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1 **Twinning in chalcostibite revisited**

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6 **Abstract:** Twinning in chalcostibite has been reported to occur on the (104) plane with respect to
7 the standard setting *Pnma* of the space group. However, different axial settings have been used for
8 this mineral, and in the literature an axial ratio which corresponds to the *Pnam* setting is often
9 reported. Unfortunately, the same indexing of the twin plane, (104), is incorrectly used for both
10 settings; this has led to an incorrect reticular analysis of the twin, which could have been an
11 example of diperiodic twin, an alleged category which has no known examples to date. In this
12 article, we trace back the origin of the inconsistent indexing, we present a revised reticular analysis
13 which puts back this twin in the category of triperiodic twins, and we discuss the atomic structure at
14 the composition plane, showing that a small adjustment of the metal-sulphur coordination is
15 required to accommodate the change in orientation occurring when the twin forms.

16 **Key-words:** chalcostibite; crystallographic orbits; twinning.

17 **1 Introduction**

18 In our review of hybrid twins in non-silicate minerals (Nespolo and Ferraris, 2009) we have shown
19 that almost all non-Friedelian twins, *i.e.* twins with a twin index beyond the empirical limit of 6, are
20 hybrid twins whose effective twin index is within or close to this limit. One remarkable exception
21 remained however, which seemed to escape the reticular theory of twinning (Friedel, 1926), even in
22 its last extension as theory of hybrid twins (Nespolo & Ferraris, 2005): (104) twin in chalcostibite
23 CuSbS_2 . In our analysis, we found two concurrent sublattices with twin indices 29 and 25, leading
24 to an effective twin index of 14.5, far too large to explain this twin on the basis of the reticular

25 theory . Chalcostibite (104) could therefore be the first example of diperiodic twin, an alleged
26 category introduced as intermediate between the usual triperiodic twins and the exceptional case of
27 monoperiodic twins discovered in Zinnwald twin of quartz (Friedel, 1933).

28 While working on the relation between diperiodic twins, of which to the best of our knowledge
29 there are no confirmed representatives to date, and plesiotwins, a type of oriented crystal association
30 based on a large coincidence site lattice (Nespolo *et al.*, 1999), we have traced back the history of
31 that (104) twin in chalcostibite and realized that, due to a variety of axial settings adopted by
32 different authors, at a certain point an error in the indexing occurred in the literature, which remains
33 in reference textbooks. In this article, we give a brief historical perspective of this twin, show that
34 once the twin plane is correctly indexed the twin is still hybrid but with a much lower effective twin
35 index (5.5 instead of 14.5), and explain its occurrence on the basis of pseudo-eigensymmetry of the
36 crystallographic orbits occupied by Cu and Sb, which is the basis of a satisfactory structural
37 restoration across the twin plane.

38 **2 Axial setting of chalcostibite and the problem of indexing the twin and** 39 **composition plane**

40 Chalcostibite (named by Glocker, 1847, p. 32) is a sulfosalt also reported under different names:
41 *kupferantimonglanz* (Zincken, 1835); *rosite* (Huot, 1841, p. 197); *wolfsbergite*, from the type
42 locality (Wolfsberg, Germany: Nicol, 1849, p. 484); *guejarite*, from Guejar in Spain (Cumenge,
43 1879).

44 Chalcostibite crystallizes in a space group of type *Pnma* (No. 62); both the point group (*mmm*) and
45 the type of unit cell (*oP*) are invariant under any permutation of the basis vectors. Such a
46 permutation does result in different settings of the space group (a recent detailed treatment is
47 available in Nespolo and Aroyo, 2016), but the structural information was not available in the old
48 mineralogical literature. Before the discovery of X-ray diffraction, the unit cell was estimated from

49 an axial ratio obtained by indexing the developed faces, and expressed in the form of a ratio $a:b:c$,
50 usually normalized with respect to b taken as the longest parameter; however, different orientations
51 resulted in different indexing of the faces. In case of orthorhombic crystals, the presence of
52 symmetry operations of the same order (binary rotations or mirror reflections) along the three basis
53 vectors made the indexing particularly disputable. As a result, different axial ratios were often
54 adopted by various authors. In the case of chalcostibite, the following ratios were reported:

- 55 • Friedel (1879): 0.7841:1:0.8220
- 56 • Groth (1889): 0.5231:1:0.6395
- 57 • Laspeyres (1891): 0.527598:1:0.618584
- 58 • Penfield and Frenzel (1897, 1898): 0.5312:1:0.63955 (from their own measurements);
59 0.5283:1:0.6364 (from measurement of Laspeyres, 1891); 0.5242:1:0.6377 (from
60 measurement of Friedel, 1879, and re-indexing forms {730} and {370} as {320} and {230}
61 respectively)
- 62 • Goldschmidt (1923): 0.8026:1:0.6275
- 63 • Ungemach (1923): 0.6275:1:2.4082
- 64 • Palache *et al.* (1952): 0.4153:1:0.2606

65 The ratios reported by Groth, by Laspeyers, and by Penfield and Frenzel (GLP in the following, for
66 short) were essentially the same. The transformations are the following¹: Friedel to GLP: **c,2a,b**;
67 Friedel to Palache: **3c,6b,-2a**; GLP to Palache: **3a,6c,-b**; Goldschmidt to Palache: **b,3a,-c**;
68 Ungemach to Palache: **b,c,a**.

69 Cell parameters obtained from X-ray diffraction were published by Hofmann (1933), for the
70 standard setting $Pnma$ of the space group, namely $a = 6.12$, $b = 3.89$, $c = 14.51$ Å, corresponding to
71 the ratio 1.5899:1:3.8254, *i.e.* 0.4156:0.2614:1, very close to Palache apart from the exchange of b

5 1 Some of the transformations given by Palache *et al.* (1952) correspond to a change to left-handed reference.
6 In these cases, we have modified a sign to obtain a right-handed setting.

72 and **c** basis vectors. Cell parameters from X-ray diffraction were also reported by Cervelle *et al.*
73 (1979) as $a = 6.026$, $b = 14.510$, $c = 3.800$ Å, without any indication of the space group; they
74 however clearly correspond to the *Pnam* setting and a ratio 0.4153:1:0.2619, very close to the ratio
75 of Palache. The transformation from Hofmann to Palache is **a,c,-b** and from Palache to Hofmann is
76 **a,-c,b**. Finally, the transformation from GLP to Hoffman is **3a,b,6c**. In other words, the *orientation*
77 of the basis vectors chosen in GLP is consistent with the cell parameters for the standard setting of
78 the space group, although the ratios differ.

79 Twinning in chalcostibite was reported by Spencer (1896) based on axial ratio of Groth (1889), as
80 occurring on the (102) plane. The same twin was also listed by Hintze (1904, page 992), who used
81 Penfield's axial ratio. The twin plane is reported to coincide with the composition plane and, with
82 respect to the cell parameters obtained from the X-ray diffraction data, it becomes (104) in the
83 *Pnma* setting or (140) in the *Pnam* setting, after removing common factors remaining by adopting
84 the transformation. Palache *et al.* (1952) adopted basis vectors which correspond to the *Pnam*
85 setting of the space group; accordingly, the twin plane should have been indicated as (140).
86 Unfortunately, the Miller indices of the twin plane were taken directly from Hofmann (1933); in
87 other words, Palache *et al.* (1952) gave the axial ratio corresponding to the *Pnam* setting of the
88 space group, but the Miller indices corresponding to the *Pnma* setting. This error was replicated in a
89 few texts and databases where the twin is mentioned, for example mindat.org (entry No. 983 for
90 chalcostibite).

91 In our survey (Nespolo and Ferraris, 2009), based on the data reported by Palache *et al.* (1952),
92 assuming that the indexing was consistent with the axial ratio, we exchanged the *k* and *l* indices
93 when computing the twin lattice. The very large effective twin index was the result of the incorrect
94 indexing of the twin plane in Palache *et al.* (1952). After discovering this error, we repeated the
95 calculations and we report the correct results here.

96 **3 Reticular analysis of the (104) twin in chalcostibite**

97 As we have shown in the previous section, the twin and composition plane reported by Hintze
98 (1904) has Miller indices (140) in the *Pnam* setting reported by Palache *et al.*, and (104) in the
99 standard *Pnma* setting. On the basis of the cell parameters reported by Razmara *et al.* (1997) for
100 *Pnma*, namely $a = 6.0160(1)$, $b = 3.7968(6)$, $c = 14.499(3)$ Å, two concurrent sublattices are based
101 on the twin plane, with quasi-perpendicular directions [302] (index 11, obliquity 0.83°) and [403]
102 (index 8, obliquity 2.12°), which lead to an effective twin index $n_E = 5.5$, as shown in Fig. 1
103 (calculations performed with the software *geminography*: Nespolo and Ferraris, 2006). This result
104 shows that (104) twin in chalcostibite is a normal, triperiodic hybrid twin; the large effective twin
105 index reported in our 2009 survey was the result of the error in the indexing of the twin plane in
106 Palache *et al.* (1952). The possibility of a diperiodic twin is therefore negated.

107 **4 Structural analysis of the (104) twin in chalcostibite**

108 Fig. 2 shows the structure of chalcostibite along the **b** axis (black: Cu; grey: Sb; white: S) in the
109 cation-centred description. Cu has a slightly distorted tetrahedral coordination with Cu-S bond
110 lengths 2.2717, 2×2.3157 and 2.3163 Å, whereas Sb has a more irregular coordination, in the shape
111 of a highly distorted tetragonal pyramid, with five bond distances at 2.4489, 2×2.5895 and
112 2×3.1288 Å; the two longer distances barely contribute to the coordination of Sb. Indeed, the
113 Effective Coordination Number (ECoN: Hoppe, 1979) for Cu and Sb is 3.99 for four Cu-S bonds
114 and 3.36 for five Sb-S bonds, showing that the coordination for Sb is much more distorted than for
115 Cu and is more realistically described a 3+2. In the anion-centred description (Fig. 3), one S (S1) is
116 coordinated by two Cu, both at 2.3157 Å, and three Sb, at 2.4489 and 2×3.1288 Å; again, the two
117 longer distances S-Sb are borderline bond contacts. The other S (S2) is coordinated by two Cu at
118 2.2717 and 2.3163 Å, and two Sb, both at 2×2.5895 Å (computations performed with the software

119 CHARDI2015: Nespolo and Guillot, 2016). The structure of minerals is commonly described as
120 based on cation-centred polyhedra, but the importance of the alternative interpretation as anion-
121 centred polyhedra has been repeatedly emphasized (see, e.g., Krivovichev *et al.*, 2013; Beck, 2014;
122 Eon and Nespolo, 2015). As it was already pointed out by Hofmann (1933), both types of metal
123 atoms are very close to the (104) plane (Fig. 4); their position should therefore not be largely
124 affected by twinning. These atoms are located at the corners of the coordination polyhedra in the
125 anion-centred description of the structure, which makes the visual comparison of the changes in
126 coordination due to twinning easier. The anion-centred description is therefore privileged below; the
127 cation-centred description leads to the same conclusions and is briefly presented in the discussion.
128 Hofmann (1933) did not provide any quantitative estimation of the perturbation the structure
129 undergoes at the formation of the twin. To obtain such a quantitative measure, we need to analyse
130 the pseudo-eigensymmetry of the crystallographic orbits, to find whether it contains an operation
131 whose linear part coincides with the twin operation. The approach has been described in details in
132 our previous articles, where the reader can find all the details; here we give just a brief summary.
133 The same approach has allowed us to explain the formation of twins in a number of minerals,
134 namely melilite (Marzouki *et al.* 2014a), staurolite (Marzouki *et al.* 2014b), aragonite (Marzouki *et*
135 *al.*, 2015), marcasite (Nespolo and Souvignier, 2015a), cassiterite and rutile (Nespolo and
136 Souvignier, 2015b), forsterite (Azevedo and Nespolo, 2017) and the Carlsbad twin in orthoclase
137 (Nespolo and Souvignier, 2017).

138 The unit cell of the twin lattice is defined by the (104) plane and the [302] direction quasi-
139 perpendicular to it. Because the twin is hybrid, more than one direction quasi-perpendicular to the
140 (104) plane could be chosen, each corresponding to a different sublattice: in this case, [302]
141 (obliquity 0.83°) and [403] (obliquity 2.12°). The former direction is chosen to describe the
142 structure of chalcostibite in the setting of the twin, because of the lower obliquity, which allows a

143 more precise estimation of the pseudo-symmetry.

144 The two shortest directions in the (104) plane are $[40\bar{1}]$ and $[010]$, which, together with $[302]$,
145 constitute the columns of the transformation matrix from the basis vectors $(\mathbf{abc})_I$ of the untwinned
146 chalcostibite to those of the twin $(\mathbf{abc})_T$ (I = individual, T = twin):

$$(\mathbf{a} \ \mathbf{b} \ \mathbf{c})_I \begin{pmatrix} 4 & 0 & 3 \\ 0 & 1 & 0 \\ \bar{1} & 0 & 2 \end{pmatrix} = (\mathbf{a} \ \mathbf{b} \ \mathbf{c})_T$$

147 *i.e.* $\mathbf{a}_T\mathbf{b}_T\mathbf{c}_T = 4\mathbf{a}_I-\mathbf{c}_I, \mathbf{b}_I, 3\mathbf{a}_I+2\mathbf{c}_I$. The cell parameters of the twin lattice are $a_T = 28.094$, $b_T = 3.797$, c_T
148 $= 34.156 \text{ \AA}$, $\beta_T = 89.17^\circ$; the unit cell of the twin lattice is primitive, monoclinic but pseudo-
149 orthorhombic, with a deviation of β which corresponds precisely to the obliquity and is eleven times
150 larger than the unit cell of the individual (this correspond to the index of the first sublattice); it
151 contains $16 \times 11 = 176$ atoms. The highest subgroup of *Pnma* compatible with this lattice is
152 obtained as $\mathcal{H} = G_1 \cap G_2$ where G_1 and G_2 are the space groups of the two individuals, both of type
153 *Pnma*, in the respective orientations. In our case, \mathcal{H} is of type $P2_1/m$. The fractional coordinates of
154 chalcostibite in the asymmetric unit of *Pnma* are given in Table 1. The Wyckoff splitting scheme to
155 the setting of the twin lattice is very simple: $4c \rightarrow 22 \times 2e$. Table 2 [Note that Table 2 is deposited,
156 not printed, and freely available as Supplementary Material linked to this article on the GSW
157 website of the journal: <http://eurjmin.geoscienceworld.org/>] gives the 88 atoms in the asymmetric
158 unit of $P2_1/m$. Crystallographic orbits having a (pseudo)-eigensymmetry containing a mirror or
159 glide plane perpendicular to the \mathbf{c} vector of the twin lattice are (quasi)-restored by the corresponding
160 operation. In the cell of the twin lattice, there are 11 positions for the (001) plane passing on or
161 close to the metal atoms, about 3.1 \AA apart. The eigensymmetry analysis can be performed about
162 any of these positions: we take the one about $z = 0.5$. The position of the metal atoms about $z = 0.5$
163 are pseudosymmetric with respect to two orthorhombic minimal (index 2) supergroups of $P2_1/m$:

164 *Pmmn* (No. 59), with the basis vector in common with the individual, and *Pbmm*, which
165 corresponds to *Pmma* (No. 51) expressed in a non-standard setting obtained with basis vector
166 transformation **c,a,b**. Table 3 gives the fractional atomic coordinates of the four independent metal
167 atoms (the other four are obtained by applying an inversion), as well as the corresponding fractional
168 atomic coordinates obtained by applying an *n*-glide reflection (for *Pmmn* pseudo-eigensymmetry)
169 and a mirror reflection (for *Pbmm* pseudo-eigensymmetry), both about $z = 0.5$. The Sb atoms are
170 restored by this operation within, respectively, 0.2625 Å and 0.2732 Å, the Cu atoms within 0.3849
171 Å and 0.3825 Å. This means that if a change of orientation occurs during the crystal growth at $z =$
172 0.5 (with respect to the unit cell of the twin lattice), only a small adjustment of the metal atoms is
173 necessary to overcome this perturbation. The two candidate restoration operations corresponding to
174 the two pseudo-eigensymmetries do not lead, however, to the same coordination environment on the
175 two sides of the twin plane. The situation is shown in Fig. 5, where the region around $z = 0.5$ is
176 shown for the untwinned crystal (bottom), the twinned model in *Pmmn* (middle), and the twinned
177 model in *Pbmm* (top). The position of the metal atoms on the twin plan being slightly different in
178 the two individuals, they are shown as split, almost overlapped atoms in the twinned models in Fig.
179 5. The coordination polyhedra share edges on the twin plane in the *Pmmn* model, as in the
180 untwinned crystal, whereas they share faces in the *Pbmm* model. Twinning by reflection on (104)
181 requires therefore a small adjustment of the metal atoms to produce a local structure at the boundary
182 which is close to that of the untwinned crystal if the restoration operation is an *n*-glide; if instead the
183 restoration operation is a mirror reflection, the coordination that results highly modified, an event
184 which would make the twin less likely to occur.

185 Now, exactly the same conclusion can be drawn for the eleven positions of the twin plan every
186 $\sim 3.1\text{Å}$. This means that during the crystal growth, twinning on (104) can be accommodated every
187 $\sim 3.1\text{Å}$, making this twinning a relatively high probability event.

188 **5 Discussion**

189 Fig 6 is obtained from the *Pmmn* twin model by taking the arithmetic average of the fractional
190 coordinates of the metal atoms almost overlapped in the Fig. 5 (middle). The coordination
191 polyhedra are essentially the same as those occurring in the untwinned mineral, but the S-metal
192 distances are in some cases severely affected, resulting in some polyhedra of unphysically small
193 size, with some S-metal distances as short at 1.6 Å. Clearly, the structural adjustment has to extend
194 further from the composition plane in order for the S-metal distances to approach their normal
195 values. From the energetic viewpoint, it is certainly more favourable if the strain occurring at the
196 composition plane is absorbed through smaller deformations on a slightly wider region than a single
197 larger deformation at the composition plane.

198 Fig. 7 is the cation-centred description of the structure of chalcostibite analogous to Fig. 5. The
199 coordination polyhedra at the twin plane for the *Pmmn* model are essentially the same as those in
200 the untwinned crystal, with the exception of one Cu site; here, one S has moved closer and another
201 one farther from Cu, leading to a triangular instead of tetrahedral coordination. The structural
202 adjustment close to the twin plane mentioned above would easily restore the normal coordination of
203 this Cu atom. In the *Pbmm* model, instead, the coordination at the twin plane is so heavily affected
204 that it would require extensive rearrangements to get closer to the normal coordination in the bulk
205 of the crystal. The *Pmmn* model is definitely more sound than the *Pbmm* model and the restoration
206 operation for this twin is an *n*-glide perpendicular to the *c* axis of the twin lattice.

207 The determination of the extent and extension of the structural adjustment around the twin plane
208 would require a high-resolution transmission electron microscopy study of (104) twin in
209 chalcostibite, which, to the best of our knowledge, has never been performed. With this study, we
210 hope to draw the attention of electron microscopists on the interest to perform such an investigation.

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284 **FIGURE CAPTIONS**

285 **Figure 1.** The lattice of chalcostibite projected along the [010] direction. drawn in scale according
286 to the cell parameters reported by Razmara *et al.* (1997). Four-pointed and five-pointed black stars
287 indicate lattice nodes belonging to the [302]/(104) and [403]/(104) sublattice respectively; nodes on
288 the (104) plane are common the two two sublattice and indicated by black circle; white circles stand
289 for lattice nodes not belonging to either of the sublattices. The unit cell based on the [302]/(104)
290 pair of lattice elements has multiplicity 11 and contains one lattice node for each sublattice, so that
291 the effective twin index is $11/2 = 5.5$.

292 **Figure 2.** The structure of chalcostibite observed down the **b** axis in the cation-centred description.
293 Cu atoms occupy a distorted tetrahedron whereas Sb atoms are at the centre of a face of a distorted
294 square pyramid (this and the following figures are drawn with VESTA: Momma and Izumi, 2011).

295 **Figure 3.** The structure of chalcostibite observed down the **b** axis in the anion-centred description.
296 The two crystallographically independent S atoms have different coordination: a 2Cu+3Sb distorted
297 square pyramid and a 2Cu+2Sb distorted tetrahedron.

298 **Figure 4.** The ball-and-stick description of the structure of chalcostibite, with the (104) plane drawn
299 in grey at the position $z = 0.5$. Metal atoms are positioned very close to this plane. Cu atoms are
300 shown in black, Sb atoms in grey, S atoms in white.

301 **Figure 5.** A portion of the structure of chalcostibite in the axial setting of the twin, drawn around
302 the twin plane in the anion-centred description. Bottom: the untwinned structure. Middle: the *Pmnm*
303 twinned model (the portion above the twin plane is obtained from the one below it by an *n*-glide
304 reflection at $z = 0.5$). Top: the *Pbmm* twinned model (the portion above the twin plane is obtained
305 from the one below it by a mirror reflection at $z = 0.5$). In both twinned models, the metal atoms
306 close to the twin plane are shown in the positions corresponding to the two individuals; these
307 positions being very close, the corresponding atoms are almost overlapped in the figure. Whereas in
308 the *Pnmm* model the coordination polyhedra on the opposite sides of the twin plane share their
309 edges, as in the untwinned crystal, in the *Pbmm* model they share their faces, leading to a physically
310 unlikely situation.

311 **Fig. 6.** A likely structural adjustment at the composition plane, obtained by taking the arithmetic
312 average of the fractional atomic coordinates of the metal atoms quasi-overlapped in Fig. 5. The S-
313 metal coordination appears very similar to that in the untwinned crystal but actually some of the
314 polyhedra have unphysically small volumes, indicating that the structural adjustment likely extends
315 for a few atomic planes in order to minimize the structural strain occurring when the twin forms.

316 **Figure 7.** A portion of the structure of chalcostibite in the axial setting of the twin, drawn around
317 the twin plane in the cation-centred description. Bottom: the untwinned structure; middle: the
318 *Pmnm* twinned model; top: the *Pbmm* twinned model (same conventions as in Fig. 5). The
319 positions of the Cu and Sb atoms on the twin plane are the arithmetic average of the positions in the
320 two individuals; no other structural adjustment is introduced. In the *Pnmm* model, the coordination
321 polyhedra are essentially the same as in the untwinned crystal, with the exception of one of the Cu
322 sites; in the *Pbmm* model, instead, the coordination around the twin plane is severely affected. A
323 structural adjustment of the S atoms close to the twin plane can restore the normal coordination in
324 the *Pmnm* model but not in the *Pbmm* model.

325 **Table 1.** Fractional atomic coordinates in the asymmetric unit of chalcostibite, setting *Pnma*. All
 326 atoms are in Wyckoff position 4c. Data from Ramzara *et al* (1997).

Cu	0.7463(6)	$\frac{3}{4}$	0.1721(2)
Sb	0.2245(2)	$\frac{1}{4}$	0.0636(1)
S1	0.624(1)	$\frac{1}{4}$	0.0960(4)
S2	0.131(2)	$\frac{3}{4}$	0.1787(5)

327 **Table 3.** Fractional atomic coordinates of metal atoms around $z = 0.5$ (label without ') and after
 328 application of a mirror reflection about $z = 0.5$ label with '), in the two models *Pmnm* and *Pbmm*.
 329 The difference is expressed both in terms of fractional atomic coordinated and in Å ($|\Delta|$).

<i>Pmnm</i>											
Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>	Δx	Δy	Δz	$ \Delta $
Sb11	0.93256	0.25	0.49808	Sb18'	0.94184	0.25	0.49728	0.00928	0	0.0008	0.2625
Sb18	0.44184	0.75	0.50272	Sb11'	0.43256	0.75	0.50192	0.00928	0	0.0008	0.2625
Cu20	0.68263	0.75	0.50526	Cu20'	0.68397	0.75	0.49406	0.00134	0	0.0112	0.3849
Cu2	0.18397	0.25	0.50594	Cu2'	0.18263	0.25	0.49474	0.00134	0	0.0112	0.3849
<i>Pbmm</i>											
Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>	Δx	Δy	Δz	$ \Delta $
Sb11	0.93256	0.25	0.49808	Sb11'	0.93256	0.25	0.50192	0	0	0.0008	0.2732
Sb18	0.44184	0.75	0.50272	Sb18'	0.44184	0.75	0.49728	0	0	0.0008	0.2732
Cu20	0.68263	0.75	0.50526	Cu2'	0.68263	0.75	0.49474	0	0	0.0112	0.3825
Cu2	0.18397	0.25	0.50594	Cu02'	0.18397	0.25	0.49406	0	0	0.0112	0.3825













