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Producing highly complicated materials. Nature does it better

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1 **Producing highly complicated materials. Nature does it better**

2
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16

17 **Abstract**

18 Through the years, mineralogical studies have produced a tremendous amount of data on
19 the atomic arrangement and mineral properties. Quite often, structural analysis has led to
20 elucidate the role played by minor components, giving interesting insights into the physico-
21 chemical conditions of minerals and allowing the description of unpredictable structures that
22 represented a body of knowledge critical for assessing their technological potentialities. Using
23 such a rich database, containing many basic acquisitions, further steps became appropriate
24 and possible, into the directions of more advanced knowledge frontiers. Some of these
25 frontiers assume the name of modularity, complexity, aperiodicity, and matter organization at
26 not conventional levels, and will be discussed in this review.

27

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73 1. Nature: A treasure-trove for structural complexity

74 The study of the materials formed by Nature, i.e. the minerals, has been always the
75 basis for the greatest breakthroughs in chemistry and solid state physics, including the
76 discovery of new elements and chemical compounds, the construction of the periodic table of
77 the elements and the deciphering of the properties of polarized light (Lima-de-Faria 1990).
78 The observations of the mineral morphologies (crystal faces) led to elaborate theories of the
79 structure of solid matter, which were experimentally confirmed in the first decades of the 20th
80 century with the studies on the interaction between X-rays and crystals. The increasingly
81 detailed definition of the physical properties (hardness, tenacity, luminescence, radioactivity,
82 magnetism, electrical and optical properties, etc.) and the compositional and structural
83 characteristics of minerals, as well as the search for natural or synthetic materials with
84 specific mechanical, electrical, magnetic and thermal properties, led to the birth of “materials
85 science” in the middle of the 20th century. The development of materials science was
86 considered as a true technological revolution, a response to precise demands related to
87 economy and industry, and which today is increasingly being used to give answers related to
88 human health and protection of the bio-geosphere.

89 There are about 90 natural chemical elements, which combine to form the *ca.* 5500
90 known terrestrial and extra-terrestrial mineral species, distinct by chemical composition
91 and/or crystal structure. Minerals represent, in the words of the great Bulgarian mineralogist
92 Ivan Kostov (1913-2004), “...*milestones of the history of the Earth and of the Cosmos*”, as
93 well as a valuable source of information for research on nanotechnologies and innovative
94 materials. They are the product of natural terrestrial and extra-terrestrial laboratories in which
95 laboratory “tests” have been carried out for *ca.* 4.8 billion years on thermodynamic systems
96 characterized by wide ranges of chemical-physical parameters and evolutionary processes
97 (temperature, pressure, activity and mobility of chemical components, electromagnetic
98 radiation, compositional, thermal and baric gradients, gravitational field, etc.).

99 Beside the use of natural compounds as technologically-important materials (Ferraris
100 and Merlini 2005; Depmeier 2009), mineral structures with their inherent complexity have
101 also represented a treasure trove for new discoveries in crystallography. For example, in the
102 field of aperiodic crystallography, the mineral calaverite ($\text{Au}_{1-x}\text{Ag}_x\text{Te}_2$, with $0 \leq x \leq 0.33$) has
103 been the ideal case to begin to shed light on incommensurability in crystals (Goldschmidt et al
104 1931). Later, mineralogy played an important role with numerous examples of mineral
105 structures exhibiting modularities (Ferraris et al. 2008), fast ion conducting properties (Kuhs
106 and Heger 1979), non-commensurate (misfit) layer structures (Makovicky and Hyde 1981),
107 currently known under the name of composite structures, and in providing the first example of
108 a (billion years old) natural quasicrystal (Bindi et al. 2009c), which settled any doubt that
109 could remain on the long-term stability of quasicrystals.

110 In this review we will focus on different aspects of the complexity of mineral
111 structures, including a quantitative definition of crystal-structure complexity (Krivovichev
112 2013a).

113 114 2. Modularity of crystal structures

115 2.1 Introduction

116 A crystal structure is composed of a very large number of atoms (neutral or ionized)
117 bonded to constitute a three-dimensional, triperiodic network of atoms and of bonds, which
118 can be represented by a graph, where atoms are vertices and bonds are edges. In molecular
119 crystals, the network of bonds can be decomposed into small sub-units (molecules)
120 characterized by stronger bonds (intramolecular bonds), connected by weaker bonds
121 (intermolecular bonds). Moreover, the transition from a state of matter to another (solid to

122 liquid, liquid to gas etc.) preserves the molecular entity: ice, water and water vapour are all
123 characterized by the same molecular component, the H₂O molecule, but differ in the way the
124 molecules interact and are arranged one with respect to the other.

125 Inorganic crystals – here we mean really inorganic crystals, not including crystals of
126 metal-organic compounds that, for some inexplicable reason, are today considered in the
127 “inorganic” realm – are mainly non-molecular: they differ from molecular crystals in that
128 bringing them to fusion (or sublimation) does not preserve structural unit common to the
129 states of matter, i.e., a molecule. The largest majority of minerals are non-molecular. Fusion
130 of halite, sphalerite, pyrite, “biotite”, pyrope... (you name it!) does not produce a liquid with
131 intra- and intermolecular bonds.

132 Nevertheless, the structure of inorganic crystals, including minerals, can too be
133 decomposed into elementary building blocks of variable size. Such a decomposition is often –
134 but not always – an interpretation of the crystal structures, rather than a physical reality. The
135 most typical example is the smallest and universally known building block: the coordination
136 polyhedron. An octahedron of NaCl₆⁵⁻ or a tetrahedron of ZnS₄⁴⁻ do not correspond to
137 chemical units comparable to a molecule: yet, the polyhedral interpretation of inorganic and
138 mineral crystals is the basis of crystal chemistry since its dawn (Pauling 1929; Wells 1975).

139 Bigger and more complex building blocks occur in modular structures, which are built
140 by juxtaposing one or more types of modules. The modules are three-dimensional but have
141 less than triperiodic components (i.e., they are periodic only along one or two directions, or
142 even non periodic at all, in the case of finite components) that can ideally be described as cuts
143 from a structurally and chemically homogeneous parent structure: the *archetype*. This
144 archetype does not necessarily correspond to a real structure. The most well-known example
145 is certainly that of structures that can be described as based on stacking of layers of equal
146 spheres. The most compact layer, in which each sphere is in contact with six other spheres,
147 has hexagonal symmetry. By stacking identical layers on the top of each other, one gets
148 infinitely many stacking variants, which have maximal compactness if the spheres on adjacent
149 layers are in contact too. This is realized when a sphere of a layer is located on the top of a
150 triangular cavity of the preceding layer. If the position of the spheres on a layer is indicated as
151 A, the two types of triangular cavities in the same layer as B and C (Fig. 1), the stacking
152 variants corresponds to sequences (periodic or non-periodic) of the three letters A, B and C
153 with the same letter never occurring in two successive positions. The archetype is a structure
154 with periodicity of one layer: its stacking sequence is therefore AA and it is not a structure
155 with maximal compactness. It does nevertheless occur in structures with covalent bonds,
156 where the overlap of orbitals determines the relative position of the layers. From this
157 triperiodic archetype, one ideally cuts out a diperiodic layer, whose repetition produces many
158 possible stacking variants. The stacking of layers results in interlayer cavities with different
159 geometry and size, which are then partially occupied by other types of atoms (normally, but
160 not always, less electronegative than the atoms represented by the spheres), leading to a large
161 variability of derivative structures (for a detailed analysis, see Umayahara and Nespolo 2018).

162 A wide range of modular structures is known in the literature. The most complete
163 account of modular structures in minerals can be found in Ferraris et al. (2008). The algebraic
164 description of modular structures requires the theory of groupoids (small categories in which
165 every morphism is invertible) and is outside the purpose of this review. Interested readers are

166 referred to the order-disorder (OD) theory (Dornberger-Schiff and Grell-Niemann 1961),
167 which is the theory of a subclass of modular structures built of diperiodic layers, although
168 generalisations to rods and blocks have been proposed (Dornberger-Schiff 1964; Belokoneva
169 2005). A generalisation has been recently introduced by Nespolo et al. (2020).

170

171 2.2 Symbolic representation of modular structures

172 Modular structures can be classified as *monoarchetypal* and *polyarchetypal*, depending
173 on whether the modules can be viewed as obtained from a single archetype or from at least
174 two different archetypes. The chemical composition of the modules of monoarchetypal
175 modular structures is identical, but the juxtaposition of modules may create or annihilate
176 coordination sites at the interface between two modules. As a consequence, the chemical
177 composition of a series of monoarchetypal structures is not necessarily constant; when it is,
178 then the modular structures are simply polytypes. On the other hand, the chemical
179 composition of a series polyarchetypal structures (polysomes) is by definition variable and
180 depends on the ratio between the number of different archetypes building the structure.

181 In the case of monoarchetypal modular structures, like those based on sphere packings,
182 it is always possible to adjust two modules one next to the other in such a way to form
183 chemical bonds between atoms exposed on the adjacent surfaces of two modules. Depending
184 on the number of possible relative orientations and positions, the number of possible modular
185 structures may increase significantly. If the coordination site at the interface is not affected by
186 the relative arrangement of the modules, then all the monoarchetypal modular structures based
187 on the same type of module are polytypes¹.

188 Let us indicate the archetype as **A** and a module extracted from it as **M**. Juxtaposing
189 modules **M** in a way to obtain back the archetype **A** can be represented as ${}^a\mathbf{M}_{na}{}^b\mathbf{M}_{nb}{}^c\mathbf{M}_{nc}$,
190 where n_j ($j = a, b, c$) indicates that number of modules **M** needed to span the unit cell of **A**
191 along the axis j of the coordinate system. Clearly, to get back the archetype, all the modules
192 are arranged with the same topology one with respect to the preceding (and following) one.
193 This notation applies to non-periodic modules; if the module is monoperiodic (rod or chain)
194 then the repetition along only two axes has to be specified, e.g., ${}^a\mathbf{M}_{na}{}^b\mathbf{M}_{nb}$ if the module is
195 periodic along c . Similarly, if the module is diperiodic (sheet or layer), then the repetition
196 along only one axis has to be specified, e.g., ${}^c\mathbf{M}_{nc}$ if the module is periodic along a and b . For
197 example, the archetype of the structures based on sphere packing is simply $\mathbf{A} = {}^c\mathbf{A}_1$, simplified
198 to $\mathbf{A} = {}^c\mathbf{A}$ because $nc = 1$, or even $\mathbf{A} = \mathbf{A}$ if it is understood that the only direction lacking
199 periodicity is taken as axis c of the coordinate system.

200 Different modular structures sharing the same archetype can be obtained if the modules
201 **M** are differently oriented and/or positioned with respect to their orientation and position in
202 the archetype. We can differentiate them by an index in parentheses. Monoarchetypal modular
203 structures can then be represented as $\mathbf{M}(1)_{n1}\mathbf{M}(2)_{n2}\dots\mathbf{M}(m)_{nm}$, where n_j is the number of
204 modules **M**(j) that occur continuously in the structure. In this example we suppose a layer
205 structure, so that only one direction of missing periodicity exists. For a rod structure, a 2×2

11 ¹According to the official definition (Guinier et al. 1984), polytypes are obtained by “stacking layers of
12 (nearly) identical structure and composition” so that the resulting triperiodic structures “differ only in their
13 stacking sequence”. The building modules are clearly requested to be layers, although “a more general definition
14 of polytypism that includes 'rod' and 'block' polytypes may become necessary in the future”. Here we adopt this
15 larger definition of polytypism.

206 matrix is in general necessary, to take into account the sequence along the two directions of
 207 missing periodicity. For a structure built by non-periodic modules, a 3×3 matrix would be
 208 required. In this section, we fix our attention, for the sake of simplicity, on modular structures
 209 built by diperiodic modules (sheets or layers) so that a row matrix of symbols is sufficient to
 210 describe it; generalization to structures built by mono-periodic or non-periodic structures
 211 simply requires adding one or two dimensions to the symbol matrix.

212 For the sake of simplicity and without loss of generality, let us go back to the case of
 213 packing of equal spheres. The three most common polytypes, the hexagonal close packing
 214 (*hcp*) or $2H$, the cubic close packing (*ccp*) or $3C$, and the double hexagonal or $4H$, correspond
 215 to the sequences AB, ABC and ABAC, respectively. Accordingly:

- 216
- 217 • $2H$: $\mathbf{M}(1) = A, \mathbf{M}(2) = B$;
 - 218 • $3C$: $\mathbf{M}(1) = A, \mathbf{M}(2) = B, \mathbf{M}(3) = C$;
 - 219 • $4H$: $\mathbf{M}(1) = \mathbf{M}(3) = A, \mathbf{M}(2) = B, \mathbf{M}(4) = C$.
- 220

221 The same orientation and position can occur in different places in a single period, as in
 222 the example $4H$ above. A somewhat more complex example is that of covellite, CuS, for
 223 which the sequence of sulfur atoms is ACAABA (copper occupies some of the cavities
 224 formed by stacking of layer of sulfur; Umayahara and Nespolo 2018), or, by a shift of the
 225 origin, AACAAAB², so that its symbolic representation is $\mathbf{M}(1)_2\mathbf{M}(2)\mathbf{M}(1)_2\mathbf{M}(3)$, where $\mathbf{M}(1)$
 226 = A, $\mathbf{M}(2) = C, \mathbf{M}(3) = B$.

227 The structure of the interface between two modules also plays a role not only in the
 228 classification of modular structures, but also for its stability. Extracting modules from an
 229 archetype and rearranging them in order to obtain a new, different structure opens the
 230 possibility of a modification of the inter-module coordination. Let us indicate as $\mathbf{I}(i/j)$ the
 231 intermodule region between modules i and j : the modular structure can then be represented as:

232

$$233 \quad [\mathbf{M}(1)\mathbf{I}(1/1)_{n_1-1}]\mathbf{M}(1)\mathbf{I}(1/2)[\mathbf{M}(2)\mathbf{I}(2/2)_{n_2-1}]\mathbf{M}(2)\mathbf{I}(2/3)\dots \mathbf{I}(m-1/m)\mathbf{M}(m)_{m_m}\mathbf{I}(m/1). \quad (1)$$

234

235 Let us again analyse a few examples of structures based on the stacking of spheres. The
 236 interlayer region between two layers with different position (A and B, B and C, C and A),
 237 contains two types of tetrahedral sites, with the triangular basis parallel to the layer and the
 238 fourth, apical corner oriented along the stacking direction (the sites are noted T^+ and T^-
 239 depending on whether the apical tetrahedron points along the positive or negative sense of the
 240 axis corresponding to the stacking direction) and an octahedral site whose opposite triangular
 241 faces are in the layers (noted O) (Fig. 2). The interlayer region between two layers with the
 242 same position (A and A, B and B, C and C), contains two types of trigonal pyramidal sites,
 243 that we will indicate as P_1 and P_2 , respectively (Fig. 3).

- 244
- 245 • Nickeline, NiAs: $2H$ stacking with the octahedral cavities occupied: COBO. $\mathbf{M}(1) = C,$
 246 $\mathbf{M}(2) = B, \mathbf{I}(1/2) = \mathbf{I}(2/1) = O$.

18 ² The sequence of layers does not impose a choice of the origin, which is instead restricted once the space-
 19 group type of the crystal structure is specified.

- 247 • Sphalerite, ZnS: 3C stacking with the T⁺ cavities occupied: AT⁺BT⁺CT⁺. **M**(1) = A,
 248 **M**(2) = B, **M**(3) = C, **I**(1/2) = **I**(2/3) = **I**(3/1) = T⁺.
 249 • Molybdenite, MoS₂: BP₁BCP₁C. **M**(1) = **M**(2) = B, **M**(3) = **M**(4) = C, **I**(1/1) = **I**(2/2)
 250 = P₁, **I**(1/2) = **I**(2/1) = ∥ (where ∥ indicates empty interlayer).
 251

252 When the intermodular region is constant, all the **I**(i/j) can be simply replaced by **I**, as in
 253 the examples of nickeline and sphalerite.

254 The range of modular structures that can be obtained from a single archetype is actually
 255 wider than what is suggested by the examples above. Identical modules obtained from the
 256 same archetype can be differently oriented with respect to the orientation in the archetype, and
 257 this modifies, sometimes profoundly, the interface.

258 A number of modular structures composed of two (possibly more) types of modules are
 259 also known. They are called *polyarchetypal* because each type of module corresponds to a
 260 different archetype. A polyarchetypal modular structure can occur if the interface between the
 261 two types of modules is compatible with the formation of chemical bonds. This requirement
 262 limits the possibilities of polyarchetypal crystal structures; putting two modules one next to
 263 the other does not necessarily results in a configuration compatible with the formation of
 264 chemical bonds. Polyarchetypal modular structures are known as *polysomatic structures*
 265 (Thompson 1978). The symbolic representation in Eq. (1) applies to polyarchetypal modular
 266 structures too; the only difference with respect to the case of monoarchetypal modular
 267 structures is that the modules **M**(j) are obtained from two or more different archetypes.

268 The scope of this brief survey being necessarily limited, we have chosen to analyse in
 269 details mono- and diarchetypal modular structures where the building blocks are di-, mono- or
 270 non-periodic modules ideally obtained from the TOT layer of phyllosilicates.
 271

272 **2.3 Modular structures whose archetype are phyllosilicates**

273 Phyllosilicates are layer minerals built by stacking layers of different structure and
 274 composition. Depending on the type of layers, several phyllosilicate archetypes exist.

275 Phyllosilicate layers are composed of two types of sheets:

276 1. corner-sharing tetrahedra (T hereafter) centred around a small cation (mainly silicon,
 277 partially substituted by aluminium, iron, titanium); the corners are occupied by oxygen atoms
 278 (Fig. 4a);

279 2. sheets of edge-sharing octahedra (O hereafter) centred around various cations
 280 (aluminium, magnesium, iron, manganese, titanium, lithium); the O sheet alone occurs in
 281 hydroxide minerals like brucite, Mg(OH)₂, in which all the octahedra are occupied (Fig. 4b),
 282 and gibbsite, Al(OH)₃, in which one third of the octahedra are vacant (Fig. 4c).

283 In the T sheet, all the tetrahedra have the same orientation with respect to the direction
 284 of stacking. Three of the four vertices define the basis of the tetrahedra and the anions on
 285 these vertices, called the basal oxygen atoms O_b, define a geometric plane. The fourth corner,
 286 occupied by the apical oxygen atoms, connects the T sheet with the O sheet, by replacing the
 287 corresponding OH group. In the so-called *Pauling model* the T sheets have hexagonal
 288 symmetry. In the real structure, because of the difference in the lateral dimensions of the T
 289 and O sheets, tetrahedra rotate around [001] by an amount that depends mainly on the
 290 chemical composition but also external conditions like temperature and pressure, so that the

291 symmetry of the T sheet is reduced to ditrigonal. The model that takes into account this
292 rotation is known as the *trigonal model* (Nespolo et al. 1999).

293 In the O sheet, the OH groups can be replaced not only by the apical oxygen atoms of
294 the T sheet, also by fluorine, chlorine, oxygen atoms not belonging to the T sheet, or, much
295 more rarely, by sulfur. In the real structure of minerals, these sheets are deformed with respect
296 to their ideal configuration: tetrahedra are actually disphenoids, octahedra are actually trigonal
297 antiprisms (eigensymmetry $\bar{3}m$) or metaprisms (eigensymmetry 32) or even polyhedra with
298 lower symmetry. However, for the sake of simplicity, we retain their idealized description.
299 Readers interested in the real structure of the phyllosilicate layers can find abundant details in
300 Ferraris and Ivaldi (2002).

301 Depending on how the sheets are arranged in the layers, several archetypes are realized.

302 1. Layer built by one T sheet and one O sheet (TO layer). Depending on whether the
303 nature of the O sheet, the layer is brucitic, like in the serpentine mineral, or gibbsitic, like in
304 the kaolinite mineral.

305 2. Layer built by one O sheet sandwiched between two T sheets (TOT layer). Depending
306 on the nature of the O sheet and of the interlayer region, a number of minerals are realized:
307 talc (brucitic TOT without interlayer cations), pyrophyllite (gibbsitic TOT without interlayer
308 cations), micas (with interlayer cations), montmorillonites (smectites) and illites (with the
309 interlayer region only partially filled with cations).

310 3. A TOT layer alternating with an O sheet, like in the chlorite minerals.

311 Depending on the distribution of cations occupying the O sheets, phyllosilicates are
312 classified into different families, with a more or less fine classification depending on the
313 purpose of investigation. Here we are interested in the modular structure of these minerals,
314 which does not significantly change with the nature of the cations. Therefore, we can simplify
315 the classification to three archetypes, differing by the type of layer (TO, TOT and TOT:O),
316 each characterised by a period of one layer along the stacking direction. In the following we
317 deal specifically with the TOT archetype, which provides a large number of modular
318 structures occurring in nature.

319 In the TOT layer, the two T sheets are actually staggered one with respect to the other
320 by about $a/3$ in the projection on the (001) plane (Fig. 5a). As a consequence, most of the
321 symmetry operations of the O sheet are not extended to symmetry operations of the whole
322 layer. Only the inversion, one of the two-fold rotations and one of the mirror reflections are
323 (Fig. 5b). Therefore, the interlayer region has trigonal symmetry (ideally hexagonal) whereas
324 the layer symmetry has only monoclinic symmetry. Stacking two TOT layers one on top of
325 the other can be realized in three orientations (six, in the Pauling model) that correspond to
326 the same configuration of the interlayer region but not of the layer. This leads to three (ideally
327 six) different mutual orientations of the same pair of layers, i.e., three (ideally six) modular
328 structures with the period of two layers, which are simply polytypes. The same situation
329 occurs for *each* pair of layers so that with the increase in the period the number of possible
330 polytypes increases significantly. Furthermore, the interlayer region may be empty or host
331 cations and small molecules, which increases the number of modular structures. Finally, a
332 different module, namely a rod, can be extracted from the same archetype, leading to a large
333 number of modular structures which differ for the relative position of these rods along *two*
334 directions and for the nature of the intermodular region.

336 2.3.1 Layer modular structures

337 Modular structures where the module is a TOT layer can be represented by Eq. (1) in
 338 which all the modules **M** have the same chemical composition and structure but differ for
 339 their relative orientation and/or position. These can be identified as follows.

- 340 • The TOT layer has monoclinic symmetry. The relative orientation of two TOT layers
 341 can be specified by the orientation of the unique symmetry direction in each of the two
 342 layers. Although in principle infinitely many relative orientations are possible, the
 343 ditrigonal (ideally hexagonal) symmetry of the plane of basal oxygen atoms actually
 344 restricts these orientations to multiples of 60° , which correspond to orientations under
 345 which the coordination sites in the interlayer region is unchanged.
- 346 • Mapping of one layer onto the adjacent one can be obtained by a twofold rotation about
 347 a direction in the interlayer region, followed by a shift along the same or another
 348 direction again in the interlayer region. In the following, we will differentiate modular
 349 structures based on the stacking of TOT layers in “zero-shift” and “non-zero-shift”,
 350 depending on whether the shift component of this mapping is absent or present. The
 351 zero-shift configuration preserves the coordination sites in the interlayer region,
 352 whereas the non-zero-shift modifies it.

353 In each TOT modular structure, the interlayer region is essentially the same between
 354 each pair of layers and can be empty or contain cations, small molecules or more complex
 355 components, like the O sheet one finds in chlorites. The archetype is simply $\mathbf{A} = \mathbf{M}$, in which
 356 the unit cell contains a single layer; two adjacent layers, in successive unit cells, are in parallel
 357 orientation and have zero-shift relative position.

358

359 2.3.2 Modular structures with empty interlayer region

360 The simplest modular structures obtained by stacking TOT layers are those in which the
 361 interlayer region is empty. Stacking the layers with parallel orientation and with the same shift
 362 results in a one-layer period. For zero-shift the result would be the archetype, which however
 363 is not realized in nature. The $1A$ (one-layer period, triclinic) polytype has a non-zero shift
 364 between the TOT layers in two successive unit cells. Fig. 6a and 6b show, respectively, the
 365 structure of talc and of pyrophyllite, which differ by the content of the O sheet (Mg filling all
 366 the octahedral cavities vs. Al filling two third of them, respectively). The lower T sheet has
 367 been removed for the sake of clarity. Fig. 7a and 7b show a different section of the same
 368 structure, with two adjacent T sheets belonging to two successive TOT layers, from which the
 369 O sheets have been removed. The ditrigonal cavities (ideally hexagonal) have parallel
 370 orientation but are shifted by about $a/3$ for talc ($0.2968a$, Fig. 7a) and about $1/10$ along the
 371 $[120]$ direction for pyrophyllite (Fig. 7b). Both talc and pyrophyllite occur also in a different
 372 polytype, $2M$ (two-layer period, monoclinic), where again adjacent layers show non-zero
 373 shift. The majority of polytypes are however disordered, i.e., without a periodicity along the
 374 stacking direction. This is the result of the weak van der Waals bonds between successive
 375 layers, which are not interlocked by the presence of cations or small molecules.

376

377 **2.3.3 Modular structures with cations in the interlayer region**

378 The presence of cations in the interlayer region is characteristic of micas. Depending on
379 whether the cations are mono- or divalent, micas are classified in *true micas* and *brittle micas*.
380 These cations lock successive TOT layers in zero-shift configuration, but the relative rotations
381 of $n \times 60^\circ$ (n integer) result in a large number of polytypes. The strong ionic bonds between the
382 cations and the basal oxygen atoms of the tetrahedra belonging to two adjacent TOT layers are
383 considered responsible for the occurrence of periodic polytypes with variable, sometimes very
384 large, periodicities (Nespolo and Āuroviĉ 2002).

385 In the Pauling model, the six $n \times 60^\circ$ orientations all correspond to the same
386 configuration of the interlayer region. In the trigonal model, this sixfold degeneration is partly
387 resolved. Even $(2n \times 60^\circ)$ orientations result in a staggered configuration of the basal oxygen
388 atoms (Fig. 8a, phlogopite-1*M*: Redhammer and Roth 2002), whereas odd $[(2n+1) \times 60^\circ]$
389 orientation in an eclipsed orientation (Fig. 8b, phlogopite-2*O*: Ferraris et al. 2001; and Fig. 8c,
390 lepidolite-2*M*₂: Guggenheim 1981). This difference is considered one of the reasons for the
391 higher occurrence frequencies of polytypes showing even orientations. Furthermore, minerals
392 with inhomogeneous occupation of the octahedral sites, in particular those where one of the
393 three independent sites is empty, result in a tilting of the tetrahedra which makes the plane of
394 the basal oxygen atoms no longer flat but corrugated, and this further destabilizes odd-rotation
395 configurations (Fig. 9).

396 Partial occupation of the interlayer region occurs in some clay minerals like illite (K-
397 poor muscovite) and montmorillonite (showing incomplete occupation of the interlayer region
398 by cations like Na⁺ and Ca²⁺). The configuration of the interlayer region in illite is essentially
399 the same as in muscovite, whereas that in montmorillonite, characterized by a lower
400 occupancy in the interlayer region, is closer to that of pyrophyllite.

401

402 **2.3.4 Modular structures with an O sheet in the interlayer region**

403 The alternate sequence of TOT layers and O sheets is typical of chlorite. The presence
404 of an O sheet in the interlayer region leads to hydrogen bonds between the hydroxyl groups
405 on the surface of this sheet and the basal oxygen plane of the TOT sheets next to it. This
406 network of hydrogen bonds results in a non-zero-shift of successive TOT layers. Fig. 10
407 shows the 1*M* polytype of chlorite (Zanazzi et al. 2007): successive TOT layers are equally
408 oriented but shifted by $0.42a$.

409 Hydrogen bonds are stronger than van der Waals bonds, but definitely weaker than ionic
410 bonds. This partly explains the scarcity of periodic polytypes in chlorite with respect to micas.

411

412 **2.3.5 Rod modular structures**

413 The TOT layer can be imagined as built by three separate sheets (two T sheets and an O
414 sheet) that are attached one on the top of the other. The apical oxygen atoms of the T sheets
415 replace two thirds of the hydroxyl groups of the O sheets. The remaining OH groups allow to
416 differentiate the octahedral sites. The primitive unit cell contains three octahedral sites: one
417 has the OH groups in *trans* configuration, the two others in *cis* configuration (Fig. 11).

418 The TOT layer can be cut in rods with different widths, which can be assembled
419 together to produce a wide range of minerals. The juxtaposition of two rods implies a

420 positional, but no rotational, degree of freedom, contrary to the case of layers, which are
 421 diperiodic. The result depends on several factors.

- 422 • The width of the rod, which is measured by the number of full octahedra it contains; a
 423 rod n -octahedra width is indicated as R_n . Fig. 12 shows rods R_5 and R_8 . Clearly,
 424 moving along a , the boundaries of a rod pass either through the oxygen atoms /
 425 hydroxyl groups (defining full octahedra) or cations (cutting through the octahedra).
 426 The former are taken as measure of the width of the rod.
- 427 • The occupation of the regions between pairs of rods, along the two directions of
 428 missing periodicity.
- 429 • The bonding scheme between pairs of rods.

430 Because the modules are monophasic, Eq. (1) has to be generalized to a 2×2 matrix
 431 form. The T and O sheet in the TOT layer become there the T and O chain of the TOT (R_n)
 432 rod. The TOT phyllosilicate archetype can be written as

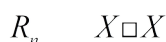


433 \square

434 where \square represents the empty region between successive layers. The first line represents the
 435 layer itself; indeed, a layer can be interpreted as an infinite juxtaposition of rods n -octahedra
 436 width for any value of n . The second line shows the interlayer region is empty. Modular
 437 structures built by the juxtaposition of rods can be represented by extending the above
 438 notation, which however cannot account for the bonding scheme between pairs of rods, which
 439 is realized in two ways:

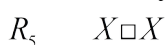
- 440 1. the OH- O_b scheme, obtained by replacing an hydroxyl group of the O chain by the
 441 basal oxygen atom of a neighbouring T chain;
- 442 2. the O_b - O_b scheme, obtained by sharing the basal oxygen atom of two neighbouring
 443 T chains.

444 The following analysis is a schematic version of the publication of Nespolo and
 445 Bouznari (2017). Rod modular structures with the OH- O_b scheme are shown in Figs. 13-15.
 446 Fig. 13 shows the structure of amphiboles, which can be interpreted as composed by R_5 rods,
 447 periodic along the c axis of the mineral, displaced one with respect to the other along the a
 448 axis. Exactly the same topology occurs in jimthompsonite, which is built by rods R_8 instead of
 449 R_5 (Fig. 14). The structure of the two minerals can be represented as



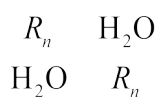
450 where \square represents empty space, X is a cation, and $n = 5$ or 8 respectively. Depending on
 451 cations occupying the O chain and the nature of the X cation amphiboles are classified in a
 452 number of different minerals. In some of these, the empty space \square is sometimes occupied by a
 453 monovalent cation, mainly sodium. A similar variation has not been found in jimthompsonite.
 454

455 Intermediate structures do exist as well. Fig. 15 shows the structure of chesterite, which
 456 can be schematically represented as

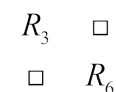


457 i.e., by an alternation of amphibole-like modules and jimthompsonite-like modules.
 458

459 Rod modular structures with the O_b-O_b scheme are shown in Fig. 16-18. The sequence
 460 of R_5 and of R_8 rods is found in palygorskite and sepiolite respectively, where water molecules
 461 occur instead of the X cations of amphiboles (Figs. 16 and 17). It can be symbolically
 462 represented as



463
 464 A further modular structure is known as well, kalifersite, which shows an alternation of
 465 R_3 and R_6 modules, i.e.,



466
 467 (Fig. 18).

468 The symbolic representation adopted here has the advantage of being synthetic and
 469 illustrative but does not have the ambition to express the difference in the relative position of
 470 the modules. Our purpose here is to point out and emphasize the tight structural relations
 471 between minerals that were only partially recognized in the past (Thompson 1978). For a full
 472 structural information, one needs a more detailed description; interested readers are referred to
 473 Nespolo et al. (2018).

474

475 **2.4 Polyarchetypal modular structures. The example of pyroxenoids**

476 Polyarchetypal modular structures are built by the juxtaposition of modules taken from
 477 two or more archetypes. A large number of examples can be found in Ferraris et al. (2008).
 478 Our aim is to illustrate the general principle in the simplest possible way. For that, we restrict
 479 our treatment to one of the two series of pyroxenoids, diarchetypal minerals whose modules,
 480 although different, can again be obtained from the TOT layer of phyllosilicates (Angel and
 481 Burham 1991).

482 Pyroxenoids are metamorphic minerals with variable chemistry and occurrence. They
 483 are classified on the basis of two parameters (Takéuchi 1997).

- 484 1. The period along the direction of the T chain, which is of three or more tetrahedra.
 485 Wollastonite, whose T chain has a period of three tetrahedra, is one archetype. The
 486 second archetype is not a pyroxenoid but a pyroxene, whose T chain has a period of
 487 two tetrahedra.
- 488 2. The width of the O chain, sandwiched between two T chains, measured roughly
 489 perpendicularly to the direction of the T chains, variable between two and three
 490 cation sites. These sites have only approximate octahedral geometry, but in the
 491 following we will treat them as octahedral for the sake of simplicity.

492 Fig. 19a shows the structure of the first archetype, wollastonite, $CaSiO_3$, along the b
 493 axis. The O chain has a width of three octahedra. Fig. 19b shows the same structure along
 494 $[101]^*$, with the cation sites in a ball-and-stick representation instead than polyhedral. The
 495 period of the tetrahedral chain is three tetrahedra. The structure of wollastonite can therefore
 496 be described as obtained by juxtaposition of TOT rods composed of tetrahedral chains with
 497 period of three tetrahedra and octahedral chains three-octahedra wide. These rods can be
 498 represented as $R^T_o = R^3_3$, where T indicates the number of tetrahedra defining the period of the
 499 T chain and $_o$ the number of octahedra defining the width of the O chain.

500 Fig. 20a and 20b show the structure of the other archetype, a pyroxene, $(M_2M_1)SiO_3$
501 ($M_2 = Ca, Mg, Fe^{2+}, Na, Li, M_1 = Mg, Fe^{2+}, Al^{3+}, Fe^{3+}$) along $[001]$ and along $[101]$
502 respectively. The larger site (white polyhedron in Fig. 20a, usually indicated as M_2 in the
503 literature) does not have an octahedral geometry but in this treatment we approximate it to an
504 octahedron. The rods building the structure of pyroxenes can therefore be represented as R_{O}^T
505 $= R_2^2$.

506 Fig. 21 shows the structure of rhodonite group minerals (Shchipalkina et al. 2019),
507 $CaMn_4Si_5O_5$, seen along $[100]^*$. This structure is composed by a regular alternation of
508 wollastonite-like slabs and pyroxene-like slabs. The slabs are cut from the rods and are
509 therefore non-periodic. We can represent it as $S^3_3S^2_2$, where S^T_O stands for “slab” O octahedra
510 thick obtained from the chain R^T_O .

511 Fig. 22 shows the structure of pyroxmangite, $MnSiO_3$, along $[100]^*$, which is composed
512 by a regular alternation of one wollastonite-like slabs and two pyroxene-like slabs. It can be
513 represented as $S^3_3(S^2_2)_2$.

514 Fig. 23 shows the structure of ferrosilite-III, $FeSiO_3$, along $[110]^*$, which is composed
515 by a regular alternation of one wollastonite-like slabs and three pyroxene-like slabs. It can be
516 represented as $S^3_3(S^2_2)_3$.

517 These five minerals can be seen as representative of a potentially large family of
518 diarchetypal modular structures, whose general member is $S^3_3(S^2_2)_n$. Members known so far
519 correspond to $n = 0$ (wollastonite, first archetype), $n = 1$ (rhodonite), $n = 2$ (pyroxmangite), n
520 $= 3$ (ferrosilite-III) and $n = \infty$ (pyroxene, second archetype). The period of the T chains is
521 $2n+3$ tetrahedra; for the pyroxene archetype, $n = \infty$ indicates the absence of wollastonite-like
522 slabs so that the period corresponds to the thickness of a S^2_2 slab, i.e. two tetrahedra.

523

524 **3. Information-based analysis of structural complexity of minerals**

525 **3.1. Introduction**

526 The problem of quantifying the complexity of natural and artificial structures is of high
527 importance for modern science that deals with more and more complex systems in the course
528 of its development. Crystals are considered as intuitively simple systems (Bennet 1990), due
529 to the periodic character of their structures, and their complexity was the subject of thought
530 for crystallographers at the very beginning of the development of X-ray diffraction analysis.
531 In particular, Pauling (1929) suggested the parsimony rule that states that ‘...the number of
532 different types of constituents in a crystal tends to be small’. The topic of structural
533 complexity of crystals reappeared in scientific literature many times (see Krivovichev (2013a,
534 2016b, 2017) for historical remarks), but only recently the universal measures were suggested
535 based upon the Shannon information theory (Krivovichev 2012a, b, 2013a, b, 2014, 2016a).
536 Below we formulate the basic principles of this method by considering an n -dimensional
537 crystal structure in order to cover both classical crystals and those that can be described using
538 superspace approach.

539

540 **3.2. Structural complexity measures**

541 The complexity of a crystal structure can be estimated as the amount of Shannon
542 information per atom (represented by a point), $^{str}I_G$, and per unit cell, $^{str}I_{G,total}$, calculated
543 according to the following equations:

34
35

544

$${}^{\text{str}}I_G = -\sum_{i=1}^k p_i \log_2 p_i \quad (\text{bits/atom}) \quad (1),$$

$${}^{\text{str}}I_{G,\text{total}} = -\nu I_G = -\sum_{i=1}^k \nu p_i \log_2 p_i \quad (\text{bits/cell}) \quad (2),$$

547

548 where k is the number of different crystallographic orbits in the structure and p_i is the
549 random-choice probability for an atom from the i th crystallographic orbit, that is:

550

$$p_i = m_i / \nu \quad (3),$$

552

553 where m_i is the number of points of the crystallographic orbit in the reduced unit cell³, and ν
554 is the total number of atoms in the reduced unit cell.

555 The Shannon information measures are applicable to any crystalline structure that can
556 be characterized by a finite amount of atoms located in a finite amount of space with defined
557 equivalence relation among atomic sites (including trivial symmetry). The two measures of
558 structural complexity, ${}^{\text{str}}I_G$ and ${}^{\text{str}}I_{G,\text{total}}$, reflect upon the two important properties of complexity,
559 size and symmetry of a system. While the parameter ${}^{\text{str}}I_G$ is sensitive to symmetry, the
560 parameter ${}^{\text{str}}I_{G,\text{total}}$ is sensitive to both symmetry and the number of translationally independent
561 sites, i.e. the size of a system.

562 The equations (1-3) do not take into account the complexity of bonding network in the
563 crystal structure, which can be accounted for by introducing additional measures (e.g., by
564 including bonds into consideration (see (Krivovichev 2013a) for more details).

565 The equations (1-3) may be used to calculate *information density*, ρ_{inf} , of a crystal
566 structure as the amount of Shannon information per volumetric unit, e.g. per cubic Ångström:

567

$$\rho_{\text{inf}} = {}^{\text{str}}I_{G,\text{total}} / V_{\text{red}} \quad (4),$$

569

570 where V_{red} is the volume of the reduced unit cell. The information density is the
571 parameter that can be strictly applied to one unit cell only and not to the whole crystal, since
572 the periodicity condition of a crystal structure would result in the redundant character of all
573 information except for the one contained in a single reduced unit cell.

574

575 3.3. Applications: general overview

576 Krivovichev (2013a, 2014) calculated information-based structural complexity
577 parameters for all known inorganic and mineral structures and classified them according to
578 their ${}^{\text{str}}I_{G,\text{total}}$ parameter value into five groups (bits/cell): very simple (0-50), simple (50-100),
579 intermediately complex (100-500), complex (500-1000), and very complex (> 1000 bits/cell).
580 The procedure of the information-based measures of structural complexity calculation in

36 ³ A reduced cell is a primitive (minimal volume) cell satisfying two restrictions on the basis vectors **a**, **b**, **c**:
37 1) of all lattice vectors, none is shorter than **a**; of those not directed along **a**, none is shorter than **b**; of those
38 not lying in the **ab** plane, none is shorter than **c**; 2) The three angles between basis vectors are either all acute
39 (type I) or all non-acute (type II).

40

41

581 incorporated into the TOPOS Pro program package (Blatov et al., 2014), which is freely
582 available for download.

583 For minerals, Krivovichev (2013a) provided the following average values of
584 information-based structural complexity measures: $\langle \text{str}I_G \rangle = 3.23(2)$ bits/atom and $\langle \text{str}I_{G,\text{total}} \rangle$
585 $= 228(6)$ bits/cell. However, these calculations were based upon partial structural information,
586 since for many crystal structures of hydrated minerals, the positions of H atoms have not been
587 determined in the original structural studies. For hydrated Ca borates, Pankova et al. (2018)
588 used the procedure of H-corrections by introducing surrogate H sites into the structure data,
589 and this procedure was recently performed for all mineral species known to date
590 (unpublished). The new average complexity parameters for minerals are: $\langle \text{str}I_G \rangle = 3.48(2)$
591 bits/atom and $\langle \text{str}I_{G,\text{total}} \rangle = 303(6)$ bits/cell. The increase in the average values is due not only
592 to the inclusion of H atoms into calculations, but also owing to the fact that more and more
593 complex minerals are discovered in nature due to the applications of novel experimental
594 techniques, including high-sensitive area detectors, the use of synchrotron radiation and the
595 advances in electron diffraction methods.

596

597 3.4. Most complex mineral structures

598 Table 1 provides the list of five most complex mineral structures known in April 2020.

599 Ewingite, $\text{Mg}_8\text{Ca}_8[(\text{UO}_2)_{24}(\text{CO}_3)_{30}\text{O}_4(\text{OH})_{12}(\text{H}_2\text{O})_8](\text{H}_2\text{O})_{130}$, is the Earth's most complex
600 mineral reported so far with the estimated complexity of 23477.507 bits/cell. The mineral was
601 found as golden-yellow crystals formed on a damp wall of the old Plavno mine of the
602 Jáchymov ore district, western Bohemia, Czech Republic (Olds et al. 2017), where
603 crystallized from low-temperature uranyl-bearing aqueous solutions. Its crystal structure
604 contains a 54-nuclear (24U + 30C) uranyl carbonate cluster $[(\text{UO}_2)_{24}(\text{CO}_3)_{30}\text{O}_4(\text{OH})_{12}(\text{H}_2\text{O})_8]^{32-}$
605 shown in Fig. 24a. Its skeletal representation (Fig. 24b), where each node corresponds either
606 to U (yellow) or to C (grey) center emphasizes the presence of four U_3 triangles (with the U-U
607 distances shorter than 4 Å) that correspond to the trimers of three $(\text{UO}_2)\text{O}_5$ pentagonal
608 bipyramids sharing the same equatorial O atom. Two other building units are the $[(\text{UO}_2)$
609 $(\text{CO}_3)_3]$ and $[(\text{UO}_2)(\text{CO}_3)_2(\text{H}_2\text{O})_2]$ hexagonal bipyramids. The visual complexity of the cluster
610 architecture can further be reduced by leaving only U atoms and the addition of the U-U links
611 corresponding to the U-U distances in between 4 and 6.2 Å (Fig. 24c). The resulting graph
612 can be considered as consisting of four U_3 trimers (U-U < 4 Å) and six U_4 dihedra of two
613 edge-sharing U_3 triangles (U-U = 4.0-6.2 Å). The centers of the trimers and the dihedra
614 (denoted by red and blue circles in Fig. 24c) form tetrahedron and octahedron, respectively,
615 with six tetrahedral edges in correspondence to six octahedral vertices (Fig. 24d). Such a
616 relation between the tetrahedral and octahedral graphs is known in graph theory as an edge-to-
617 vertex duality. The octahedral graph can be obtained from the tetrahedral graph K_4 by
618 associating a vertex with each edge of the K_4 graph and connecting two vertices with an edge
619 if the corresponding edges of K_4 have a vertex in common (Gross and Yellen 2006).
620 Therefore, the topology of the uranyl carbonate cluster in ewingite, in addition to its extreme
621 complexity, has the interesting property of being self-edge-to-vertex dual.

622 Morrisonite, $\text{Ca}_{11}[\text{As}^3+\text{V}^{4+}_2\text{V}^{5+}_{10}\text{As}^{5+}_6\text{O}_{51}]_2 \cdot 78\text{H}_2\text{O}$, has 13558.354 bits of Shannon
623 information per unit cell and, after ewingite, is the second most complex mineral known so
624 far. The vanarsite-group minerals (Kampf et al. 2016, 2020) contain unique and previously
625 unknown type of the V-As POM cluster with the composition $[\text{As}^3+\text{V}_{12}\text{As}^{5+}_6\text{O}_{51}]$. The cluster
626 consists of twelve (VO_6) octahedra forming wheel- or corona-shaped unit centered by As^{3+}
627 cation in a trigonal-pyramidal coordination (due to the stereoactivity of a lone-electron pair)
628 and surrounded by six $(\text{As}^{5+}\text{O}_4)$ tetrahedra (Fig. 25). The vanarsite-group minerals form from
629 low-temperature aqueous solutions with V and As derived from the oxidation of primary
630 unoxidized phases.

631 Ilmajokite, $\text{Na}_{11}\text{KBaCe}_2\text{Ti}_{12}\text{Si}_{37.5}\text{O}_{94}(\text{OH})_{31}\cdot 29\text{H}_2\text{O}$, is the third most complex mineral,
632 which was first reported from the hydrothermal vein in Karnasurt Mountain, Lovozero, Kola
633 Peninsula, Russia (Bussen et al. 1972). The mineral easily dehydrates in air, which prevented
634 its structure solution for more than forty-five years. Recently, Zolotarev et al. (2020) were
635 finally able to solve the crystal structure and described it as a multilevel hierarchical
636 framework structure (Fig. 26). The crystal structure is based upon a 3D titanosilicate
637 framework consisting of trigonal prismatic titanosilicate (TPTS) clusters centered by Ce^{3+} in
638 [9]-coordination. There are two symmetry-independent clusters within the unit cell (Fig. 27).
639 In each cluster, three $[\text{Ti}_2\text{O}_{10}]$ dimers of edge-sharing TiO_6 octahedra in parallel orientation
640 form a trigonal prism centered by Ce^{3+} cations. The triple-dimer titanate structure is
641 surrounded by SiO_4 tetrahedra to form a TPTS cluster. Four adjacent TPTS clusters are linked
642 into four-membered rings within the (010) plane and linked into ribbons parallel to $[\bar{1}01]$. The
643 ribbons are organized into layers parallel to (010) and modulated with a modulation
644 wavelength of 32.91 Å and an amplitude of 13.89 Å. The layers are further linked into a the
645 titanosilicate framework via additional SiO_4 tetrahedra. The Na^+ , K^+ , Ba^{2+} and H_2O groups
646 occur in the framework cavities and have different occupancies and coordination
647 environments. As it was mentioned above, the crystal structure of ilmajokite possesses a
648 multilevel hierarchical structure (Fig. 28). The first (lowest) level consists of atoms that are
649 grouped into coordination polyhedra (second level). The TiO_6 octahedra are linked to form
650 dimers (third level). The dimers together with SiO_4 tetrahedra and centering Ce^{3+} cations
651 comprise TPTS clusters (fourth level). The clusters are linked to form four-membered rings
652 (fifth level), which are further interlinked to form ribbons (sixth level). The ribbons are united
653 into a three-dimensional octahedral-tetrahedral framework (seventh level), which, together
654 with alkali metal, Ba^{2+} cations and H_2O molecules complete the structure organization (eighth
655 level). The hierarchical complexity is reflected in the high amount of Shannon information,
656 11990.129 bits per unit cell after H-correction.

657 Paulingite-(Ca) (Lengauer et al. 1997) and fantappieite (Cámara et al. 2010) are two
658 aluminosilicates based upon frameworks consisting of corner-sharing TO_4 tetrahedra (T = Al,
659 Si). Both frameworks can be considered as built up by the linkage of polyhedral cages as
660 described elsewhere (Krivovichev 2013a,b). The two minerals represent good examples
661 illustrating the variety of contributions to the total structural complexity, including the
662 difference between structural and *topological* complexity, when the latter is estimated as a
663 Shannon information content of the ideal structure with the maximal possible symmetry
664 (Krivovichev, 2018). For instance, the topological complexity parameters for the paulingite
665 framework (PAU) are 1008 atoms per cell, 4.726 bit/atom and 4763.456 bit/cell with the
666 maximal symmetry space group $Im\bar{3}m$ identical to that of the mineral (Table 1). The addition
667 of interstitial species (Ca^{2+} cations and H_2O molecules) results in the approximately doubling
668 increase of the number of atoms (from 1008 to 1988) and the total information per cell (from
669 4763 to 11591 bits). In the case of fantappieite, the situation is different. The topological
670 symmetry of the framework is $R\bar{3}$, which is higher than the space group of the mineral, $P\bar{3}$.
671 The topological complexity of the tetrahedral framework per cell is 878.790 bits, but the
672 perfect Al/Si ordering over tetrahedral sites results in the decrease of the symmetry from $R\bar{3}$ to
673 $P\bar{3}$ (which is the *topochemical* symmetry group for the framework) and the increase of the
674 structural information per cell from ~879 to ~2636 bits (Krivovichev 2013b). The filling of

675 the framework cavities by cations and H₂O molecules more than doubles the complexity to
676 ~6112 bits per cell.

677 The five most complex mineral structures reflect the basic mechanisms of the
678 generation of crystal-structure complexity of minerals: the formation of nanoscale large
679 polyatomic clusters (usually polyoxometalates (Krivovichev 2020)) and the modular
680 architecture, when the structure is based upon a combination of one or several large modules
681 (Krivovichev 2013a). The high hydration states also favor the high Shannon information
682 content, due to the high number of H atoms.

683

684 **3.5. Information-density analysis**

685 The structural information densities for ewingite, morrisonite and ilmajokite are in the
686 range of 0.488-0.793 bits Å⁻³, which is equivalent to 4.88-7.93·10²³ bits cm⁻³. However, it
687 should be taken into account that the information density is the function of the size of the
688 atoms, and the high hydration states of the three minerals contribute essentially to the ρ_{inf} high
689 values. For anhydrous minerals, the information density is much lower. The variations of
690 information density versus the ionic size can be illustrated by the example of suanite,
691 Mg₂B₂O₅, and natrosilite, Na₂Si₂O₅, which have the same total structural information content,
692 114.117 bits/cell (Krivovichev 2013a). However, their information densities are drastically
693 different (0.333 and 0.242 bits Å⁻³, respectively), which is an obvious consequence of the
694 different ionic radii of the Mg²⁺ and Na⁺ ions, on one hand, and of the B³⁺ and Si⁴⁺ ions, on the
695 other.

696 It is notable that the structural information density of minerals (~n·10²³ bit cm⁻³) is many
697 orders higher than the volumetric densities of information of hard disks and flash memory
698 (~10¹³ and 10¹⁶ bit cm⁻³, respectively), and even exceeds those of DNA memory in both liquid
699 and crystalline states (~10¹⁹ and 10²¹ bit cm⁻³, respectively) (Zhirnov et al. 2016). However, it
700 should be kept in mind that the Shannon information in crystals is redundant due to their
701 periodic structure, and the original information is restricted to one reduced unit cell only. On
702 the other hand, the estimate of ~n·10²³ bit cm⁻³ can be seen as a possible maximum for
703 information storage attainable by the manipulation of matter on the atomic scale, if future
704 technologies would allow to build an aperiodic structure with each atom having a precise
705 position relative to its environment. It should also be mentioned that the information density
706 discussed herein and in the section 3.2 relates to the ideal crystalline state and does not take
707 into account other information contained in each mineral crystal such as defects, trace and
708 minor elements, isotopes and other chemical inhomogeneties, etc., which bears on the unique
709 geological and geochemical history of minerals. In order to quantify this information, one has
710 to develop other approaches, perhaps exceeding the limits of the Shannon theory.

711

712 **3.6. Chemical complexity**

713 The information-theoretic approach allows for the investigation of relations between
714 structural and chemical complexity. The latter can be defined by analogy with the structural
715 complexity (equations 1-4) as the amount of chemical Shannon information per atom and per
716 formula unit (f.u.). In order to do this, the crystal chemical formulae of minerals should be
717 written in a canonical way in order to determine the minimal set of species-defining
718 constituents (i.e., chemical elements that are dominant in particular sites in a crystal

719 structure). It should be noted that the assignment of an element as species-defining is
 720 determined by the rules of the definition of new mineral species given by the International
 721 Mineralogical Association (Mandarino et al. 1984; Nickel 1992, 1995). The ‘canonical’
 722 formulae of minerals are stored in the official IMA list of mineral species continuously
 723 updated by Pasero (2020).

724 The information-based analysis of chemical complexity was first suggested in (Siidra et
 725 al. 2014). Following this approach, for the idealized chemical formula of a mineral or
 726 inorganic compound, $E^{(1)}_{c_1}E^{(2)}_{c_2}\dots E^{(k)}_{c_k}$, where $E^{(i)}$ is an i th chemical element in the formula
 727 and c_i is its integer coefficient, the chemical information can be calculated as follows:

728

$$729 \quad {}^{\text{chem}}I_G = - \sum_{i=1}^k p_i \log_2 p_i \quad (\text{bits/atom}) \quad (5),$$

$$730 \quad {}^{\text{chem}}I_{G,\text{total}} = e \cdot {}^{\text{chem}}I_G = - \sum_{i=1}^k c_i \log_2 p_i \quad (\text{bits/f.u.}) \quad (6),$$

731

732 where k is the number of different elements in the formula and p_i is the random-choice
 733 probability for an atom of the i th element, that is:

734

$$735 \quad p_i = c_i / e \quad (7),$$

736

737 where e is the total number of atoms in the chemical formula:

738

$$739 \quad e = \sum_{i=1}^k c_i \quad (8).$$

740

741 The average chemical complexity values obtained from the analysis of chemical
 742 complexity of all mineral species known today are: $\langle {}^{\text{chem}}I_G \rangle = 1.62(2)$ bits/atom and \langle
 743 ${}^{\text{chem}}I_{G,\text{total}} \rangle = 62(6)$ bits/cell. Note that the chemical complexity parameters are smaller than the
 744 structural complexity ones. It was shown that the structural and chemical complexities of
 745 minerals correlate strongly, though the character of this correlation is different for different
 746 measures (Krivovichev et al. 2018).

747 Fedorov (1913, 1914) and Groth (1921) pointed out that, in general, symmetry of
 748 crystalline compounds correlates with their chemical complexity. Less complex compounds
 749 (e.g., elements) tend on average to have higher symmetries than compounds consisting from
 750 two elements, etc. Both Fedorov and Groth pointed out that this empirical observation, also
 751 known as a Fedorov-Groth law, has an ‘approximate’ character only, i.e. is of statistical nature
 752 that allows exceptions, but works on a global scale. Recently, it was demonstrated that the
 753 Fedorov-Groth law is valid and statistically meaningful, when chemical complexity is
 754 expressed according to the equation (5) as the amount of Shannon chemical information per
 755 atom and the degree of symmetry as the order of the point group of a mineral (Krivovichev,
 756 Krivovichev 2020).

757

758 **4. Structural complexity, disorder phenomena and the rise of ionic** 759 **properties**

760 **4.1 Introduction**

761 One of the most fascinating aspects related to the complexity of mineral structures is
762 related to the concept of disorder, and, to be more specific, to ionic conduction phenomena
763 related to disorder. Although in an ideal periodic compound there is little space for an atom to
764 diffuse, structural defects due to minor positional disorder (slight deviations from the ideal
765 stacking) commonly exist. What seems an unimportant disorder may be responsible for the
766 existence of different polytypes of the same compound and for the stabilization of different
767 structures as a function of temperature and pressure. From a thermodynamic point of view, at
768 0 Kelvin the atoms of an ideal crystal are arranged in a way to get the lowest free energy. With
769 increasing temperature, the entropic contribution (a measure to quantify the disorder) to the
770 free energy becomes important. As a consequence, there is the occurrence of crystal defects,
771 which can be simply considered the response of the system to reduce the free energy through
772 an increase in the entropy. Crystal defects that play an active role in ion conduction are
773 ‘Schottky’ and ‘Frenkel’ defect, the so-called ‘point defects’ in crystals. Thanks to them, ions
774 can be either brought across the solid giving rise to conductivity (*vacancy migration*) or
775 moving to an interstitial site and then subsequently jump to a neighbouring interstitial site and
776 so on, resulting in long distance motion of the ion (*interstitial migration*).

777 From the discussion above it is evident that there is a close interplay between the ion
778 motion and the crystal structure where the motion occurs. Indeed, the long-range motions of
779 ions that lead to high conductivity in solids require high density of mobile-ion-sites along
780 with a network of ‘smooth’ conduction channels connecting them (Padma Kumar and
781 Yashonath 2006). For this reason, a detailed understanding of the structural features is of
782 particular importance in the context of ionic conductors.

783 Superionic conductors or fast ion conductors have a massive use in diverse
784 technological applications: as electrolytes in batteries used in pace-makers, mobile
785 telephones, laptops, and in electrochemical devices as electrode materials. Interestingly, some
786 of them have been discovered in nature and characterized before their use as synthetic
787 compounds. In other cases, Nature has been of inspiration for new technologically-important
788 materials.

789 Among the most important materials for solid electrolyte applications there are
790 “NASICONs compounds”, NaSbO_3 , known in nature as the mineral brizziite (Olm and
791 Sabelli 1994), and Ag-Cu sulfosalts (e.g., Bindi and Biagioni 2018). Below, a brief description
792 of the first two compounds together with a more exhaustive essay of Ag-Cu-sulfosalts is
793 reported.

794

795 **4.2 NASICON**

796 The term “NASICON” is applied to the solid with chemical formula $\text{Na}_4\text{Zr}_2(\text{SiO}_4)_3$.
797 Actually, it describes a series of compounds with the general formula $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$,
798 where $0 < x < 3$. There are a number of chemically and structurally related compounds to
799 NASICONs, including langbeinite, $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$ (Mereiter 1979), a very well-known mineral
800 for its technological importance (Krivovichev 2009). The structure of NASICON is based
801 upon the octahedral-tetrahedral framework shown in Fig. 29. Each octahedron shares vertices
802 with six adjacent tetrahedra and each tetrahedron shares vertices with four adjacent octahedra.

803

804 **4.3 NaSbO_3 , brizziite**

805 The structure of brizziite is similar to those of the ilmenite group minerals and consists
806 of gibbsite-type octahedral sheets, perpendicular to the *c* axis (Fig. 30). The bond distances of

807 the Na-polyhedron are in the range 2.25-2.78 Å, whereas the Sb-octahedron exhibits a mean
808 bond distance of 1.989 Å. Each Na and Sb octahedron shares edges with three symmetry-
809 related octahedra to form Na and Sb layers, respectively. Each octahedron also shares a face
810 with another octahedron of an adjacent layer, but the opposite face is unshared. Thus, pairs of
811 Na and Sb octahedra alternate with octahedral holes along the *c* axis. There are six alternating
812 Na and Sb sheets in the unit cell, to form a hexagonal close-packed framework. Such a
813 structure is responsible for the high ionic conductivity measured (Wang et al. 1994).

814

815 4.4 Ag- and Cu-bearing sulfosalts

816 Most of Ag- and Cu-bearing sulfosalts represent an outstanding example of complex
817 structures associated with ionic conduction. Their structural complexity is mainly due to the
818 difficulty in accurately describing the Ag⁺ or Cu⁺ electron density. Indeed, both Ag⁺ or Cu⁺ *d*¹⁰
819 elements easily adopt various complex asymmetric coordinations due to an *s/d* orbital mixing
820 and/or polarization factors (Gaudin et al. 2001 and references therein). Therefore, both these
821 ions can be found in different, but very close sites, which favour the presence of strong ionic
822 conductivity. As described above, the ease to deform the electron density lowers the activation
823 energy of the site-to-site jumps giving rise to some disorder in the crystal structure. In fast
824 ionic conductors, an ionic species can move easily, giving a liquid-like structure in an open
825 framework (tunnels, layers, etc.).

826

827 4.4.1 Pearceite, polybasite and fettelite

828 The pearceite-polybasite minerals have been known for a long time and were divided by
829 Frondel (1963) into two series: the first one, formed by pearceite (Ag,Cu)₁₆(As,Sb)₂S₁₁ and
830 antimonpearceite (Ag,Cu)₁₆(Sb,As)₂S₁₁, characterized by a “small” unit cell [labeled 111] and
831 high Cu content, and the second one, formed by polybasite (Ag,Cu)₁₆(Sb,As)₂S₁₁ and
832 arsenpolybasite (Ag,Cu)₁₆(As,Sb)₂S₁₁, with double unit-cell parameters [labeled 222] and low
833 Cu content. Moreover, the existence of an intermediate type of unit cell labeled 221 was
834 claimed for both polybasite (Harris *et al.* 1965; Edenharter *et al.* 1971) and arsenpolybasite
835 (Minčeva-Stefanova *et al.* 1979). From the crystallographic point of view these minerals were
836 initially reported as monoclinic *C2/m*, although dimensionally pseudo-hexagonal (Peacock
837 and Berry 1947; Frondel 1963; Harris *et al.* 1965; Hall 1967; Sugaki *et al.* 1983). Bindi *et al.*
838 (2006a) solved and refined the crystal structure of pearceite in a space group of type *P* $\bar{3}m1$
839 (Fig. 31). They showed that the pearceite structure can be described as a regular alternation of
840 two module layers stacked along the *c* axis: a first module layer (labeled *A*), with general
841 composition [(Ag,Cu)₆(As,Sb)₂S₇]²⁻, and a second module layer (labeled *B*), with general
842 composition [Ag₉CuS₄]²⁺. The fast ion conductivity occurs in the latter module layer (Fig. 32).
843 Although no long-range ordering at low temperature could be established for pearceite, this
844 ordering was shown in different samples of polybasite by Evain *et al.* (2006), who evidenced
845 complex polytypism phenomena (i.e., 221 and 222 unit-cell types).

846 These authors solved and refined the crystal structure of both polybasite-221 (space-
847 group type *P* $\bar{3}21$; Fig. 33) and polybasite-222 (space-group type *C2/c*; Fig. 34) and proposed
848 a possible mechanism regulating the ordering in these minerals.

849 The crystal structures of the remaining members of the group (i.e., antimonpearceite,
850 arsenpolybasite-221 and -222) were studied at room temperature by Bindi *et al.* (2006b).
851 These authors showed that antimonpearceite possesses the same structural arrangement
852 observed for pearceite and that the polytypism phenomena occurring in different
853 arsenpolybasites (i.e., 221 and 222 unit-cell types) show strong analogies with those observed

854 in polybasites. The complexity of these minerals can be evidenced by the number of unit-cell
855 types used to describe all the members of the group (Fig. 35).

856 It was then clear that all the members of the pearceite-polybasite group present the same
857 high-temperature structure and that it is observed at room temperature either in their high
858 temperature (HT) fast ion conductivity form (pearceite) or in one of the low temperature (LT)
859 fully ordered (222), partially ordered (221) or still disordered (111) forms, with transition
860 temperatures slightly above or below room temperature. A detailed investigation of the phase
861 transitions, by means of conductivity and calorimetric studies and *in situ* single-crystal X-ray
862 diffraction experiments, was carried out by Bindi *et al.* (2006b).

863 Following the determination of the crystal structures for all the members of this group
864 and the elucidation of the conducting mechanism, these minerals were considered as a family
865 of polytypes. Indeed, the solution of the crystal structure allowed also the understanding of
866 the doubling of the unit-cell parameters, that is related to the Ag ordering. In agreement with
867 this deeper knowledge, a revision of the nomenclature was proposed by Bindi *et al.* (2007).
868 The old names antimonpearceite and arsenpolybasite were discredited, whereas the names
869 pearceite and polybasite, previously defined on structural basis (i.e., 111 and 222,
870 respectively), were redefined on chemical basis, with As > Sb for the former and Sb > As for
871 the latter.

872 If silver is the main driving force responsible for the fast ionic conductivity, copper
873 seems to play an important role in the disorder of particular portions of the structure. Bindi *et al.*
874 (2007) showed that not all the 111 aristotype structures give a long range ordered low-
875 temperature structure. There are indeed Cu-poor pearceite-polybasite minerals that remain
876 trigonal with the 111 cell and $P\bar{3}m1$ space-group type, and intermediate pearceite-polybasite
877 minerals with the 221 cell and $P321$ space-group type. This particularity is to be related to the
878 disorder occurring, whatever the temperature, within the $[(Ag,Cu)_6(As,Sb)_2S_7]^{2-}$ *A* module
879 layer. Indeed, with the lowest (1.54, 1.29, 1.08) and the highest (4.5) Cu content, Bindi *et al.*
880 (2006b) obtained two different fully ordered structures. As the Cu content increases (2.29,
881 1.69, and 1.55) from the lowest values, 221 compounds with only a partial ordering were
882 observed. For a further increase of the Cu content (3.8) the structure remained disordered (111
883 cell), whatever the temperature.

884 In conclusions, the pearceite-polybasite group of minerals can be considered as a series
885 with the same aristotype, fast ion conducting form at high temperature. Depending upon the
886 Cu content, an ordering occurs with transition temperatures related to that content: the lower
887 the Cu content, the higher the transition temperature from the fast ion conducting HT form to
888 the non ion conducting form.

889 Another interesting mineral structure, which shows similarities with those of the
890 pearceite-polybasite minerals, is that of fettelite, $[Ag_6As_2S_7][Ag_{10}HgAs_2S_8]$. The crystal
891 structure of fettelite (Bindi *et al.* 2009a) consists of an alternation of two kinds of layers along
892 the *c*-axis: layer *A* with general composition $[Ag_6As_2S_7]^{2-}$ and layer *B* with general
893 composition $[Ag_{10}HgAs_2S_8]^{2+}$ (Fig. 36). In this structure, the Ag atoms adopt different
894 coordinations, extending from quasi linear to quasi tetrahedral, the AsS₃ groups form trigonal
895 pyramids as are typically observed in sulfosalts, and Hg links two sulfur atoms in a linear
896 coordination. By means of an integrated high-temperature single-crystal X-ray diffraction
897 (HT-SCXRD), differential scanning calorimetry (DSC), and complex impedance spectroscopy
898 (CIS) study, Bindi and Menchetti (2011) showed that fettelite exhibits a ionic-transition at
899 about 380K toward a disordered phase having a trigonal symmetry with the *a* and *b* unit-cell

900 parameters halved. In the HT-structure, what induces the disorder in the *B* layer are both Ag
901 and Hg cations, which are found in various sites corresponding to the most pronounced
902 probability density function locations of diffusion-like paths (Fig. 37). So, even if Hg is a
903 minor element in fettelite, it does play a very important role in the stabilization of the
904 disorder. The study by Bindi and Menchetti (2011) indicated that at least two polytypes could
905 exist for fettelite, the ordered, monoclinic RT-structure (space-group type *C2*), and a fast ion
906 conducting, trigonal, disordered HT-form (space-group type $P\bar{3}m1$) with *a* and *b* parameters
907 halved.

908

909 4.4.2 Argyrodite-canfieldite series

910 The minerals of the argyrodite group mainly consist of three members: argyrodite
911 Ag_8GeS_6 , canfieldite Ag_8SnS_6 , and putzite $(\text{Cu}_{4.7}\text{Ag}_{3.3})\text{GeS}_6$. According to Wang (1978),
912 argyrodite and canfieldite are isostructural (space-group type *Pna2*₁ or *Pnam*), and a solid
913 solution exists between these two minerals. The crystal structure of argyrodite was published
914 by Eulenberger (1977) and that of a tellurian variant of canfieldite was reported by Bindi *et al.*
915 (2012a). Several structural studies on synthetic argyrodite-type compounds have been
916 reported, mainly because such phases are of interest for their manifold structural and physical
917 properties, for example, as electrolytes (e.g., Evain *et al.* 1998; Gaudin *et al.* 2001; Rao and
918 Adams 2011). These compounds undergo three phase transitions: the high-temperature, ionic-
919 conducting phase crystallizes in the space-group type $F\bar{4}3m$ (Fig. 38). The medium-
920 temperature phase has space-group type *P2*₁3, and, finally, the low-temperature phase has an
921 apparent space-group type $F\bar{4}3m$, but it actually adopts an orthorhombic symmetry (space-
922 group type: *Pna2*₁, *Pnam* or *Pmn2*₁).

923 Recently Bindi *et al.* (2017a) reported a heretofore unobserved compound belonging to
924 the argyrodite group, named spryite, exhibiting the ideal formula $\text{Ag}_8(\text{As}^{3+}_{0.5}\text{As}^{5+}_{0.5})\text{S}_6$, which
925 represents the first As^{3+} -bearing member of the argyrodite group (Fig. 39). It was found in the
926 Ag- and Mn-rich zone of the Uchucchacua polymetallic deposit, Oyon district, Catajambo,
927 Lima Department, Peru, a complex vein-type deposit related to a dacitic intrusion cutting
928 through Cretaceous and Tertiary formations on the West side of the Occidental Cordillera of
929 Central Andes (Oudin *et al.* 1982). From a structural point of view, spryite is intimately
930 twinned with six twin domains. The most peculiar feature is that arsenic is present in both
931 trivalent and pentavalent state. As^{3+} forms AsS_3 pyramids typical of sulfosalts, (Ge^{4+} , As^{5+})
932 links four S atoms in a tetrahedral coordination, and Ag occupies sites with coordination
933 ranging from quasi linear to almost tetrahedral connected into a framework (Fig. 40).

934 Noteworthy, a network of non-interacting Ag cations is established for spryite. This
935 behavior is different with respect to that usually reported for argyrodite-like compounds
936 (Belin *et al.* 2001), which show a strong disorder in the sub-lattice of the moving cations at
937 room temperature. In this light, spryite represents the first argyrodite-type compound which
938 does not behave as a fast ionic conductor. Likely, the presence of As^{3+} inhibits the typical
939 ionic conductivity observed in these compounds. The presence of partially occupied As^{3+}S_3
940 pyramids could indeed hinder the formation of the ‘quasi-liquid like’ structure of the mobile
941 ions which usually are highly delocalized over the sites available to them. The free energy

942 associated with the regular sites in spryite is likely higher than that of the interstitial sites, thus
943 making the conduction mechanism highly unfavorable.

944

945 **5. Structural complexity in sulfosalts and the role of minor constituents**

946 **5.1 Introduction**

947 Sulfosalts are an informal group of chalcogenides (Moëlo *et al.* 2008), often
948 characterized by very complex crystal structures. Dittrich *et al.* (2009) reviewed some
949 interesting properties and applications of these minerals. For instance, due to the strong
950 anisotropy of the crystal structures of several sulfosalts, the crystal growth velocities can be
951 severely anisotropic, giving rise to individuals characterized by aspect ratios of more than
952 1000, with potential application in nanotechnology (Fig. 41). Other interesting applications
953 are in photovoltaics, thermoelectrics, phase change memory, X-ray detectors, and so on.

954 Sulfosalt crystal structures are sometimes very complex, with large numbers of
955 independent atomic positions and large unit-cell volumes. Actually, these crystal structures
956 can be broken up into relatively simpler fragments (“modules”; see Section 2.2) that are
957 recombined through the action of structure-building operators. Among sulfosalts, a large
958 group is represented by the so-called rod-based sulfosalts. They are represented by Pb/Sb and
959 Pb/Bi sulfosalts whose building principles were worked out by Makovicky (1993, 1997).
960 Their crystal structures can be described as formed by cut outs of basic structures like
961 PbS(NaCl) or SnS; these building units (rods) have generally a lozenge cross-section, are
962 several PbS/SnS subcells wide and two or more atomic layers thick. These building units are
963 then connected and stacked to give rise to three-dimensional structures. Usually, these phases
964 show a distinct partitioning of Sb and Bi within rod interiors, where lone-electron-pair
965 micelles are formed, and of Pb on the rod surfaces. Mixed Pb/(Sb,Bi) positions in the rod
966 interiors can occur, in order to maintain charge balance and minimizing structural distortion.
967 Makovicky (1993) proposed three fundamental categories of rod-based structures, i.e., (i) the
968 layer-, (ii) the chess-board, and (iii) the cyclic category (Fig. 42). The next step in structural
969 complexity was represented by the so-called boxwork structures.

970

971 **5.2 Boxwork structures**

972 Boxwork structures are the currently known most complex modular category of
973 sulfosalts. This term was first introduced by Makovicky *et al.* (2001) during the description of
974 neyite, a silver-copper sulfobismuthite with formula $Ag_2Cu_6Pb_{25}Bi_{26}S_{68}$. Meanwhile, a series
975 of Pb/Sb oxy-sulfosalts and oxy-chloro-sulfosalts were described by a French-Italian research
976 group of the Nantes and Pisa Universities, showing the same kind of very complex crystal
977 structures (Table 2). These latter authors defined the occurrence of three different kinds of
978 rods, namely rods A, B, and C₁-C₂ (Moëlo *et al.* 2000; Palvadeau *et al.* 2004). Makovicky and
979 Topa (2009) gave a formal definition and a description of the architecture of these complex
980 sulfosalts. A boxwork structure (Fig. 43) can be described as formed by three structural
981 elements:

982 i) *walls* (= rods C₁-C₂), based on double layers of SnS or more rarely PbS archetype (see
983 Section 2.1). Walls are sinuous and start on one side of the wall and end on the other side. It is
984 worth noting that such a sinuosity can be obtained through the insertion of peculiar structural
985 features, e.g., kermesite-like fragments like in scainiite (Moëlo *et al.* 2000) or an Hg-centered
986 octahedron as in marrucciite (Orlandi *et al.* 2007).

987 ii) *partitions* (= rods A), usually represented by four-atomic-layers-thick lozenge-shaped
988 rods based on the SnS archetype. Only in marrucciite, partitions based on PbS archetype have
989 been observed. In neyite, the partitions are only two-atomic-layer-thick. The width varies
990 between two and four polyhedra.

991 iii) *fill elements* (= rods B) are rods of SnS archetype and, less frequently, Pb archetype.
992 The fill element composition varies between MS_4 (where M is a cation) (e.g. in vurroite –
993 Pinto *et al.* 2008) and $M_{18}S_{26}$ for chovanite (Makovicky and Topa 2009; Biagioni and Moëlo
994 2017).

995 It is worth noting that such a structural complexity seems to be closely related to the
996 occurrence of minor constituents. In particular, Makovicky and Topa (2009) highlighted the
997 role played by oxygen in generating the so-called “kermesite-like configuration”, as first
998 defined by Moëlo *et al.* (2000). Indeed, Makovicky (1993) showed that only a limited number
999 of rod shapes and sizes can be combined forming rod-layer sulfosalts and chessboard-type
1000 sulfosalts. The existence of additional new sulfosalts, containing in particular antimony, can
1001 be related to the occurrence of this structural feature, similar to that described in the oxy-
1002 sulfide kermesite, Sb_2S_2O (e.g., Bonazzi *et al.* 1987), and acting as a structure modifier,
1003 favouring the fitting of the structural modules. Kermesite-like configurations observed in
1004 scainiite and other lead-antimony oxy-sulfosalts are shown in Figure 44. The most common
1005 configuration is represented by the alternation, along the rod extension, of an oxygen atom
1006 and a vacancy. Usually, taking into account the strongest bonds for Sb^{3+} and As^{3+} (i.e., those
1007 having *Me*–S distance shorter than 2.70 Å), a trigonal pyramidal coordination is typically
1008 observed, satisfying the bond-valence requirements. In the kermesite-like configurations, only
1009 two short *Me*–S distances are present, and the third bond is represented by *Me*–O bond, with
1010 the oxygen atom above or below Sb/As. Clearly, the crystallization of such complex structures
1011 is strictly related to peculiar $f(O_2)/f(S_2)$ conditions (e.g., Orlandi *et al.* 1999).

1012 Vurroite and its isotype tazieffite are two other sulfosalts showing a boxwork structure,
1013 stabilized by Sn and Cl and Cd and Cl as minor chemical constituents, respectively (Fig. 45).
1014 Actually, these minerals can be really considered a masterpiece of structural complexity,
1015 showing a very complex crystal structure, an order-disorder⁴ (OD) character, and the
1016 occurrence of a widespread polysynthetic twinning. The two latter features (OD nature and
1017 twinning) are intimately related. On the basis of the characteristic shown by X-ray diffraction
1018 patterns, Pinto *et al.* (2008) derived the possible polytypes of vurroite and demonstrated their
1019 occurrence in the studied material. The extensive polysynthetic twinning shown by vurroite is
1020 related to the OD nature of this mineral. Following the solution of the crystal structure of
1021 vurroite, Zelenski *et al.* (2009) reported the structural features of isotypic tazieffite.

1022 The role of minor elements (both cations and anions) in stabilizing complex compounds
1023 is exemplified by several sulfosalts having a boxwork structure. For instance, Sn and Cl
1024 favours the crystallization of vurroite (Garavelli *et al.* 2005), whereas Cu, Hg, and O are
1025 pivotal for the crystallization of rouxelite (Orlandi *et al.* 2005). In this latter mineral, distorted
1026 HgS_{2+4} octahedra occur in the walls; this distortion, related to the tendency of Hg^{2+} to form
1027 two linear short bonds, favours the insertion of CuS_4 tetrahedra in the crystal structure,
1028 adjacent to the walls. In this way, Hg acts as a structure modifier. In addition, in the crystal
1029 structure of rouxelite, portions with Sb atoms showing the kermesite-like configuration occur.

1030

1031 **5.3 Other zinkenite-related complex sulfosalts**

1032 The description of these complex crystal structures using the modular approach
1033 developed by Makovicky (1993, 1997) can neglect some strong bonds. Since the first
1034 description of lead-antimony sulfosalts by the Nantes-Pisa research group (e.g., Moëlo *et al.*
1035 2000), another type of layer definition was proposed, taking into account the distribution of
1036 strong and weak bonds. In this alternative (and in some ways complementary) approach,

60 ⁴ Order-disorder structures are formed by one or more kind of layers (not necessarily structural layers) stacked
61 according to two or more geometrically equivalent ways (Ferraris *et al.* 2008 and references therein). An infinite
62 number of different layer sequences are possible, both ordered and disordered. Ordered sequences are known as
63 polytypes, corresponding to Maximum Degree of Order (MDO) sequences.

1037 complex rod layers are defined, their boundaries passing through lone-electron-pair micelles
1038 and through interfaces between archetype rods. This description highlights the organization of
1039 crystal structures around pseudotrigonal columns (see for instance the crystal structure of
1040 chovanite in Figure 43) usually organized around a Pb_6S_{12} triangular core.

1041 This latter structural motif, typical of zinkenite, $\text{Pb}_9\text{Sb}_{22}\text{S}_{42}$ (Biagioni *et al.* 2018), occurs
1042 also in other related phases having crystal structures not belonging to the boxwork group but
1043 to the chess-board type. However, their structural complexity is still very relevant. Moëlo *et al.*
1044 (2012) reported the crystal structure of two complex Ag-Pb sulfosalts, sterryite and
1045 parasterryite, $\text{Cu}(\text{Ag,Cu})_3\text{Pb}_{19}(\text{Sb,As})_{22}(\text{As}_2)\text{S}_{56}$ and $\text{Ag}_4\text{Pb}_{20}(\text{Sb,As})_{24}\text{S}_{58}$, respectively. These
1046 two minerals, along with ciriottiite, $\text{Cu}(\text{Cu,Ag})_3\text{Pb}_{19}(\text{Sb,As})_{22}(\text{As}_2)\text{S}_{56}$ (Bindi *et al.* 2016a), are
1047 expanded derivative of owyheeite, $\text{Ag}_3\text{Pb}_{10}\text{Sb}_{11}\text{S}_{28}$ (Moëlo *et al.* 1984; Laufek *et al.* 2007), a
1048 rare Ag-Pb sulfosalt showing an OD nature (Makovicky and Olsen 2015). Figure 46 shows
1049 some structural features of sterryite and parasterryite. Moëlo *et al.* (2012) defined complex
1050 columns representing the fundamental building blocks of these compounds, principally
1051 considering the surfaces of weakest bonding. In this way, a triangular prismatic core can be
1052 distinguished; around this core, two arms of unequal length, indicated as “long” and “short”,
1053 are organized. It is worth noting that sterryite and parasterryite have the same triangular
1054 prismatic core, a very similar long arm, and a $(\text{Sb,As})_2\text{S}_4$ group at the basis of the short arm.
1055 The similarity index between these two structures, defined as the ratio between the common
1056 positions and the total atoms in the formula unit, is close to 90%, being 94/103 in sterryite (94
1057 being the common positions and 103 the total number of atoms) and 94/106 in parasterryite.
1058 The difference between these two complex minerals occurs at the end of the short arm (Fig.
1059 46). In particular, sterryite (Fig. 46a) shows a partially occupied Cu site and an As–As pair
1060 (Fig. 46b and c), with As–As distance of 2.63 Å, comparable with those observed in realgar
1061 As_4S_4 (2.566 Å – Mullen and Nowacki 1972) and in wakabayashilite (2.656 Å – Bonazzi *et al.*
1062 2005). In parasterryite, the short arm is Ag-rich, with four Ag sites (Fig. 46d and e). It is
1063 interesting to observe that this chemical difference of two small structural fragments
1064 connected to topologically identical complex columns has a relevant consequence on the
1065 general organization of the crystal structures of sterryite and parasterryite, resulting in two
1066 different choices corresponding to the $P2_1/n$ and $P2_1/c$ settings of the space group,
1067 respectively.

1068 Still more complex is the crystal structure of meerschautite, $\text{Ag}_{5.5}\text{Pb}_{42.4}\text{Sb}_{45.1}\text{S}_{112}\text{O}_{0.8}$,
1069 based on two different complex columns (Biagioni *et al.* 2016). This mineral differs from
1070 sterryite and parasterryite for the space group symmetry, $P2_1$, and for the configuration of the
1071 short arms connecting successive pseudotrigonal columns (Fig. 47). One of these arms is Ag-
1072 rich (Fig. 47a and b), whereas the other displays localized Sb–O–Sb bonds, in a kermesite-
1073 like configuration (Fig. 47c and d). Meerschautite is the lead-antimony sulfosalt with the
1074 largest unit-cell content (more than 200 atom positions) showing only one O specific position
1075 (Biagioni *et al.* 2016). A mineral that is likely structurally related to sterryite, parasterryite,
1076 and meerschautite is tubulite, $\text{Ag}_2\text{Pb}_{22}\text{Sb}_{20}\text{S}_{53}$ (Moëlo *et al.* 2013). What is interesting is the
1077 tubular morphology characterizing several samples of this mineral, like those shown in Fig.
1078 41 for robinsonite. The origin of this unusual morphology is probably due to extrinsic factors,
1079 related to the crystallization environment and likely acting on extremely thin lath-like
1080 individuals at the early stages of crystal growth.

1081 5.4 Information-based complexity in sulfosalts

1082 A quantitative estimation of the structural complexity of these sulfosalts can be
1083 achieved using the method recently proposed by Krivovichev (2013a) and based on the
1084 information contents of their crystal structures. Table 3 gives the information-based
1085 complexity parameters for the sulfosalts here discussed.
1086

1087 Sulfosalts having a boxwork structure have usually structural information complexities
1088 $^{str}I_{G,total}$ in the range 500 – 1000 bits/cell, thus being classifiable as “complex”, according to
1089 Krivovichev (2013a). Two of them, marrucciite and pillaite, could seem to be not so complex,
1090 having $^{str}I_{G,total}$ of ~450 and 480 bits/cell, respectively, corresponding to an intermediate
1091 complexity. Actually, this apparently relatively low complexity is due to the fact that the
1092 calculations given in Table 3 have been usually performed on the 4 Å sub-structure of
1093 boxwork structures. The superstructure reflections doubling the 4 Å periodicity are usually
1094 very weak and in several cases it was not possible to refine the actual 8 Å structure. This point
1095 is particularly important, as exemplified by chovanite, the mineral showing the largest infill
1096 elements currently known (Makovicky and Topa 2009; Biagioni and Mořlo 2017). Indeed, the
1097 $^{str}I_{G,total}$ of the 4 Å sub-structure is ~ 800 bits/cell, and consequently this mineral could be
1098 considered as “complex”. However, when the real 8 Å structure is taken into account, a
1099 definitely higher $^{str}I_{G,total}$ value is obtained, 3753 bits/cell, agreeing with the very complex
1100 nature of this compound. Similarly, the chess-board structures of sterryite, parasterryite, and
1101 meerschautite, with $^{str}I_{G,total}$ in the range 2800 – 3200 bits/cell, can be considered “very
1102 complex”. It is interesting to observe that the pair vurroite/tazieffite, whose studies faced up
1103 to a series of complicated crystallographic issues, has a $^{str}I_{G,total}$ value lower than those shown
1104 by other phases. Indeed, the structural information complexity index $^{str}I_{G,total}$ takes into account
1105 only the amount of information contained in a mineral species, whereas it neglects other
1106 factors like OD phenomena, twinning, and modulation, which represent a different kind of
1107 complexity that, in some cases, may preclude the full understanding of the actual structural
1108 information hosted within a crystal structure.

1109

1110 5.5 Role of minor constituents

1111 Sulfosalts characterized by boxwork structures and other very complex Ag-Pb sulfosalts
1112 (e.g., sterryite, parasterryite, and meerschautite) reveal that in the crystallization of such very
1113 complicated phases a key role is played by minor components, both cations and anions. The
1114 crystal structure solution and refinement of these minerals increase our understanding of the
1115 role of minor constituents, with potential implications in the synthesis of peculiar
1116 technological compounds.

1117 Minor constituents could also give rise to incommensurate structures. In the sulfosalt
1118 realm, a simple example is represented by meneghinite, $CuPb_{13}Sb_7S_{24}$ (Fig. 48). Euler and
1119 Hellner (1960) and Hicks and Nuffield (1978) interpreted additional weak reflections in the
1120 single-crystal X-ray diffraction patterns as due to a commensurate superstructure. Recently,
1121 Bindi *et al.* (2017b), using a sample from the Bottino mine (Tuscany, Italy), where this
1122 mineral was originally described in the XIX Century, clearly observed a small (but detectable)
1123 departure of the position of the additional reflections, apparently doubling a 4 Å periodicity,
1124 from the commensurate value 0.5. The crystal structure of meneghinite has been consequently
1125 solved and refined as an incommensurate structure in a four-dimensional superspace (see
1126 Section 6.2), describing the modulation of occupancy of Cu, Pb, and Sb atoms, related to the
1127 substitution mechanism $Cu^+ + Pb^{2+} = \square + Sb^{3+}$. The small departure from the commensurate
1128 structure suggests that other commensurate superstructures observed in complex sulfosalts
1129 could be due, in some cases, to some kinds of incommensurate chemical modulation.

1130 Indeed, until now, classical examples of incommensurability in sulfosalts are
1131 represented by members of the cylindrite homologous series (e.g., Makovicky and Hyde
1132 1992). This is a peculiar kind of incommensurability related to the occurrence of a
1133 pseudotetragonal Q layer, two to four atoms thick and with a PbS archetype, and a
1134 pseudo-hexagonal H layer of CdI_2 -type or NbS_2/TaS_2 -type. The misfit between these two kinds
1135 of layers is at the origin of the incommensurate nature of this group of minerals. A recent and
1136 spectacular example is merelaniite, $Mo_4Pb_4VSbS_{15}$ (Jaszczak *et al.* 2016 – Fig. 49). The

1137 tubular morphology of these minerals is due to intrinsic factors. Indeed, the nucleation of
1138 crystals of cylindrite homologues starting from a pair of Q and H layers can induce a
1139 curvature of the constitutive layers, resulting in a macroscopic cylindrical crystal.

1140 Incommensurate modulated and composite structures are a peculiar kind of aperiodic
1141 structures, as will be discussed in the next chapter.

1142

1143 **6. Aperiodic minerals**

1144 **6.1 Introduction**

1145 Aperiodicity in minerals refer to the aperiodic nature of their crystal structures. Since
1146 the 1970s, we have learned that crystal structures do not necessarily obey the classical concept
1147 of three-dimensional periodicity of their atomic arrangements. First, *incommensurately*
1148 *modulated* structures were observed, followed by another family of structures called
1149 *composites* and finally, *quasicrystals* were discovered. These three types of complex
1150 structures are currently referred by the generic term of *aperiodic structures*. They all share in
1151 common the property that their diffraction patterns are essentially discrete but cannot be fully
1152 indexed with the usual triplets of hkl integers as is the case for the classical model of crystals.
1153 The discrete nature of diffraction pattern is a consequence of the long-range order of the
1154 corresponding crystal structures but the fact that three integers do not suffice any more is a
1155 consequence of a new type of order which will be presented in this section.

1156 It is interesting to note here the important role played by the study of mineral structures
1157 to the historical development of the concept of aperiodicity in crystals. Mineral structures of
1158 *calaverites*, *natrites* or *labradorites* for example were fundamental for the theoretical
1159 development of aperiodicity (see below).

1160 Before describing a few interesting aperiodic mineral structures, a brief description of
1161 the basic concepts used to characterize them will be presented. For a deeper understanding of
1162 the subject, the interested reader may refer to the dedicated literature (e.g., van Smaalen 2012,
1163 Janssen et al. 2018).

1164 Due to space limitations, examples of the third category of aperiodic minerals, namely
1165 composites, will not be presented here. Their structures have been shortly presented in Section
1166 5.5 and appear essentially in two different families, layered and columnar. In the first case,
1167 two or more layers with their own periodicities are stacked periodically in the third
1168 dimension. In the second case, different columns with their own periodicities form two
1169 dimensional periodic arrays. The world of natural minerals is also very rich in
1170 incommensurate examples of composites. The interested users may consult the pioneering
1171 works of Makovicky and Hyde (1981, 1992) to discover additional interesting examples of
1172 aperiodic minerals.

1173

1174 **6.2 Short theoretical presentation**

1175 Any conventional crystal structure can be described by the individual positions of each
1176 atom contained in its unit cell characterised by the three lattice vectors \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 and the three
1177 angles α_1 , α_2 , α_3 . The determination of the lattice constants is usually performed by diffraction
1178 methods (X-rays, neutron, electron) and therefore it is convenient to introduce the reciprocal
1179 lattice vectors \mathbf{a}_i^* where the scalar product satisfies the conditions

1180

$$1180 \mathbf{a}_i \cdot \mathbf{a}_j^* = \delta_{ij} \quad (1)$$

1181

1182 Here δ_{ij} is the Kronecker symbol, which is 1 if $i=j$ and 0 if $i \neq j$.

1183 Diffraction patterns of classical crystals are usually analysed in terms of the reciprocal
1184 lattice vectors with basis \mathbf{a}_1^* , \mathbf{a}_2^* and \mathbf{a}_3^* by assigning each discrete diffracted intensity to a

1185 reciprocal lattice node which is uniquely characterised by the three integers hkl mentioned
 1186 before. Once the full set of diffracted intensities is measured, it is in principle straightforward
 1187 to obtain the positions of each atom contained in the unit cell.

1188 Let us analyse the following reciprocal lattice layer of diffracted intensities of the
 1189 mineral natrite (Dušek et al. 2003; Arakcheeva and Chapuis 2005; Arakcheeva et al. 2010)
 1190 illustrated in Figure 50.

1191 It is obvious in this layer that the full set of reflections cannot be characterized in terms
 1192 of only two indices h and l . The additional reflections lay on parallel lines and are
 1193 equidistantly distributed on both side of each node $h2l$. It is convenient to define an additional
 1194 vector \mathbf{q} expressed in terms of the reciprocal vectors \mathbf{a}_i :

$$1195 \quad \mathbf{q} = \alpha_1 \mathbf{a}_1^* + \alpha_2 \mathbf{a}_2^* + \alpha_3 \mathbf{a}_3^* \quad (2)$$

1196 In the specific case, two coefficients α_1 and α_3 , are irrational and $\alpha_2 = 0$. In the general
 1197 case, we can define a set \mathbf{H} of lattice vectors to describe the full set of diffraction reflections:

$$1198 \quad \mathbf{H} = h_1 \mathbf{a}_1^* + h_2 \mathbf{a}_2^* + h_3 \mathbf{a}_3^* + m \mathbf{q} \quad (3)$$

1199 Here the integer coefficients h_i instead of the equivalent triplet hkl are used. If the
 1200 integer $m = 0$, \mathbf{H} describes a *main* reflection whereas if $m \neq 0$, \mathbf{H} describes a *satellite* reflection.

1201 We are thus faced with the necessity to increase the number of vectors in reciprocal
 1202 space and consequently its dimensionality in order to characterize the full set of reflections.
 1203 This can be done according to the following embedding given in Figure 51.

1204 The new space embedding to describe the full set of reciprocal vectors is called
 1205 superspace and in our particular case, we introduce the four new basis vectors $\mathbf{a}_{S1}^*, \dots, \mathbf{a}_{S4}^*$
 1206 expressed in terms of their external and internal components. Once the reciprocal vectors are
 1207 defined, we can use the orthogonality relation to obtain the corresponding direct space basis
 1208 vectors given in the next relation.

$$1209 \quad \left. \begin{array}{l} \mathbf{a}_{S1}^* = (\mathbf{a}_1^*, 0) \\ \mathbf{a}_{S2}^* = (\mathbf{a}_2^*, 0) \\ \mathbf{a}_{S3}^* = (\mathbf{a}_3^*, 0) \\ \mathbf{a}_{S4}^* = (\mathbf{q}, 1) \end{array} \right\} \rightarrow \mathbf{a}_{Si} \cdot \mathbf{a}_{Sj}^* = \delta_{ij} \rightarrow \left\{ \begin{array}{l} \mathbf{a}_{S1} = (\mathbf{a}_1, -\mathbf{q} \cdot \mathbf{a}_1) \\ \mathbf{a}_{S2} = (\mathbf{a}_2, -\mathbf{q} \cdot \mathbf{a}_2) \\ \mathbf{a}_{S3} = (\mathbf{a}_3, -\mathbf{q} \cdot \mathbf{a}_3) \\ \mathbf{a}_{S4} = (\mathbf{0}, 1) \end{array} \right. \quad (4)$$

1210 The next challenge is to find a suitable embedding of the three-dimensional structure
 1211 into superspace and a way to reinterpret crystal structures in this new reference frame.

1212 The origin of the satellite reflections observed on diffraction patterns was already
 1213 known long before the 1970s. However, Korekawa (1967) was the first to present some
 1214 theoretical backgrounds explaining the origin of the satellite reflections in “labradorite” and
 1215 other minerals. Their structures were interpreted as periodic displacement of atoms with an
 1216 additional periodicity, different from the three unit-cell lattice constants. Any periodic
 1217 perturbation can be represented by a series of Fourier terms and this is specifically what is
 1218 used to represent the displacements we are referring to.

1219 Let us reinterpret a structure in superspace with the simplest possible displacement or
 1220 *modulation* function, i.e., a sinusoidal displacement as represented in Figure 52a. The
 1221 description of the structure in superspace can be thus analysed in terms of two-dimensional
 1222 sections just like architect’s plans of a complex building are analysed in terms of 2-d sections.
 1223 Practically, a limited amount of sections is sufficient to fully characterize the structure. From
 1224 Figure 52b we can see that the real crystal structure is not analysed in terms of the natural
 1225

1226 variable x_4 but rather by the variable t which is related to x_4 by the relation $t = x_4 - \mathbf{q} \cdot \mathbf{r}$. For the
 1227 specific case of natrite, it turns out that only four reciprocal basis vectors are necessary to
 1228 fully characterize the diffraction pattern with integer coefficients. In general, this is not
 1229 always the case and examples of structures with up to six reciprocal basis vectors have been
 1230 found. This is for example the case for icosahedral quasicrystals. The number of reciprocal
 1231 basis vectors necessary to fully characterize the structure is called the *rank*. Therefore, if the
 1232 rank is equal to the dimension of the periodic object, the structure is *periodic*. Otherwise, if
 1233 the rank is larger than the dimension, the structure is *aperiodic*.

1234 As in periodic structures, the resolution of aperiodic crystal structures consists of
 1235 determining the electron density (if X-ray are used) from the structure factors by Fourier
 1236 transform. For a structure with rank 4, described in (3+1)D superspace, the structure factor
 1237 $F(\mathbf{H})$ is given by the relation:

$$1238 \quad F(\mathbf{H}) = \sum_j f_j(\mathbf{H}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j) \quad (5)$$

$$\times \int_0^1 dt p_j(t) \exp\{2\pi i (\mathbf{H} \cdot \mathbf{u}_j(t) + h_4 t)\}$$

1239 On the first line we recognise the classical part of the structure factor with the atomic
 1240 scattering factors f_j whereas the second line is dedicated to the modulated part of the structure
 1241 which is characterized by the functions $\mathbf{u}_j(t)$, for each atom in the unit cell. As mentioned
 1242 before, the variable t is more convenient for the analysis of the geometrical characteristics
 1243 between atoms and is favoured instead of x_4 . The probability factor $p_j(t)$ allows to characterise
 1244 structures with *substitution modulations* or defects.

1245 More complex modulation functions $\mathbf{u}_j(t)$ can obviously be obtained by adding a series
 1246 of harmonic terms to optimize the best fitting function. Other possibilities however have been
 1247 proposed like crenel or step-like, sawtooth and zigzag functions (Petříček *et al.* 2014). An
 1248 important ingredient for the description of crystal structures concern the space group
 1249 symmetry used to characterize periodic structures. For aperiodic structures, however a
 1250 generalization of the symmetry concept has been introduced in order to fully describe them,
 1251 the so-called superspace groups. This is not our intention to deal here with the theoretical
 1252 basis of superspace symmetry. Bibliographic references may be found in Janssen *et al.* (2008)
 1253 and van Smaalen *et al.* (2013).

1254 One may wonder what kind of structure solutions methods can be applied to solve
 1255 aperiodic structures. Fortunately, some efficient and recently developed algorithms have been
 1256 designed (see for instance Oszlányi and Sütő 2004; Palatinus and Chapuis, 2007) to solve any
 1257 type of structures in any dimension perhaps with some caveat on macromolecular structures.
 1258 These methods are based on *dual space phase retrieval algorithms*. They are iterative
 1259 methods which attempt to estimate the phases of the structure factors (reciprocal space) by
 1260 forcing them to satisfy the conditions that the atomic density of the structure (direct space)
 1261 cannot be negative. The program package JANA2006 (Petříček *et al.* 2014) is a very efficient
 1262 tool to solve and refine both periodic and aperiodic structures in any dimension.

1263 Finally, we can conclude this paragraph by giving some specific characteristics about
 1264 possible aperiodic structures. In our introduction, we have enumerated the three main families
 1265 of aperiodic structures which have been identified, namely the incommensurately modulated
 1266 structures, the composites and the quasicrystals. According to Yamamoto (1996), the best way
 1267 to distinguish the categories is to look at their diffraction patterns which are schematically
 1268 represented in Figure 53. In modulated structures, we can always distinguish a series of main
 1269 reflections along the external space dimension R_e and in addition a series of satellites with
 1270 embedding along the internal space dimension R_i . In composites, we can always distinguish
 1271 two or more series of main reflections and in addition satellites may also occur. In

1272 quasicrystals however, the distinction between main and satellite reflections can no longer be
 1273 made and the important reflections have no periodicities. Quasicrystals can always be clearly
 1274 distinguished whereas we can find limiting cases where the distinction between modulated
 1275 and composite crystal is not clear cut.

1276 In the next paragraphs, we shall present a few characteristic aperiodic mineral structures
 1277 and illustrate their specific properties.

1278

1279 6.3 Natrite, Na₂CO₃

1280 As mentioned earlier, natrite was at the origin of a new revolution of the concept of
 1281 crystals. The first hints aroused when de Wolff and his group (Brouns et al. 1964) realised that
 1282 they could not fully index its powder diffraction pattern. The solution of the problem was
 1283 found a decade later when van Aalst et al. (1976) proposed for the first time the embedding of
 1284 the diffraction pattern in higher dimensional space. In addition, they introduced the concept of
 1285 high-dimensional symmetry of modulated structures and proposed a structural model of
 1286 Na₂CO₃ in the harmonic approximation. Shortly following this paper, the concept of
 1287 superspace symmetry was introduced by de Wolff et al. (1981).

1288 We have to mention at this point that many publications prior to de Wolff's work were
 1289 published pointing to the existence of modulated structures in various systems. Unfortunately,
 1290 these studies proposed *ad hoc* structural solutions but failed to develop a valid concept to
 1291 generalize the symmetry properties which is a prerequisite for any structural studies. The
 1292 work initiated by the Dutch groups was the trigger which started the rapid development of the
 1293 new structural paradigm.

1294 Coming back to the structure of natrite, we should mention here that most of the
 1295 structural studies performed have been done on synthetic samples (Dušek et al., 2003;
 1296 Arakcheeva and Chapuis 2005). A study by Arakcheeva et al. (2010) comparing natural
 1297 natrites and synthetic Na₂CO₃ shows very similar structures with some minor discrepancies in
 1298 the phase transition temperatures which can easily be explained by various impurities always
 1299 present in natural samples.

1300 Na₂CO₃ exhibits numerous phases depending on the temperatures (Dušek et al. 2003;
 1301 Arakcheeva and Chapuis 2005) which are schematically indicated below.

1302

α	754K	β	605K	γ'	530K	γ	170K	δ
<i>hexagonal</i>		<i>monoclinic</i>		<i>monoclinic incom.</i>		<i>monoclinic incom.</i>		<i>monoclinic lockin</i>

1303

1304

1305 The structure of γ -Na₂CO₃ is best described in terms of graphite-like layers formed by
 1306 Na³⁺ and CO₃²⁻ ions as illustrated in Figure 54. Na1 and Na2 are located between the layers.
 1307 Both are coordinated by 6 oxygens forming octahedra. For Na3 however, the octahedra are
 1308 strongly distorted. The Na1,2–O distances vary between 2.3 and 2.4 Å whereas for Na3–O the
 1309 distances vary between 2.5 and 2.9 Å. In all the phases, the distinction between the two Na1,2
 1310 and Na3 can always be observed and although they are the same atomic species they behave
 1311 like two stereo-chemically distinct groups of atoms.

1312 In order to understand the nature of the incommensurate character of γ -Na₂CO₃, let us
 1313 analyse this structure in terms of Na and C containing planes illustrated in Figure 55 and
 1314 neglect the oxygen atoms. In the inset, we can distinguish two types of planes, namely m_M and
 1315 m_V. The m_M plane is the monoclinic (*a*, *c*) plane which can be also seen in Figure 54. The
 1316 other m_V planes are rotated by $\pm 60^\circ$ along the direction of the hexagonal channels.

1317 The atomic arrangement of both m_M and m_V planes are identical in the high-temperature
 1318 hexagonal phase α . At $T \leq 754$ K, the m_M plane and the corresponding configuration remains
 1319 stable and unchanged in all the lower-temperature phases including the incommensurate ones.

1320 The atomic arrangement observed in the m_V planes attempts to remain identical to the m_M
 1321 plane but the monoclinic distortion does not allow it. By decreasing temperature from 754 K
 1322 down to 605 K, the distortion of the m_V plane increases in the β phase until it transforms into
 1323 the incommensurate γ phase. In the γ phase, the atomic arrangement of the m_V plane is a
 1324 compromise of a sequence of different configurations observed in the β phase at different
 1325 temperatures (Fig. 55). This is at the origin of the incommensurability of the γ phase.

1326 It is important to note here the origin of the driving force in the sequence of phases
 1327 observed in this compound which is also valid for the incommensurate phase. It is not the
 1328 interactions of sodium with its first coordination sphere, i.e., O atoms, but it is the interactions
 1329 with sodium with its second coordination sphere consisting of Na and C atoms as shown in
 1330 the study by Arakcheeva and Chapuis (2005).

1331 We can follow the evolution of the sequence of phases by focusing on the Na atoms in
 1332 the vicinity of the C atoms, which gives the following coordination scheme while limiting the
 1333 $C \cdots Na$ contacts to 3.1 Å

1334

Phase	α	β	γ'	γ	δ
CN	3	4	5	6 – 7	7

1335

1336

1337 The intra layers contact distances between of C and Na3 atoms remain practically
 1338 unchanged over the temperature range. Thus, the increase of coordination number is
 1339 essentially due to the Na1,2 channel atoms. None of them participate in the coordination
 1340 sphere in phase α whereas all of them are bonded in the lock-in phase δ .

1341 It should be mentioned that a detailed study of structure modulations in natural natrites
 1342 from different origins (Arakcheeva et al. 2010) gives valuable information on the history of
 1343 the mineral transformation as a function of their occurrences.

1344

1345

6.4 Calaverite $Au_{1-x}Ag_xTe_2$

1346 Calaverite, a mineral with the composition of $Au_{1-x}Ag_xTe_2$, where $0 \leq x \leq 0.15$ is an
 1347 important gold-bearing ore and another interesting case of a modulated structure which has
 1348 first challenged mineralogists and later structural scientists until its secret could be uncovered.
 1349 Already in the beginning of the 20th century, before the diffraction method was discovered, the
 1350 attempts by mineralogists to index the faces of calaverite according to Haüy's law of rational
 1351 indices failed. After many attempts to solve this puzzle, an important study was published by
 1352 Goldschmidt et al. (1931) presenting an extended analysis of 105 different calaverite samples
 1353 originated from all over the world and identified 92 different crystal forms. The conclusion of
 1354 their work was that the law of rational indices was not of general validity. They were
 1355 obviously right but the tools to solve the problem were not ready yet.

1356 The resolution of the incommensurate structures of calaverite by Schutte and de Boer
 1357 (1988) based on the full set of diffracted intensities including satellite reflections was
 1358 fundamental to understand the origin of its incommensurability.

1359 The average structure of calaverite solved by neglecting the satellite reflection is
 1360 illustrated in Figure 56a. It consists of a series of parallel layers of edge sharing Te octahedra
 1361 centred by (Au,Ag) atoms. The geometrical properties of the incommensurate structure can
 1362 best be explained in terms of a t -plot as introduced in Figure 52. The distance t -plot illustrated
 1363 in Figure 56b gives all the (Au,Ag)-Te < 3.3 Å distances. Note that t -plots conveniently
 1364 summarize all the possible configurations which exist in the crystal but do not include
 1365 information about orientation and position of the other atoms located in the extended
 1366 neighborhood.

1367 The analysis of the t -plot indicates that for $t \approx \frac{1}{4}$ and $\frac{3}{4}$ (Au,Ag) is surrounded by only
 1368 four close Te atoms with (Au,Ag)-Te distances of about 2.7 Å (numbers 1,2,3,4 and 1,2,5,6,

1369 respectively, Fig. 56b). Two other distances of 3.2 Å are too long to take part in the
1370 coordination sphere. Knowing that the corresponding t -plot of the angles are close to 90°, we
1371 can conclude that somewhere in the crystal space, we shall find square planar (Au,Ag)Te₄
1372 configurations with the coordination number CN = 4 for (Au,Ag). Other t -intervals can be
1373 characterized with CN = 4 + 2. For a deeper analysis of the properties of the structure, we
1374 need to represent a portion of the modulated structure with many basic unit cells.

1375 Figure 57 shows a portion of the Au_{0.9}Ag_{0.1}Te₂ structure with ordered distribution of Ag
1376 (Bindi et al. 2009b). The blue circles indicate sites where Ag replaces some of the Au atoms in
1377 the octahedra with CN = 4+2. The remaining octahedra contain only Au. Schutte and de Boer
1378 (1988) proposed that the origin of the modulation in calaverite was due to the presence of
1379 Au¹⁺ and Au³⁺ with the electronic configuration 5d¹⁰ respectively 5d⁸, since Au³⁺ prefers a
1380 square planar coordination with Te. However, X-ray absorption spectroscopy experiments
1381 reported by Ettema et al. (1994) unequivocally shows only Au¹⁺ in calaverites. This
1382 conclusion is confirmed by a comprehensive structural study by Bindi et al. (2009b) with
1383 examples from a series of calaverites with different Ag compositions 0 ≤ x ≤ 0.33. The
1384 modulation of the oxidation state of Au has also been estimated between 0.9 and 1. This study
1385 has demonstrated that the Ag distribution on the Au position plays a key role in the structure
1386 formation. The ordered distribution of silver reinforces the valence fluctuation of Au and the
1387 structure modulation. A random distribution of Ag suppresses the valence fluctuation of Au
1388 and, therefore, their structural modulations. Apparently, natural samples can be found with the
1389 same composition but with both types of Ag ordering, which is not surprising considering the
1390 various growth conditions of the minerals.

1391 Calaverite is a member of a more general family of pseudo-binary system Au_{1-x}Ag_xTe₂
1392 with a silver content up to $x=0.5$. In the mineral krennerite, the silver content varies between
1393 0.2 ≤ x ≤ 0.28. The mineral sylvanite exists in two forms: one with $x = 0.5$ and the second
1394 with x slightly smaller than 0.5. It is interesting to note that the superspace model applied to
1395 calaverite is able to reproduce the complete set of structures of the pseudo-binary system by
1396 adapting the modulation vector \mathbf{q} with commensurate or incommensurate components and
1397 adjusting the t -plot of the variable x .

1398 Finally, we would like to conclude this paragraph by returning back to the famous
1399 conclusion of Goldschmidt et al. (1931) about the impossibility of indexing the faces and the
1400 rejection of the law of rational indices. Shortly after the resolution of the incommensurate
1401 structure of calaverite, Janner and Dam (1989) managed to unambiguously index all the
1402 possible faces identified in the 1931 paper. The solution was to use four indices for each face,
1403 i.e, a number equal to the rank of the structure as previously defined. Figure 58 illustrates the
1404 indexation of the faces. Janner and Dam (1989) could identify two twin samples and
1405 moreover, from the measurements of Goldschmidt et al. (1931), they could deduce the exact
1406 components of the modulation vector \mathbf{q} up to a precision comparable to that obtained by the
1407 X-ray diffraction measurements!

1408 The example of calaverite is by no means an exception and other examples have been
1409 found in metal-organic materials where the temperature dependence of the modulation vectors
1410 could be deduced from the observations of the crystal forms (Dam and Janner 1986).

1411 Häüy's law is thus still valid provided that we extend the number of indices to the rank
1412 of the structure.

1413

1414 **6.5 Melilite (Ca,Na)₂(Mg,Fe²⁺,Al)[(Al,Si)SiO₇]**

1415 The group of melilite minerals include generally solid solution of åkermanite and
1416 gehlenite with chemical composition Ca₂MgSi₂O₇ and Ca₂Al(AlSiO₇), respectively. The
1417 overall formula can be expressed as X₂T1T₂O₇ with T1 and T2 atom species tetrahedrally
1418 coordinated by oxygens. The basic structural features of the mineral family have been known

1419 since the 1930s but the incommensurability was discovered much later by Hemingway et al.
1420 (1986).

1421 The structure of melilite consists essentially of corner sharing tetrahedra layers
1422 alternating with X containing layers as represented in Figure 59. The T2 tetrahedra always
1423 appear in pairs forming bow-tie whereas the T1 tetrahedra are linked to four T2 tetrahedra.
1424 Each layer consists of irregular pentagonal rings surrounded by two T1 and three T2
1425 tetrahedra. The X atoms are located between the tetrahedra layers and are linked to the
1426 oxygens of the nearest layers.

1427 It is clear that this structure allows a large degree of freedom to accommodate many
1428 different chemical substitutions for the T1, T2 and X cations. The tetrahedral layers can easily
1429 accommodate different T cations with variable size by permitting rotational and translational
1430 displacements.

1431 Since the discovery of the incommensurate nature of some melilite structures, many
1432 structural studies appeared with various compositions and temperatures. A selection of
1433 references can be found in Bindi et al. (2001). The incommensurate structures have been
1434 solved in (3+2)D superspace group with tetragonal symmetry. The origin of the
1435 incommensurability is essentially due to positional rather than substitutional changes. The
1436 coordination of the X cations by O atoms within a single incommensurate structure may vary
1437 between 6 and 8 and a flattening of the T1 tetrahedra may also occur. Occupational
1438 modulation wave has also been observed in some cases pointing to ordered distribution of
1439 some cations. Superstructures which can also be interpreted as *commensurately* modulated
1440 structures have also been observed.

1441 The resolution of a natural incommensurately modulated melilite sample from Umbria
1442 (Italy) presented here was published by Bindi et al. (2001). Only first order satellites were
1443 observed. A portion of the incommensurate layer structure is presented in Figure 60a. A close
1444 analysis of the pentagonal rings mentioned above shows a large variation of deformation
1445 extending in the layer plane. The most important feature of the deformation can best be
1446 understood in terms of the T1-X coordination sphere as represented in the *t*-plot of Figure
1447 60b. Here we concentrate on the X neighbourhood of T1. We can essentially distinguish two
1448 zones, one in the vicinity of $t = \frac{1}{2}$ and one in the vicinity of $t = 0$ or 1. Close to $t = \frac{1}{2}$ T1 has 8
1449 X neighbours with distances up to 4 Å located approximately on the vertices of a cube (see
1450 inset). Close to $t = 0$ or 1, T1 has only four X neighbours forming a tetrahedron. Figure 60a
1451 illustrates another feature of the structure based on the X-O coordination polyhedra. In the
1452 average structure of melilite they are slightly distorted trigonal prism with 6 oxygens. In the
1453 incommensurate structure, we observe that the 6-coordinated X atoms form clusters with four
1454 long T1-X distances surrounding the T1 tetrahedra indicated on Figure 60a by black
1455 tetrahedra. The clusters are regularly located on various circles with 8 members which recalls
1456 to some extent similar distributions in quasicrystals! The small 8-membered ring has also
1457 been observed in a synthetic $\text{Ca}_2\text{CoSi}_2\text{O}_7$ (Riester et al. 2000) by X-ray diffraction and in
1458 $\text{Ca}_2\text{ZnGe}_2\text{O}_7$ (van Heurck et al. 1992) by electron microscopy.

1459 The X-O polyhedra deformation is certainly not the only distortion observed in melilite.
1460 The T1-O distances and O-T1-O angles are also affected according to various *t*-plot
1461 calculations. The departure from the ideal angle of 109° may vary between 103 and 123°.

1462 Here again as in the other mineral structures presented above, we can find a common
1463 justification for the origin of the incommensurability. In melilite, the presence of impurities
1464 and the relative size of the X and T cations create disparities in the coordination polyhedra.
1465 The ideal 6 coordinated X-O polyhedra can only be accommodated locally, however not
1466 stochastically but in a very ordered way in the form of various circular distributions as
1467 indicated on Figure 60a.

1468

1469 6.6 Natural Quasicrystals

1470 The discovery of synthetic quasicrystals by Shechtman et al. (1984) extended further the
1471 concept of aperiodicity in crystals beyond incommensurately modulated and composites
1472 structures. Following this discovery, a large number of Al ternary alloys with quasicrystalline
1473 structures could be produced and analyzed by diffraction methods. Two families of
1474 quasicrystals essentially emerged in these studies, namely icosahedral and decagonal
1475 quasicrystals. During that period, it appeared however that the world of mineralogy would
1476 remain exempt of *natural* quasicrystalline materials. The situation changed a quarter of a
1477 century later when Bindi et al. (2009c) discovered the first naturally occurring sample of a
1478 quasicrystal. The discovery did not occur by serendipity but following not only a systematic
1479 analysis of all metallic alloys which could be found in structural databases but also by
1480 analyzing various notable mineral collections (Bindi 2020). Finally, the search focused around
1481 the mineral kathyrkite (Cu,Zn)Al₂ originating from the Koryak Mountains in the northeast of
1482 the Kamchatka Peninsula in Russia. From a sample size of sub- μm , the authors could locate
1483 an area which did produce the characteristic diffraction pattern with ten-fold symmetry
1484 illustrated in Figure 61a obtained by HRTEM. The chemical analysis of the sample yielded
1485 the composition Al₆₃Cu₂₄Fe₁₃, which is very close to the already known synthetic face-
1486 centered icosahedral phase (FCI). In addition to the ten-fold symmetry pattern, the authors
1487 could also locate the six- and two-fold patterns at angles corresponding to the FCI pattern.
1488 Another convincing argument of the icosahedral symmetry of the sample is given in Figure
1489 61b. The plot lists the intensity weighted $|\Delta|$ where Δ is the absolute deviation of each
1490 scattering vector \mathbf{H} from the nearest matching FCI peak versus the intensity-weighted average
1491 of \mathbf{H} . The center grey zone corresponds to a large number of classical structures extracted
1492 from the ICDD database whereas the symbols \ominus and \circ represent well identified QC
1493 structures. The vertical and horizontal dotted lines represent 1σ confidence intervals. It is thus
1494 clear that the mineral (\blacktriangle) confirms the nature of its QC structure.

1495 The natural QC mineral was subsequently given the official name *icosahedrite* (Bindi et
1496 al. 2011) and a further analysis (Bindi et al. 2012b) gave evidence of the extraterrestrial origin
1497 of the sample. The formation of the sample was estimated to be approximately 4.5 Gya under
1498 extreme conditions, i.e., shock pressures ≥ 10 GPa and temperatures ≥ 1500 K. The meteoritic
1499 origin of stable QC forms is thus clearly demonstrated.

1500 The analysis of the famous kathyrkite sample reserved another surprise, namely the
1501 discovery of a decagonal quasicrystalline phase (Bindi et al. 2015) with composition
1502 Al₇₁Ni₂₄Fe₅. This chemical composition has also been observed in synthetic samples.
1503 Decagonal quasicrystals with rank = 5 can be described by a periodic stacking of
1504 quasicrystalline layers. Thus, contrary to the icosahedral QC, only ten- and two-fold symmetry
1505 diffraction pattern can be observed but no six-fold symmetry.

1506 Yet, the kathyrkite sample delivered a third quasicrystalline phase with the chemical
1507 composition Al₆₂Cu₂₁Fe₇ (Bindi et al. 2016b). Contrary to the previously discovered natural
1508 QC, this new icosahedral phase did not have any synthetic equivalent and its composition
1509 seemed to be outside the previously expected equilibrium stability field under standard
1510 pressure. Noteworthy, the synthetic analogue of natural Al₆₂Cu₂₁Fe₇ was recently obtained by
1511 a collision experiment simulating the impact between asteroids in outer space (Hu et al.
1512 2020).

1513 Synthetic QC often exhibits so-called *phason strains*. Phason strains are elastic modes
1514 which diffuse in the structure and often relax. They cause systematic shift of the Bragg
1515 reflections and the shifts from the ideal positions are inversely related to the intensity of the
1516 peak. They are usually observed on samples subject to rapid quenching during the synthesis.
1517 It appears that the two natural QC crystalline samples described here are exempt of phason
1518 strains and thus depart significantly from synthetic samples formed under strictly controlled

1519 laboratory conditions (Bindi and Stanley 2020). This feature gives also an important indicator
1520 about the long-term stability of natural QC phases.

1521

1522 **6.7 The puzzle of “labradorite”**

1523 The variety of anorthite known as “labradorite” is notable for the iridescent effect
1524 observed on some specimens as illustrated in Figure 62a. It belongs to the family of the
1525 plagioclase feldspars with composition $\text{Ca}_x\text{Na}_{1-x}\text{Al}_{1+x}\text{Si}_{3-x}\text{O}_8$ which form solid solution with the
1526 two end members *albite* ($\text{NaAlSi}_3\text{O}_8$) and *anorthite* ($\text{CaAl}_2\text{Si}_2\text{O}_8$).

1527 Plagioclase feldspars can be considered as an important diagnostic tool for petrological
1528 studies. The nearly continuous composition variable x is at the origin of structural
1529 complexities which have filled many volumes of studies dedicated to a better understanding
1530 of their structures. The observation of superstructures, diffuse scattering and the presence of
1531 satellite reflections in the diffraction patterns have been the subject of many interesting model
1532 proposals since more than 60-70 years. Korekawa and Jagodzinski (1967) were the first to
1533 report the observation of two types of satellite reflections relating to two scale lengths in the
1534 diffraction patterns of labradorite with an anorthite content of 52%. One series of satellites
1535 (called e-satellites) is associated with a modulation periodicity of 50 Å and the other series (s-
1536 satellites) is associated with another type of modulation with a much larger periodicity and
1537 which is related to the iridescent (or schiller) effect (Fig. 62b). The periodicity of the violet
1538 color is approximately 1800 ± 200 Å and 1400 ± 200 Å for the ultraviolet.

1539 A more recent publication by Boysen and Kek (2015) attempts to propose an improved
1540 model of labradorite on the basis of X-ray synchrotron radiation data. The tentative schematic
1541 model illustrated in Figure 63 gives an interpretation of the origin of the two scale lengths.
1542 The large domains D1 and D2 exhibit anorthite content differences of up to 10% and are
1543 related to the modulation given by the s-satellites. Within each domain D_i , we observe another
1544 modulation sequence related to the e-satellites. The origin of this modulation is also due to
1545 variations of the Na/Ca content but the role of the Si/Al distribution is not clarified.

1546 It is surprising that a complete and satisfactory structure solution has not yet been
1547 proposed despite the numerous studies on the problem published up to these days (Jin and Xu
1548 2017). The difficulty lies in finding a single structural model which is capable of handling
1549 simultaneously both types of modulations with two independent and very different length
1550 scales. This would solve the problem of existing correlations with the different Ca/Na and
1551 Si/Al contents in different domains and which are completely neglected if the structure
1552 solution neglects one or the other type of satellite. Another difficulty resides in the accurate
1553 measurements of very narrow and weak satellite reflections even on current synchrotron
1554 facilities. It is thus probable that a definitive solution of the structure of labradorite will
1555 possibly emerge from a new refinement in a (3+2)D structure model, i.e., with rank 5 instead
1556 of rank 4.

1557

1558 **6.8 When “disorder” turns out in aperiodicity**

1559 The analysis of aperiodic crystal structures often reveals very subtle atomic interactions
1560 which are difficult to detect with classical structures. This is not only valid for minerals but
1561 for any aperiodic structure. Another interesting aspect is that a single atomic species may
1562 occur in the same structure with different crystal-chemical environments and different valence
1563 states giving clues on its electronic state. This is the case for instance of Na in natrite and Au
1564 in calaverite.

1565 It turns out that the usefulness of the tools which have been developed for the analysis
1566 and solution of aperiodic structures (Petříček et al. 2014) goes much beyond these goals. They
1567 also have been useful for the prediction and design of new structures. They are also helpful in
1568 discovering new relations between various structures as in the case of scheelite (Arakcheeva

1569 and Chapuis 2008). The use of the superspace concept is by far not limited to aperiodic
1570 structures but represent a very powerful link between the periodic and aperiodic allowing to
1571 extend the notion of structure type.

1572 The discovery of aperiodic structure has had an enormous impact on pushing back the
1573 frontier of so-called disordered structures. Before the concept was well established, many
1574 different structures have been published with some caveats on the existence of additional
1575 (usually weak) peaks which could not be explained. They were mostly attributed to
1576 “impurities” or “disorder”. It turns out that these structures were very well ordered but with an
1577 aperiodic character.

1578

1579 **7. Conclusion and perspectives**

1580 Researches and studies dealing with the complexity of mineral structures are continually
1581 moving forward. In recent years, the new generation of instruments (with new super-sensible
1582 CCD and imaging plate systems) considerably improved the sensitivity of data collection for
1583 complex mineral structures of very small samples, in particular incommensurately modulated
1584 and disordered structures. Several computer programs are nowadays able to deal with these
1585 structures. Beside X-ray diffraction, precession electron diffraction methods are increasing
1586 their power allowing the determination of structures from very small particles, down to a few
1587 nanometers (e.g., Mugnaioli and Gemmi 2018). Given this extraordinary range of techniques
1588 and instrumentations, we think that, beside the ongoing work to determine still-unknown
1589 mineral structures, a broader vision is called for in considering the future of mineralogical
1590 crystallography. Mineralogy can indeed continue to surprise us and have a strong impact on
1591 other disciplines, including chemistry, condensed matter physics, materials science and
1592 engineering.

1593

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1604

1605

1606

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1985
1986

1987 **Figure captions**

1988 **Figure 1.** Hexagonal compact layer of equally sized spheres, with the two differently
1989 oriented triangular cavities indicated as B and C. The centres of the spheres are indicated as
1990 A.

1991 **Figure 2.** The octahedral (O) and the two tetrahedral (T) cavities in the region between
1992 two compact layers of equally sized spheres in which the spheres in upper layer are positioned
1993 on one of the triangular cavities of the lower layer.

1994 **Figure 3.** The two trigonal prismatic (P_1 and P_2) cavities in the region between two
1995 compact layers of equally sized spheres in which the spheres in upper layer are positioned
1996 above the spheres of the lower layer. This and the following figures, up to Fig. 23, drawn with
1997 VESTA (Momma and Izumi 2011).

1998 **Figure 4.** The tetrahedral (T) and octahedral (O) sheets building the layer phyllosilicates
1999 (a) Perspective view of the T sheet. (b). The dioctahedral sheet seen along $[001]^*$. Red
2000 spheres are oxygen atoms, smaller white spheres are hydrogen atoms. Dashed segments
2001 represent hydrogen bonds. (c). The trioctahedral sheet seen along $[001]^*$. Same colour scheme
2002 as in (b).

2003 **Figure 5.** The TOT layer seen (a) along $[010]$ and (b) along $[001]^*$. In (a), the two T
2004 sheets are staggered one with respect to the other by about $-a/3$. In (b), the ideal configuration
2005 of the T sheet (hexagonal) symmetry is shown, which is however seldom realized in
2006 phyllosilicates, a ditrigonal rotation of the tetrahedra being very common. Red and blue
2007 spheres are oxygen atoms and hydroxyl groups, respectively. The conventional (rectangular in
2008 projection) and primitive (rhomb-shaped in projection) unit cells are shown. The symmetry
2009 elements of the point group are also shown: a two-fold axis parallel to b (thin line ending with
2010 the oval symbol of a twofold rotation axis), a mirror plane normal to it (thick line) and an
2011 inversion centre (small white circle at the intersection of the rotation axis and the mirror
2012 plane).

2013 **Figure 6.** The real configuration of the T sheet in a trioctahedral (a) and dioctahedral (b)
2014 TOT layer. The ditrigonal rotation, which depends on the actual chemistry of the mineral, is in
2015 general more important for the dioctahedral layer because of the size difference between the
2016 empty and the occupied octahedral sites.

2017 **Figure 7.** The real structure of the T sheet in talc and pyrophyllite. Two adjacent T
2018 sheets belonging to two successive TOT layers, from which the O sheets have been removed.
2019 The ditrigonal cavities (ideally hexagonal) have parallel orientation but are shifted by about
2020 (a) $a/3$ for talc ($0.2968a$) and (b) about $1/10$ along the $[120]$ direction for pyrophyllite.

2021 **Figure 8.** The real structure of the T sheet in micas. Two successive TOT layers from
2022 which the O sheets have been removed. Between the two T sheets, the interlayer cation
2023 (purple) is shown. Even ($2n \times 60^\circ$) orientations result in a staggered configuration of the basal
2024 oxygen atoms (Fig. 8a, phlogopite- $1M$), whereas odd $[(2n+1) \times 60^\circ]$ orientation in an eclipsed
2025 orientation (Fig. 8b, phlogopite- $2O$, and Fig. 8c, lepidolite- $2M_2$).

2026 **Figure 9.** In trioctahedral TOT layers the tetrahedra of the same T sheet have parallel or
2027 quasi-parallel orientation (a), whereas in dioctahedral TOT layers, because of the size
2028 difference between empty and occupied O sites, these tetrahedra are tilted about the basal
2029 bridging oxygen atoms.

2030 **Figure 10.** The interlayer region of 1M polytype of chlorite, containing an isolated O
2031 sheet, with two T sheets belonging to successive TOT layers. These are equally oriented by
2032 shifted by $0.42a$.

2033 **Figure 11.** The O sheet seen along $[001]^*$. In red, positions of the hydroxyl groups that
2034 are replaced by apical oxygen atoms of the T sheet when forming the TOT layer. In blue,
2035 hydroxyl groups the remain in the TOT sheet (the white small circles are hydrogen atoms).
2036 Octahedral sides with OH groups in *trans* configurations are shown in white, those with OH
2037 groups in *cis* configuration in yellow. replace two thirds of the hydroxyl groups of the O
2038 sheets. The remaining OH groups allow to differentiate the octahedral sites. The rhombic-
2039 shaped primitive unit cell, shown in the figure, contains one *trans* and two *cis* octahedral
2040 sites; the origin has been moved onto the *trans* site to enhance readability of the figure.

2041 **Figure 12.** Selection of R_5 (a) and R_8 (b) rods from the TOT layer. Numbers identify the
2042 octahedra spanning the width of the rod.

2043 **Figure 13.** The structure of amphiboles, seen along $[001]$. This structure can be
2044 interpreted as composed by R_5 rods, periodic along the c axis of the mineral, displaced one
2045 with respect to the other along the a axis, according to the OH- O_b bonding scheme.
2046 Depending on cations occupying the O chain and the nature of the X cation amphiboles are
2047 classified in a number of different minerals. In some of these, the empty space \square is
2048 sometimes occupied by a monovalent cation, mainly sodium.

2049 **Figure 14.** The structure of jimthompsonite, seen along $[001]$. This structure can be
2050 interpreted as composed by R_8 rods, periodic along the c axis of the mineral, displaced one
2051 with respect to the other along the a axis, according to the OH- O_b bonding scheme.

2052 **Figure 15.** The structure of chesterite, seen along $[001]$. This structure can be
2053 interpreted as composed by R_5 and R_8 rods alternating, according to the OH- O_b bonding
2054 scheme, i.e. by an alternation of amphibole-like modules and jimthompsonite-like modules.

2055 **Figure 16.** The structure of palygorskite, seen along $[001]$. This structure can be
2056 interpreted as composed by R_5 rods, periodic along the c axis of the mineral, displaced one
2057 with respect to the other along the a axis, according to the O_b - O_b bonding scheme. Water
2058 molecules occur in the regions between the rods.

2059 **Figure 17.** The structure of sepiolite, seen along $[001]$. This structure can be interpreted
2060 as composed by R_8 rods, periodic along the c axis of the mineral, displaced one with respect
2061 to the other along the a axis, according to the O_b - O_b bonding scheme. Water molecules occur
2062 in the regions between the rods.

2063 **Figure 18.** The structure of kalifersite, seen perspectively along $[001]$. This structure
2064 can be interpreted as composed by an alternation of R_3 rods and R_6 rods, periodic along the c
2065 axis of the mineral, displaced one with respect to the other along the a axis, according to the
2066 O_b - O_b bonding scheme.

2067 **Figure. 19.** The structure of wollastonite, $CaSiO_3$. (a) Projection along the b axis,
2068 showing that the O chain has a width of three octahedra. (b) projection along $[101]^*$, with the
2069 cation sites in a ball-and-stick representation. The period of the tetrahedral chain, between two
2070 horizontal black lines, is three tetrahedra.

2071 **Figure 20.** The structure of pyroxenes, $MSiO_3$ ($M = Ca, Mg$ for diopside, shown in this
2072 figure) seen (a) along $[001]$ and (b) along $[101]$. The larger site, white polyhedron in (a),
2073 usually indicated as M2 in the literature, is assimilated to an octahedron for the sake of

2074 comparison with the other structure, although in pyroxenes it does have a octahedral
2075 geometry. The period of the tetrahedral chain, between two horizontal black lines, is two
2076 tetrahedra. Structural data from Cameron et al. (1973).

2077 **Figure 21.** The structure of rhodonite, $(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg}, \text{Ca})\text{SiO}_3$ seen along $[100]^*$. The
2078 period of the tetrahedral chain, between two horizontal black lines, is five tetrahedra. This
2079 structure is composed by a regular alternation of wollastonite-like slabs and pyroxene-like
2080 slabs, shown between horizontal red lines. Structural data from Peacor et al. (1978).

2081 **Figure 22.** The structure of pyroxmangite, MnSiO_3 , seen along $[100]^*$. The period of
2082 the tetrahedral chain, between two horizontal black lines, is seven tetrahedra. This structure is
2083 composed by a regular alternation of one wollastonite-like slabs and two pyroxene-like slabs,
2084 shown between horizontal red lines. Structural data from Pinckney and Burnham (1988).

2085 **Figure 23.** The structure of ferrosilite-III, FeSiO_3 , seen along $[110]^*$. The period of the
2086 tetrahedral chain, between two horizontal black lines, is nine tetrahedra. This structure is
2087 composed by a regular alternation of one wollastonite-like slabs and three pyroxene-like
2088 slabs, shown between horizontal red lines. Structural data from Weber (1983).

2089 **Figure 24.** The $[(\text{UO}_2)_2(\text{CO}_3)_3\text{O}_4(\text{OH})_{12}(\text{H}_2\text{O})_8]$ cluster in ewingite (a), its skeletal
2090 representation (b), the U core (c; the U–U contacts shorter than 4 Å are shown as thick black
2091 lines; those between 4 and 6.2 Å as thin black lines; red and blue points indicate centres of the
2092 U_3 trimers and midpoints of the shared U–U edges of the U_4 dihedra, respectively), and the
2093 arrangements of the red and blue circles that correspond to the intersection of tetrahedron and
2094 octahedron, respectively (d).

2095 **Figure 25.** The $[\text{As}^{3+}\text{V}^{4+}_2\text{V}^{5+}_{10}\text{As}^{5+}_6\text{O}_{51}]$ cluster in morrisonite in polyhedral (a) and
2096 skeletal (b) representations.

2097 **Figure 26.** The projection of the crystal structure of ilmajokite along the c axis. Legend:
2098 Si tetrahedra = yellow, Ti octahedra = blue; H_2O molecules, Na, K, Ba, and Ce atoms are
2099 shown as red, light-blue, green, brown, and orange spheres, respectively (after Zolotarev et al.
2100 2020).

2101 **Figure 27.** Trigonal-prismatic titanosilicate (TPTS) clusters in the crystal structure of
2102 ilmajokite shown in polyhedral (a, c) and nodal (b, d) representations. The numbering scheme
2103 corresponds to the numbering of Si and Ti atoms from the experiment. The Ce-centered Ti_6
2104 trigonal prism is highlighted in yellow. Legend as in Figure 26 (after Zolotarev et al. 2020).

2105 **Figure 28.** The hierarchical organization of the crystal structure of ilmajokite separated
2106 into eight hierarchy levels (highlighted in grey).

2107 **Figure 29.** The crystal structure of langbeinite, $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$ (Mereiter 1979), projected
2108 down $[001]$. (SO_4) -tetrahedra are given in yellow and (MgO_6) -octahedra in green. Purple and
2109 red circles indicate K and O atoms, respectively. The unit cell and the orientation of the
2110 structure are outlined.

2111 **Figure 30.** The crystal structure of brizziite, NaSbO_3 (Olimi and Sabelli 1994). (SbO_6) -
2112 octahedra are given in green. Yellow and red circles indicate Na and O atoms, respectively.
2113 The unit cell and the orientation of the structure are outlined.

2114 **Figure 31.** Structure of $(\text{Ag}, \text{Cu})_{16}(\text{As}, \text{Sb})_2\text{S}_{11}$, showing the stacking of the
2115 $[(\text{Ag}, \text{Cu})_6(\text{As}, \text{Sb})_2\text{S}_7]$ and $[\text{Ag}_9\text{CuS}_4]$ layers (see text). The former layer is shown as ball-and-
2116 stick, with grey, violet, and yellow circles representing $(\text{Ag}, \text{Cu})_1$, (As, Sb) , and S sites,
2117 respectively. In the latter layer, the positions of Ag atoms (grey circles), are those obtained at
2118 RT; Cu is shown as blue circles.

2119 **Figure 32.** Non-harmonic joint probability density iso-surface for Ag at RT in the
2120 $[\text{Ag}_9\text{CuS}_4]$ layer extended with S2 atoms, exhibiting the Ag diffusion in the ab plane. Level of
2121 the map: 0.05 \AA^{-3} . Sulfur and Cu atoms are shown at arbitrary sizes.

2122 **Figure 33.** Projection of the crystal structure of polybasite-221 along the hexagonal *a*
2123 axis. Silver, Cu, Sb, and S atoms are shown as grey, blue, brownish, and yellow circles.

2124 **Figure 34.** Projection of the crystal structure of polybasite-222 structure along the
2125 monoclinic *b* axis, emphasizing the succession of the $[(\text{Ag,Cu})_6\text{Sb}_2\text{S}_7]^{2-}$ A (A_0) and
2126 $[\text{Ag}_9\text{CuS}_4]^{2+}$ B (B_0) module layers. Same symbols as in Figure 5.

2127 **Figure 35.** Different unit-cell type in the pearceite-polybasite group of minerals.

2128 **Figure 36.** Projection of the crystal structure of fettelite along the monoclinic *b* axis,
2129 emphasizing the succession of the $[\text{Ag}_6\text{As}_2\text{S}_7]^{2-}$ *A* and $[\text{Ag}_{10}\text{HgAs}_2\text{S}_8]^{2+}$ *B* module layers. Grey,
2130 dark violet, red and yellow circles indicate Ag, As, Hg and S atoms, respectively. The unit cell
2131 is outlined.

2132 **Figure 37.** Non-harmonic joint probability density iso-surface for Ag/Hg in the HT-
2133 structure of fettelite exhibiting the Ag diffusion in the *ab* plane. Part of the *B* layer extended
2134 with S atoms. Level of the map: 0.05 \AA^{-3} . Sulfur atoms in arbitrary size.

2135 **Figure 38.** (a) Three-dimensional representation of a joint probability density iso-
2136 surface (at the 90 \AA^{-3} level) for the gamma form of Ag_7PSe_6 at 473 K, showing Ag diffusion
2137 paths within a cluster centered on Se3. Se atoms are represented as spheres of arbitrary size
2138 (Evain et al. 1998). (b) Three-dimensional representation of a joint probability density iso-
2139 surface (at the 20 \AA^{-3} level) showing the cluster connection around the Se2 atom. Se atoms are
2140 represented as spheres of arbitrary size and the Se2 splitting is not taken into account for the
2141 sake of clarity (Evain et al. 1998).

2142 **Figure 39.** Spryite, $\text{Ag}_8(\text{As}^{3+}_{0.5}\text{As}^{5+}_{0.5})\text{S}_6$, equant crystals surrounding proustite
2143 (Ag_3AsS_3) crystals on Mn-bearing calcite. Field of view 1.6 cm.

2144 **Figure 40.** Crystal structure of spryite as seen down $[010]$ (a). White, light blue, red,
2145 and yellow circles correspond to Ag, (Ge, As^{5+}), As^{3+} and S, respectively. (b) Portion of the
2146 crystal structure of spryite highlighting the split *M1-M2* positions (see text for explanation). In
2147 light blue the *M1* tetrahedron and with a red circle the *M2* atom.

2148 **Figure 41.** Unusual cylindrical aggregates of thin robinsonite fibers from the Monte
2149 Arsiccio mine, Apuan Alps, Tuscany, Italy. The aspect ratio of these aggregates, where fibers
2150 can show thickness down to less than 500 nm, are larger than 100,000.

2151 **Figure 42.** Sulfosalt structures showing the three main categories of rod-based
2152 structures, i.e., rod layers (boulangerite, $\text{Pb}_5\text{Sb}_4\text{S}_{11}$ – a), chess-board (izoklakeite,
2153 $(\text{Cu,Fe,Ag})_2\text{Pb}_{27}(\text{Sb,Bi})_{19}\text{S}_{57}$ – b), and cyclic (zinkenite, $\text{Pb}_9\text{Sb}_{22}\text{S}_{42}$ – c).

2154 **Figure 43.** The crystal structure of chovanite, seen down *b*, shown as an example of
2155 boxwork structure. Different colors indicate walls (yellow), partitions (light blue), and fill
2156 elements (pink). Light blue ellipses indicate the lone-electron-pair micelles, whereas red
2157 triangles show the pseudotrigonal axes. Dotted lines indicate the surfaces of weakest bonding.

2158 **Figure 44.** Two different kermesite-like configurations observed in scainiite. In (a), a
2159 Sb_2O_2 ladder can be recognized, whereas (b) shows Sb–O chains (i.e., half of the ladder). The
2160 configuration shown in (b) has been reported in several other lead-antimony oxy-sulfosalts.
2161 Oxygen, S, Sb, and Pb atoms are shown as red, yellow, brownish, and grey circles,
2162 respectively.

2163 **Figure 45.** The crystal structure of vurroite, as seen down *a*. Circles represent Pb (grey),
2164 Bi (violet), As (dark violet), S (yellow), and Cl (green) sites. Sn sites are shown as brown
2165 polyhedra.

2166 **Figure 46.** Structural details of the sterryite – parasterryite pair. (a) Crystal structure of
2167 sterryite as seen down *a*; (b) complex column of sterryite. The red ellipse indicates the short
2168 arm, whose arrangement is shown in (c). Parasterryite has a similar complex column (d),
2169 differing mainly for the short arm (red ellipse), shown in (e). Ag, Cu, Pb, Sb, As, and S atoms
2170 are shown as grey, blue, dark grey, brownish, dark violet, and yellow circles, respectively.

2171 **Figure 47.** The two complex columns characterizing the crystal structure of
2172 meerschautite (a, c) and details of their short arms (b, d).

2173 **Figure 48.** Meneghinite, as lead grey striated prismatic crystals, up to 1 cm long,
2174 associated with siderite and quartz, from the Bottino mine (Tuscany, Italy) (a) and its crystal
2175 structure as seen down the 4 Å axis. Copper, Pb, Sb, and S atoms are shown as blue, dark
2176 grey, brownish, and yellow circles, respectively.

2177 **Figure 49.** Merelaniite, black whiskers up to ~ 3 mm in length associated with tabular
2178 colorless crystals of “stilbite”, showing inclusions of black flattened crystals of graphite. The
2179 specimen is from Merelani, Lelatema Mountains, Tanzania.

2180 **Figure 50.** Reconstructed reciprocal space layer of natrite with indices of diffraction
2181 reflections $h2l$. In addition to the main reflections at the lattice nodes $h2l$ defined by the two
2182 vectors \mathbf{a}_1^* and \mathbf{a}_3^* , we observe a series of equidistant reflections aligned along the vector \mathbf{q}
2183 called satellite reflections.

2184 **Figure 51.** Embedding of the three-dimensional reciprocal space into a higher
2185 dimensional space called superspace. The additional reciprocal space vector \mathbf{a}_{s4}^* consists of
2186 two components, the *external* component \mathbf{q} and the *internal* component \mathbf{e}_4^* .

2187 **Figure 52.** (a) A sinusoidal displacement modulation along \mathbf{a}_2 . The period of the
2188 modulation λ is the inverse of $\|\mathbf{q}\|$. Corresponding 2-dimensional section in the $\mathbf{a}_{s2}, \mathbf{a}_{s4}$ plane.
2189 The displacements from the average positions along \mathbf{a}_2 is given by the intersections of the
2190 sinusoidal curve along the “real crystal” line.

2191 **Figure 53.** Distinction between the three families of aperiodic structures based on their
2192 reciprocal space embeddings.

2193 **Figure 54.** Portion of γ - Na_2CO_3 , the room temperature phase of natrite. Oxygen forming
2194 triangular coordination around the C atoms (black) are omitted. The links between atoms are
2195 contact distances between Na and C atoms shorter than 3.4 Å. The structure can be interpreted
2196 as a series of parallel graphite-like C-Na₃ layers stacked along the c axis. Na1 and Na2 are
2197 located between the layers.

2198 **Figure 55.** Analysis of the incommensurate structure of γ - Na_2CO_3 in terms of the m_M
2199 and m_V planes containing the Na and C atoms. Links are only indicated for Na, C contact
2200 distances smaller than 3.1 Å.

2201 **Figure 56.** (a) Average structure of calaverite consisting of parallel edge-sharing layers
2202 of Te octahedra with (Au,Ag) atoms at their centre. (b) t -plot representation of the (Au,Ag)-Te
2203 distances from the refinement in superspace in the incommensurate structure of $\text{Au}_{0.9}\text{Ag}_{0.1}\text{Te}_2$
2204 with ordered Ag distribution. Numbers refer to the six independent (Au,Ag)-Te distances in
2205 each [(Au,Ag)Te₆]-octahedron.

2206 **Figure 57.** Portion of the incommensurate structure of $\text{Au}_{0.9}\text{Ag}_{0.1}\text{Te}_2$ with ordered
2207 distribution of Ag on the Au position. The thick grey lines indicate the (Au,Ag)-Te distances
2208 shorter than 3.1 Å. The blue circles represent the (Au,Ag) positions, which incorporate Ag.

2209 **Figure 58.** Indexation of the calaverite faces by Janner and Dam (1989) with four
2210 indices according to the crystal model of Goldschmidt et al. (1931). The colors indicate the
2211 two twin components.

2212 **Figure 59.** The average melilite layer structure with general composition $\text{X}_2\text{T1T}_2\text{O}_7$
2213 viewed along the normal to the layers (a) and in the perpendicular direction (b). X atoms are
2214 violet. The blue T2 tetrahedra always form bow tie whereas the yellow T1 tetrahedra are
2215 always surrounded by four T2 tetrahedra.

2216 **Figure 60.** (a) Representation of a layer portion of a natural melilite with an
2217 incommensurately modulated structure and composition $(\text{Ca,Na})_2(\text{Al,Mg,Fe}^{2+})[(\text{Al,Si})\text{SiO}_7]$.
2218 The black T1 tetrahedra are those surrounded with only six coordinated X-O distances and
2219 four T1-X distances. (b) t -plot of the T1-X (Mg-Ca) distances. Two zones can be
2220 distinguished, one with $t \cong \frac{1}{2}$ where 8 X atoms (violet) can be found in the vicinity of T1

2221 (yellow) with distances shorter than 4.0 \AA and $t \cong 0$ or 1 where 4 X can be found within the
2222 same limit.

2223 **Figure 61.** (a) HR TEM diffraction pattern of icosahedral QC $\text{Al}_{63}\text{Cu}_{24}\text{Fe}_{13}$ with ten-fold
2224 symmetry. (b) See text for the explanation of the plot.

2225 **Figure 62.** (a) Iridescent “labradorite”, a plagioclase feldspar with composition $\text{Ca}_x\text{Na}_{1-x}\text{Al}_{1+x}\text{Si}_{3-x}\text{O}_8$. (b) Schematic representation of the main and satellite reflections based on
2226 Boysen and Kek (2015) data.

2227 **Figure 63.** Schematic model of the labradorite structure with two different types of
2228 domains as proposed by Boysen and Kek (2015). The large domains D_i are linked to the s-
2229 satellites and also to the iridescent property whereas the smaller domains are linked to the e-
2230 satellites.
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2233 **Table captions**

2234 **Table 1.** Five most structurally complex minerals and information-based parameters of
2235 their complexity.

2236 **Table 2.** Sulfosalt species characterized by boxwork structure.

2237 **Table 3.** Information-based complexity parameters for selected sulfosalts.

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2277 **Table 1.** Five most structurally complex minerals and information-based parameters of their complexity

Mineral name	Chemical composition	G	ν [atoms]	$^{str}I_G$ [bits/atom]	$^{str}I_{G,total}$ [bits/cell]	ρ_{inf} [bits Å ⁻³]	Re f.
Ewingite	Mg ₈ Ca ₈ [(UO ₂) ₂₄ (CO ₃) ₃₀ O ₄ (OH) ₁₂ (H ₂ O) ₈]·130H ₂ O	<i>I4</i> ₁ /	3088	7.603	23477.507	0.793	1
Morrisonite	Ca ₁₁ [As ³⁺ V ⁴⁺ ₂ V ⁵⁺ ₁₀ As ⁵⁺ ₆ O ₅₁] ₂ ·78H ₂ O	<i>P2</i> ₁ /	1576	8.622	13588.354	0.791	2
Ilmajokite	Na ₁₁ KBaCe ₂ Ti ₁₂ Si _{37.5} O ₉₄ (OH) ₃₁ ·29H ₂ O	<i>C2</i> / <i>c</i>	1416	8.468	11990.129	0.730	3
Paulingite-(Ca)	Ca ₅ [Al ₁₀ Si ₃₂ O ₈₄]·34H ₂ O	<i>Im</i> $\bar{3}$	1988	5.730	11590.532	0.535	4
Fantappieite	[Na ₉₉ Ca ₃₃] _{$\Sigma=132$} [Si ₉₉ Al ₉₉ O ₃₉₆](SO ₄) ₃₃ ·6H ₂ O	<i>P</i> $\bar{3}$	839	7.285	6111.824	0.488	5

2278 References: (1) Olds et al. 2017; (2) Kampf et al. 2016; (3) Zolotarev et al. 2020; (4) Lengauer et al. 1997; (5) Cámara et al. 2010.

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Table 2 – Sulfosalt species characterized by boxwork structure.

Mineral	Chemical formula	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)	s.g.	Ref.
Chovanite	Pb ₂₈ Sb ₃₀ S ₇₂ O	34.05	8.20	48.08	106.3	12892	<i>P2₁/c</i>	[1]
Marrucciite	Hg ₃ Pb ₁₆ Sb ₁₈ S ₄₆	48.32	4.12	24.06	118.8	4192	<i>C2/m</i>	[2]
Neyite	Ag ₂ Cu ₆ Pb ₂₅ Bi ₂₆ S ₆₈	37.53	4.07	43.70	108.8	6319	<i>C2/m</i>	[3]
Pellouxite	(Cu,Ag) ₂ Pb ₂₁ Sb ₂₃ S ₅₅ ClO	55.82	4.09	24.13	113.1	5065	<i>C2/m</i>	[4]
Pillaite	Pb ₉ Sb ₁₀ S ₂₃ ClO _{0.5}	49.49	4.13	21.83	99.6	4394	<i>C2/m</i>	[5]
Rouxelite	Cu ₂ HgPb ₂₂ Sb ₂₈ S ₆₄ (O,S) ₂	43.11	4.06	37.87	117.4	5887	<i>C2/m</i>	[6]
Scainiite	Pb ₁₄ Sb ₃₀ S ₅₄ O ₅	52.00	8.15	24.31	104.1	9990	<i>C2/m</i>	[7]
Tazieffite	Pb ₂₀ Cd ₂ (Bi,As) ₂₂ S ₅₀ Cl ₁₀	8.35	45.59	27.26	98.8	10257	<i>C2/c</i>	[8]
Vurroite	Pb ₂₀ Sn ₂ (As,Bi) ₂₂ S ₅₄ Cl ₆	8.37	45.50	27.27	98.8	10265	<i>C2/c</i>	[9]

2281 [1] Biagioni and Moëlo 2017; [2] Orlandi et al. 2007; [3] Makovicky et al. 2001; [4] Palvadeau et al. 2004; [5] Meer-
 2282 schaut et al. 2001; [6] Orlandi et al. 2005; [7] Moëlo et al. 2000; [8] Zelenski et al. 2009; [9] Pinto et al. 2008.

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Table 3 – Information-based complexity parameters for selected sulfosalts.

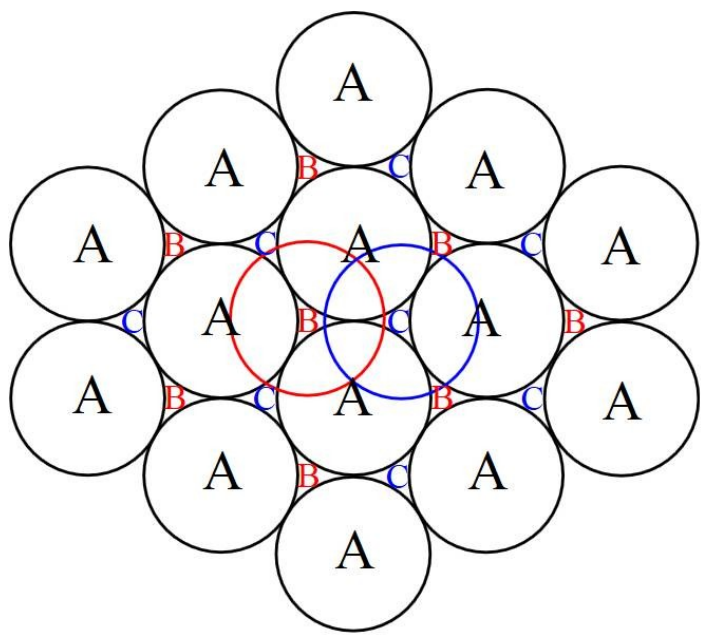
v_1 –	Mineral	Chemical formula	v_1	v_2	$^{chem}I_G$	$^{str}I_G$	$^{chem}I_{G,total}$	$^{str}I_{G,total}$
	Chovanite ^{SS}	Pb ₂₈ Sb ₃₀ S ₇₂ O	66	132	1.526	6.044	100.709	797.860
	Chovanite	Pb ₂₈ Sb ₃₀ S ₇₂ O	66	532	1.526	7.055	100.709	3753.410
	Marrucciite ^{SS}	Hg ₃ Pb ₁₆ Sb ₁₈ S ₄₆	83	83	1.581	5.387	131.234	447.128
	Meerschautite	Ag _{5.5} Pb _{42.4} Sb _{45.1} S ₁₁₂ O _{0.8}	411	414	1.595	7.693	655.636	3185.104
	Neyite^{SS}	Ag ₂ Cu ₆ Pb ₂₅ Bi ₂₆ S ₆₈	127	127	1.715	5.997	217.803	761.563
	Parasterryite	Ag ₄ Pb ₂₀ (Sb,As) ₂₄ S ₅₈	53	424	1.815	6.728	96.220	2852.638
	Pellouxite ^{SS}	(Cu,Ag) ₂ Pb ₂₁ Sb ₂₃ S ₅₅ ClO	103	104	1.712	5.700	167.772	592.846
	Pillaite ^{SS}	Pb ₉ Sb ₁₀ S ₂₃ ClO _{0.5}	87	88	1.643	5.459	142.958	480.430
	Rouxelite ^{SS}	Cu ₂ HgPb ₂₂ Sb ₂₈ S ₆₄ (O,S) ₂	119	119	1.679	5.903	199.774	702.483
	Scainiite	Pb ₁₄ Sb ₃₀ S ₅₄ O ₅	76	206	1.242	6.182	94.416	1273.419
	Sterryite	CuAg ₃ Pb ₁₉ Sb ₂₂ (As) ₂ S ₅₆	103	424	1.692	6.728	172.561	2852.638
	Tazieffite	Pb ₂₀ Cd ₂ As ₂₂ S ₅₀ Cl ₁₀	52	208	1.874	5.739	97.446	1193.691
	Vurroite	Pb ₂₀ Sn ₂ Bi ₂₂ S ₅₄ Cl ₆	52	208	1.770	5.739	92.015	1193.691

2286 number of atoms in the chemical formula; v_2 – number of atoms within the reduced unit cell; $^{chem}I_G$ – the amount of
 2287 chemical Shannon information per atom (bits/atom); $^{str}I_G$ – the amount of structural Shannon information per atom
 2288 (bits/atom); $^{chem}I_{G,total}$ – the amount of chemical Shannon information per formula (bits/formula); $^{str}I_{G,total}$ – the amount of
 2289 structural Shannon information per unit cell (bits/cell). ^{SS} = 4 Å sub-structure.

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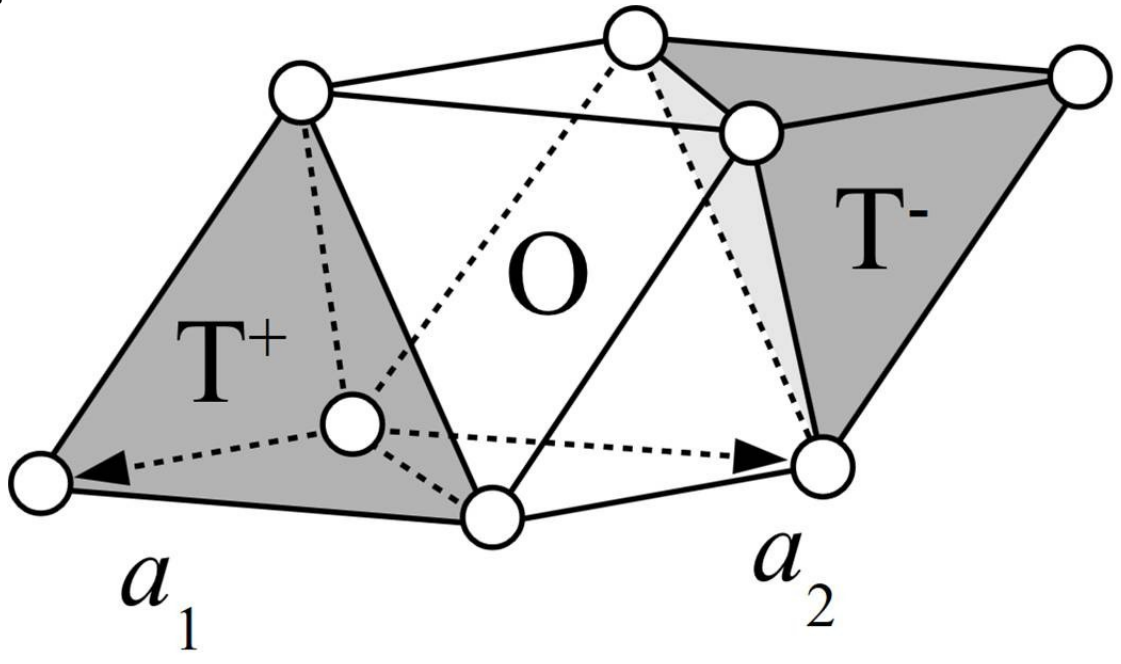
Figure 1

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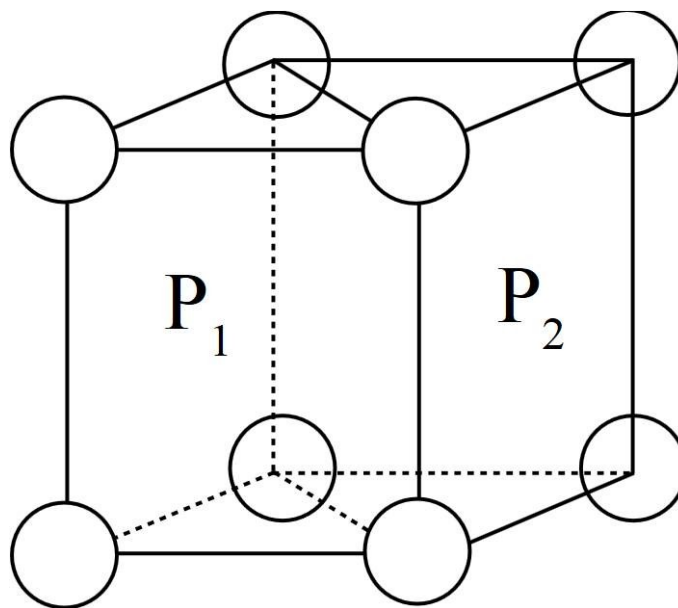
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Figure 2



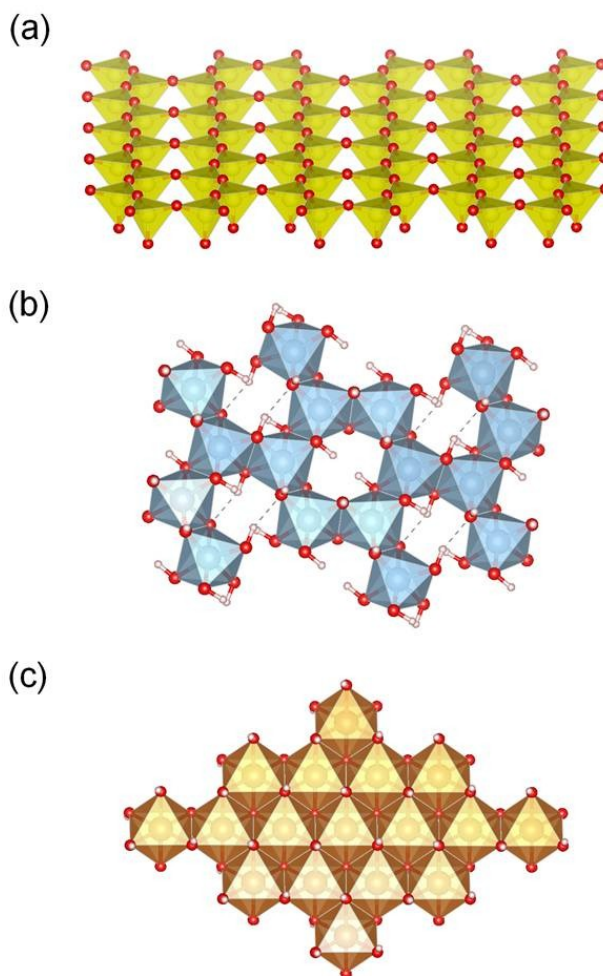
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Figure 3



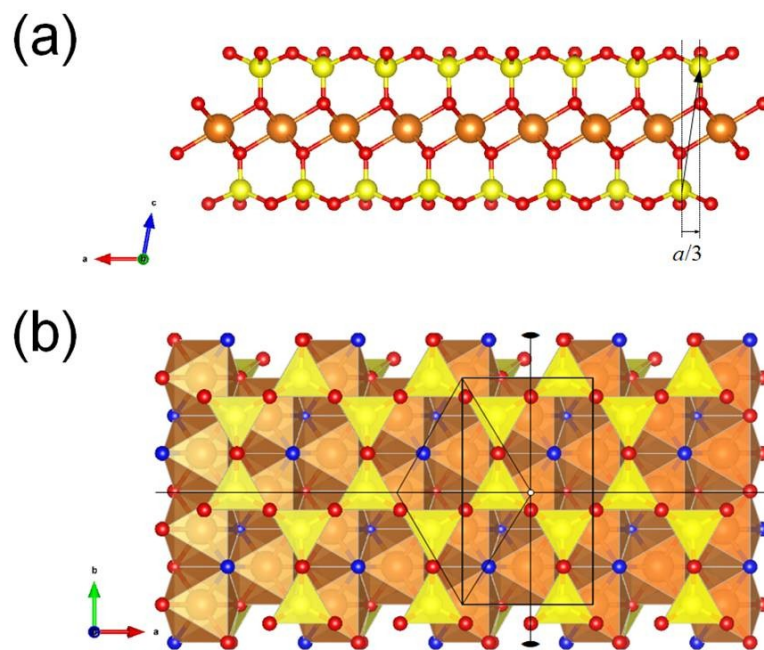
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Figure 4



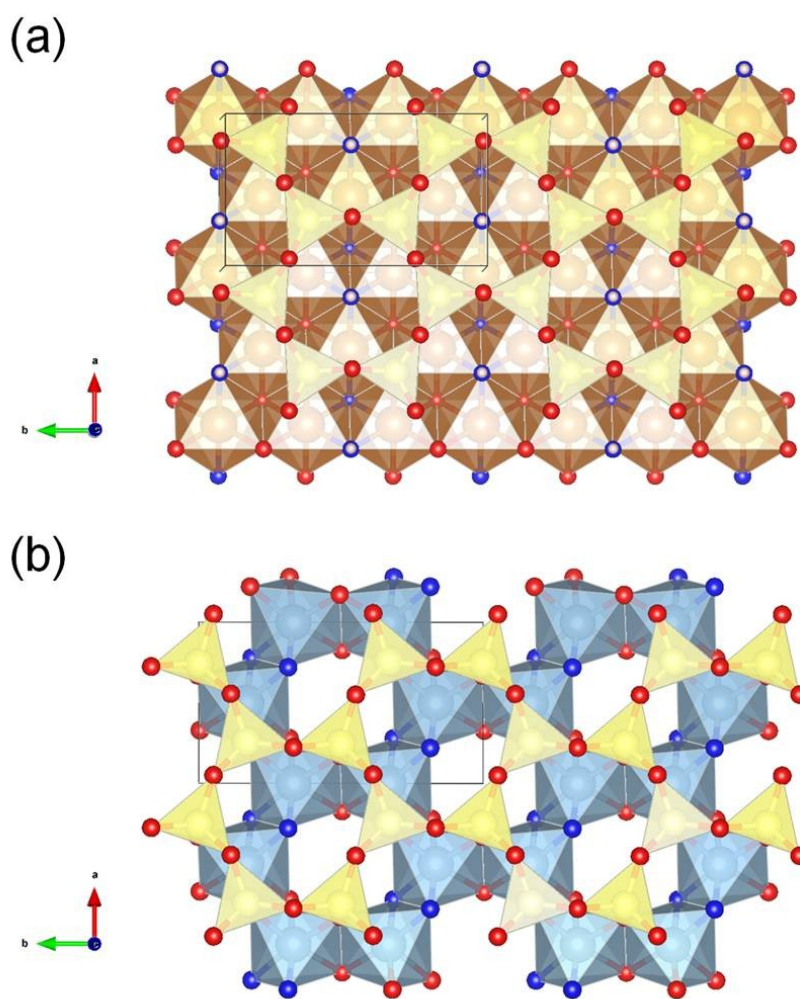
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Figure 5



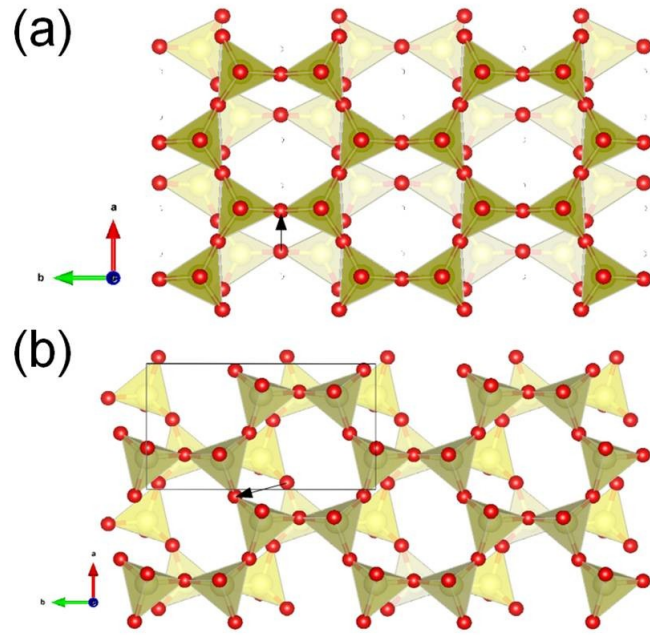
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Figure 6



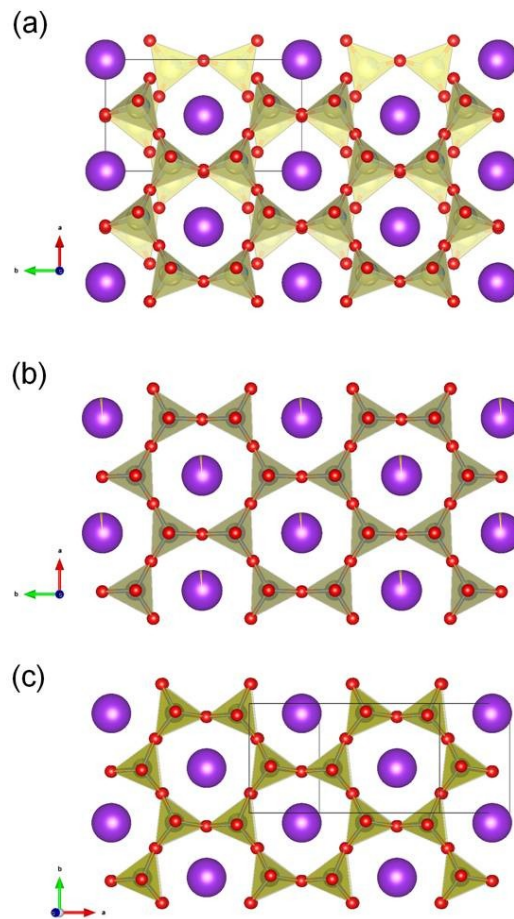
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Figure 7



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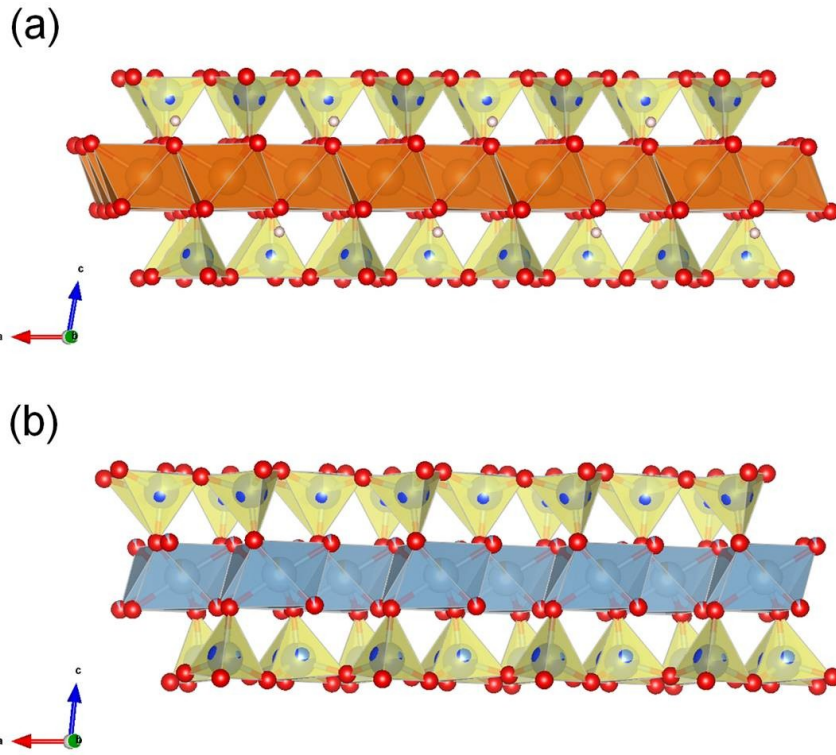
Figure 8



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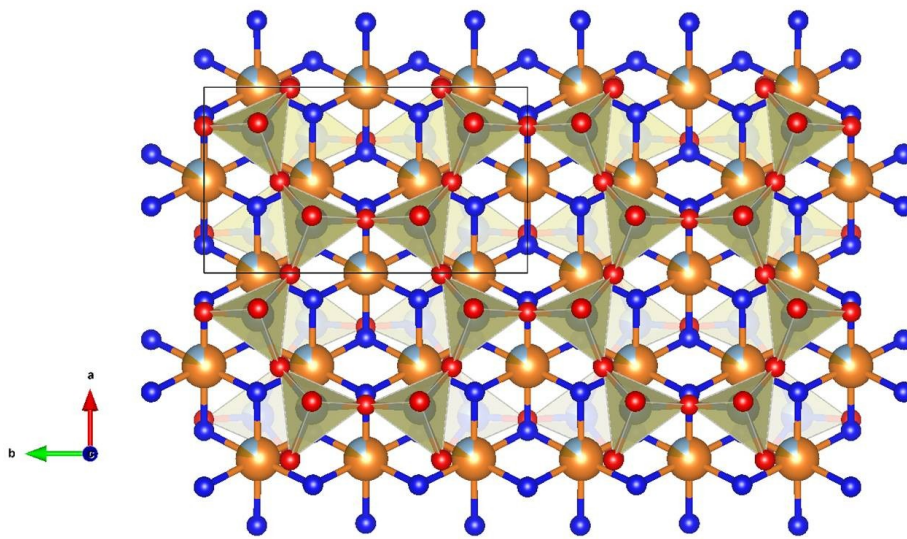
Figure 9

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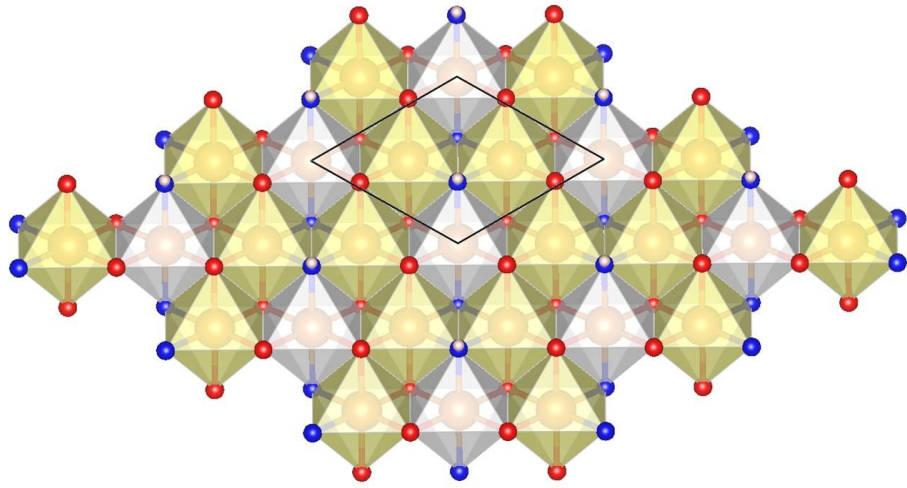
Figure 10



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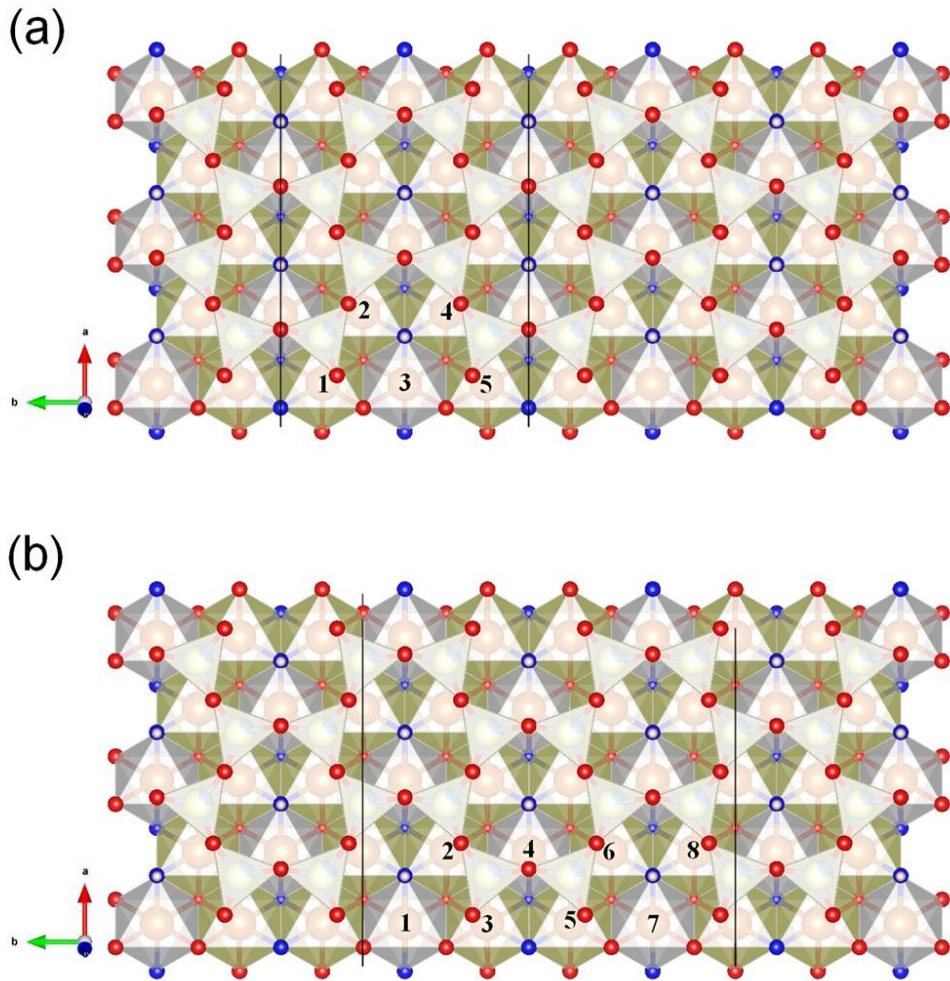
Figure 11

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Figure 12

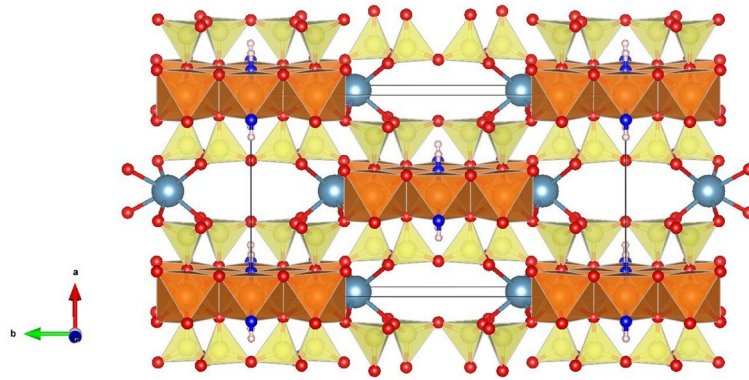


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Figure 13

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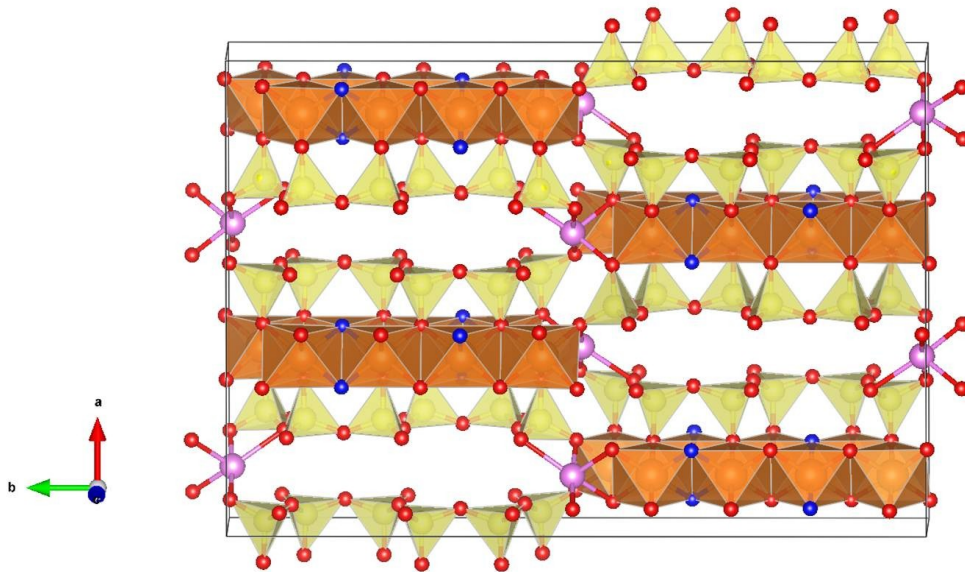
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Figure 14



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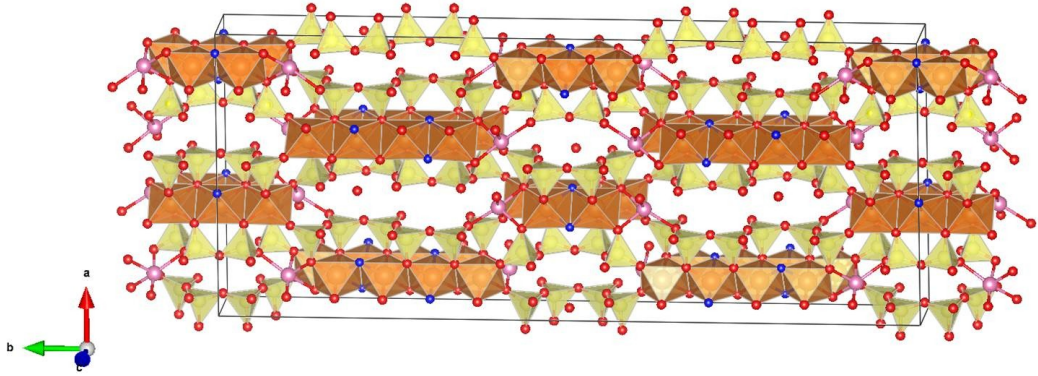
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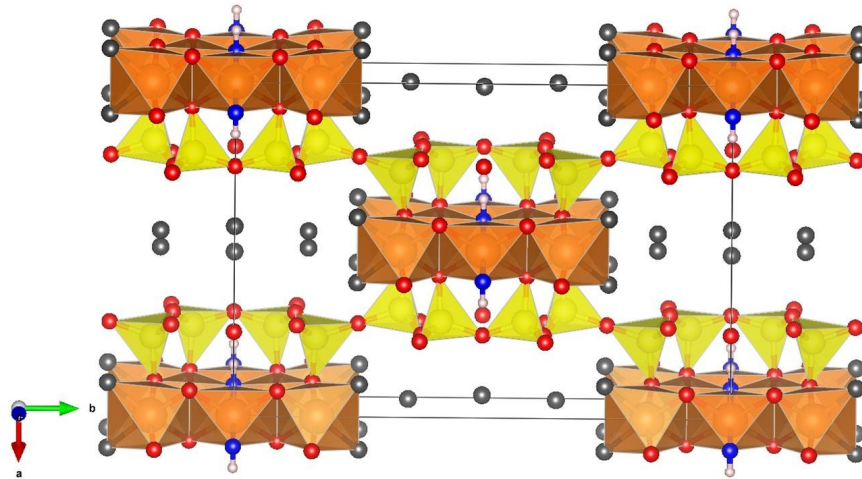
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Figure 15



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Figure 16

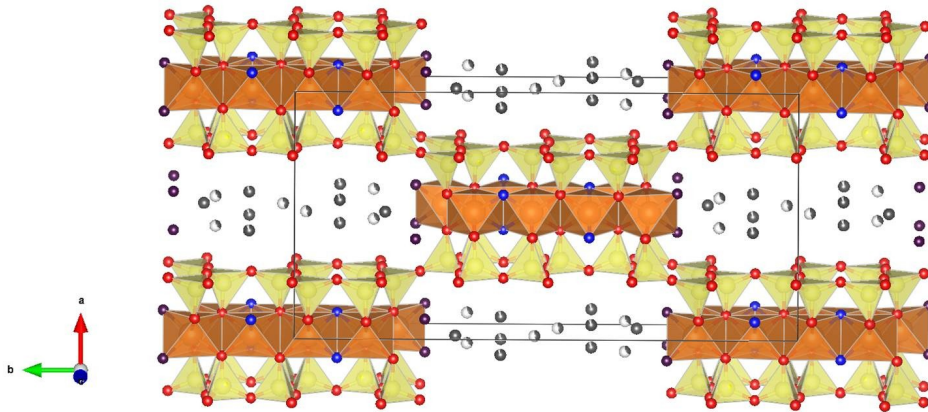


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Figure 17



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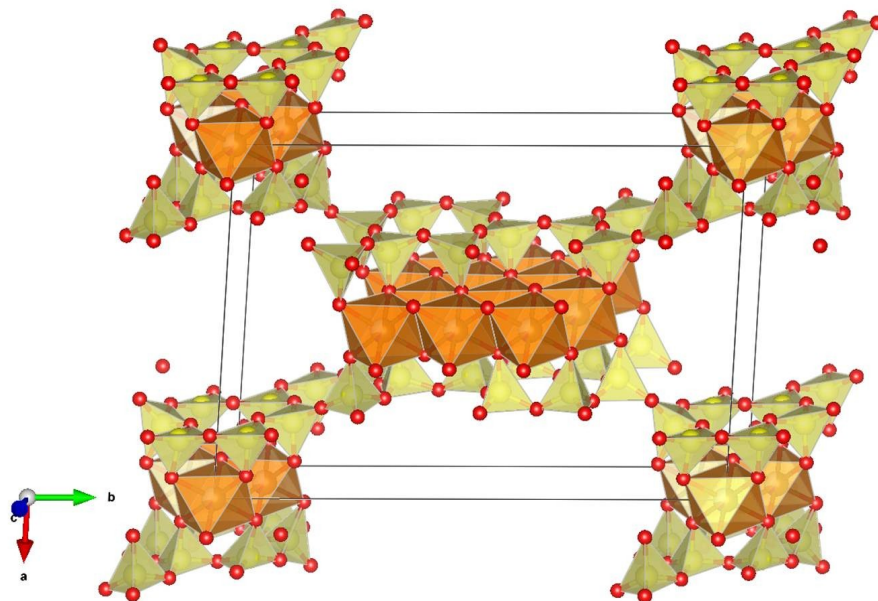
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Figure 18



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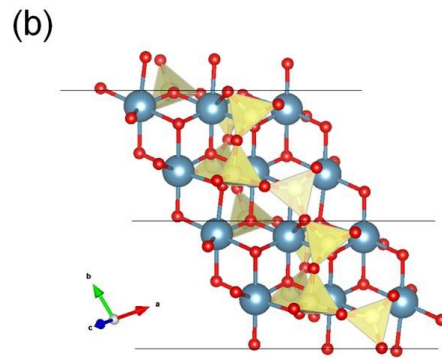
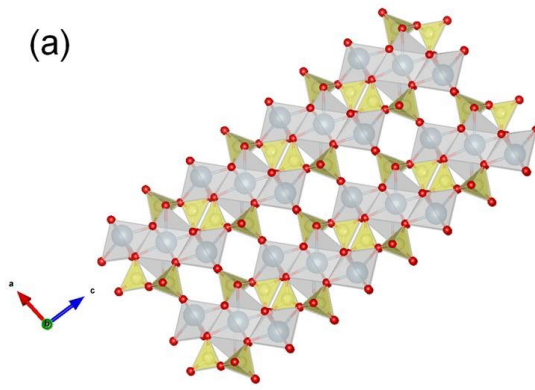
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Figure 19

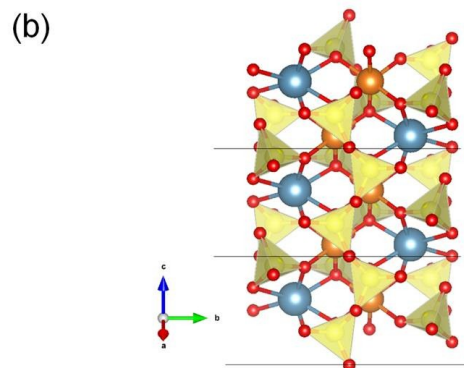
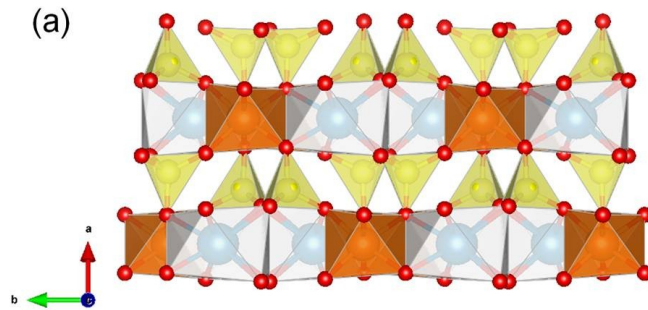
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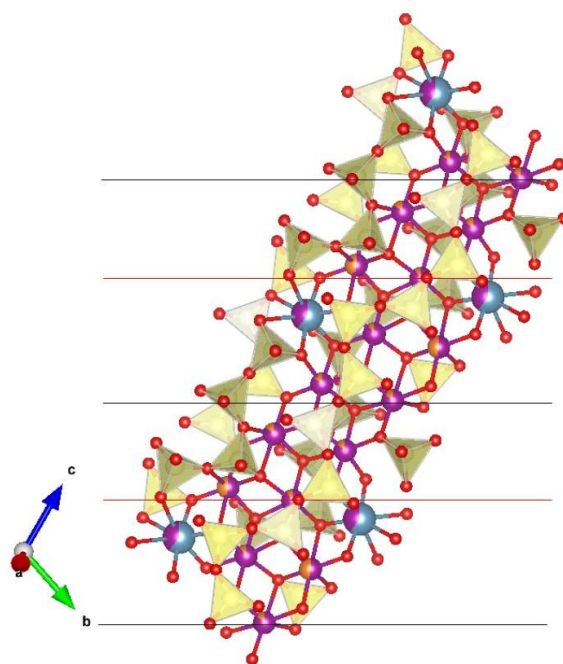
Figure 20



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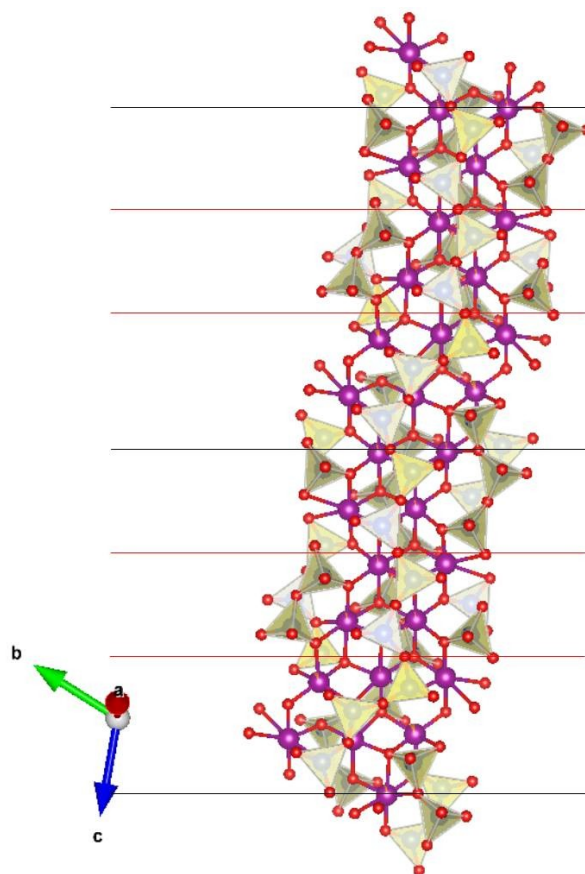
Figure 21

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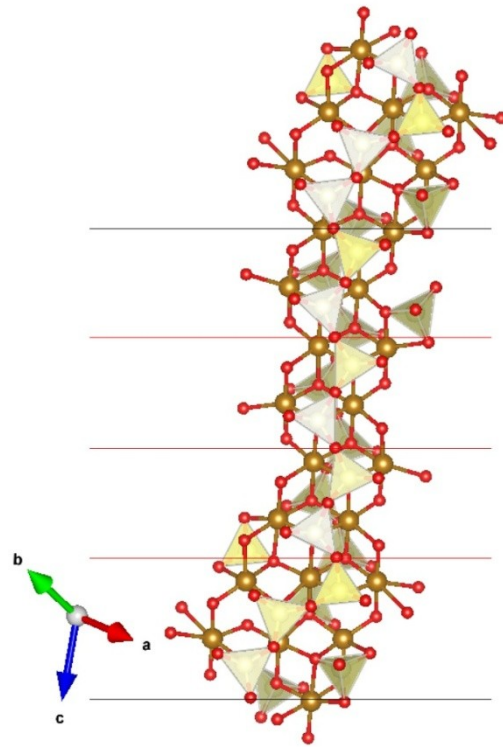
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Figure 22



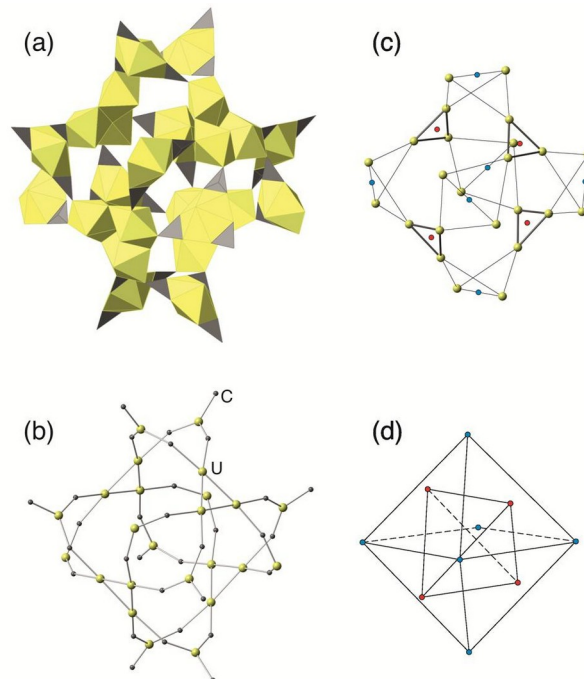
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Figure 23



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Figure 24

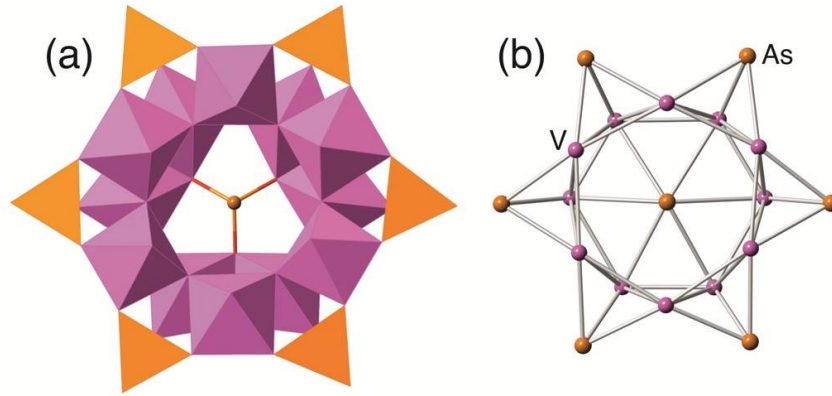


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Figure 25



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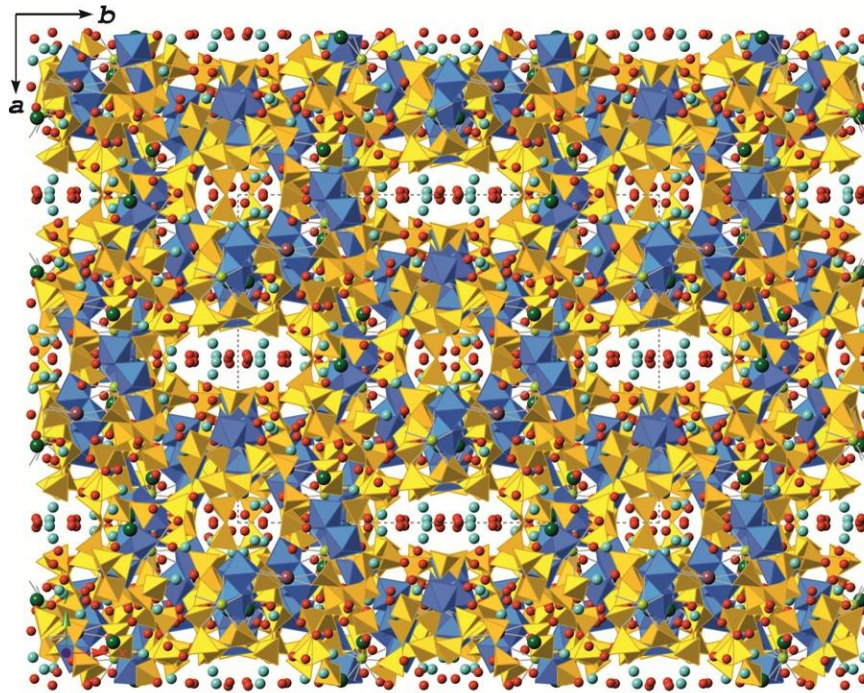
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Figure 26



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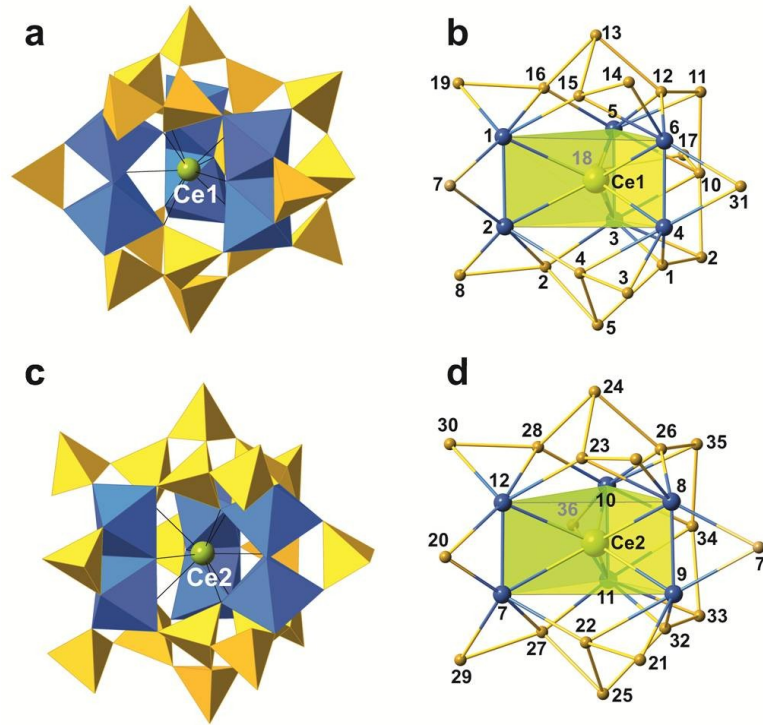
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Figure 27

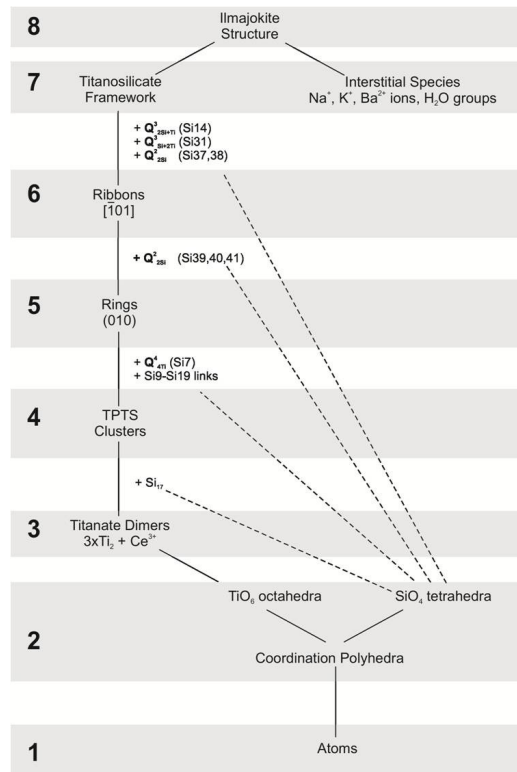
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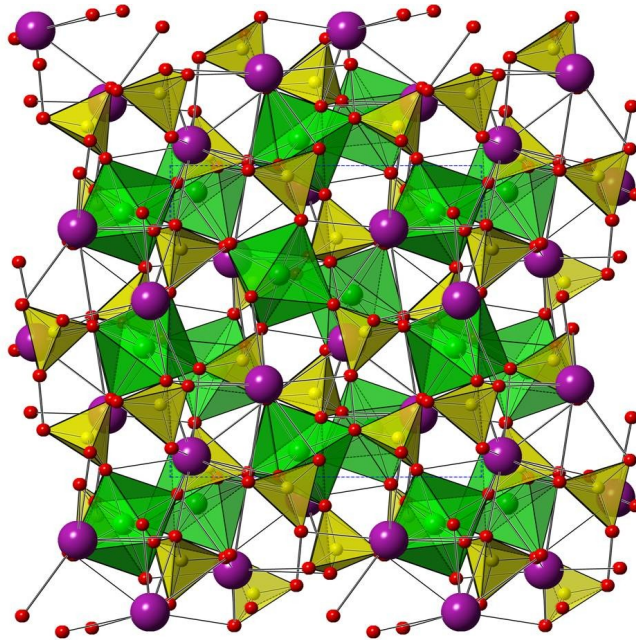
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Figure 28



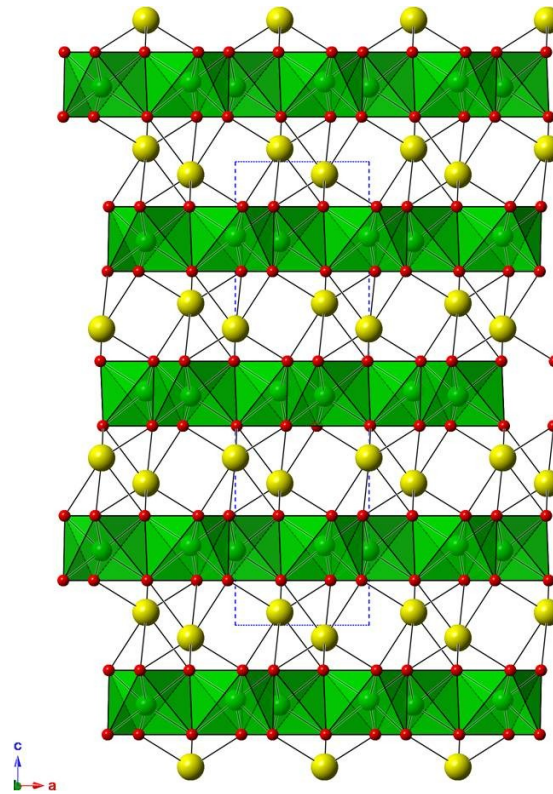
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Figure 29



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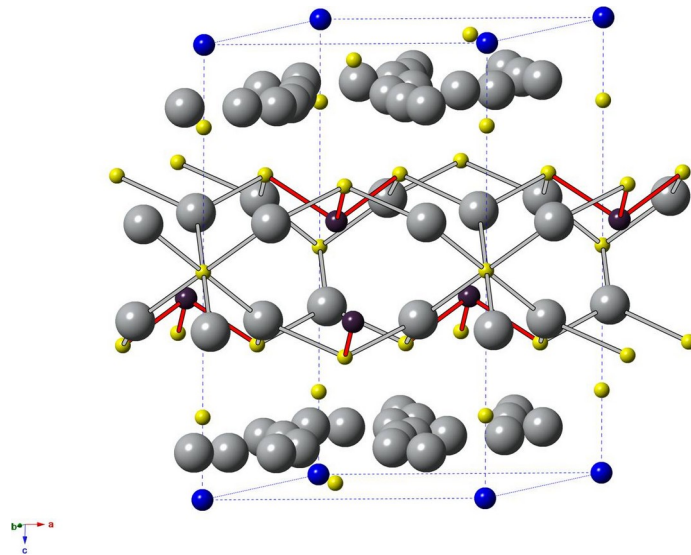
Figure 30



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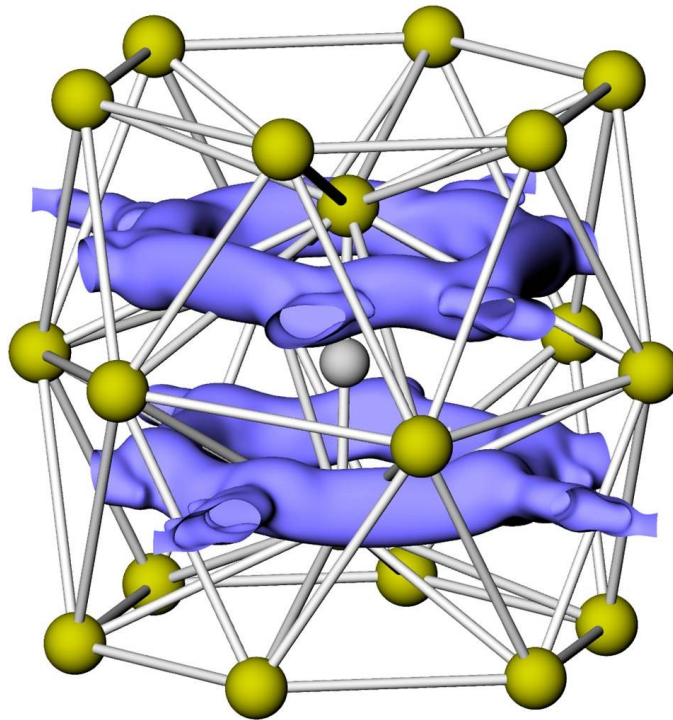
Figure 31

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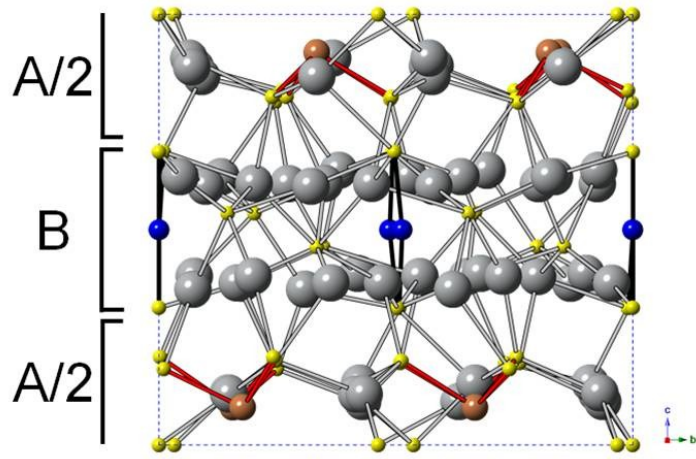
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Figure 32



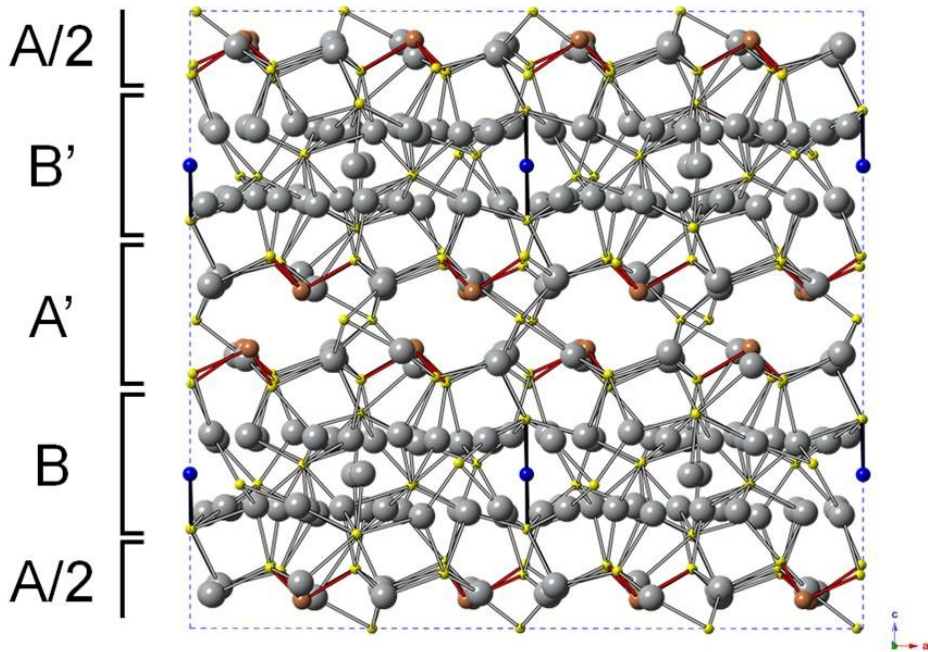
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Figure 33



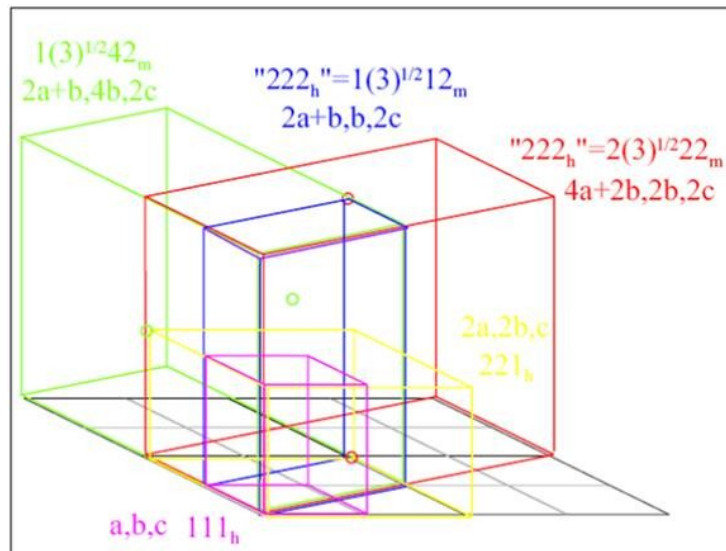
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Figure 34



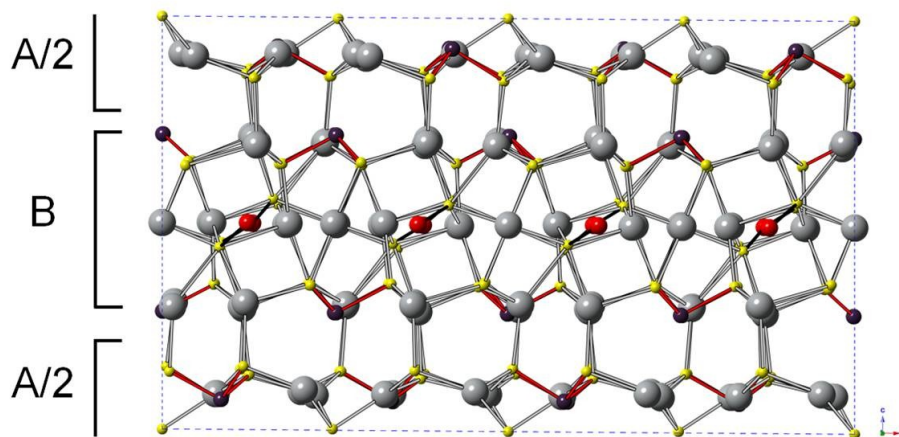
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Figure 35



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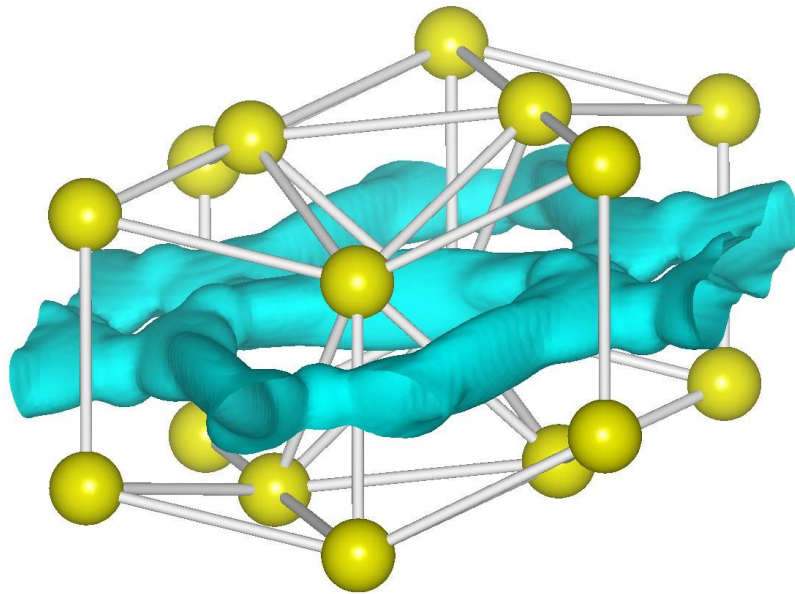
Figure 36



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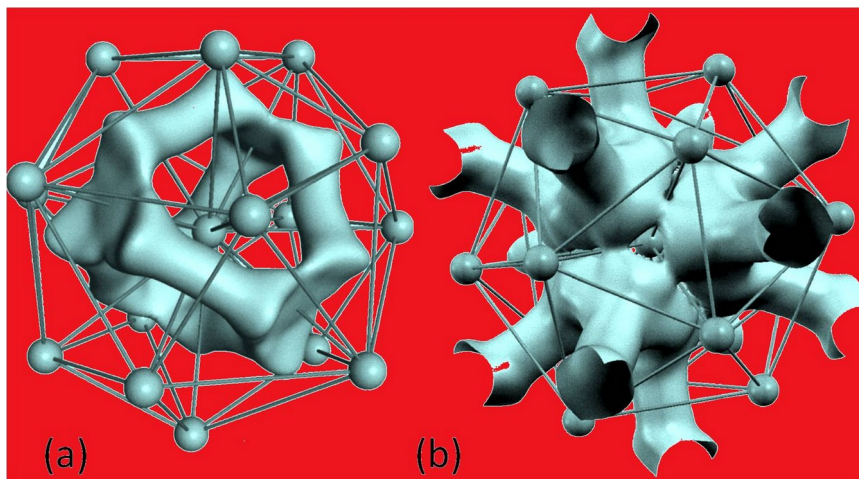
Figure 37

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Figure 38



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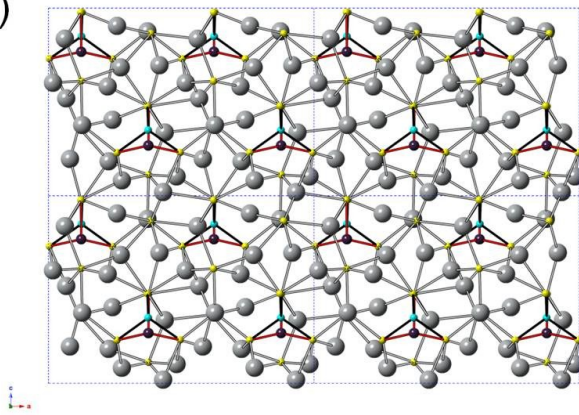
Figure 39



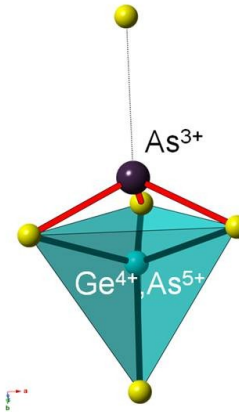
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Figure 40

(a)

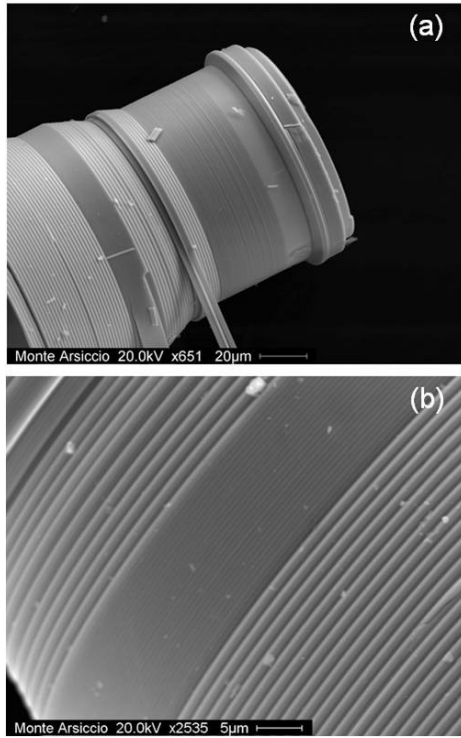


(b)



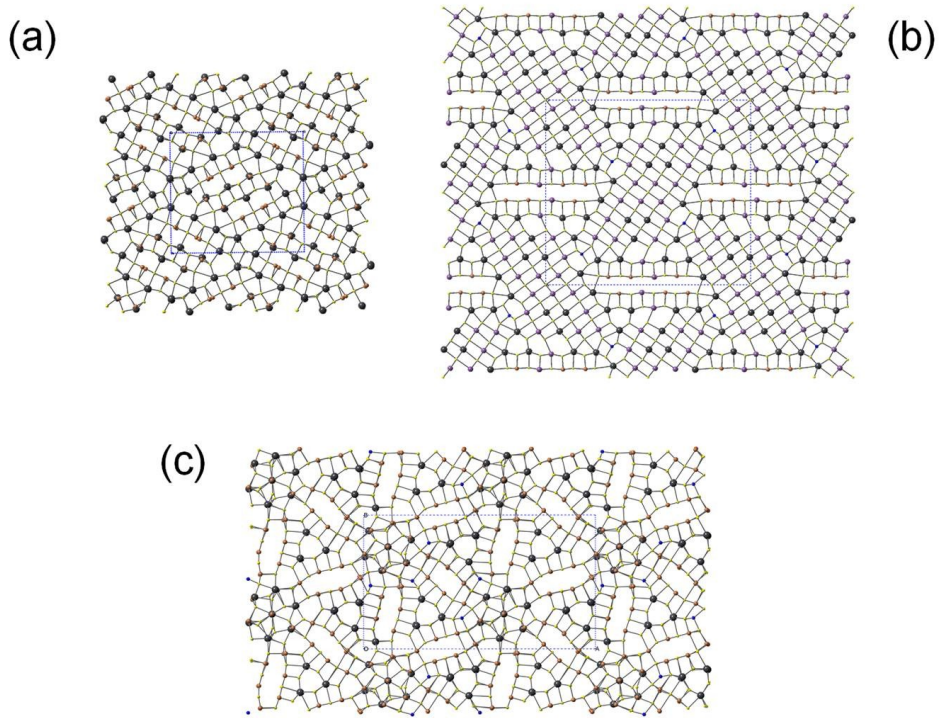
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Figure 41



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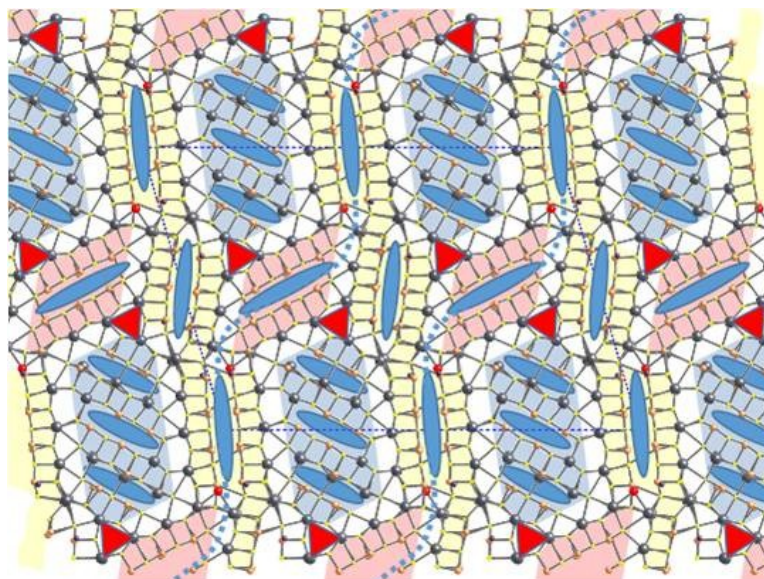
Figure 42



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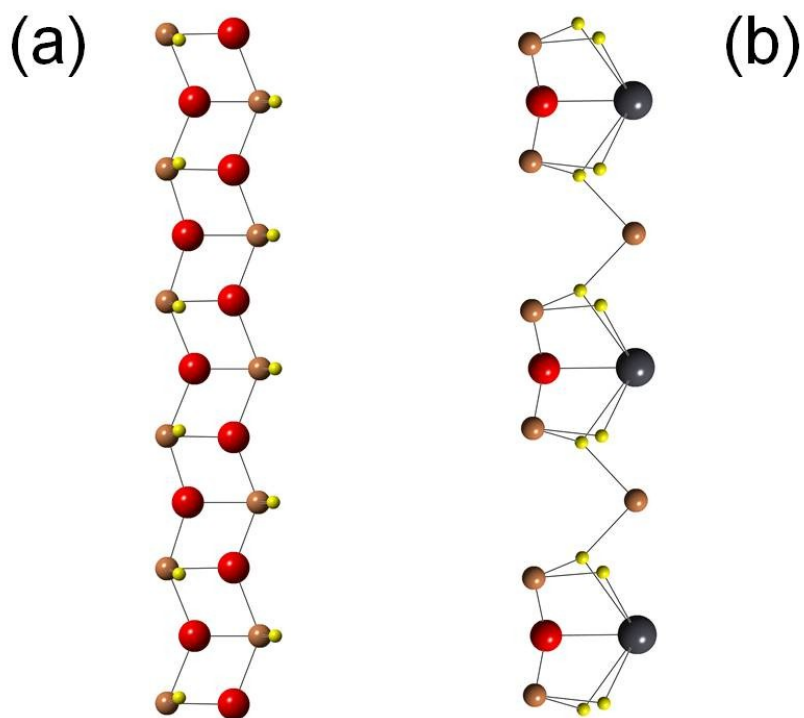
Figure 43

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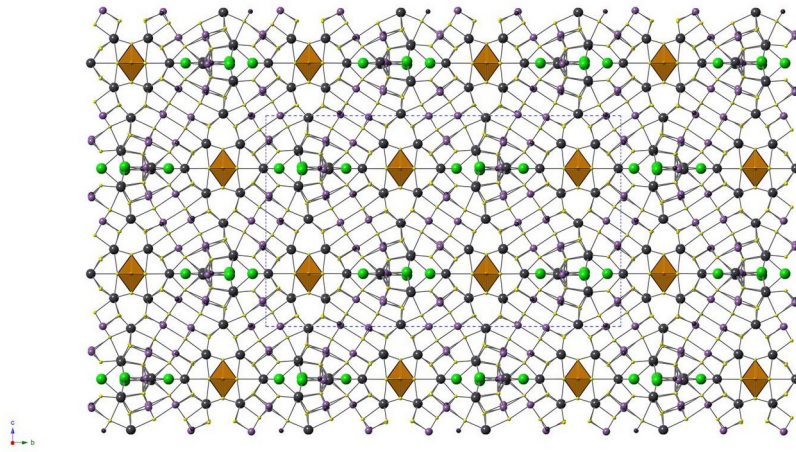
Figure 44



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Figure 45



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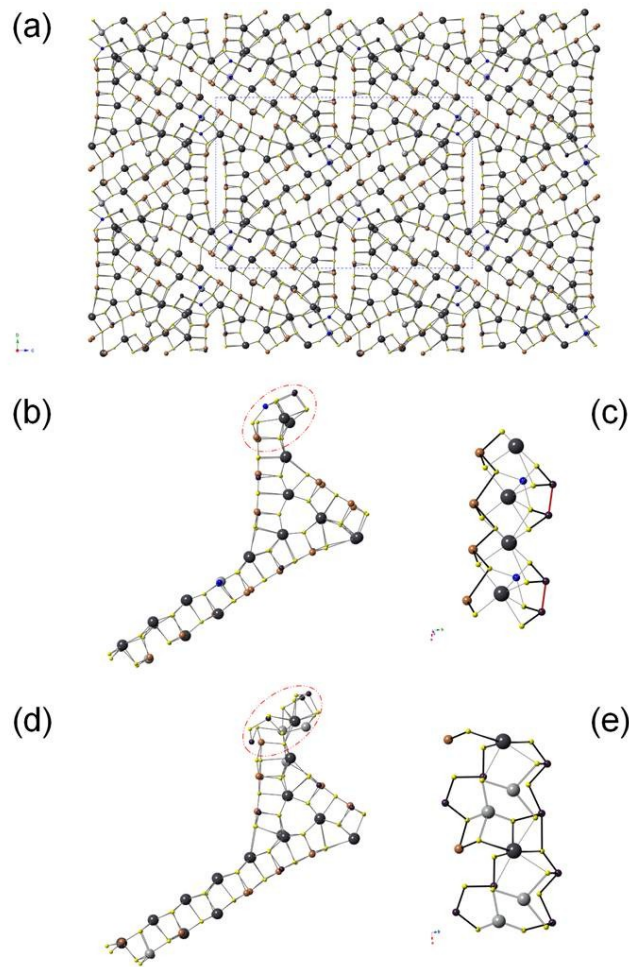
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Figure 46



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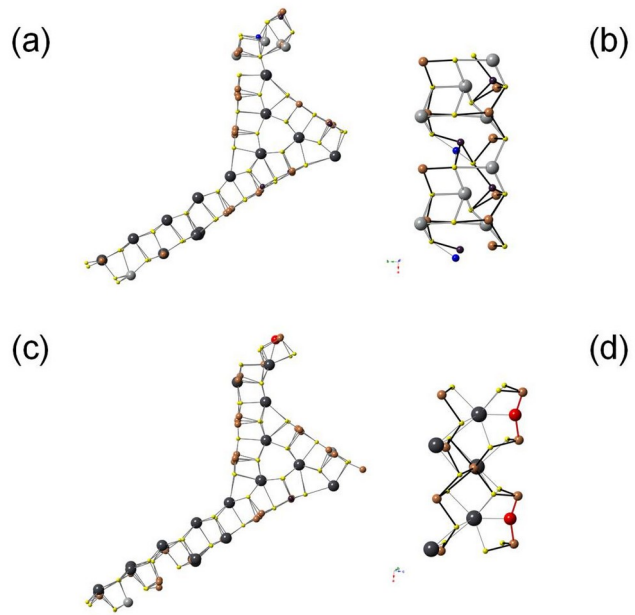
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Figure 47

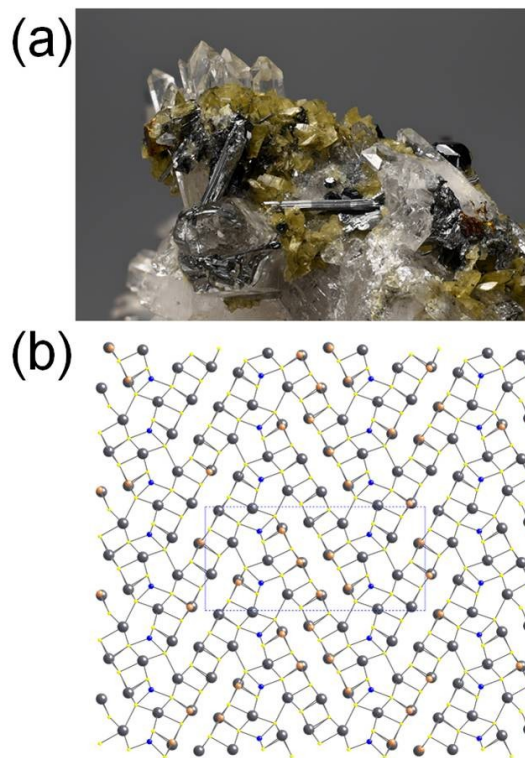
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Figure 48



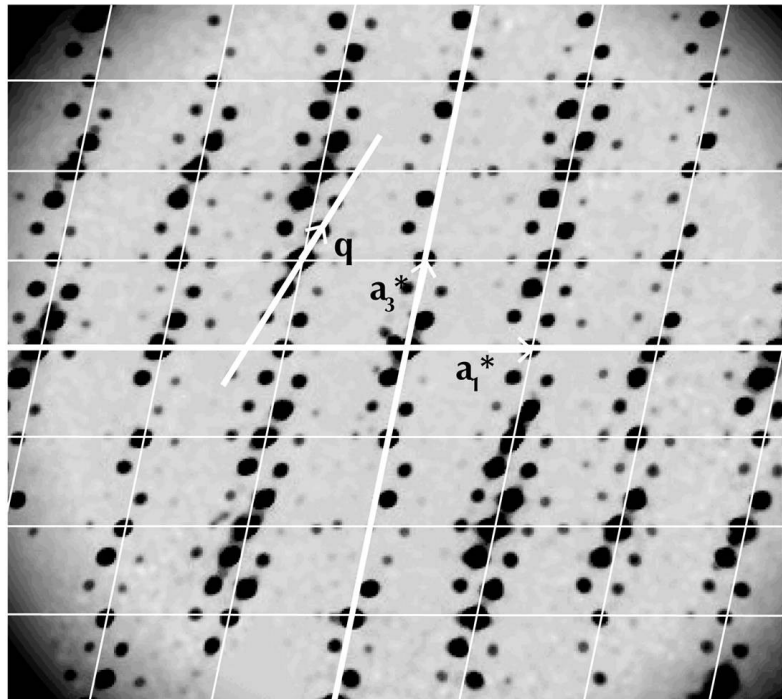
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Figure 49



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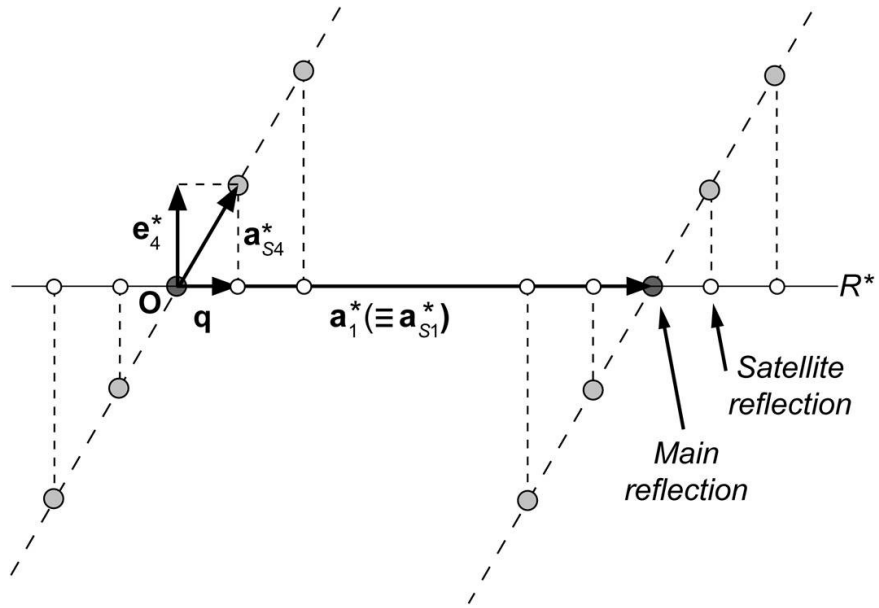
Figure 50



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Figure 51

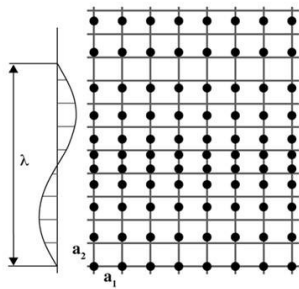
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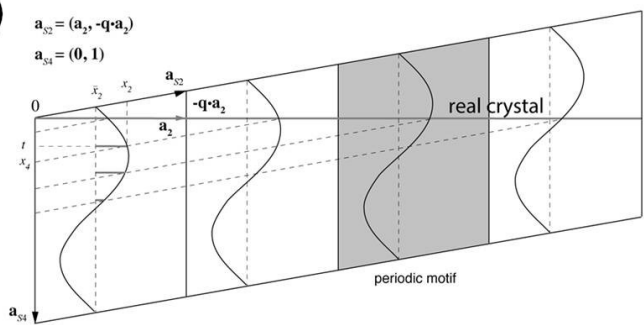
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Figure 52

(a)



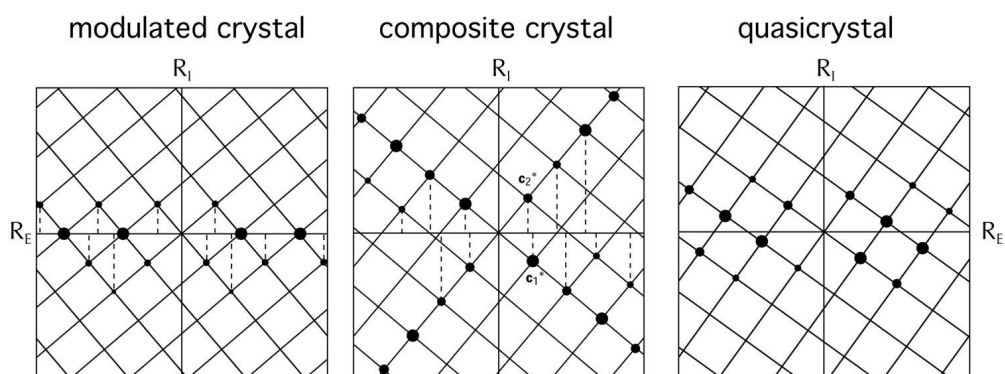
(b)



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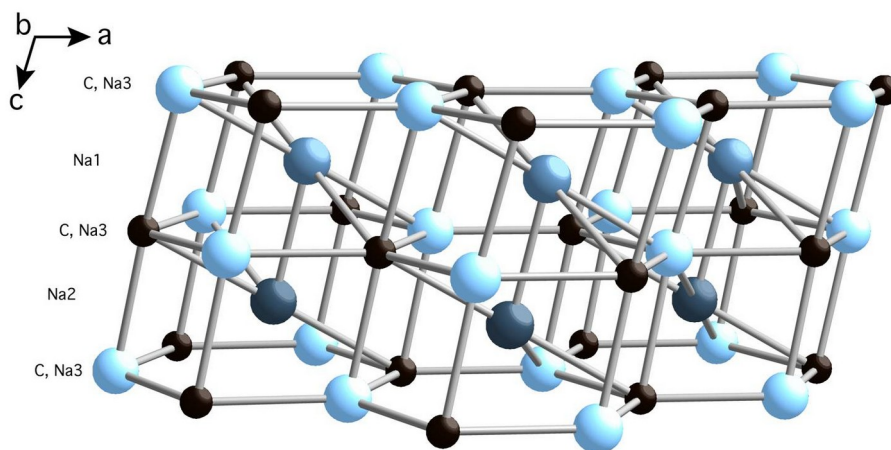
Figure 53

Reciprocal space embeddings of aperiodic crystals



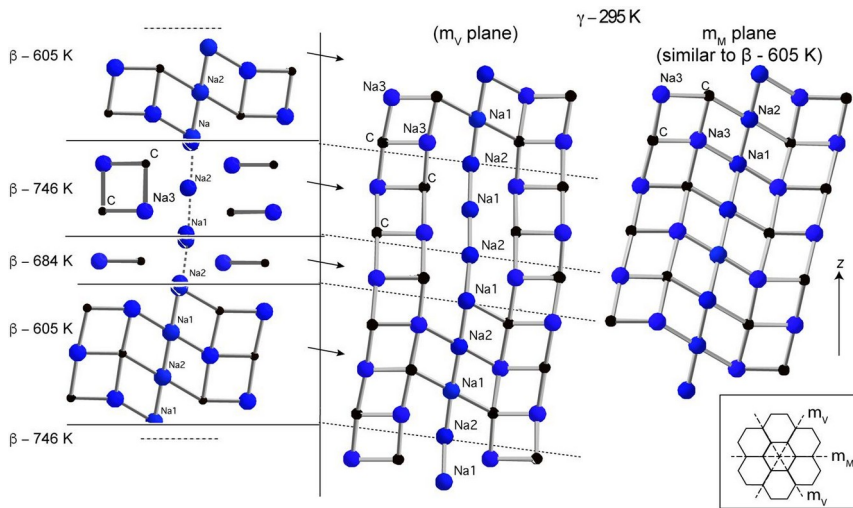
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Figure 54



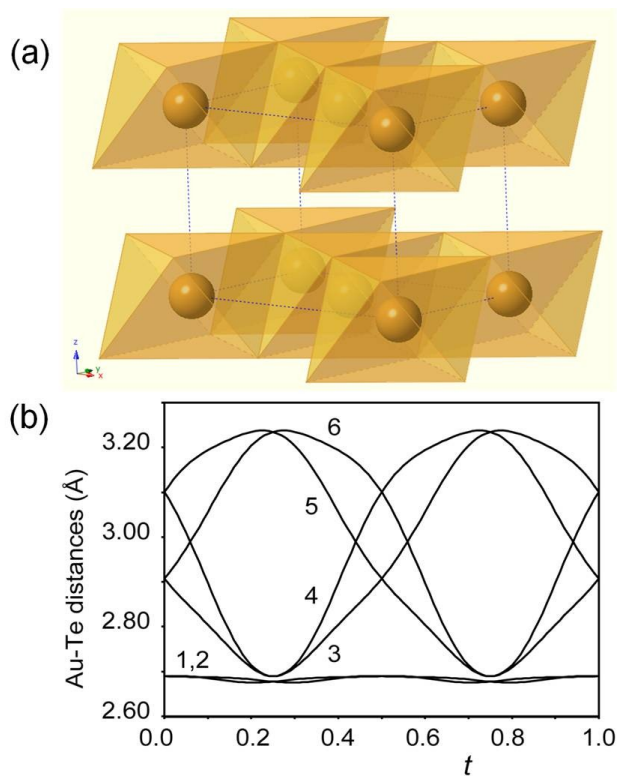
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Figure 55



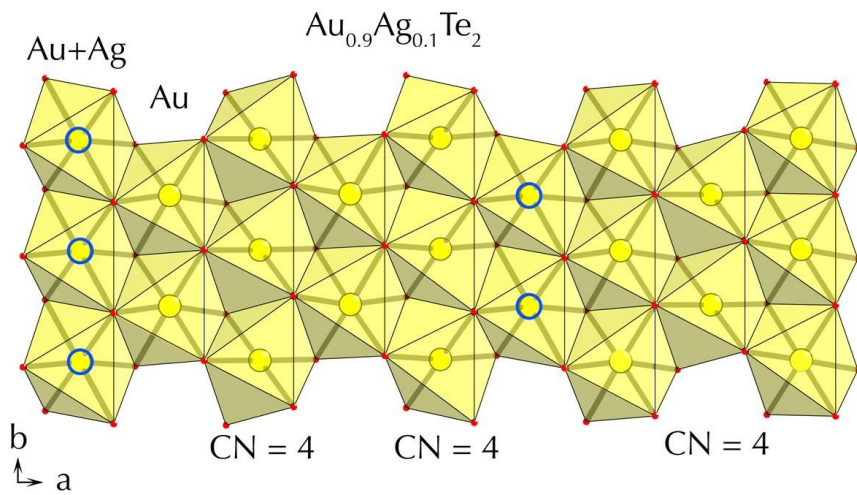
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Figure 56



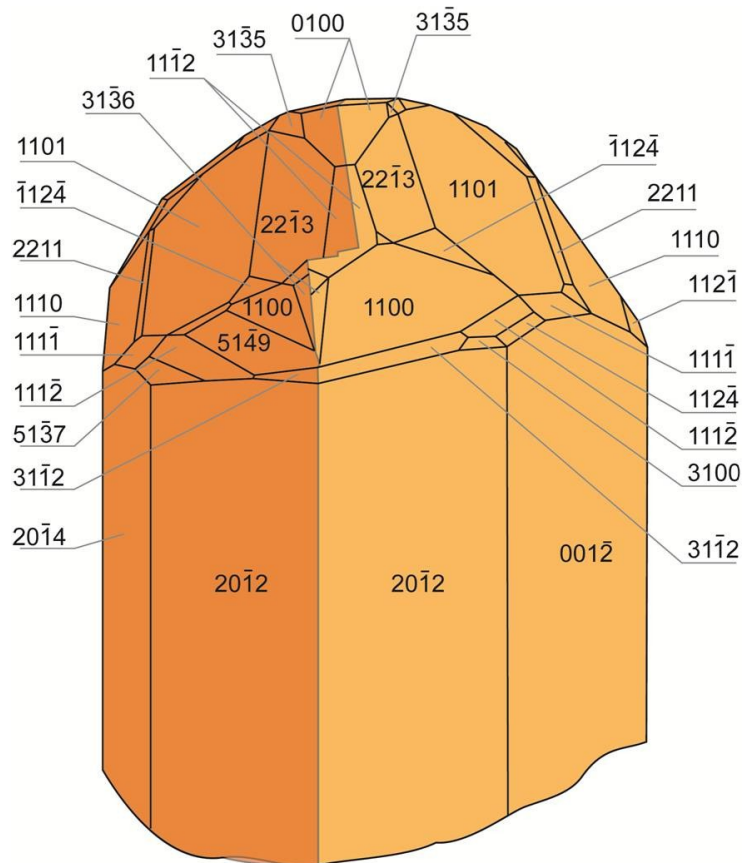
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Figure 57



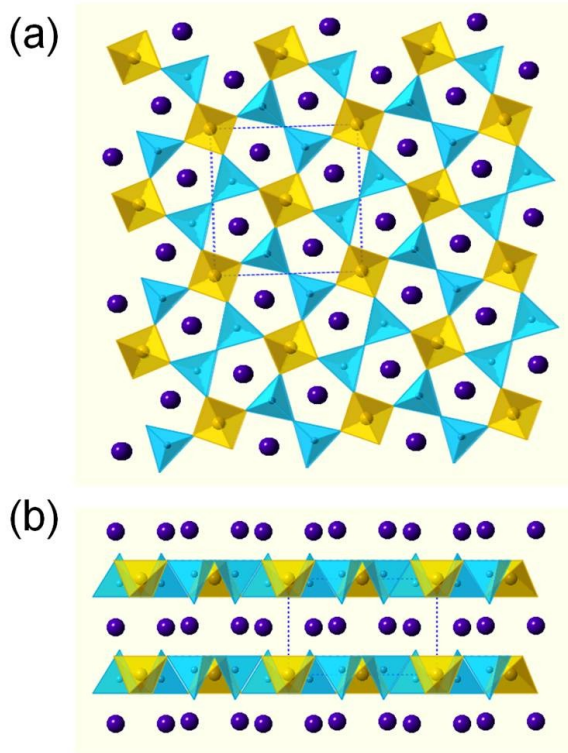
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Figure 58



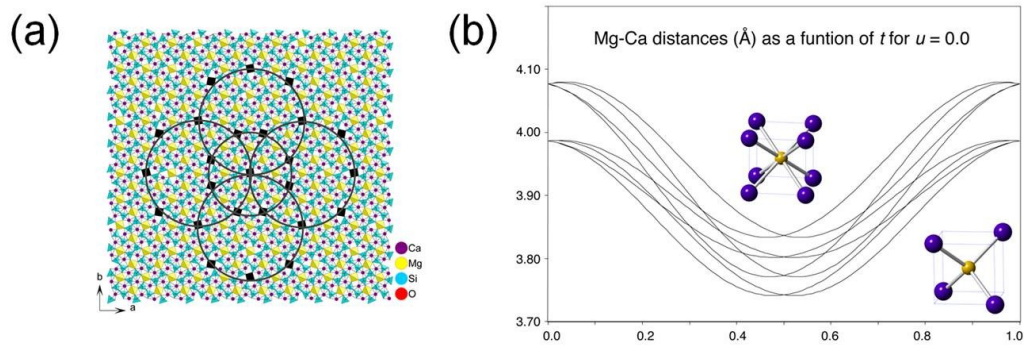
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Figure 59



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Figure 60

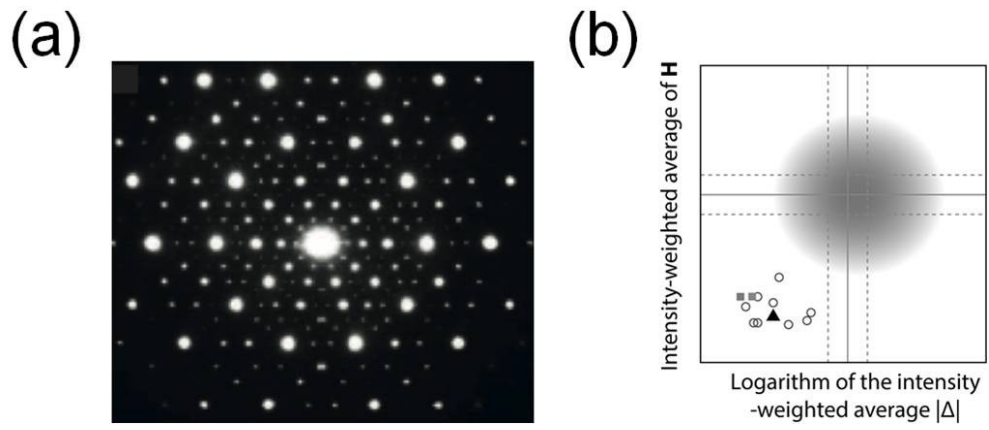


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Figure 61



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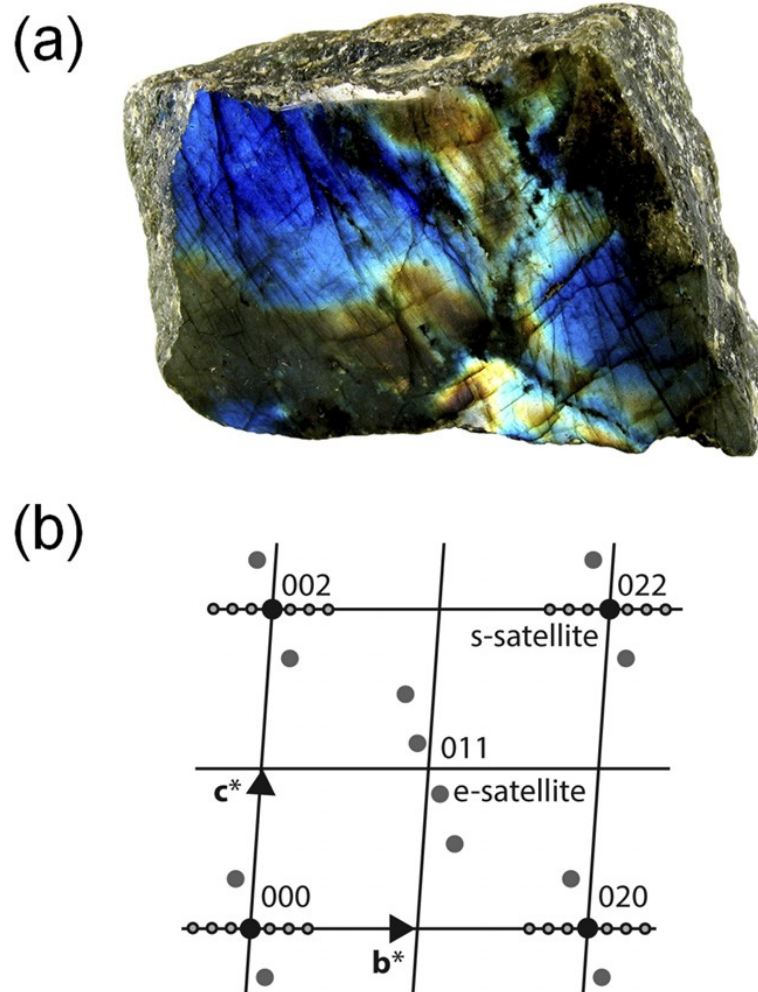
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Figure 62

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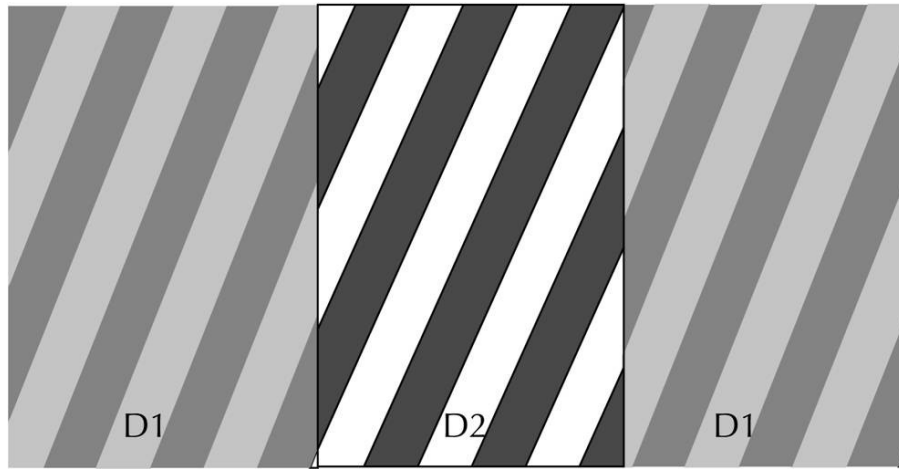


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Figure 63



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