,32	16,34	19,31	12,38	14,36	11,39	8,22	6,24	9,21
M _{C1}	2,28	5,26	1,30	17,33	20,31	16,35	13,37	11,40	15,36	7,23	10,21	6,25
M _{A2}	16,31	17,32	18,33	1,26	2,27	3,28	6,21	8,23	7,22	11,36	13,38	12,37
M _{B2}	18,32	16,34	19,31	3,27	1,29	4,26	8,22	9,21	6,24	12,38	11,39	14,36
M _{C2}	17,33	20,31	16,35	2,28	5,26	1,30	7,23	6,25	10,21	13,37	15,36	11,40
M _{A3}	11,36	12,37	13,38	6,21	8,23	7,22	1,26	2,27	3,28	1,31	18,33	17,32
M _{B3}	12,38	14,36	11,39	8,22	9,21	6,24	2,27	1,29	4,26	18,32	19,31	16,34
M _{C3}	13,37	11,40	15,36	7,23	6,25	10,21	2,28	5,26	1,30	17,33	16,35	20,31
M _{A4}	6,21	7,22	8,23	11,36	13,38	12,37	16,31	18,33	17,32	1,26	2,27	3,28
M _{B4}	8,22	6,24	9,21	12,38	11,39	14,36	18,32	19,31	16,34	3,27	1,29	4,26
M _{C4}	7,23	10,21	6,25	13,37	15,36	11,40	17,33	16,35	20,31	2,28	5,26	1,30



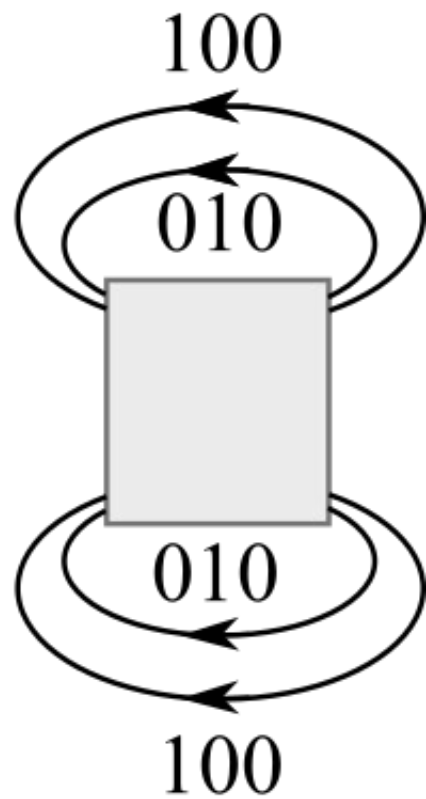
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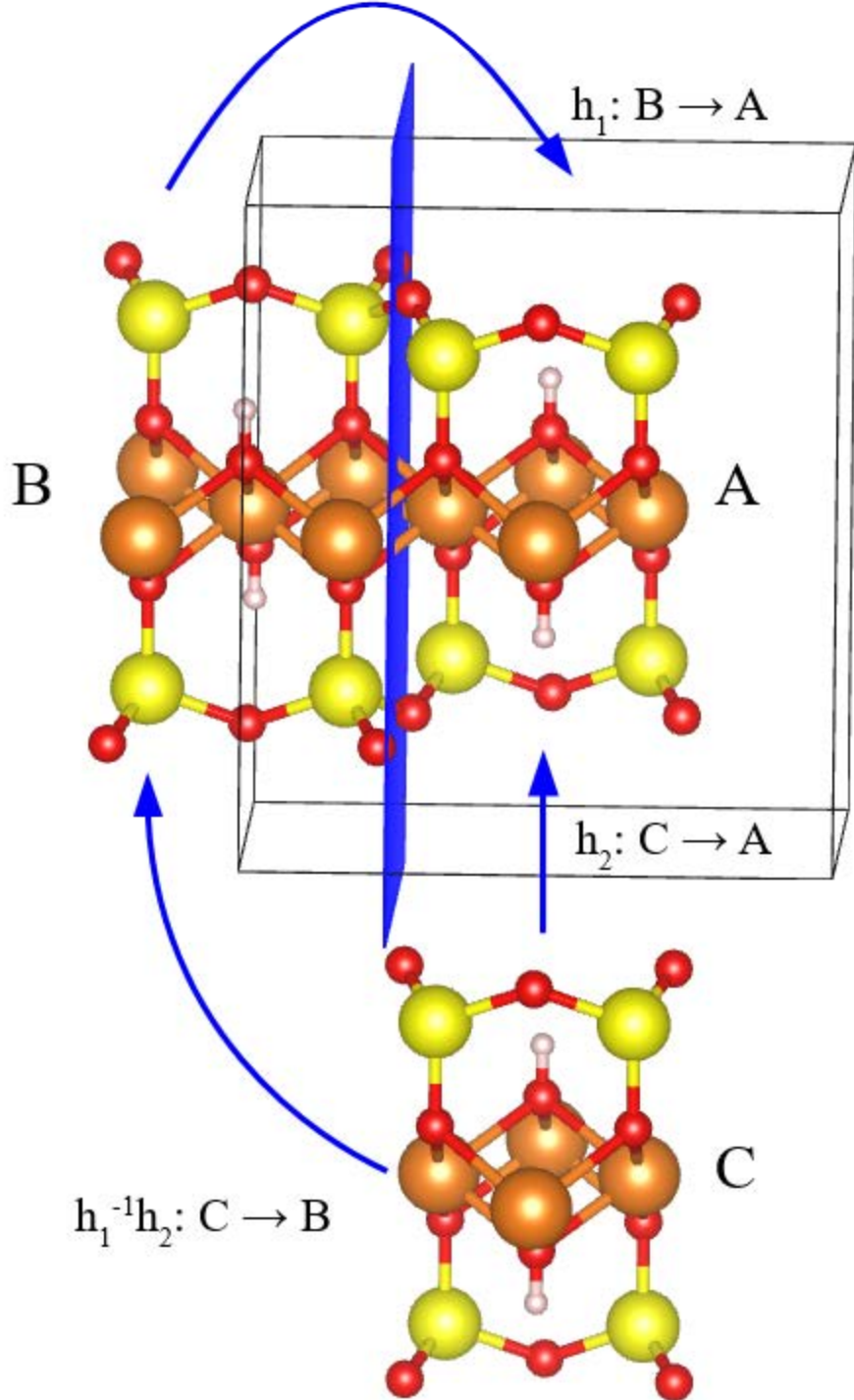
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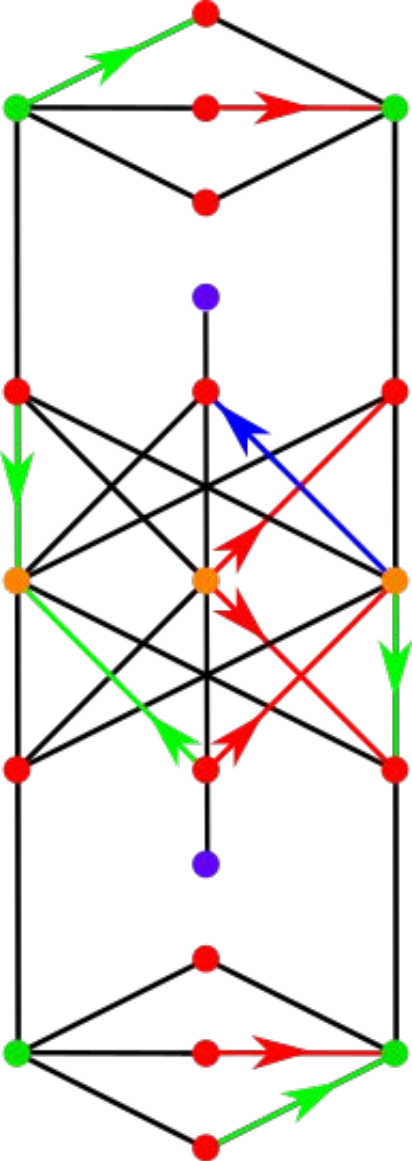
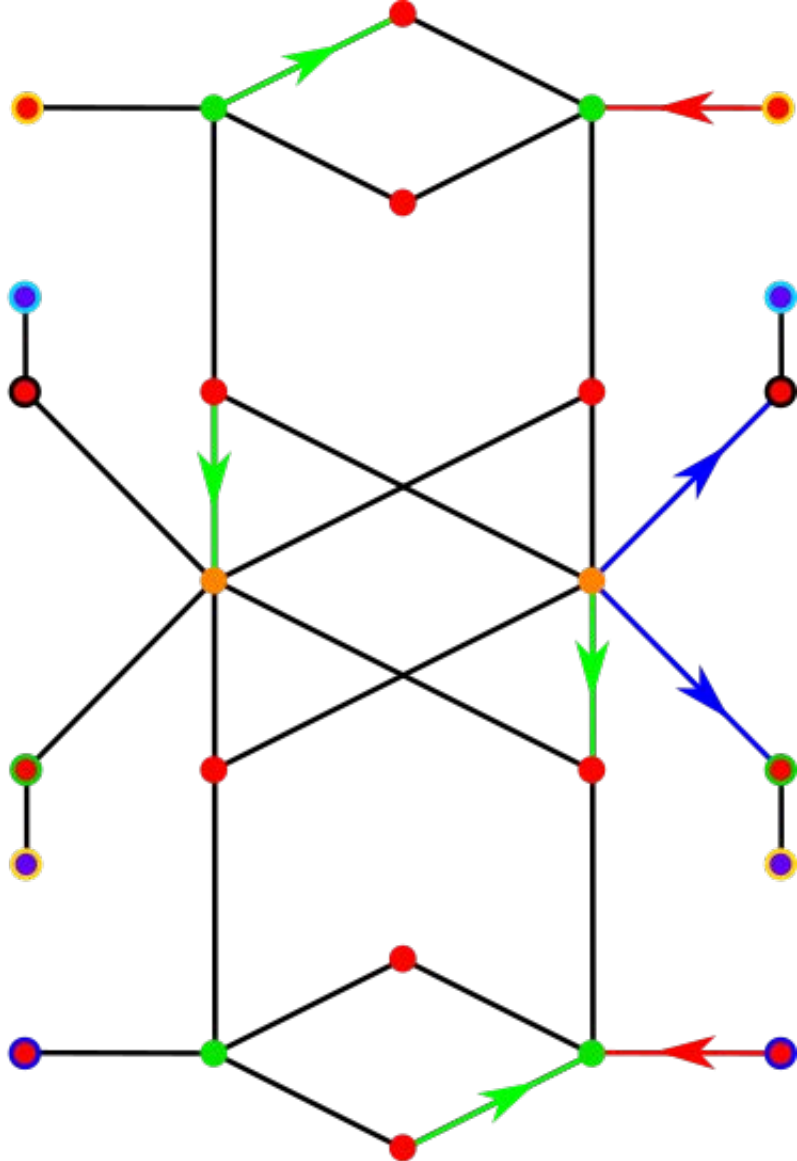


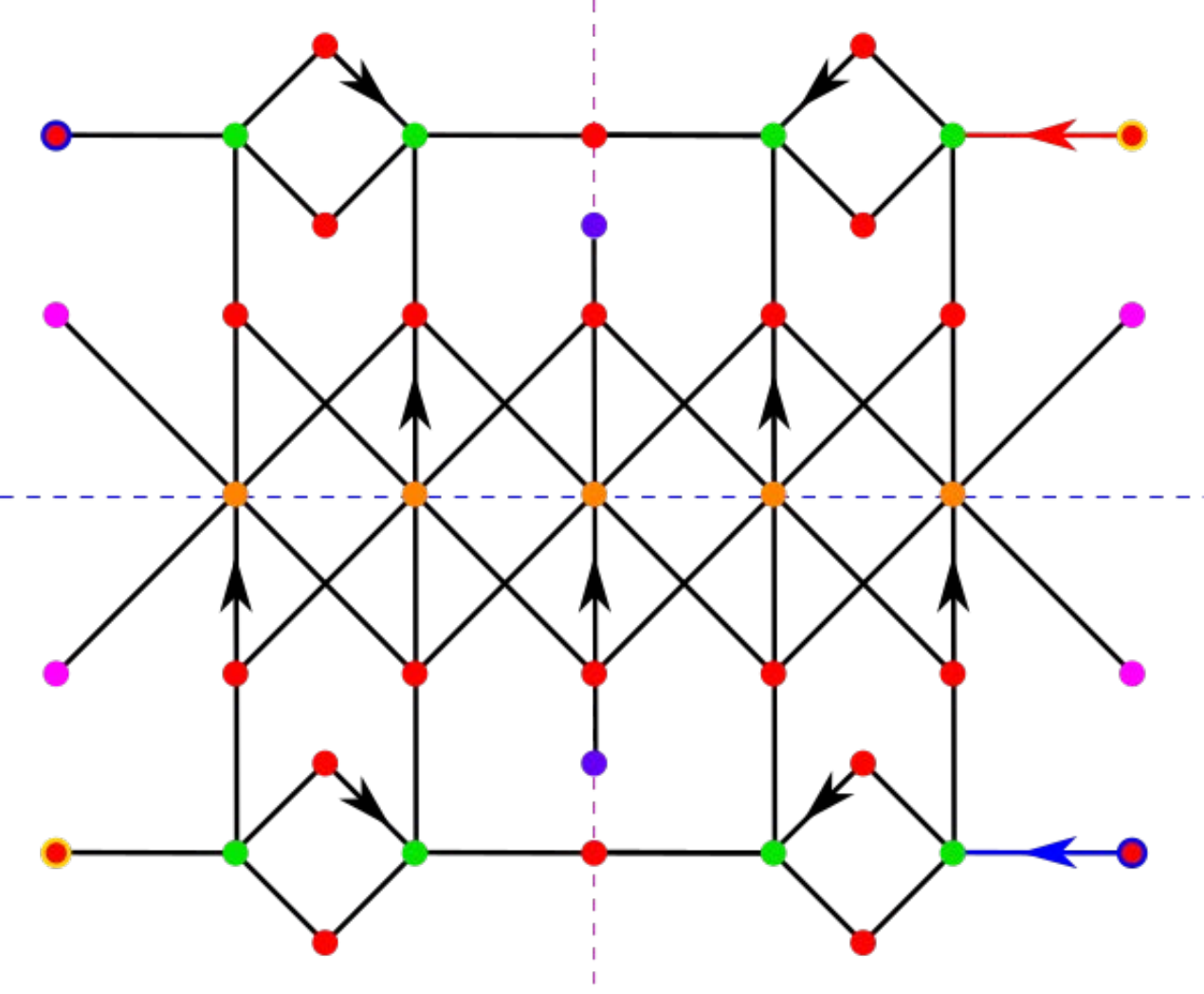
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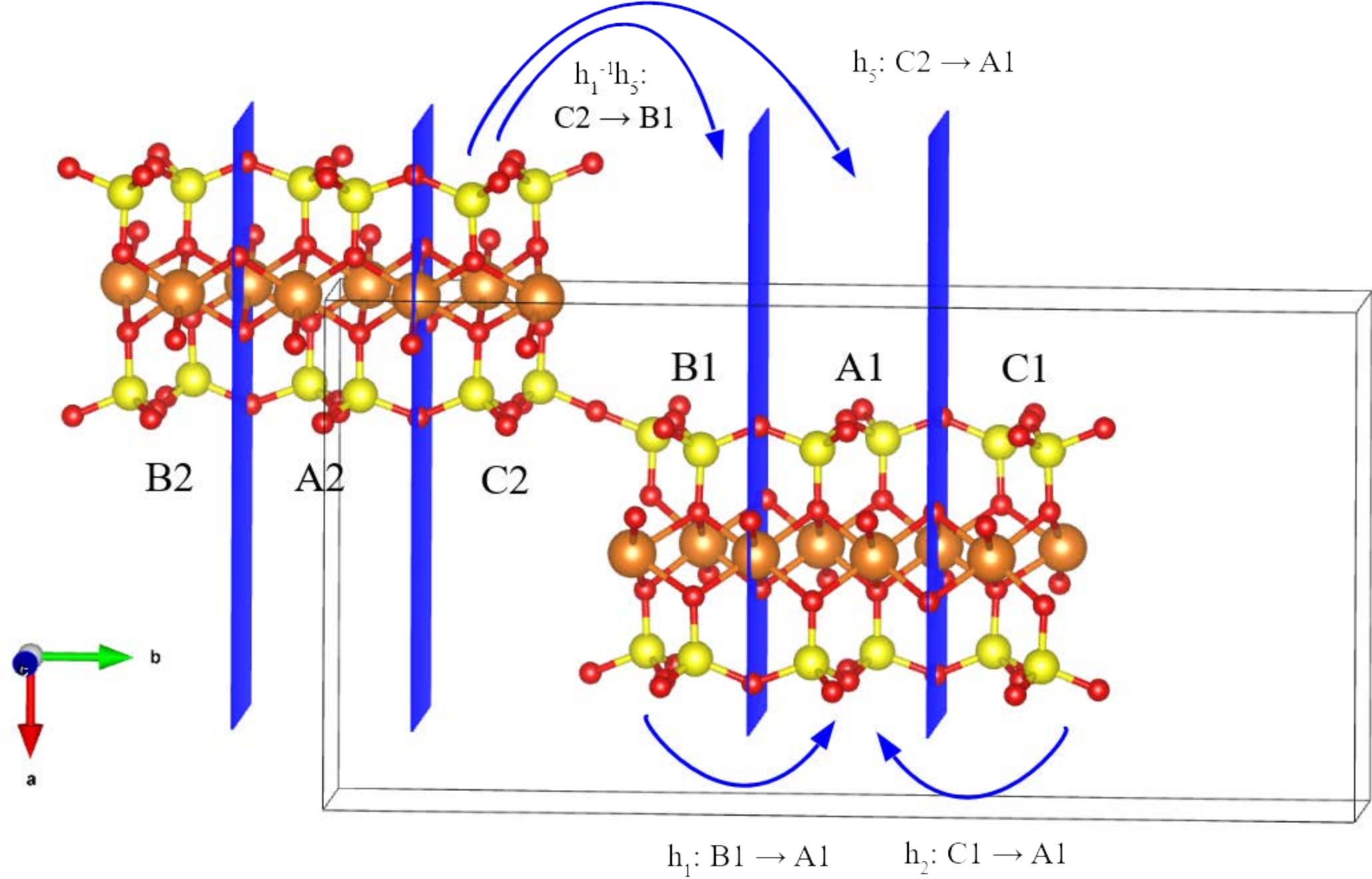


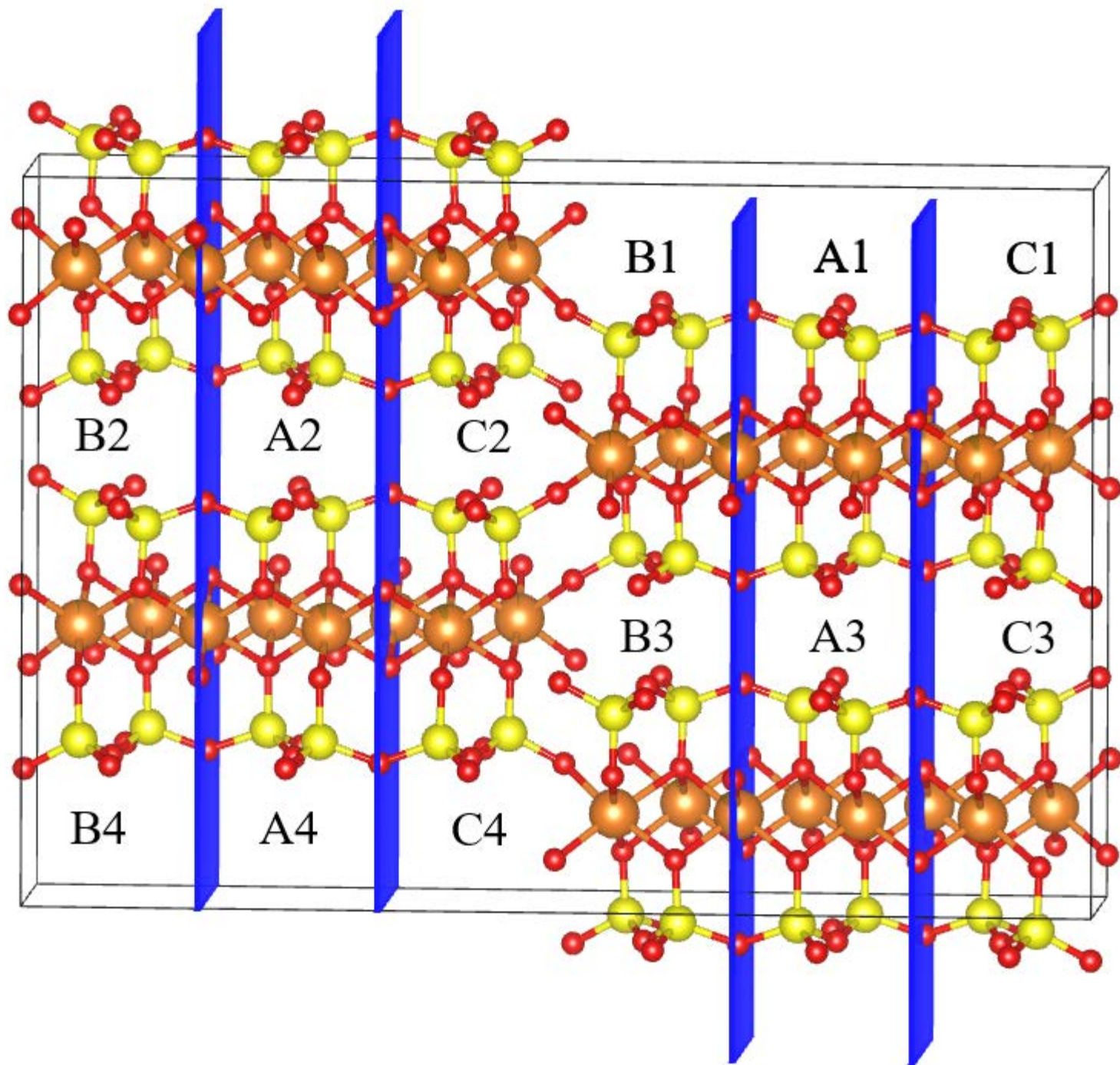
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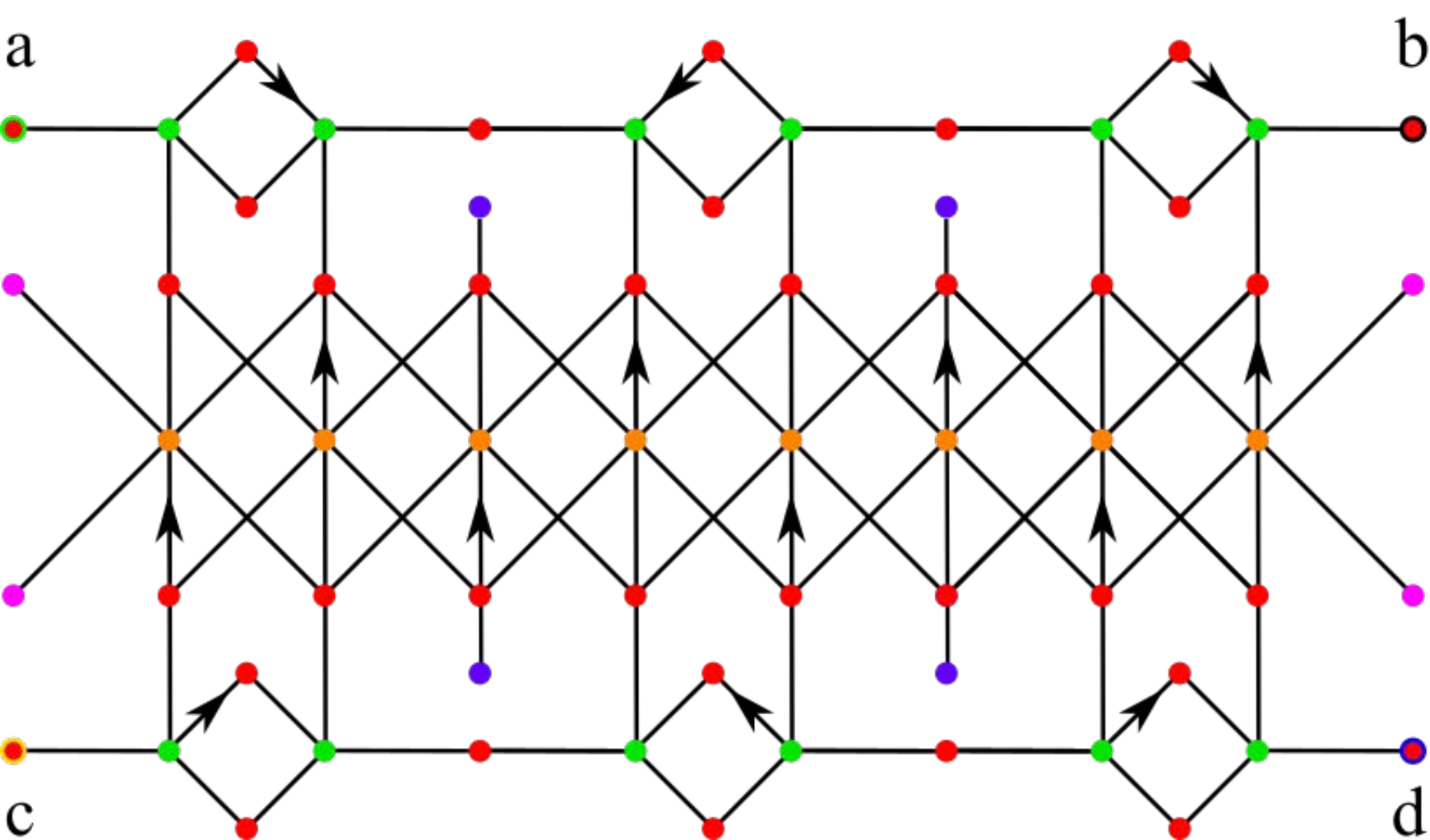
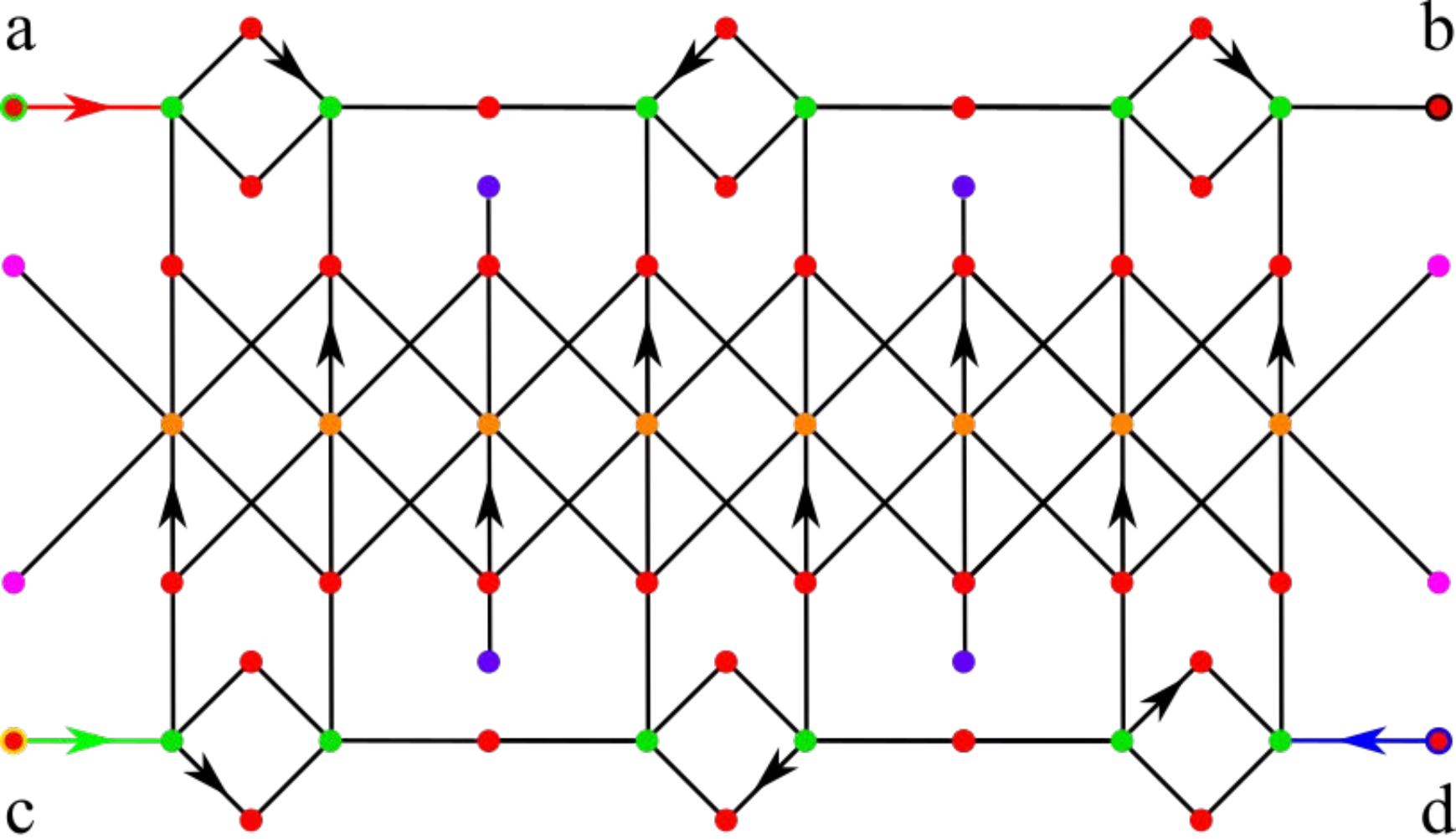


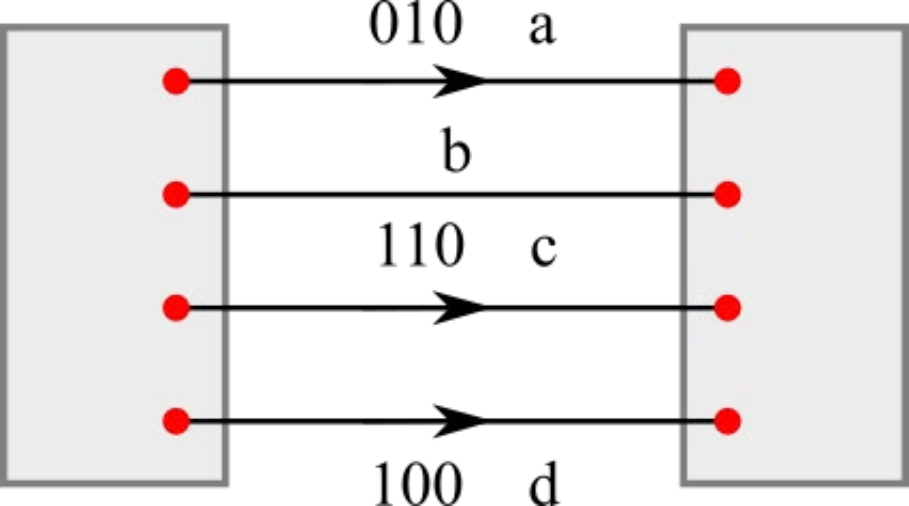
 a 
$$b$$

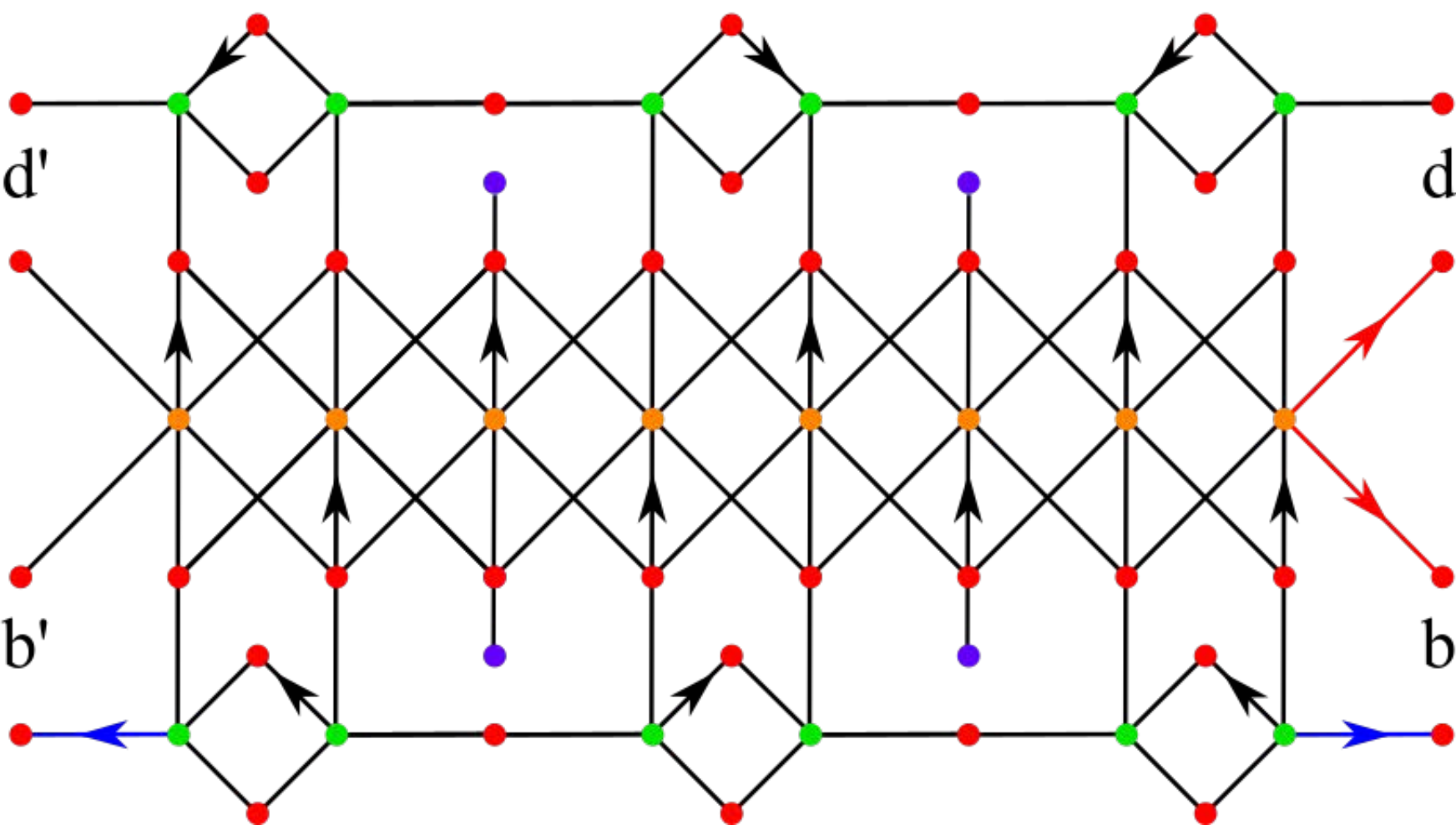
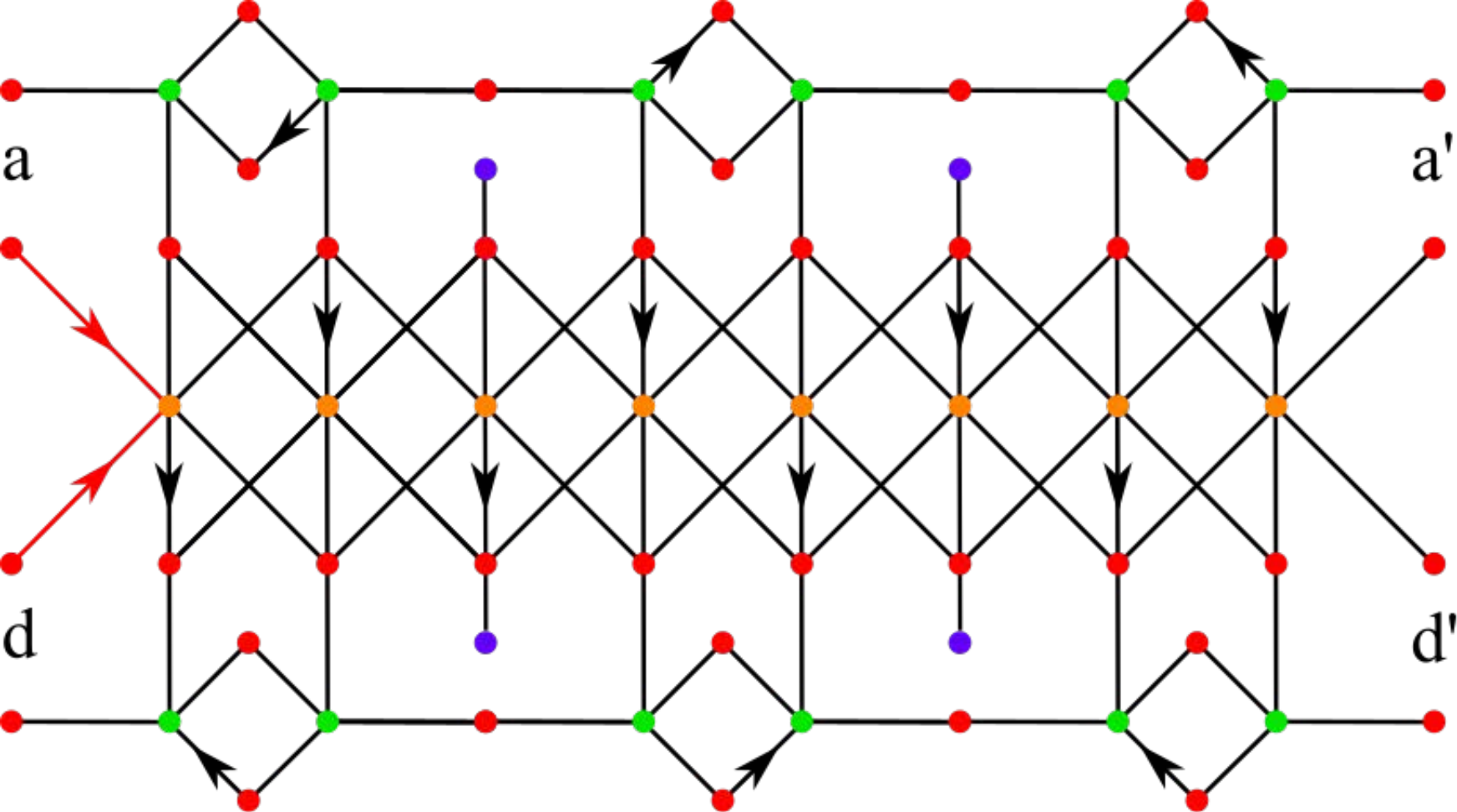


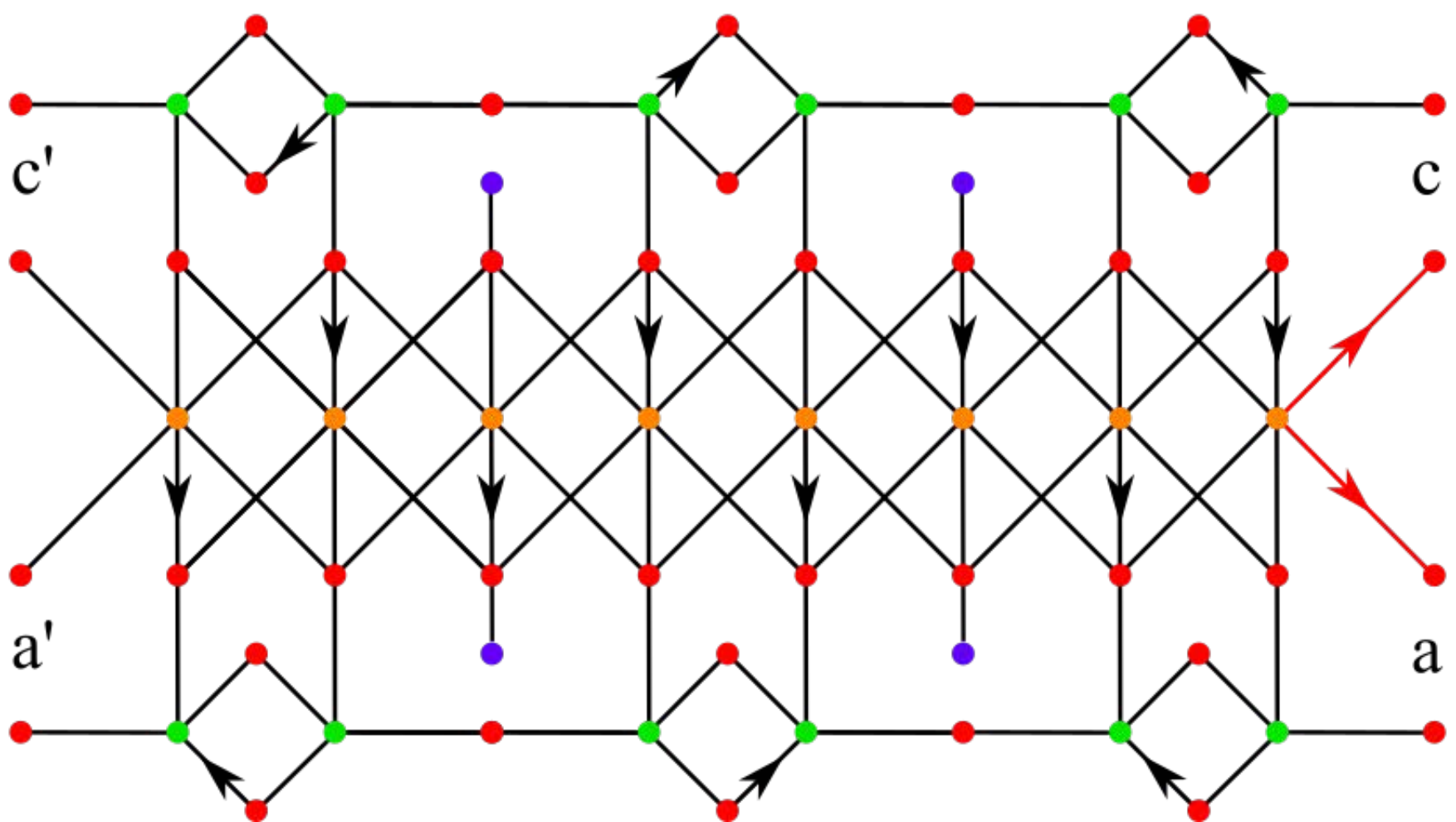
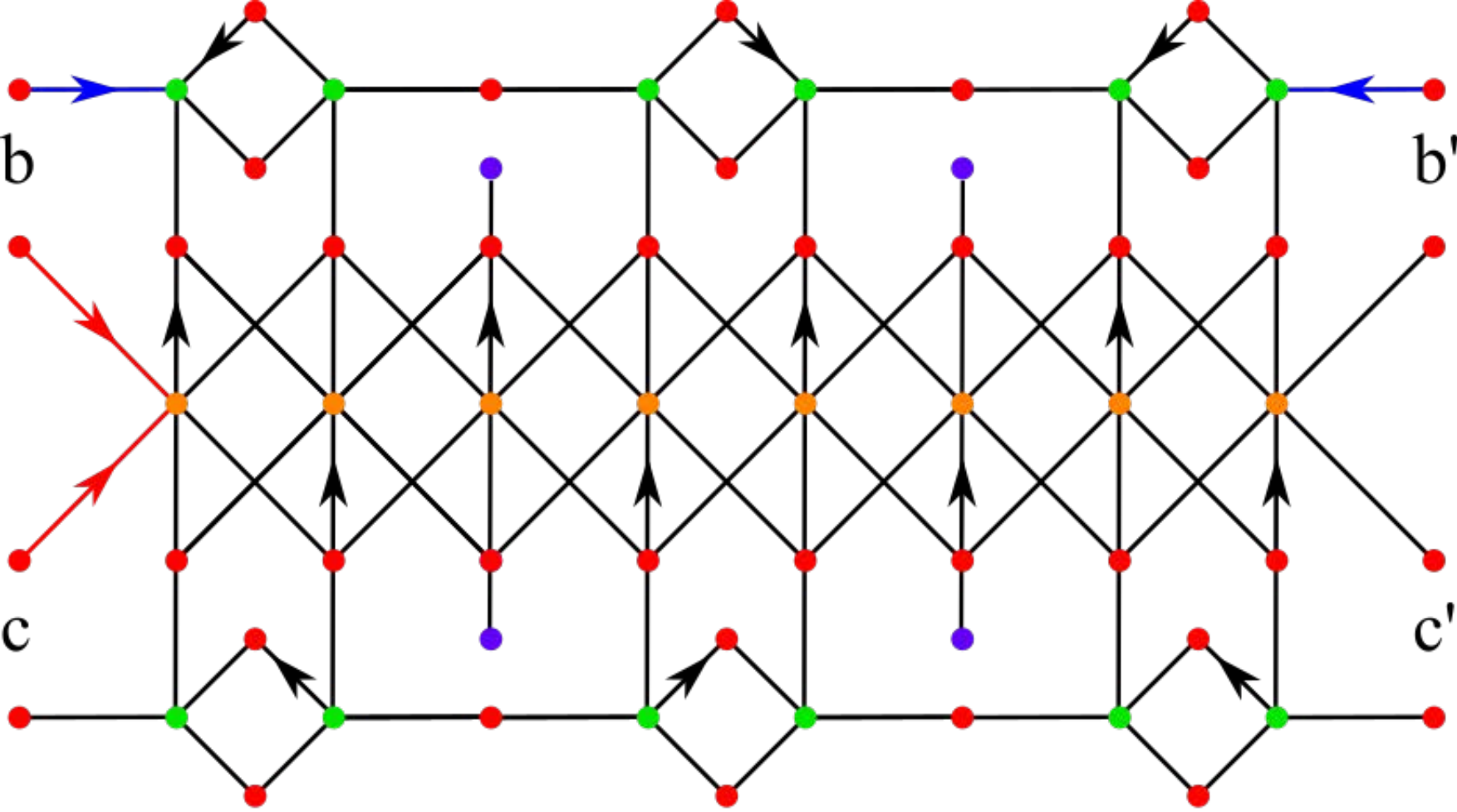


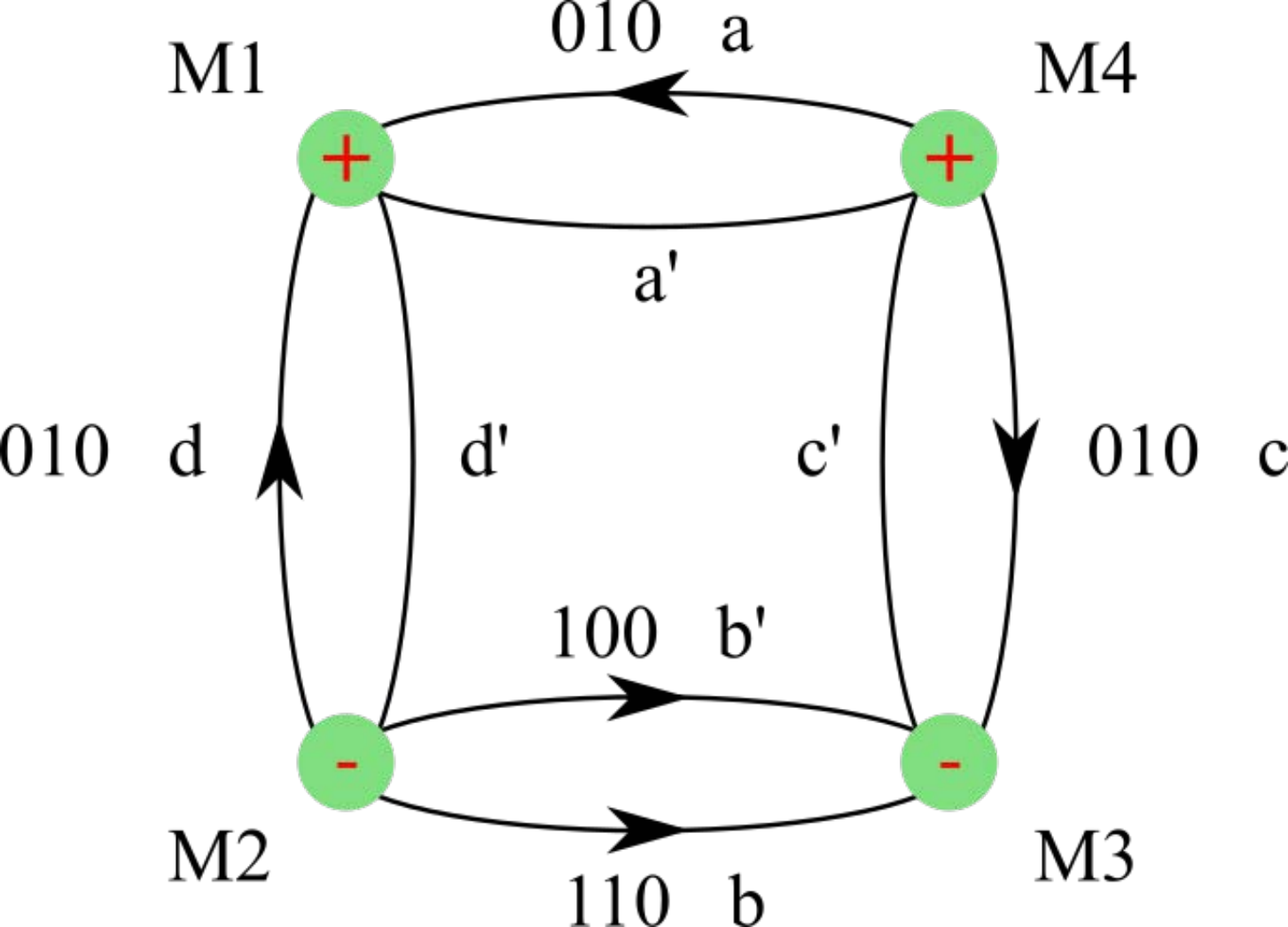


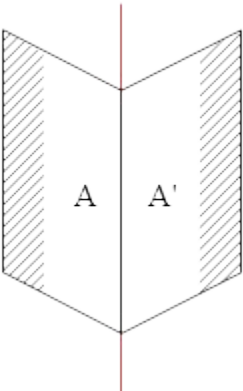
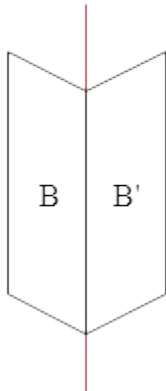










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