

The staurolite enigma solved

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Staurolite has been long considered an enigma because of its remarkable pseudosymmetry and the frequent twinning. Staurolite gives two twins whose occurrence frequency seems to contradict the condition of lattice restoration requested by the reticular theory of twinning, in that the more frequent one (Saint Andrews cross twin) has a twin index of 12, whereas the less frequent one (Greek cross twin) has a twin index of 6. The hybrid theory of twinning shows that the former is actually a hybrid twin with two concurrent sublattices and an effective twin index of 6.0. However, this is still not sufficient to explain the observed higher occurrence frequency of the Saint Andrews twin. The (pseudo)-eigensymmetry of the crystallographic orbits of staurolite has been analysed and it was found that the whole substructure built on anions is restored (with small deviations) by both twin laws, which explains why twinning is frequent in staurolite. On the other hand, 45% of the cation sites are quasi-restored in the Saint Andrews cross twin, against only 19% for the Greek cross twin: this difference finally explains the different occurrence frequencies of the two twins.

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1. Introduction

The first structural study of staurolite was reported by Cardoso (1928), who suggested the space-group type *Ccmm*. The following year, and by adopting the same type of space group, Náray-Szabó (1929) succeeded in solving the structure. However, the correct space group had not been determined yet. In fact, Juurinen (1956) suggested *C222₁* and the same year Hurst *et al.* (1956) proposed *C2/m*, which was then confirmed by Náray-Szabó & Sasvári (1958).

Nowadays, the crystal structure and chemistry of staurolite are well known: it crystallizes in the space group *C2/m* (No. 12) with cell parameters $a = 7.8695$, $b = 16.60759$, $c = 5.6658$ Å, $\beta = 90.001^\circ$ (Hawthorne *et al.*, 1993). The metric of the lattice is thus orthorhombic and this explains the previous uncertainties in the determination of its space group. The atomic coordinates are given in Tables 1 and 2.

The idealized formula of staurolite can be written as $HX_9Y_2Z_4O_{24}H$, with $X = (Al^{3+}, Mg^{2+}, Fe^{2+})$, $Y = (Fe^{2+}, Mg^{2+})$ and $Z = Si^{4+}$. The structure is based on a slightly distorted face-centred cubic (f.c.c.) packing of oxygen atoms with the cations partly occupying the octahedral and tetrahedral cavities, which can be represented by the symmetrical packing symbol $A(- - 2/3)B(1/4 1/4 1/4)C(- 2/3 -)A(1/4 1/4 1/4)B(2/3 - -)C(1/4 1/4 1/4)$ (Zoltai & Stout, 1984). This symbol gives the fractional occupation of the independent polyhedra (two tetrahedra and one octahedron) formed by a pair of hexagonal sheets of spheres, representing the anions (oxygen atoms

here). The idealized structure of staurolite consists thus of an f.c.c. stacking of anions with an alternation, along the stacking direction, of cationic planes occupying alternatively one-quarter of each cavity and two-thirds of the octahedral cavities only. The closeness of the oxygen packing to a truly f.c.c. packing is shown in Table 2, where the fractional coordinates are idealized to multiples of one-twelfth and the corresponding displacement from the actual positions are given: the largest displacement is only 0.35 Å. The real and idealized oxygen substructures are compared visually in Fig. 1 (figures are drawn with *VESTA*; Momma & Izumi, 2011).

Staurolite gives two twins, known as the 90° twin or *Greek cross* twin and the 60° twin or *Saint Andrews cross* twin, whose relative occurrence frequency remains so far unexplained and is one of the reasons why Smith (1968) called staurolite 'an enigma'. The reticular theory of twinning (*cf.* Friedel, 1904, 1926) considers a high degree of lattice restoration as a necessary condition for the formation of twins and relates the probability of occurrence of a twin with the degree of overlap of the lattices of the individuals. The latter is measured by two parameters: the obliquity and the twin index. The twin lattice L_T is defined by two elements mutually (quasi)-perpendicular, the plane $(hkl)_T$ and the direction $[uvw]_T$: one is the twin element, the other the lattice element (quasi)-perpendicular to it. The angle between $[hkl]^*$ and the direction $[uvw]$ quasi-perpendicular to (hkl) (for reflection twins), or between $(uvw)^*$ and the plane (hkl) quasi-perpendicular to $[uvw]$ (for rotation twins) is the obliquity ω , which measures deviation

Table 1

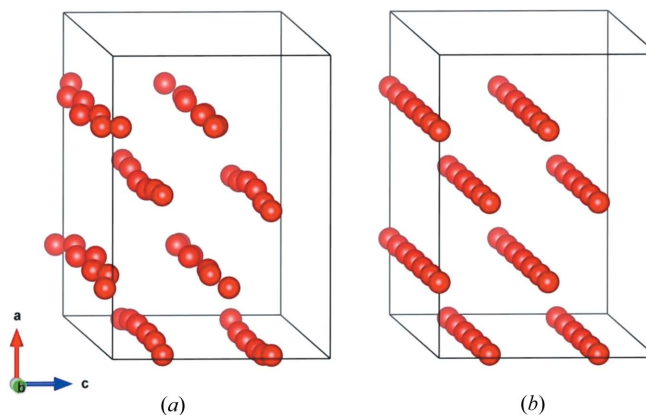
Atomic coordinates of cations in staurolite in the setting of the individual.

Site	Wyckoff position	Coordinates
X1	4g	1/2, 0.17511, 0
X2	4h	1/2, 0.17511, 1/2
X3	8j	0.26288, 0.41053, 0.25011
X4	2a	0, 0, 0
X5	2c	0, 0, 1/2
Y	4i	0.39107, 0, 0.24991
Z	8j	0.13416, 0.16612, 0.24996
Fe1	2b	1/2, 0, 0
Fe2	2d	1/2, 0, 1/2

from perfect overlap of the lattice nodes of the individuals forming the twin; correspondingly, twins are classified in TLS (twin lattice symmetry) and TLQS (twin lattice quasi symmetry), respectively (Donnay & Donnay, 1974).¹ The twin index n is the inverse of the fraction of lattice nodes restored (exactly, for TLS; approximately, for TLQS) by the twin operation and corresponds to the ratio between the volumes of the primitive cells of the twin and the individual: $n = V(\mathbf{L}_T)/V(\mathbf{L}_{ind})$. As a heuristic rule, the lower the obliquity and the twin index, the higher is the occurrence probability of the twin. Friedel (1904, 1926) reported an empirical limit for the occurrence of twins as $n \leq 6$ and $\omega \leq 6$. Twins that respect these limits are called *Friedelian twins* (Nespolo & Ferraris, 2005).

Staurolite twins are often reported in the literature as reflection twins on (031) (Greek cross) and (231) (Saint Andrews cross), the corresponding twin indices are 6 and 12, respectively. The Saint Andrews cross is thus a non-Friedelian twin, which should have a low occurrence probability but instead occurs more frequently than the Greek cross (Hurst *et al.*, 1956) and seems to contradict the assumption that a high degree of lattice restoration is a prerequisite for the formation of twins, which is at the core of the reticular theory. Hurst *et al.* (1956) have demonstrated that staurolite twins are actually rotation twins: the Greek cross twin is obtained by either 90° rotation around [100] or 180° around [013] and the Saint Andrews cross by either 120° rotation around [102] or 180° around [313] (Nespolo & Ferraris, 2007). Ericksen (2003) presented a detailed mathematical analysis trying to confirm or refute the interpretation of Hurst *et al.* (1956), without however coming to a definite conclusion. The rotation (rather than reflection nature) does not change the reticular interpretation of the Greek cross twin. For the Saint Andrews twin, however, there are two coexisting sublattices, which make this twin *hybrid*: for the full lattice restoration both sublattices have to be taken into account and the degree of lattice restoration is measured by the *effective twin index* n_E (Nespolo & Ferraris, 2006), which is defined as the ratio between the lattice nodes of the individual and the lattice nodes belonging to any of the quasi-restored sublattices. The Saint Andrews

¹ For manifold twins (*i.e.* twins in which the twin operation is higher than twofold), a zero-obliquity TLQS may occur. In this case, a different parameter is necessary to measure the deviation from the exact restoration of lattice nodes, like the twin misfit introduced by Nespolo & Ferraris (2007).

**Figure 1**

View of the (pseudo)-f.c.c. packing formed by the oxygen atoms in staurolite; (a) exact coordinates and (b) idealized coordinates.

cross twin is found to be a hybrid twin with two concurrent sublattices leading to an effective twin index of $n_E = 6.0$. The hybrid interpretation no longer contradicts the necessary condition of a good lattice restoration (Nespolo & Ferraris, 2009). It cannot, however, explain the higher frequency of the Saint Andrews cross twin: for this a detailed analysis of the structural restoration is required.

2. The common substructure of oxygen atoms

Under the action of the symmetry operations of the space group \mathcal{G} , each atom with coordinates r_i generates a crystallographic orbit O_i with eigensymmetry \mathcal{E}_i . If \mathcal{G} is a proper subgroup of \mathcal{E}_i , O_i is called a *non-characteristic orbit*. The eigensymmetry group of O_i may contain the twin operation t : in this case, the orbit O_i is restored by the twin operation and forms a substructure which continues unperturbed across the composition surface and can justify the formation of the twin. The orbit O_i can also be only pseudosymmetric: in this case some operations in the eigensymmetry group \mathcal{E}_i are only approximate symmetry operations for O_i and thus the substructure undergoes a limited perturbation across the surface; the closer the pseudosymmetries of the orbit are to proper symmetry operations, the lower the perturbation of the substructure across the surface. The union of two or more orbits may also have an eigensymmetry higher than \mathcal{G} : in this case, the substructure crossing the composition surface unperturbed or only slightly perturbed is composed of the union of orbits and the twin operation restores one orbit to one or more different orbits in this union. In order for two orbits to be considered in the union, the atoms occupying those orbits must play a similar structural role: for example, be of the same chemical species or have the same type of coordination environment (Marzouki *et al.*, 2014).

As we have seen, the structure of staurolite is based on a pseudo-f.c.c. packing of oxygen atoms: this means that the union of the corresponding orbits must have a pseudo-cubic symmetry. Indeed, Naray-Szabo (1929) had already recognized that the 48 oxygen atoms in the unit cell form a pseudo-

Table 2

Idealization of oxygen coordinates in the individual and pseudo-cubic basis.

Oxygen atom	Wyckoff position	Coordinates r_i in individual basis	Approximate coordinates in the individual basis	Absolute displacement (Å)	Idealized $(\mathbf{P}, \mathbf{p})^{-1} \cdot r_i$ in cubic cell
O1	4i	0.23461, 0, 0.96468	1/4, 0, 0	0.23360	1/2, 0, 0
O2	4i	0.23493, 0, 0.53474	1/4, 0, 1/2	0.23081	0, 1/2, 0
O3	8j	0.25523, 0.16128, 0.01537	1/4, 1/6, 0	0.1240	0, 1/2, 0
O4	8j	0.25503, 0.16129, 0.48467	1/4, 1/6, 1/2	0.12985	1/2, 0, 0
O5	8j	0.00152, 0.08876, 0.24971	0, 1/12, 1/4	0.09147	0, 0, 1/2
O6	8j	0.02140, 0.24936, 0.25018	0, 1/4, 1/4	0.1687	1/2, 1/2, 1/2
O7	8j	0.52671, 0.09997, 0.24994	1/2, 1/12, 1/4	0.34720	0, 0, 1/2

f.c.c. substructure. This pseudo-cubic symmetry is confirmed by the analysis of the union of oxygen orbits with the *PSEUDO* program (Capillas *et al.*, 2011) at the Bilbao Crystallographic Server (Aroyo *et al.*, 2006). The computation shows that the eigensymmetry for this union is $Fm\bar{3}m$ (No. 225) with transformation matrix (\mathbf{P}, \mathbf{p}) relating an eigensymmetry basis $(abc)_u$ to the individual basis $(abc)_I$ defined as follows:

$$(abc)_I(\mathbf{P}, \mathbf{p}) = (abc)_u, \mathbf{P}^{-1} = \begin{pmatrix} 0 & 3 & 1 \\ 0 & -3 & 1 \\ 2 & 0 & 0 \end{pmatrix}, -\mathbf{P}^{-1}\mathbf{p} = \begin{pmatrix} 1/2 \\ 0 \\ 1/2 \end{pmatrix}.$$

The cell shrinking corresponds to the determinant of the matrix \mathbf{P} , namely 1/12.

The seven orbits of oxygen atoms in the individual basis, whose idealized coordinates (expressed as closest multiple of 1/12) are given in Table 2, coalesce into a single oxygen orbit O_u under the action of the eigensymmetry group of the union of all oxygen atoms. This orbit corresponds to the Wyckoff position $4b$ in the space-group type $Fm\bar{3}m$. The union of oxygen orbits in the individual basis becomes thus one single orbit in the cubic basis $(abc)_u$ with multiplicity 4 (due to the F -centring) which, considering that the transformation matrix has determinant 12, corresponds to the 48 oxygen atoms in the unit cell defined by $(abc)_u$, as found by Naray-Szabo (1929).

As seen in the previous section, the twin axes for staurolite can be chosen as [100], [013] (Greek cross twin), [102] and [313] (Saint Andrews cross twin). These directions are transformed by the matrix \mathbf{P}^{-1} above to lattice symmetry directions in the cubic basis $(abc)_u$ (Table 3), which confirms that the union of oxygen atoms, with cubic (pseudo)-symmetry, is fully restored by the twin operations. The substructure built on the oxygen atoms is thus equally restored in both twins and cannot explain the different occurrence frequency of these two twins. Consequently, the restoration of the cations must be the discriminating factor.

3. Analysis of the pseudo-eigensymmetry of the cation substructure

Let $[uvw]_T$ be the twin axis, $(hkl)_T$ the lattice plane (quasi)-perpendicular to it, and \mathbf{v}_1 and \mathbf{v}_2 two vectors defining a two-dimensional unit cell in $(hkl)_T$. The three linearly independent vectors \mathbf{v}_1 , \mathbf{v}_2 and $[uvw]_T$ form the basis of the twin lattice,

Table 3

Expression of the twin element in the pseudo-cubic basis.

Twin element in the individual basis	Twin element in the cubic basis
$4_{[100]}$	$4_{[001]}$
$2_{[013]}$	$2_{[100]}$
$3_{[102]}$	$3_{[111]}$
$2_{[313]}$	$2_{[101]}$

denoted by $(abc)_T$, which is related to the basis $(abc)_I$ of the lattice of the individual by a basis transformation \mathbf{P} :

$$(abc)_I\mathbf{P} = (abc)_T. \quad (1)$$

Given the coordinates

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}_I$$

of an atom in the individual basis, the new coordinates

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}_T$$

of this atom in the twin basis are obtained by

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}_T = \mathbf{P}^{-1} \begin{pmatrix} x \\ y \\ z \end{pmatrix}_I.$$

The twin operation t maps the first individual of the twinned crystal onto the second one, thus the space group of the second individual is the conjugate group $t\mathcal{G}t^{-1}$. The subgroup \mathcal{H} of \mathcal{G} compatible with the twin lattice is the intersection group of the space groups of the two conjugated individuals, *i.e.* $\mathcal{H} = \mathcal{G} \cap t\mathcal{G}t^{-1}$ (Marzouki *et al.*, 2014). Each atom with coordinates r_i generates a crystallographic orbit $O_i = \{g r_i, g \in \mathcal{G}\}$ with eigensymmetry \mathcal{E}_i under the action of the symmetry operations of the space group \mathcal{G} . The atoms belonging to the orbit O_i have $\mathbf{P}^{-1} \cdot g \cdot r_i$ as coordinates in the twin basis. With respect to the intersection group \mathcal{H} , the points in O_i are in general no longer all equivalent but split into two or more orbits O_{ij} under \mathcal{H} , with eigensymmetry groups \mathcal{E}_{ij} (Wondratschek, 1993). If the twin operation t belongs to \mathcal{E}_{ij} , then the atoms forming O_{ij} are restored by t and O_{ij} belongs to the substructure that crosses the composition surface unperturbed. It may, however, also happen that the twin operation t

Table 4

Degree of quasi-restoration of octahedral sites for the Greek cross twin.

In all cases the (pseudo)-eigensymmetry is $P4/m$. As the accepted tolerance is 1 Å, d_{\min} is given with two decimal places.

Orbit or union of orbits	d_{\min} (Å)
$X_{12} \cup X_{14}$	0.20
$X_{21} \cup X_{53}$	0.14
X_{54}	0
$X_{23} \cup X_{24}$	0.20
$X_{16} \cup X_{43}$	0.14
X_{44}	0

belongs to the eigensymmetry of the union of two or more orbits, $\cup_{ij} O_{ij}$: in this case, atoms belonging to a split orbit in one individual can be restored onto atoms belonging to a different split orbit in another individual, as we have seen for the set of oxygen atoms.

For the analysis of the restoration of cations in staurolite, three cases are possible.

(1) Neither the orbit O_{ij} nor its union with other orbits is restored by t ; the substructure defined by O_{ij} does not continue across the composition surface.

(2) The orbit O_{ij} or the union of O_{ij} with other orbits is restored by t ; the substructure defined by O_{ij} continues across the interface and is restored, within some tolerance, to itself or to another orbit.

(3) The orbit O_{ij} and the union of O_{ij} with other orbits is restored by t ; the substructure defined by O_{ij} continues across the interface and is restored, within some tolerance, to itself and to another orbit; this is possible because of the accepted tolerance; obviously, the restoration to one orbit is better than that on the other. The former will be retained because it represents a better explanation for the formation of the twin; the latter would not appear at a lower level of accepted tolerance.

In the staurolite structure, the sites of the cations are situated in two different coordination environments: tetrahedral and octahedral. The tetrahedral sites are occupied by the cations Y and Z . The octahedral sites are occupied by the cations X . Further sites, listed as Fe1 and Fe2 in Table 1, have an atom site occupancy of only 5% and 4.5%, respectively; this is too low to influence the restoration of the structure and will be neglected in the further analysis.

4. Results

The crystal structure of staurolite has a space group \mathcal{G} of type $C2/m$ (No. 12) with a metrically orthorhombic lattice. Conjugation by each of the two twin operations fixes the identity and the inversion, but neither the twofold rotation nor the mirror reflection normal to it are conjugated to an operation in \mathcal{G} . Therefore, the point group of the twin lattice is of type $\bar{1}$, with the twin lattice obtained by $\mathbf{L} \cap t\mathbf{L} = \mathbf{L}_T$ (Marzouki *et al.*, 2014). The twin operation $4_{[100]}$ fixes a tetragonal lattice with basis vectors $[0\bar{1}3]$, $[013]$ and $[100]$, which define the basis of the twin lattice for the Greek cross twin. However, the centring vector

Table 5

Degree of quasi-restoration of tetrahedral sites for the Saint Andrews cross twin.

In all cases the (pseudo)-eigensymmetry is $P2/m$.

Orbit or union of orbits	d_{\min} (Å)	Orbit or union of orbits	d_{\min} (Å)
Y_2	0.18	$Z_{16} \cup Z_{25}$	0.10
$Y_3 \cup Z_8$	0.14	$Z_{22} \cup Y_{22}$	0.15
$Y_4 \cup Z_{33}$	0.15	Z_{31}	0.11
Z_5	0.11	Z_{37}	0.09
Z_{14}	0.09	$Z_{44} \cup Y_{23}$	0.14
$Z_{15} \cup Z_{38}$	0.10	Y_{24}	0.18

Table 6

Degree of quasi-restoration of octahedral sites for the Saint Andrews cross twin.

In all cases, the (pseudo)-eigensymmetry is $P2/m$.

Orbit or union of orbits	d_{\min} (Å)	Orbit or union of orbits	d_{\min} (Å)
$X_{301} \cup X_{104}$	0.08	$X_{324} \cup X_{115}$	0.27
$X_{201} \cup X_{110}$	0.24	$X_{211} \cup X_{120}$	0.14
X_{513}	0	$X_{326} \cup X_{218}$	0.08
$X_{302} \cup X_{215}$	0.27	$X_{212} \cup X_{507}$	0.14
X_{413}	0	$X_{405} \cup X_{117}$	0.14
X_{304}	0.28	$X_{329} \cup X_{407}$	0.14
X_{103}	0.14	X_{114}	0.24
X_{202}	0.14	$X_{213} \cup X_{122}$	0.24
$X_{203} \cup X_{502}$	0.14	X_{512}	0
$X_{501} \cup X_{106}$	0.14	X_{331}	0.29
X_{307}	0.04	$X_{216} \cup X_{411}$	0.14
$X_{311} \cup X_{403}$	0.14	$X_{340} \cup X_{511}$	0.14
X_{313}	0.25	X_{341}	0.15
$X_{205} \cup X_{404}$	0.14	$X_{118} \cup X_{345}$	0.08
$X_{206} \cup X_{116}$	0.14	$X_{119} \cup X_{410}$	0.14
$X_{318} \cup X_{217}$	0.08	X_{219}	0.14
$X_{319} \cup X_{504}$	0.14	$X_{220} \cup X_{348}$	0.27
X_{321}	0.15	$X_{508} \cup X_{123}$	0.14
$X_{107} \cup X_{325}$	0.27	X_{343}	0.04
X_{109}	0.24	X_{346}	0.25
X_{209}	0.24	X_{124}	0.14
X_{210}	0.24	X_{412}	0
$X_{503} \cup X_{406}$	0		

[003] is also compatible with the twin operation (Nespolo & Ferraris, 2007), therefore $\mathcal{H} = \mathcal{G} \cap t\mathcal{G}t^{-1}$ is of type $C\bar{1}$ (No. 2, non-conventional setting). The twin operation $2_{[313]}$ fixes the lattice with basis $[\bar{1}\bar{1}1]$, $[10\bar{2}]$ and $[313]$, which defines a primitive basis for the Saint Andrews cross twin. In this case, the intersection group $\mathcal{H} = \mathcal{G} \cap t\mathcal{G}t^{-1}$ is of type $P\bar{1}$ (No. 2). The transformation matrix \mathbf{P} in equation (1) thus takes the form

$$\mathbf{P}_{\text{Gc}} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & -1 & 0 \\ 3 & 3 & 0 \end{pmatrix} \text{ and } \mathbf{P}_{\text{SA}} = \begin{pmatrix} 1 & 3 & 1 \\ 0 & 1 & -1 \\ -2 & 3 & 1 \end{pmatrix}$$

for the Greek cross twin (Gc) and the Saint Andrews cross twin (SA), respectively. The corresponding cell parameters are $a = b = 23.7424$, $c = 7.8695$ Å, $\alpha = \beta = 90.001$, $\gamma = 88.772^\circ$ for the Greek cross twin and $a = 13.7796$, $b = 33.4821$, $c = 19.2283$ Å, α

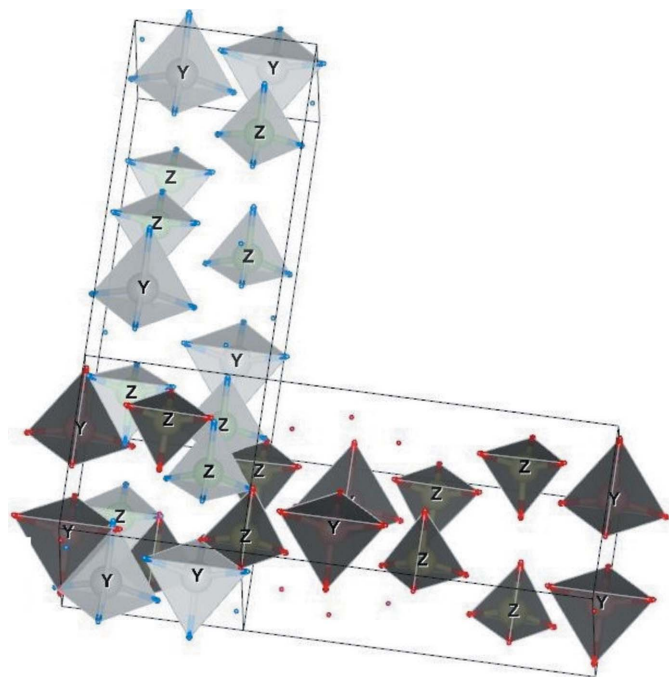


Figure 2
View of the tetrahedra in the unit cell of the individual in its original orientation (dark tetrahedra, oxygen atoms in red) and after applying a $4_{[100]}$ rotation (light tetrahedra, oxygen atoms in blue). The common part of the figure corresponds to the common volume of a penetration Greek cross twin, octahedra omitted. Whereas the oxygen atoms are almost restored, this is not the case for the tetrahedra: the twin operation maps a filled tetrahedron onto an empty one and *vice versa*.

$= 89.472$, $\beta = 61.629$, $\gamma = 35.049^\circ$ for the Saint Andrews cross twin.

The orbits at the cation sites $X1$ – $X5$, Y and Z undergo splitting when the action is restricted to the intersection group \mathcal{H} . The tolerance on the (quasi)-restoration for the cations, d_{\min} , is taken as 1 \AA , as in our previous analysis of melilite twins (Marzouki *et al.*, 2014). Tables S1, S2 and S3 (available in the supporting information²) give the splitting scheme for those orbits for which at least one split orbit is quasi-restored, as obtained by *WYCKSPLIT* (Kroumova *et al.*, 1998): when none of the split orbits is restored, the splitting scheme is omitted for the sake of brevity. The quasi-restored orbits and unions of orbits are given in Tables 4, 5 and 6, together with the achieved restoration accuracy d_{\min} .

The minimal supergroup \mathcal{E} of \mathcal{H} containing the twin operation t is of type $P4/m$ (No. 83) for the Greek cross twin and of type $P2/m$ (No. 10) for the Saint Andrews cross twin. The corresponding coordinate transformation from \mathcal{H} to \mathcal{E} is simply the transformation $(1/2 \ 1/2 \ 0, -1/2 \ 1/2 \ 0, 0 \ 0 \ 1)$ from the C to the P cell for the Greek cross twin and the identity matrix for the Saint Andrews cross twin (no shift of origin in both cases).

For the octahedral sites (X), the restoration is much higher in the Saint Andrews cross twin (136 atoms out of 240, 57%)

Table 7

Summary of the percentage of the polyhedra quasi-restoration by the twin operations $4_{[100]}$ and $2_{[313]}$ for the Greek cross twin and Saint Andrews cross twin, respectively.

Twin	Octahedral sites restored (%)	Tetrahedral sites restored (%)	Cation sites restored (%)
Greek cross	30	0	19
Saint Andrews cross	56	25	45

than for the Greek cross twin (36 atoms out of 120, 30%). None of the 72 atoms in tetrahedral coordination (Y and Z sites) is restored for the Greek cross twin, whereas on these sites 36 atoms out of 144 (25%) are restored for the Saint Andrews cross twin (Table 7).

Fig. 2 shows the substructure of staurolite built on tetrahedra, in the original orientation and after a $4_{[001]}$ rotation which corresponds to a Greek cross twin operation. Although the staurolite structure is based on a distorted f.c.c. lattice formed by the oxygen atoms, the $4_{[001]}$ rotation is not a pseudosymmetry operation for the structure because of the cation distribution, expressed by the symmetrical packing symbol. In fact, this operation approximately maps filled tetrahedra of one individual onto empty tetrahedra of the other individual and *vice versa*: none of the tetrahedra is therefore restored by the twin operation. Furthermore, when the twin cell of the Greek cross twin is viewed from the side with the twin axis as vertical axis (see Fig. 3), it becomes evident that the tetrahedra are arranged in layers perpendicular to the twin axis. Within each layer, all tetrahedra have the same orientation, whereas tetrahedra in neighbouring layers have opposite orientation. Since the $4_{[001]}$ rotation reverses the orientation of the tetrahedra, this again demonstrates that none of the tetrahedra can be restored in the Greek cross twin.

5. Conclusions

The crystallographic orbit analysis explains both the frequent twinning in staurolite and the different occurrence frequency of the two types of twins. The complete quasi-restoration of the substructure built on oxygen atoms is the structural reason behind the high frequency of twinning. The significant difference in the restoration of the cations (19% *versus* 45%: Table 7) explains why the Saint Andrews twin is more frequent than the Greek cross twin. The ‘staurolite enigma’ is therefore finally solved.

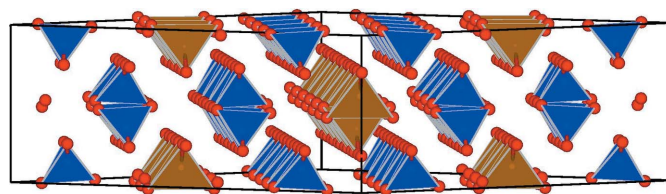


Figure 3
Twin cell of the Greek cross twin viewed with the twin axis as the vertical axis. The tetrahedra are arranged in layers perpendicular to the twin axis, within each layer all tetrahedra have the same orientation.

² Supporting information for this paper is available from the IUCr electronic archives (Reference: PC5038).

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