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► **To cite this version:**

Massimo Nespolo, Akihiro Umayahara, Jean-Guillaume Eon. A groupoid and graph-theoretical analysis of the biopyribole-palysepiole series. *European Journal of Mineralogy*, 2018, Minerals and materials: building principles and applications, 30 (3), pp.413 - 428. 10.1127/ejm/2018/0030-2726 . hal-01872490

**HAL Id: hal-01872490**

**<https://hal.univ-lorraine.fr/hal-01872490v1>**

Submitted on 12 Sep 2018

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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; trochochemical 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 trochochemical-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  $X = A, B, C...$  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:

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

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 series<sup>1</sup> 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.

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

## 117 2 Elements, operations and symbols

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

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

142 For screw rotations, a special symbol is normally used only for symmetry elements. If  $p$  is the  
143 screw component (then  $q$  and  $r$  are related to the location of the geometric element with respect to  
144 the origin), the defining operation is the one with the largest  $n$  and the smallest positive  $p$  ( $0 \leq p <$   
145  $n$ ); the symmetry element is then indicated as  $n_p^3$ . For example, among the operations  $n(p,0,0)$   
146 sharing the line  $x,0,\frac{1}{4}$ , there are  $n$  possible operations, corresponding to values of  $p$  restricted from 0  
147 to  $n-1$ ; if  $p = 0$ , then the defining operation is a pure rotation and the symmetry element is a rotation  
148 axis, although it is shared also by an infinite number of screw rotations  $n(n,0,0)$ ,  $n(2n,0,0)$   $n(3n,0,0)$   
149 and so on. If  $p > 0$ , then the defining operation is a screw rotation, there is no pure rotation in the  
150 element set and the symmetry element is therefore called a screw axis. For the sake of brevity, when  
151  $p$  takes an integer value, the same shortened notation used for symmetry elements can be used also  
152 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)  
153  $x,0,\frac{1}{4}$  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

9 2 The values of  $p,q,r$  that correspond to a half- or quarter-diagonal depend on how the geometric element is  
10 oriented with respect to the basis vectors.

11 3 We need to specify “the largest  $n$ ” because rotations of different order may share the same geometric  
12 element. For example, about the same line (geometric element) we may have operations 4,  $4^2 = 2$ ,  $4^3$  and  $4^4 = 1$ .  
13 The largest  $n$ , in this example  $n = 4$ , corresponds to the defining operation and the symmetry element is a fourfold  
14 rotation axis.

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

### 161 3 Topological analysis based on the Labelled Quotient Graph (LQG)

162 The so-called *vector method* uses graph-theoretical techniques to represent and analyse the  
163 combinatorial topology of crystal structures. The method has been extensively described in two  
164 recent papers of one of the authors (Eon, 2016; 2017) but goes back to the work of Chung *et al.*  
165 (1984). As a rough guide to the reader, this section summarizes the main features of the method  
166 needed to follow our interpretation of modular structures. The case of diopside, with the  
167 characterization of the  $R_2$  rod, will be examined as an illustration of the abstract concepts. In the  
168 next sections we will focus on the description of phlogopite, palygorskite, sepiolite and  
169 jimthompsonite using the  $R_2$  rod. Only the main components of each structure are taken into  
170 account.

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

189 Given a periodic structure and a reference unit cell, the respective labelled quotient graph can be  
190 constructed in two steps. Initially, every atom in the unit cell is represented by an isolated vertex (a  
191 point)  $V_i$  ( $i=1,n$ ) and all bonds between atoms in the unit cell are represented by an edge (a line  
192 segment or an arc) joining the representative vertices, thus giving a finite graph  $G$  associated to the  
193 combinatorial topology of the unit cell. In a 3-dimensional framework, some atoms in the unit cell  
194 must obviously be linked to atoms in neighbouring cells. Suppose that atom  $V_i$  in the reference cell,  
195 is bonded to atom  $V'_j$  in a neighbouring unit cell such that the translation  $\{1 \mid pqr\}$  (in the Seitz  
196 notation: Glazer *et al.*, 2014) maps atom  $V_j$  in the reference unit cell to this atom  $V'_j$ . Then we add  
197 an edge  $V_iV_j$  to our graph  $G$ ; this edge is oriented from  $V_i$  to  $V_j$  and carries the triple label  $pqr$  that,  
198 in topological graph theory, is called the **voltage** on the edge  $V_iV_j$ . 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  $\text{Si}_2\text{O}_2$  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  $Z^3$  (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





271 lattice translation about  $\mathbf{b}$  is obtained by applying twice the partial operation  $2_1 \frac{1}{4}, y, \frac{1}{2}$ . The  
 272 operations that look different in the two hybrid groups are simply related by a unit translation in  
 273 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  $\mathbf{a}$ ,  
 274  $\bar{1}_{0, 0, \frac{1}{2}}$  from  $\bar{1}_{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}}$  and a unit translation along  $\mathbf{a} + \mathbf{b}$ ,  $m_{x, 0, z}$  from  $m_{x, \frac{1}{2}, z}$  and a unit translation along  $\mathbf{b}$ .  
 275 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  
 276 explicitly in this analysis because they are at the boundary of the pair of modules BA but are  
 277 generated when combining the  $a$ -glide reflection at  $x, \frac{1}{4}, z$  with a full translation along  $\pm \mathbf{b}$ . These are  
 278 therefore global operations for the layer.

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

- 284 •  $t(0, 0, 1)$  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  
 285 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  $a$   $-2\mathbf{c}$  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.

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

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

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

## 305 5 Structures built on $R_5$ rods: amphiboles and palygorskite

306 The  $R_5$  rods, whose rod symmetry (kernel) is  $\mu_c 12/m1$ , occur in amphiboles and in palygorskite.  
 307 The partial operation is a  $C$ -centring translation in both cases; the unit cell having different  
 308 dimensions, the resulting structure is different, but the symmetry (type of group) is the same. The  
 309 groupoid is therefore composed by two hybrid groups, each containing a kernel and a hull.

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

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

310  
311

and, by specifying the operations:

$$1, 2 \, \frac{1}{2}, y, \frac{1}{2}, \bar{1} \, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, m \, x, \frac{1}{2}, z \quad \cup \quad t^{(1/2,1/2,0)}, 2_1 \, \frac{1}{4}, y, \frac{1}{2}, \bar{1} \, \frac{1}{4}, \frac{1}{4}, \frac{1}{2}, a \, x, \frac{1}{4}, z$$

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

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

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

## 327 6 Structures built on $R_8$ rods: sepiolite and jimthompsonite

328 As shown by Nespolo and Bouznari (2017), the  $Z_8$  module, and thus the  $R_8$  rod, can be almost  
329 exactly reconstructed by expanding the  $Z_5$  module through the action of a pseudo-partial mirror,  
330 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  
331 along  $-\mathbf{b}$  so that the  $R_8$  rod can be ideally separated into three  $R_2$  rods, below labelled as A (middle),

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

333  $\not\mu_c 1c1$  respectively for sepiolite and jimthompsonite. The octahedral cations and oxygen atoms at the  
334 boundaries between the rods, *i.e.* approximately on the pseudo-partial mirrors, are the additional  
335 components necessary to obtain the  $R_8$  rod from the stacking of  $R_2$  rods. The unit cell of sepiolite  
336 contains two  $Z_8$  modules and the unit cell of jimthompsonite four; these are related by one and three  
337 partial operations respectively. These, and the corresponding  $R_8$  rods, are labelled sequentially from  
338 1 to 2 and from 1 to 4 respectively; the same numbering scheme is applied to the  $R_2$  components A,  
339 B and C. Concretely, the structure of the two title minerals can be obtained in two steps (Figures 6  
340 and 7).

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

25  
26

344 (jimthompsonite), mapping A1 to C1; complete the  $R_8$  rod with the additional atoms;  
345 2. build the structure of the two minerals by applying the mapping of different  $R_8$  rods; this leads  
346 automatically to the mappings of (Aj,Bj,Cj)  $R_2$  rods in the  $j > 1$   $R_8$  rod to the corresponding  
347 (A1,B1,C1)  $R_2$  rods in target  $R_8$  rod.

348 For sepiolite the operation in step 2 is an  $n$ -glide reflection at  $\frac{1}{4},y,z$ , whereas for jimthompsonite,  
349 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  
350 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  
351  $12^2 = 144$  blocks for jimthompsonite. This means we have to derive  $4 \times 36 = 144$  and  $2 \times 144 = 288$   
352 operations respectively, not all of which will turn out to be different; some of the operations  
353 obtained in this way will actually be global operations building the space group of the mineral.

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

361 Table 1 presents the groupoid structure of sepiolite. The 144 combinations  $h_j^{-1}K_A h_i$  ( $i,j = 0,1,2$ ,  $h_0$   
362 = identity), result in 40 operations, listed with a sequence number in Table 2. Finally, Table 3 gives  
363 the operations in each kernel and hull by the sequential number defined in Table 2. To be noted that  
364 some of the operations obtained in this way are *not* the defining operations of the corresponding  
365 symmetry element. For example, the operations No. 33,  $2_2 \frac{1}{4},\frac{1}{4},z$ , which is a shorthand notation for  
366  $2(0,0,1) \frac{1}{4},\frac{1}{4},z$ , is a screw rotation about the direction  $\frac{1}{4},\frac{1}{4},z$  with screw component corresponding  
367 to a full translation along  $c$ . The defining operation is  $2 \frac{1}{4},\frac{1}{4},z$  and does also occur when  $2_2 \frac{1}{4},\frac{1}{4},z$   
368 is combined with a lattice translation along  $-c$ , which belongs to the rod symmetry.

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

373 Figure 8 displays the LQG of sepiolite evidencing the structural role of two  $R_8$  rods and their  
374 relations with the  $R_2$  rod of diopside. Indeed, one can look at each  $R_8$  rod as built from three  
375 interlinked  $R_2$  rods stuffed by two octahedral cations at the third and sixth position, starting from the  
376 left or from the right of the figure. Alternatively, one can build the  $R_8$  rod by interlinking an  $R_5$  rod  
377 with an  $R_2$  rod and stuffing it with an additional octahedral cation in the third ( $R_2 + R_5$ ), or  
378 equivalently in the sixth position ( $R_5 + R_2$ ). Figure 9 shows the simplified LQG of sepiolite  
379 representing the linkage of the  $R_8$  rods. This LQG is that of the **sql** lattice in a body-centred cell,  
380 which indicates that the two  $R_8$  rods are related by a translation in the (001) plane. This centring  
381 translation is associated to the permutation  $\phi_1 = (a,d)(b,c)$ , also exchanging the two rods M1 and  
382 M2, which leaves invariant every net voltage over the cycles of the simplified LQG. However, the  
383 permutation induced by  $\phi_1$  in the full LQG of sepiolite realizes an inversion of the [001] direction.  
384 This permutation must therefore be associated to the glide reflection  $n(\frac{1}{2}, \frac{1}{2}, 0)$ . Partial operations  
385 between the three  $R_2$  rods forming the  $R_8$  rod can be deduced from those of palygorskite using the  
386 ( $R_2 + R_5$ ) or ( $R_5 + R_2$ ) construction. Indeed, the central  $R_2$  rod A of  $R_8$  belongs to the  $R_5$  rod in both  
387 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  
388 or C, by a partial mirror reflection with mirror plane going through the added octahedral cations.  
389 The orientation of the mirror plane can be obtained from a complete analysis of the other two  
390 generators of the symmetry group of sepiolite using the two LQGs. It can be seen that the

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

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

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

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

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

## 438 7 Chesterite as a contracted twin of jimthompsonite

439 Chesterite is composed by an alternation along the  $\mathbf{b}$  axis of  $R_8$  and  $R_5$  rods. The unit cell  
440 contains four  $Z_8$  and four  $Z_5$  modules; pairs of modules of the same type are related by an  $A$   
441 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  
442  $n$ -glide about the plane  $x,y,1/4$ . The kernel is  $\mu_c1c1$  for  $Z_8$  and  $\mu_c1m1$  for  $Z_5$ . The two structure-  
443 building operations applied to the two modules produce the space group of chesterite, of type  
444  $A2_1ma$ ; the groupoid degenerates to a group, as in the case of phlogopite, palygorskite and  
445 tremolite.

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

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

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

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

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

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

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

## 493 8 Discussion

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

511 **Acknowledgments.** This article is devoted to Professors Giovanni Ferraris and Stefano Merlino,  
512 pioneers of the study of modularity in crystal structures and mentors of the first author, on occasion  
513 of their 80<sup>th</sup> birthday. This research has been conducted during a short term study abroad stay (AU)  
514 at Université de Lorraine, France, funded by the Tobitate Japan Scholarship Program. JGE thanks  
515 CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico of Brazil) for support  
516 during this work. The critical remarks by two anonymous reviewers are gratefully acknowledged.

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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  $\rightarrow A1): n_{\frac{1}{4},y,z}$ ;  $h_4 (B2 \rightarrow A1) = h_1 h_3 = 2_1 \frac{1}{4},0.17215,z$ ;  $h_5 (C2 \rightarrow A1) = h_2 h_3 = 2_1 x,0.3294,z$ .

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

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 | $2 (0,0,-158,0) \frac{1}{2},y,\frac{1}{2}$ | 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.

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

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  $A1): a_{x,y,\frac{1}{4}}$ ;  $h_7 (B3 \rightarrow A1) = h_1 h_6 = 2_{1 x,0.6662,\frac{1}{4}}$ ;  $h_8 (C3 \rightarrow A1) = h_2 h_6 = 2_{1 x,0.83407,\frac{1}{4}}$ ;  $h_9 (A4 \rightarrow A1): \bar{1}_{\frac{1}{2},\frac{1}{2},\frac{1}{2}}$ ;  
642  $h_{10} (B4 \rightarrow A1) = h_1 h_9 = 2 (0,0.3324,0)_{\frac{1}{2}y,0}$ ;  $h_{11} (C4 \rightarrow A1) = h_2 h_9 = 2 (0,0.66814,0)_{\frac{1}{2}y,0}$ .

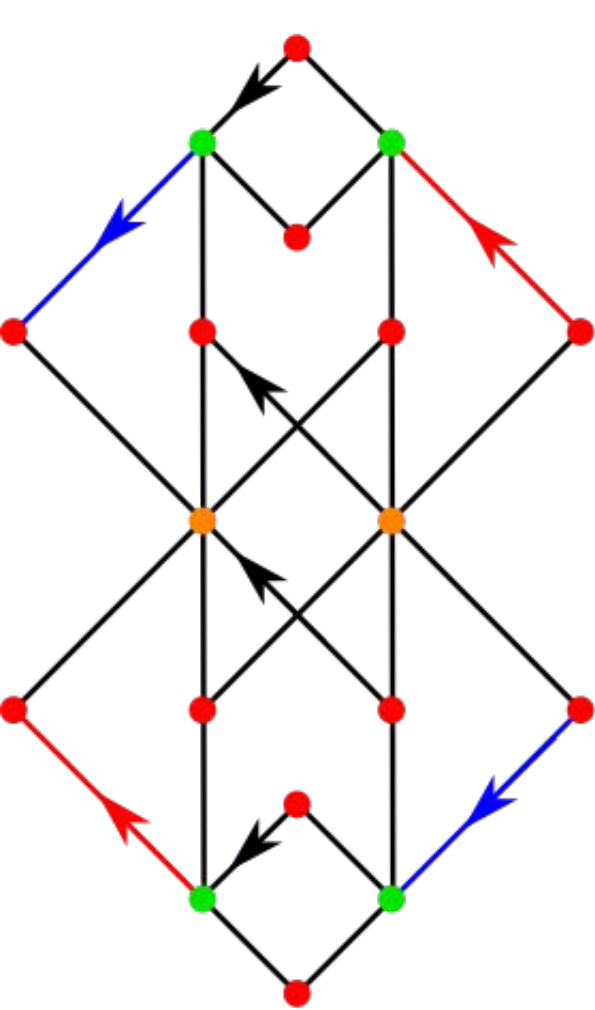
|                     |                        |                        |                        |                        |                        |                        |                        |                        |                        |                           |                        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

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.

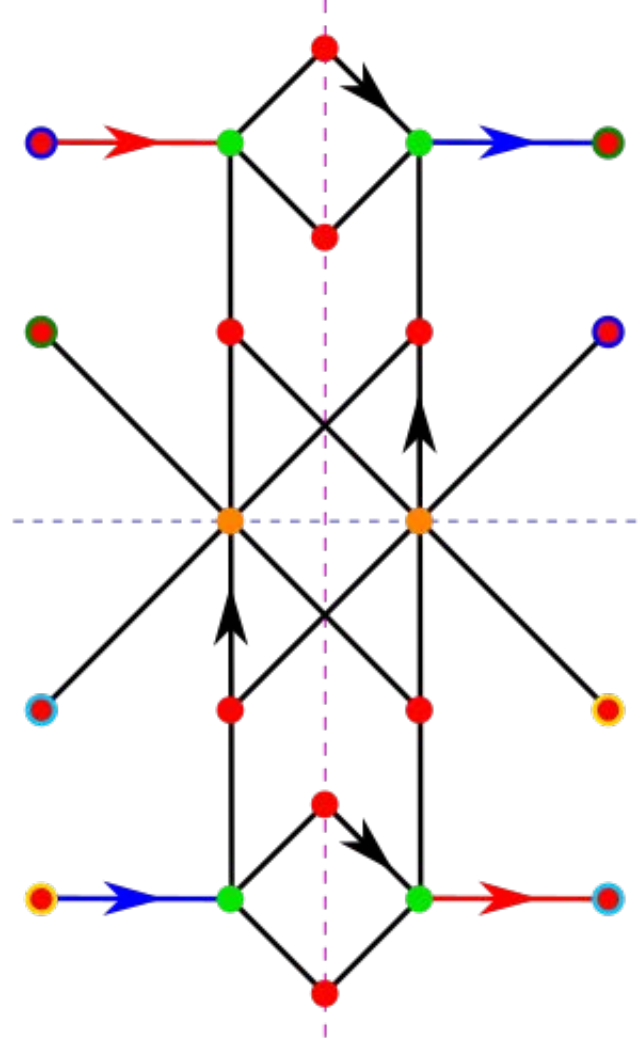
| No | Op.                              | Fr | No | Op.   | Fr | No | Op.                                  | Fr | No | Op.   | Fr |
|----|----------------------------------|----|----|---|----|----|--------------------------------------|----|----|---|----|
| 1  | 1                                | 12 | 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 | $2\bar{1} x, 0.666065, \frac{1}{4}$             | 8  | 22 | $2(0, 1.33213, 0) 0, y, 0$           | 8  | 32 | $2\sqrt{4}, -0.083935, z$                       | 8  |
| 3  | $t(0, -0.16787, 0.5)$            | 8  | 13 | $2\bar{1} x, 0.833935, \frac{1}{4}$             | 8  | 23 | $2(0, 1.66787, 0) 0, y, 0$           | 8  | 33 | $2\sqrt{4}, 0.083935, z$                        | 8  |
| 4  | $t(0, -0.33574, 0.5)$            | 4  | 14 | $2\bar{1} x, 0.58213, 0$                        | 4  | 24 | $2(0, 1.16426, 0) 0, y, \frac{1}{4}$ | 4  | 34 | $2_1 \sqrt{4}, -0.16787, z$                     | 4  |
| 5  | $t(0, 0.335746, 0.5)$            | 4  | 15 | $2\bar{1} x, 0.91787, 0$                        | 4  | 25 | $2(0, 1.83574, 0) 0, y, \frac{1}{4}$ | 4  | 35 | $2_1 \sqrt{4}, 0.16787, z$                      | 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  | $\bar{1} 0, 0.083935, \sqrt{4}$  | 8  | 17 | $g(0, -0.33213, \frac{1}{2}) \frac{1}{4}, y, z$ | 8  | 27 | $m x, 0.666065, z$                   | 8  | 37 | $g(\sqrt{2}, 0.16787, 0) x, y, 0$               | 8  |
| 8  | $\bar{1} 0, -0.083935, \sqrt{4}$ | 8  | 18 | $g(0, -0.66787, \frac{1}{2}) \frac{1}{4}, y, z$ | 8  | 28 | $m x, 0.8343935, z$                  | 8  | 38 | $g(\sqrt{2}, -0.16787) x, y, 0$                 | 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.

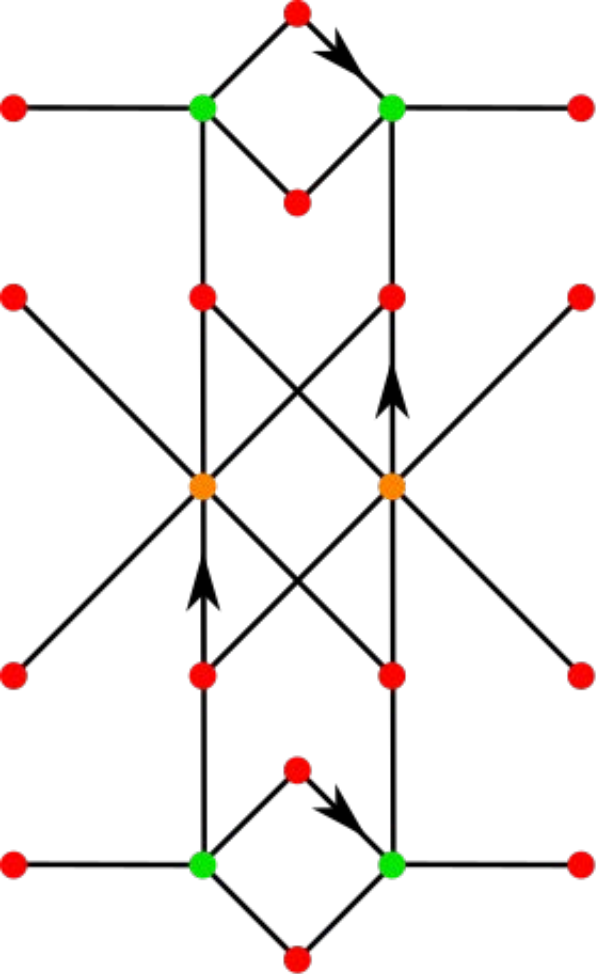
|          |              |              |              |              |              |              |              |              |              |              |              |              |
|----------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|---------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



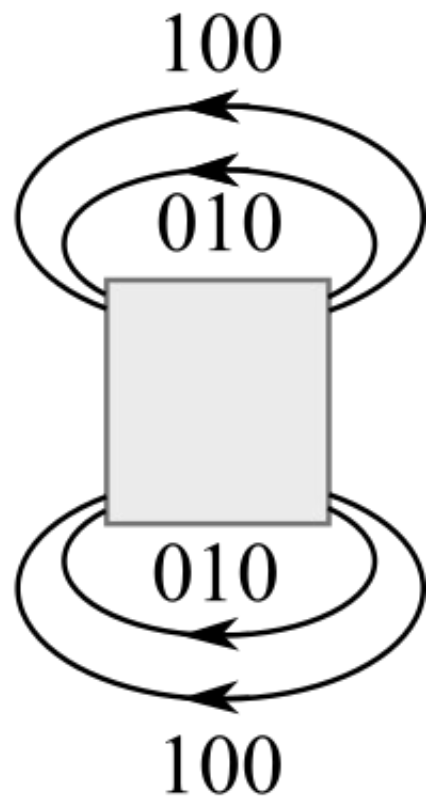
*a*



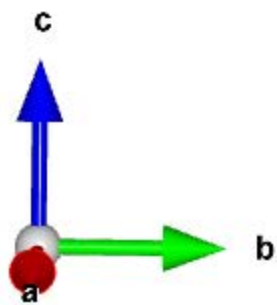
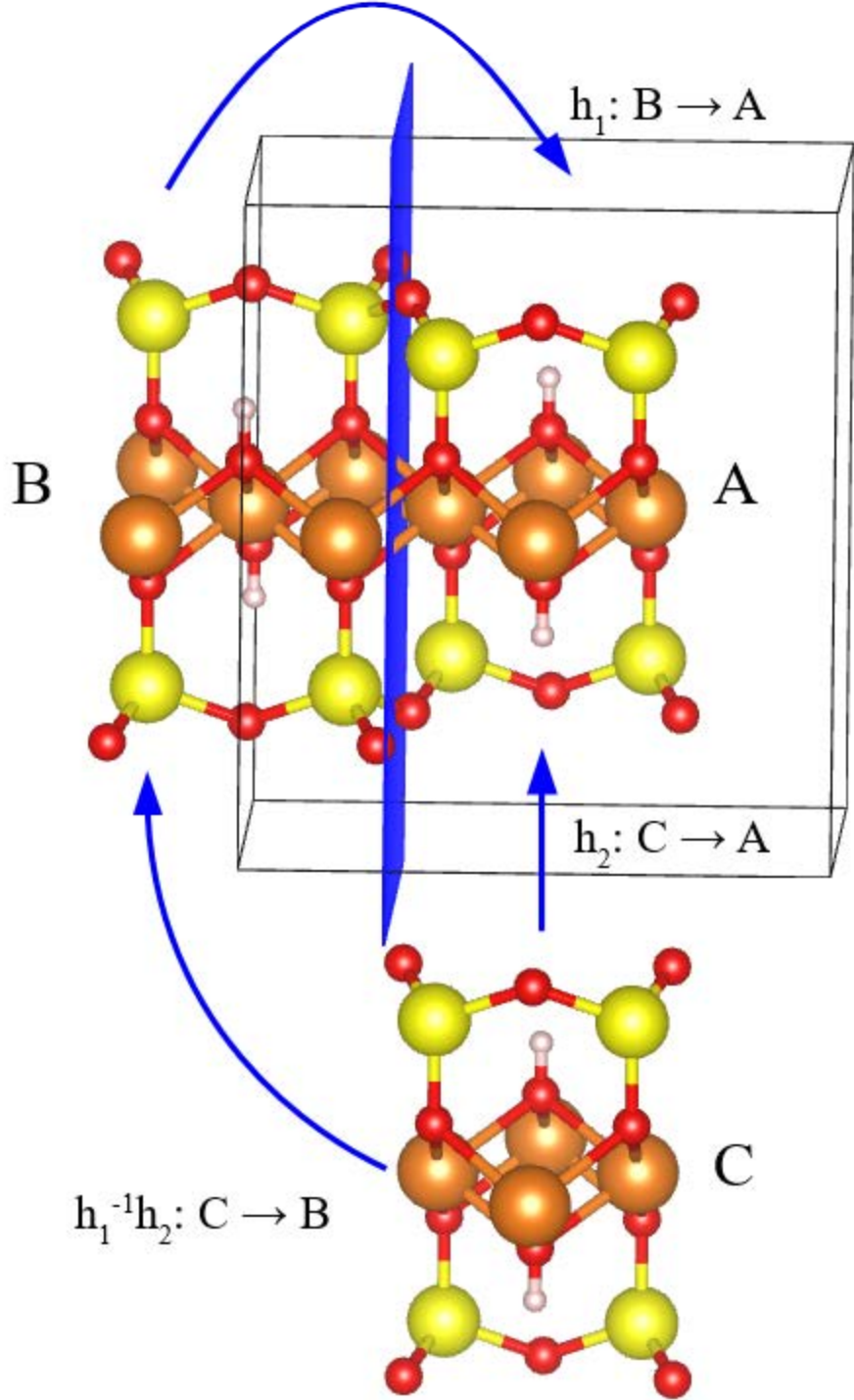
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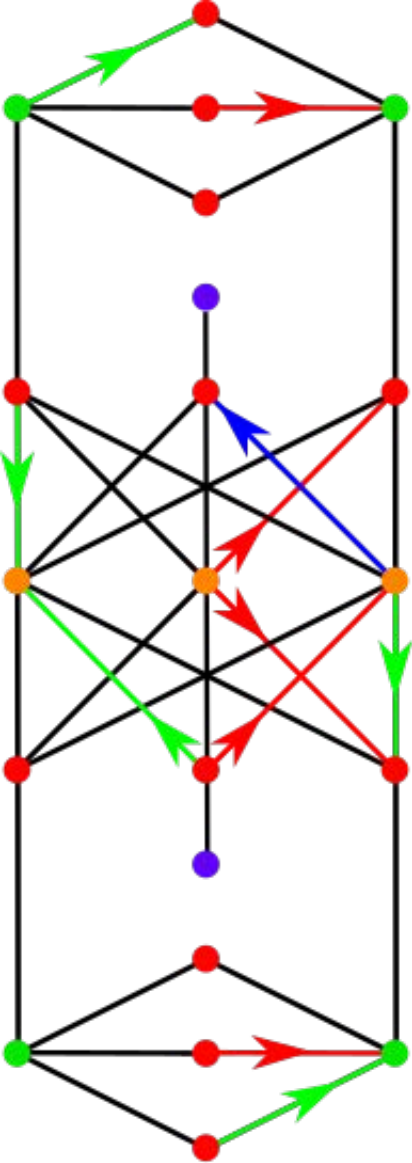


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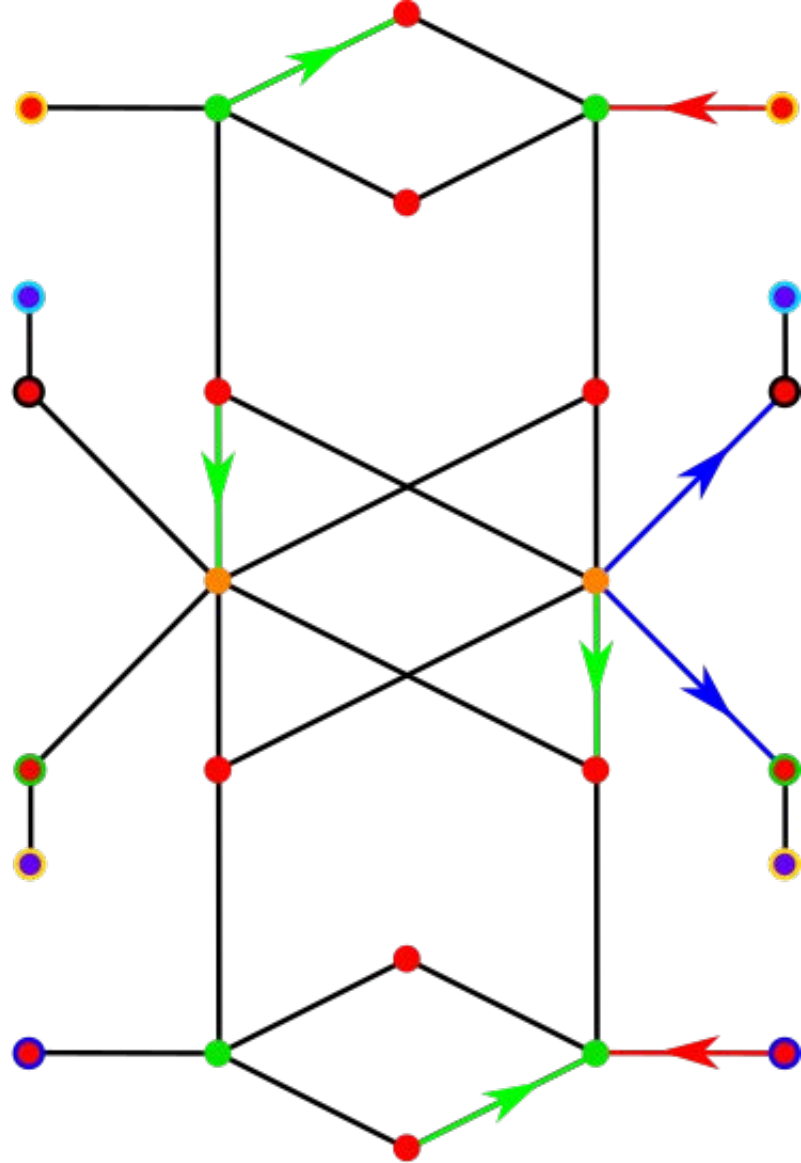


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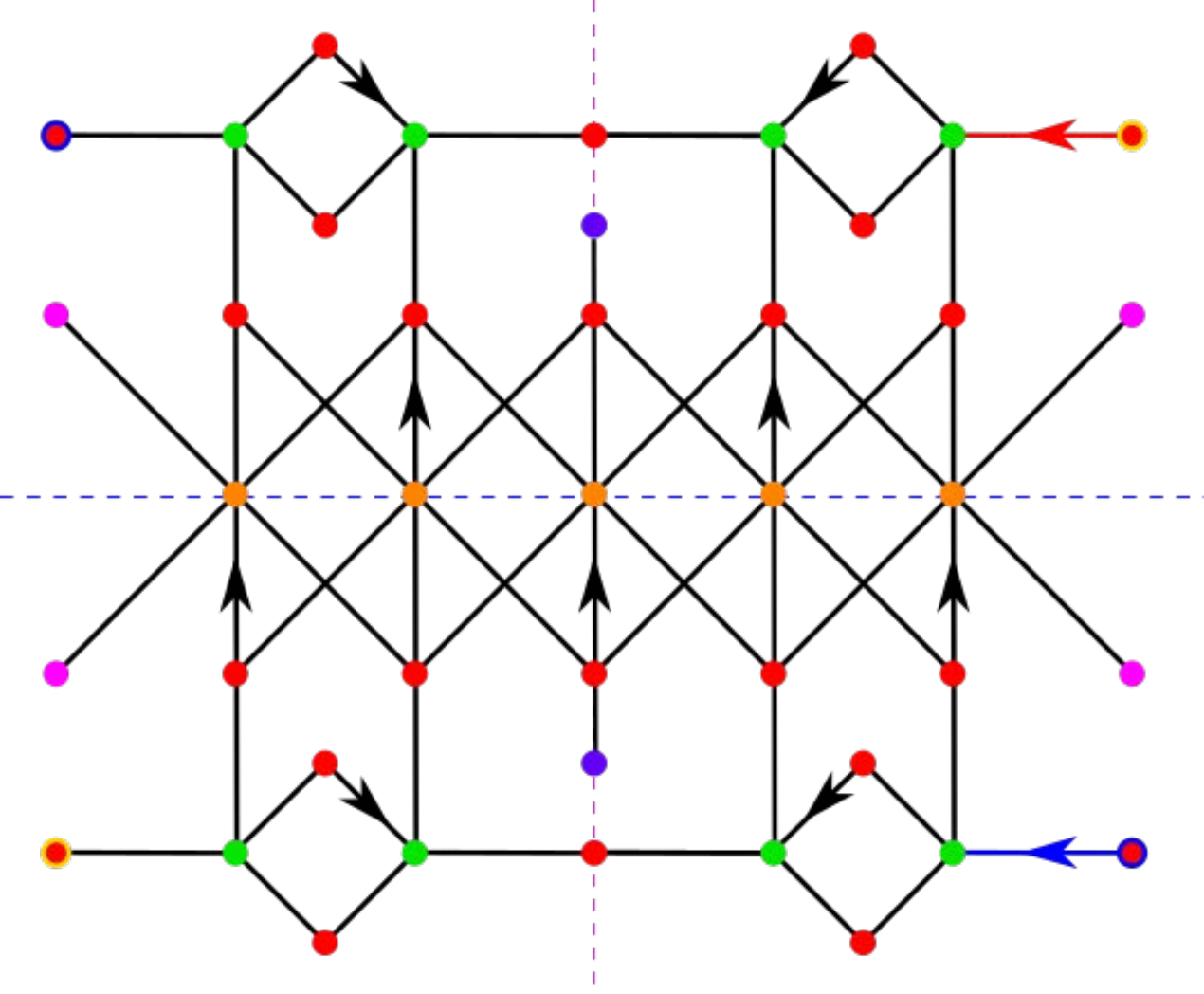


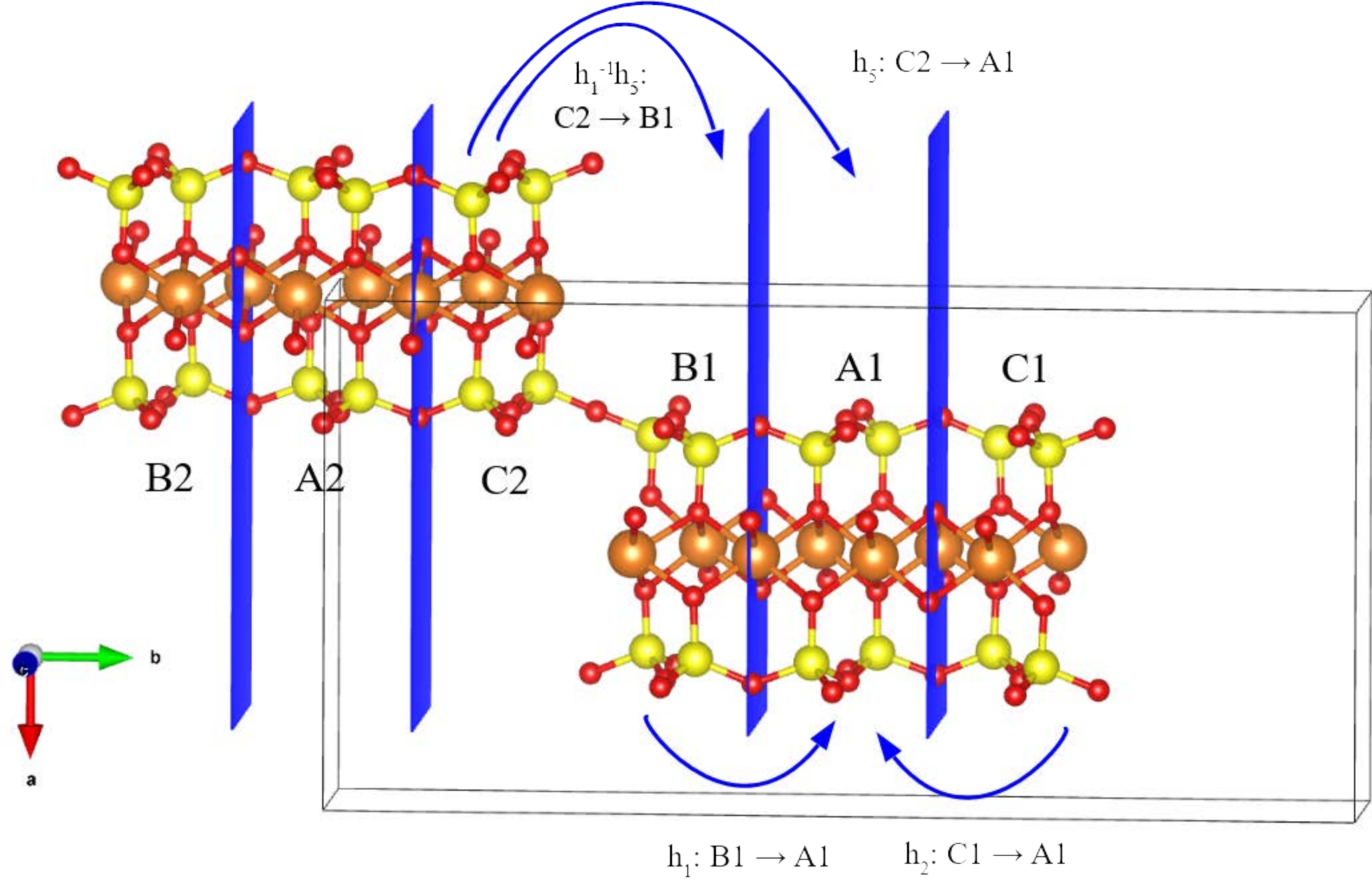
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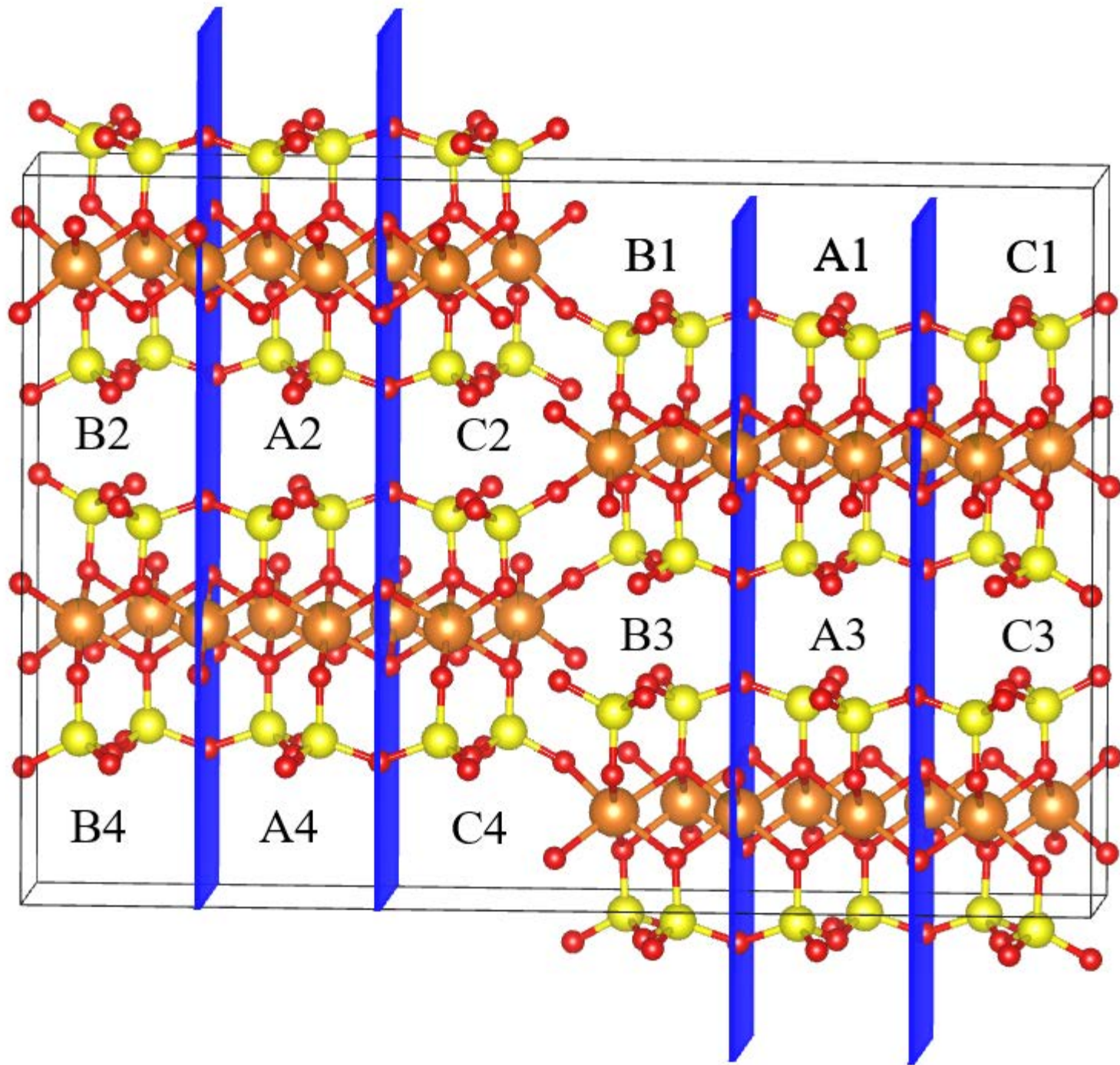


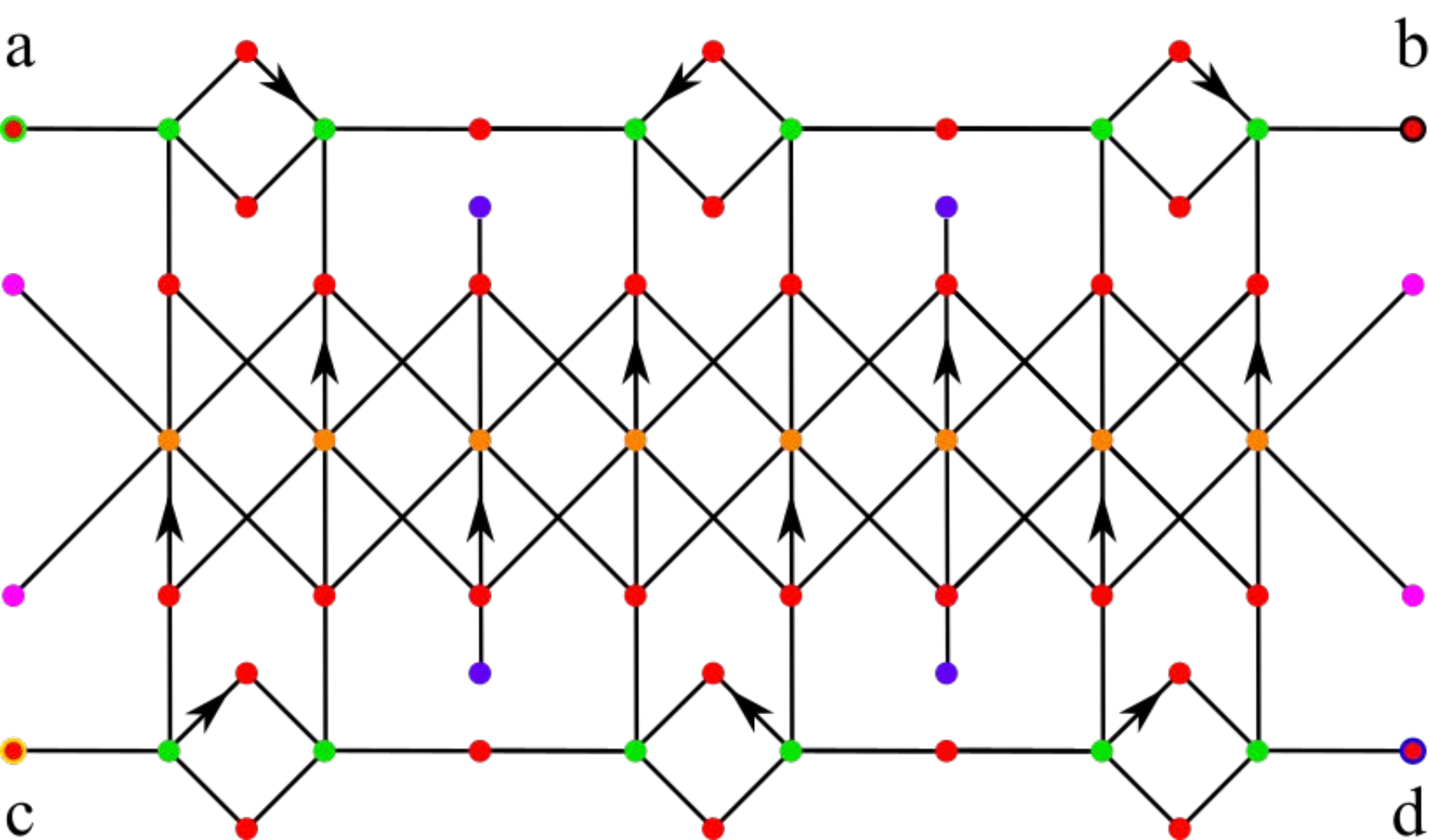
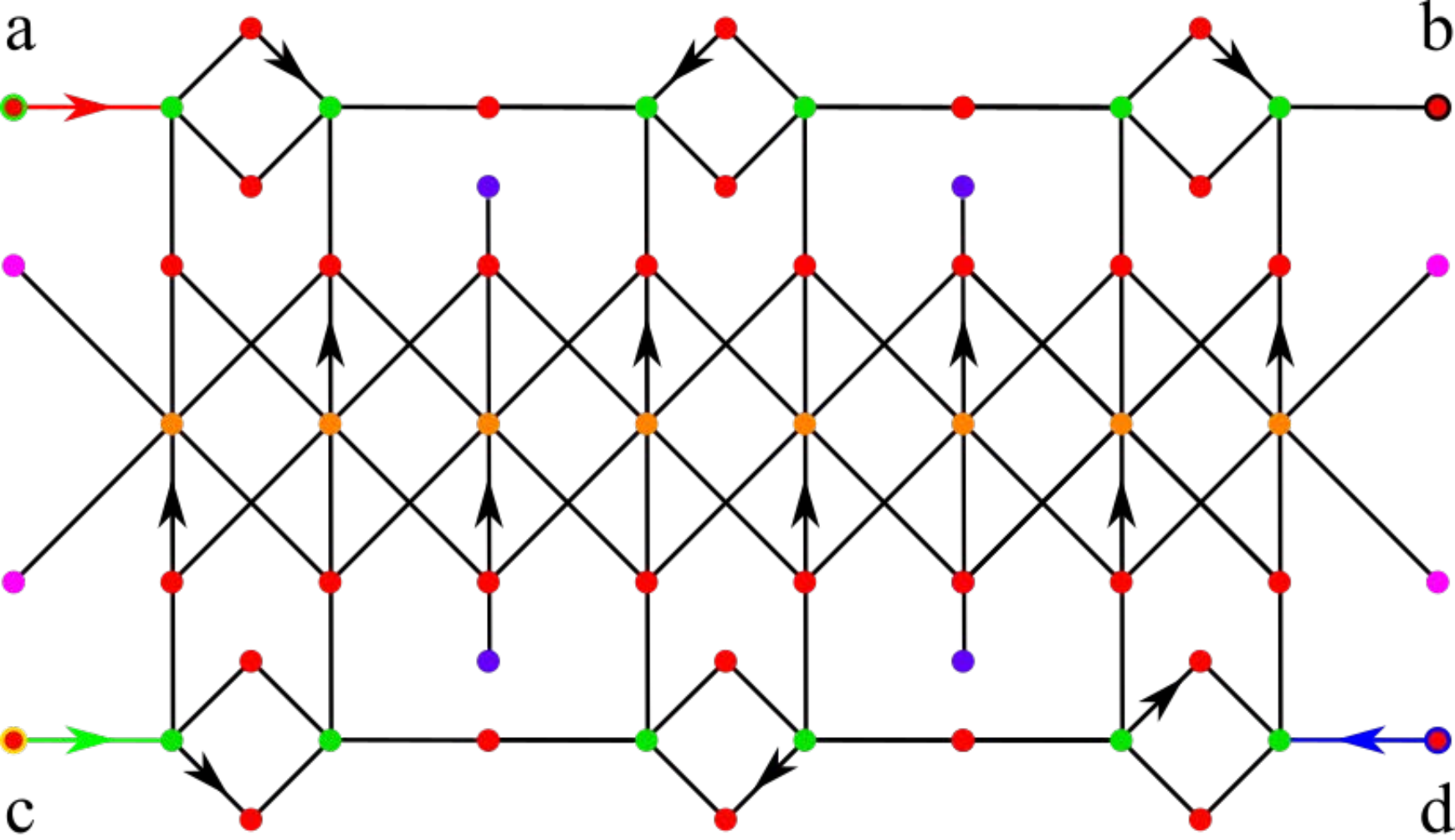
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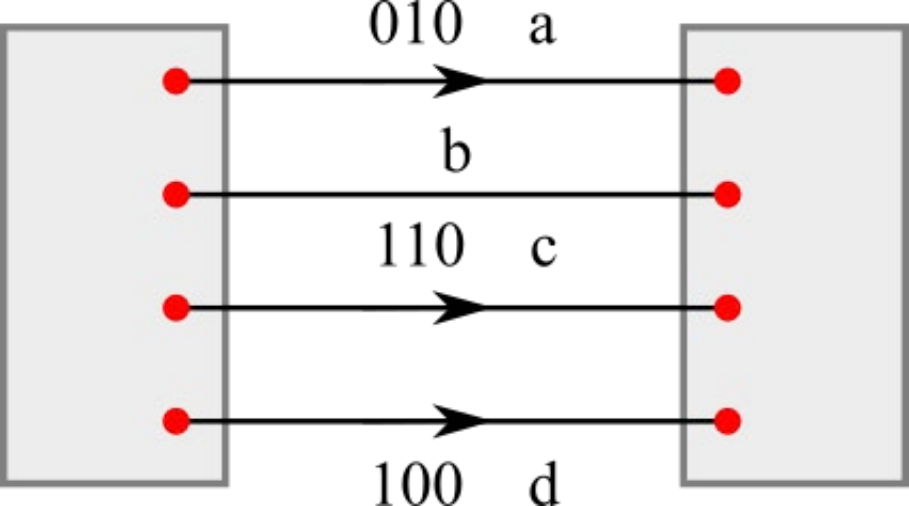




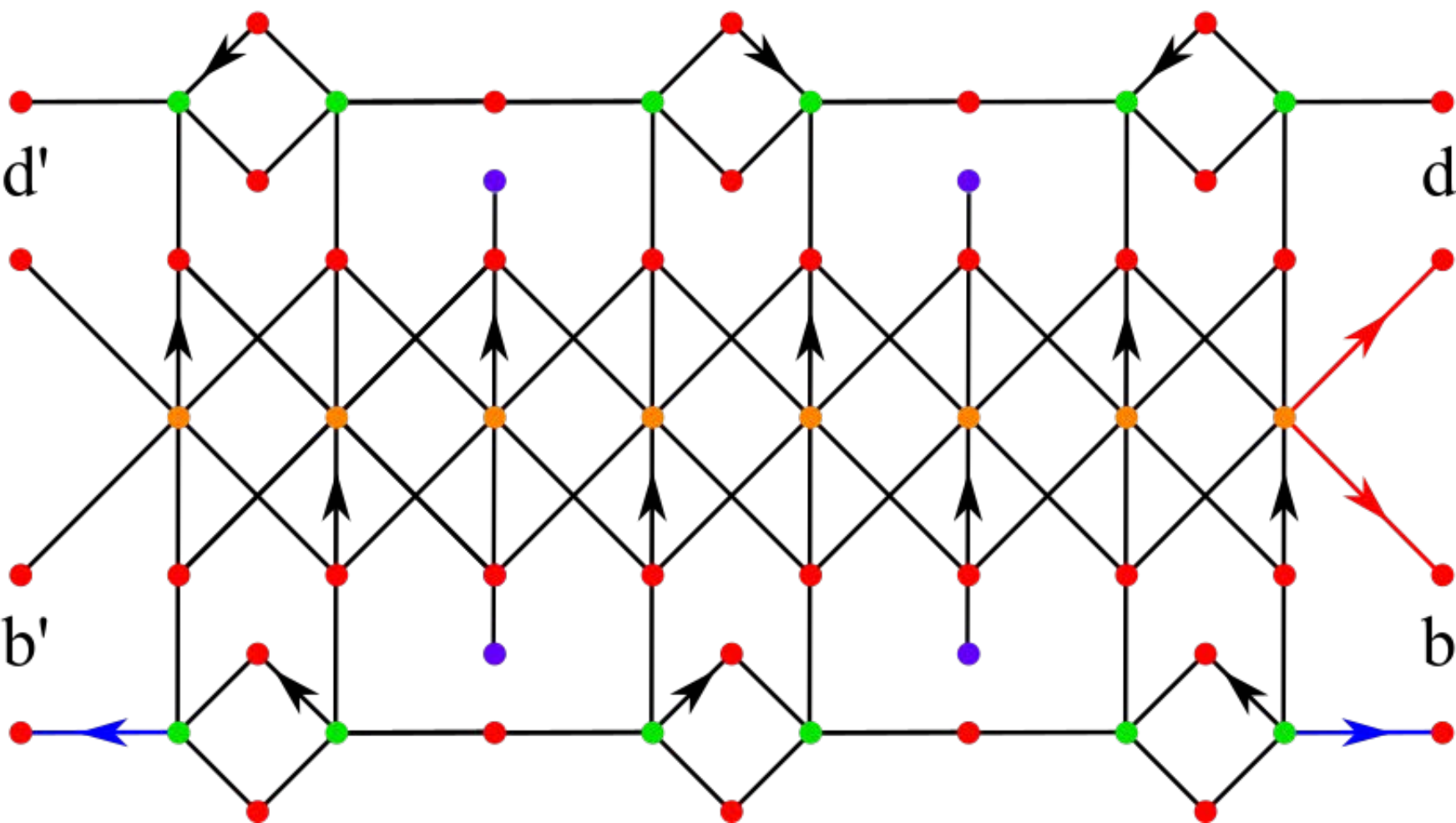
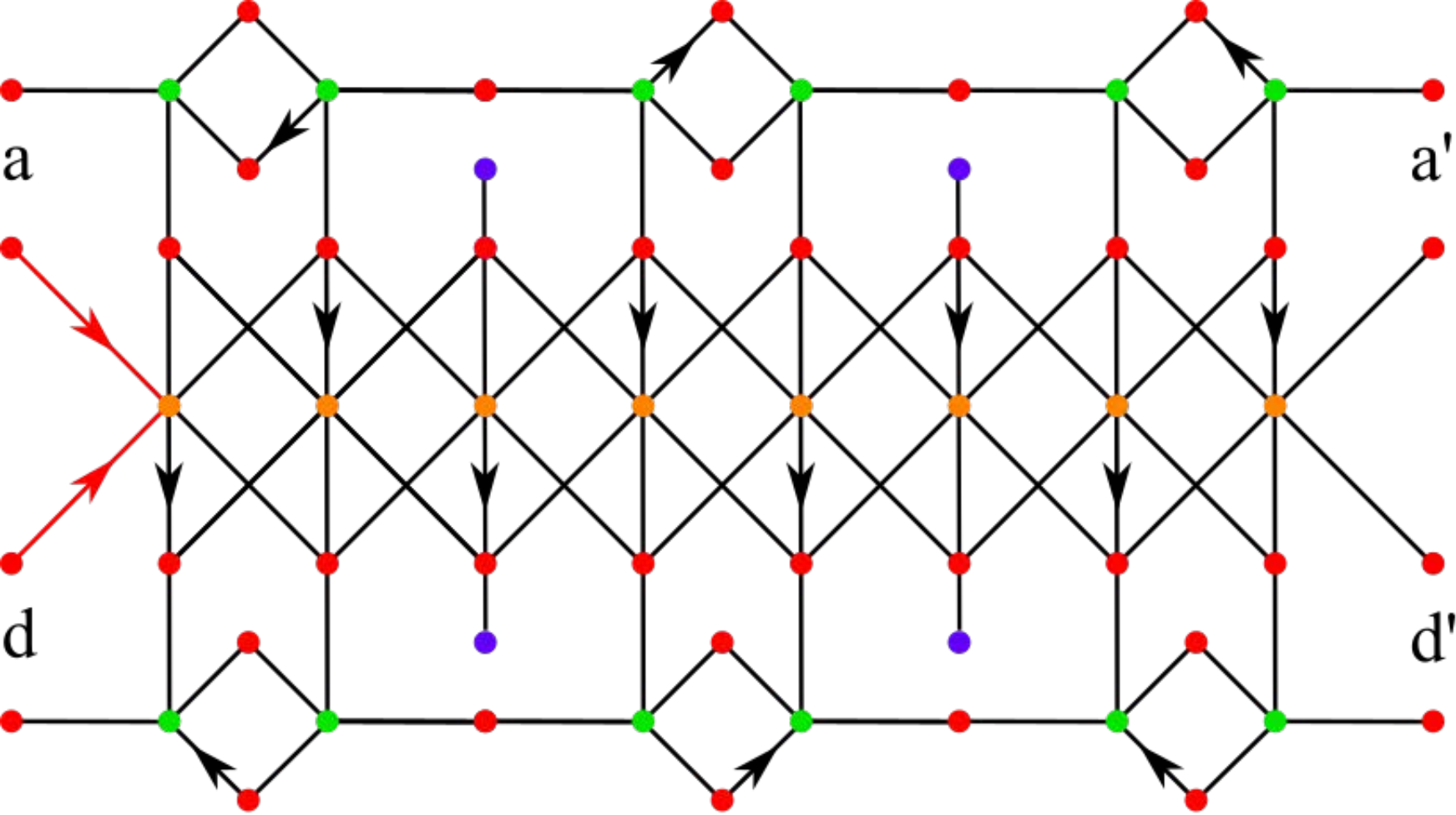


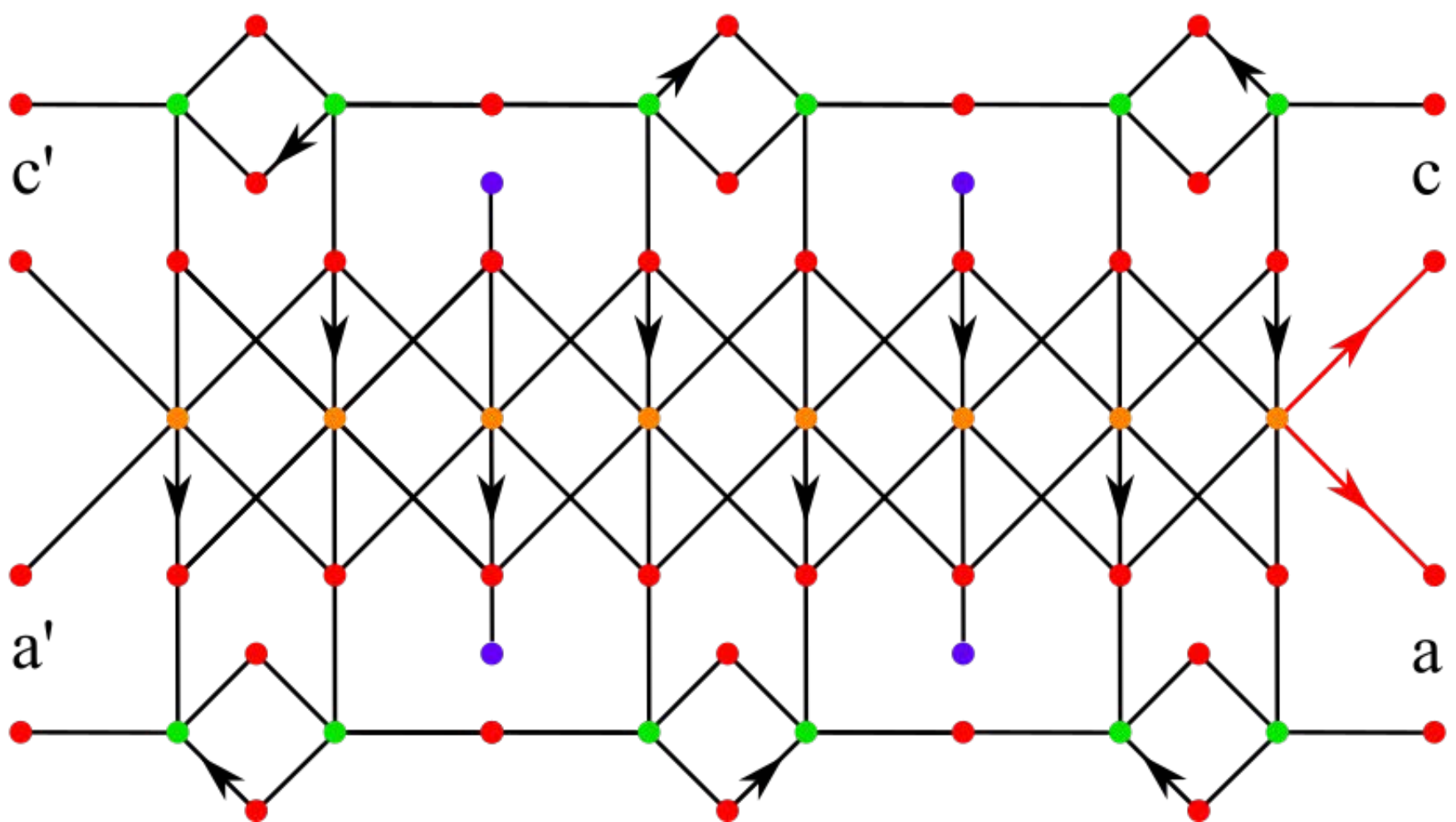
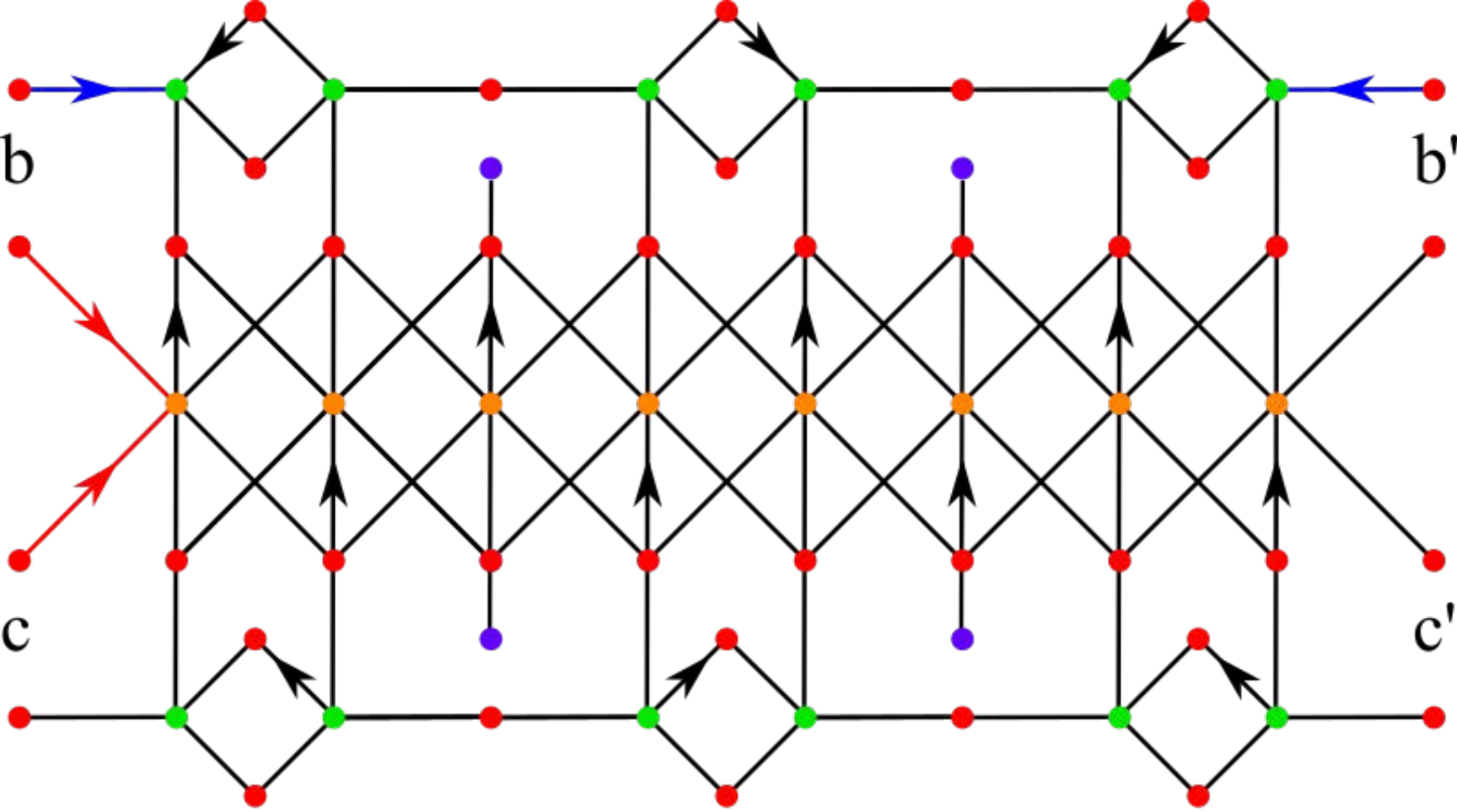


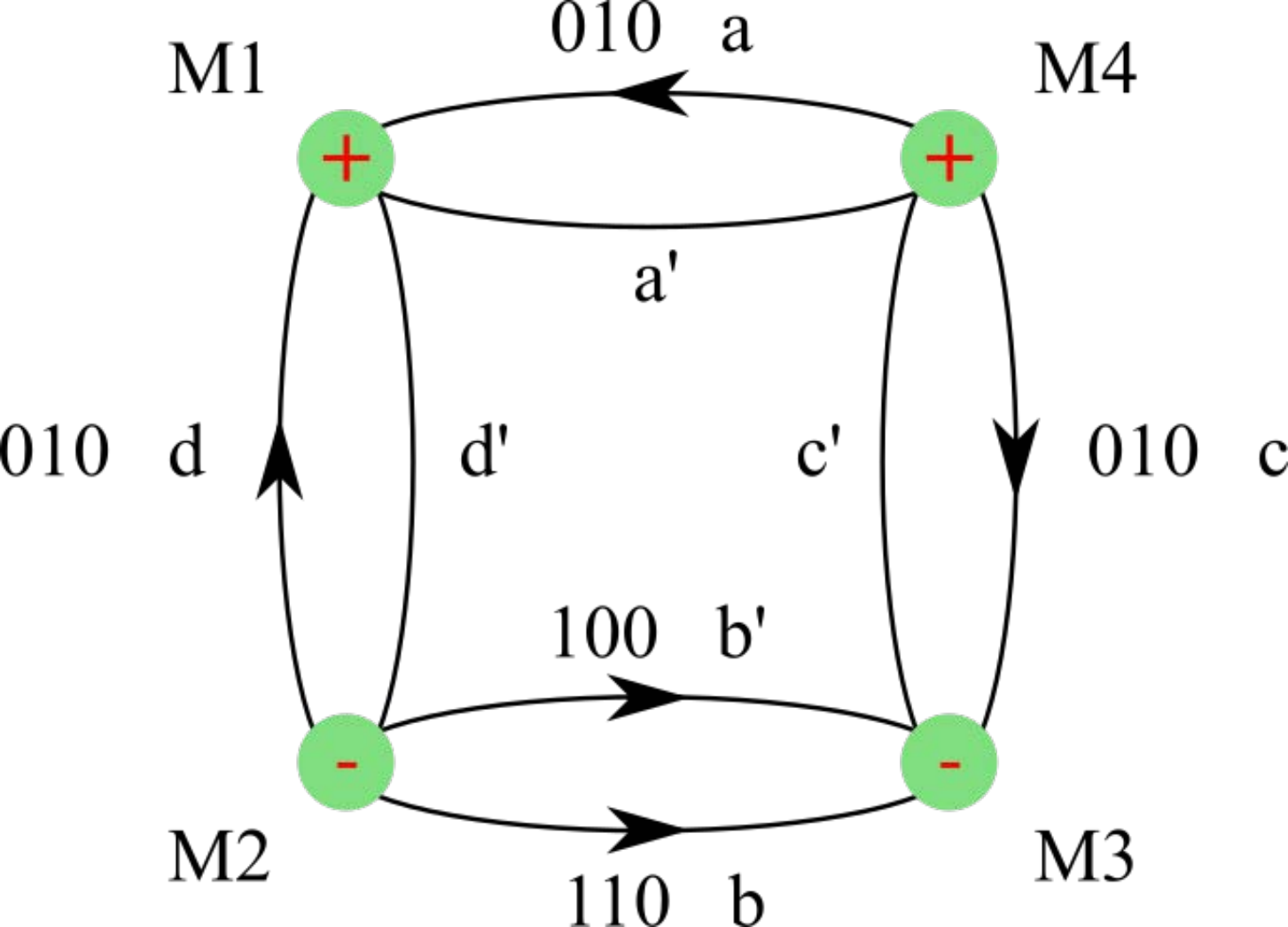




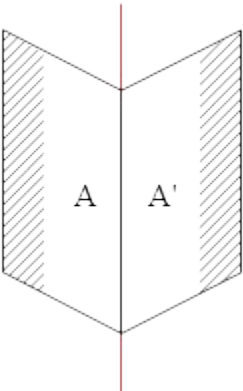
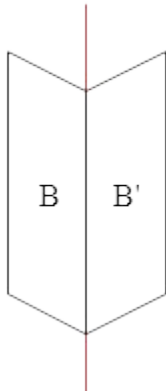










$m$  $m$  $m$ 