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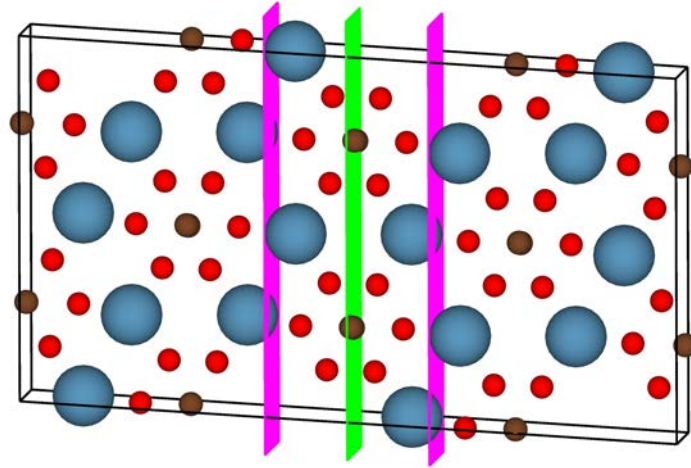
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# Group-theoretical investigation



**of the structural basis for the formation**



**of twinned crystals**

Mohamed Amine Marzouki



# Group-theoretical investigation of the structural basis for the formation of twinned crystals.

Proefschrift

ter verkrijging van de graad van doctor

aan de Radboud Universiteit Nijmegen

op gezag van de rector magnificus prof. dr. Th.L.M. Engelen,

volgens besluit van het college van decanen

en ter verkrijging van de graad van doctor in de Natuurwetenschappen

aan de Université de Lorraine

op gezag van de president professor P. Mutzenhardt

in het openbaar te verdedigen op woensdag 9 september 2015

om 12.30 uur precies

door

Mohamed Amine Marzouki

geboren op 6 juli 1985

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# Group-theoretical investigation of the structural basis for the formation of twinned crystals.

Doctoral Thesis

to obtain the degree of doctor

from Radboud University Nijmegen

on the authority of the Rector Magnificus prof. dr. Th.L.M. Engelen,

according to the decision of the Council of Deans

and to obtain the degree of doctor in Physics from Université de Lorraine

on the authority of the President professor P. Mutzenhardt

to be defended in public on Wednesday, September 9, 2015

at 12.30 hours

by

Mohamed Amine Marzouki

Born on July 6, 1985

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# ACKNOWLEDGEMENTS

First, I would like to thank my two PhD advisors and mentors, Professor Massimo NESPOLO and Dr. Bernd SOUVIGNIER, for supporting me during these past four years. You have provided me with a tremendous amount of advices and you have significantly shaped my work. I would like to thank you for encouraging me, for trusting me and for paving my way as a research scientist. Your advice, time, and guidance on both scientific as well as career level have been priceless. You have taught me how good and sound mathematical modeling must be done. And for all these reasons, I'm deeply grateful.

I would like also to thank all the members of my PhD committee, Professors Annalisa FASOLINO, Mois AROYO, and Denis GRATIAS for accepting to evaluate my work.

I will forever be thankful to my fellow colleagues and researchers in the two laboratories IMAPP-Nijmegen, The Netherlands & CRM2-Nancy. Especially, Prof. Dominik SCHANIEL, Dr. Christian JELSCH, Prof. Benoit GUILLOT, Dr. Sebastien LESEGUE, Dr. Dario ROCCA, they have been enormously helpful in providing advices and useful comments in many occasions during the writing process of my thesis. Also, my warm thanks to my brother Dr. Yousri MARZOUKI for his tutoring advices and to my friend Dr. Laurent BATTISTI for his nudges at the software & computing level.

All my thanks, also, go to many of my professors from my previous years of High school, Bachelor and Master degree. It is obvious that without their priceless help and support I would not be where I'm today.

I would like to thank the administration personnel of my two universities, Radboud University Nijmegen, The Netherlands & Université de Lorraine, Nancy, France for their understanding, patience and for facilitating the administration procedures.

A special thank to my Graduate School “Ecole doctorale SESAMES” for the financial support for my PhD.

Finally, I express my most sincere thanks to my family and to my friends for their unconditional support, encouragement and love. Your warm thoughts have been my



guide during the whole process. I hope that you'll find in these few words the genuine expression of my deep gratitude.

# Abstract

This thesis addresses the structural rationale behind the formation of growth twins, with the purpose of opening a route to the future development of synthesis protocols to reduce the occurrence frequency of twinning. The reason for this effort is that twinning affects negatively the physico-chemical properties of materials and biomaterials of technological interests and reduces the quality of the experimental data on which the structural investigation is based.

While on the one hand the reasons for twinning in transformation and mechanical twins are well understood, in the case of growth twins twinning is still seen as an accident linked to aleatory conditions where kinetics, rather than thermodynamics, plays a principal role.

A general approach known as the reticular theory of twinning has been developed since the XIX century, based on the existence of a sublattice common to the twinned crystals, which gives the minimal necessary conditions for the occurrence of a twin. This approach is, however, insufficient to discriminate between twins with the same degree of lattice overlap but showing a fairly different occurrence frequency. A structural approach, based on the analysis of the eigensymmetry of the crystallographic orbits building a crystal structure was proposed more than half a century ago (Donnay and Curien, 1960) but remained at an embryonic state, despite some recent revival (Nespolo and Ferraris, 2009). Also, the idea that a slice common to the twinned individuals may contain an operation mapping these individuals was proposed (Holser, 1958) but never brought to a full development. In this thesis, we present a full development of these ideas and show that the structurally necessary conditions for the formation of a growth twin can be described on the basis of the eigensymmetry of the crystallographic orbits and on the sectional layer group giving the symmetry of the common slice.

The detailed analysis of three well-know twins demonstrates a clear correlation between the degree of structural restoration by the twin operation and the occurrence frequency of the twins. The analysis of a negative example, i.e. of a hypothetical twin which one would expect on the basis of the reticular theory but has never been observed, strengthens the evidence of this correlation, because of the low structural

restoration one would observe in that twin.

We expect that the generalisation of the approach presented in this thesis through a semi-automatic procedure will provide crystal growers with a powerful tool to modulate the occurrence frequency of twinning through a modification of the crystal morphologies towards a larger exposure and development of crystal faces which represent an unfavorable interface for twinning.

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# Symbols

$(\mathbf{a}, \mathbf{b}, \mathbf{c})$ : basis vectors of the unit cell;

$a, b, c$ : length of basis vectors;

$\mathcal{P}$ : point group of the individual crystal;

$\mathcal{G}$ : space group of the individual,  $\mathcal{G} = \{g_1, g_2, \dots\}$ , with  $g_1 = 1$  the identity element of  $\mathcal{G}$ ;

$\mathcal{H}$ : space group associated with the structure of the twinned crystal;

$\mathbf{r}_i = |\mathbf{r}_i\rangle = \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}$  : ket-vector, coordinates of the  $i$ -th crystallographically independent atom  $A_i$ ;

$\langle \mathbf{r}_i | = (x_i, y_i, z_i)$ : bra-vector of  $\mathbf{r}_i$ ;

$O_i$ : orbit of  $\mathbf{r}_i$  under  $\mathcal{G}$ ,  $O_i = \{\mathbf{r}_i, g_2\mathbf{r}_i, \dots\} = \{\mathbf{r}_i^1, \mathbf{r}_i^2, \dots\}$  with  $\mathbf{r}_i^k = g_k\mathbf{r}_i$  for  $g_k \in \mathcal{G}$ ;

$O_{ij}$ : splitting of the orbit  $O_i$  under the action of a subgroup of  $\mathcal{G}$ ;

$m(O_i)$ : multiplicity of the orbit  $O_i$ , defined as the number of equivalent points in the conventional unit cell of  $\mathcal{G}$ ;

$\mathcal{S}_i$ : site-symmetry group of  $\mathbf{r}_i$ ;

$\mathcal{E}(O_i)$ : eigensymmetry of the orbit  $O_i$ ;

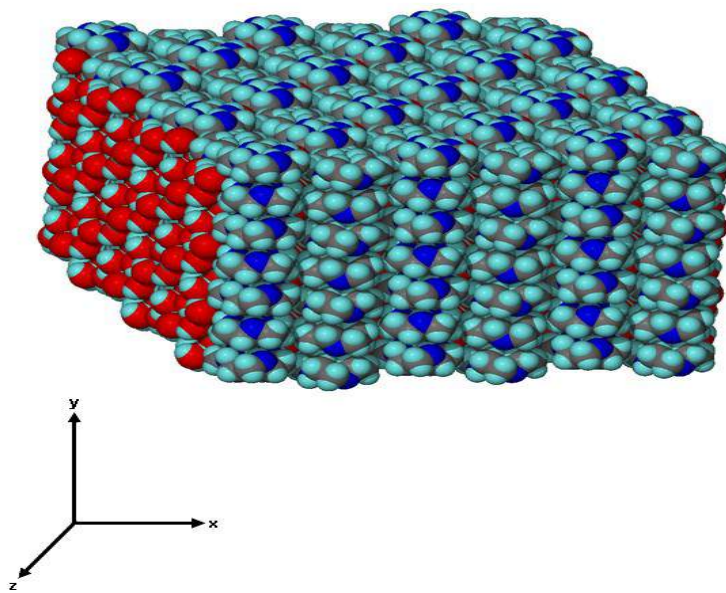
$(\mathbf{P}, \mathbf{p})$ : matrix-column pair representing a change of coordinate system; composed of a  $3 \times 3$  matrix  $\mathbf{P}$  and a  $3 \times 1$  column  $\mathbf{p}$ ;

$\mathcal{T}$ : matrix representation of the twin operation in the basis of the twin.

# Chapter I. Introduction

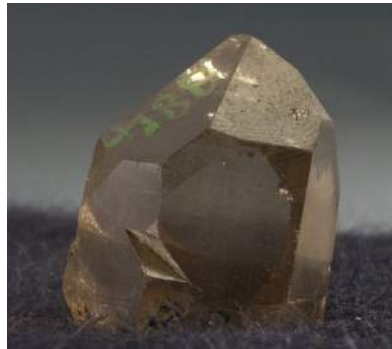
The subject of this thesis is the investigation of twinned crystals (twins) based on the symmetry properties of these crystals and of their individual components.

Abstracting from static and dynamic defects, a crystal is a solid material with a homogeneous ordered distribution of its microscopic structure, such as atoms, molecules or ions. The crystal structure forms an atomic pattern that is repeated in three independent directions of physical space (Figure 1.1). In the mathematical idealisation, the pattern is regarded as extending infinitely in every direction. This assumption is reasonable, since the ratio between the size of the crystal (usually in the order of at least  $10^{-3}$  m) and the microscopic periodicity (typically some  $10^{-10}$  m) is several orders of magnitude.



**Figure 1.1:** Atom packing with translations in three independent directions of space.

From a morphological point of view, if the sample is euhedral, i.e. with well-developed faces, macroscopic single (untwinned) crystals are usually recognised by their geometrical shape, consisting of flat faces with sharp angles (Figure 1.2). In contrast, the presence of re-entrant angles is a distinctive feature of twinned crystals, whereas their absence cannot be taken as a conclusive argument for the absence of twinning.



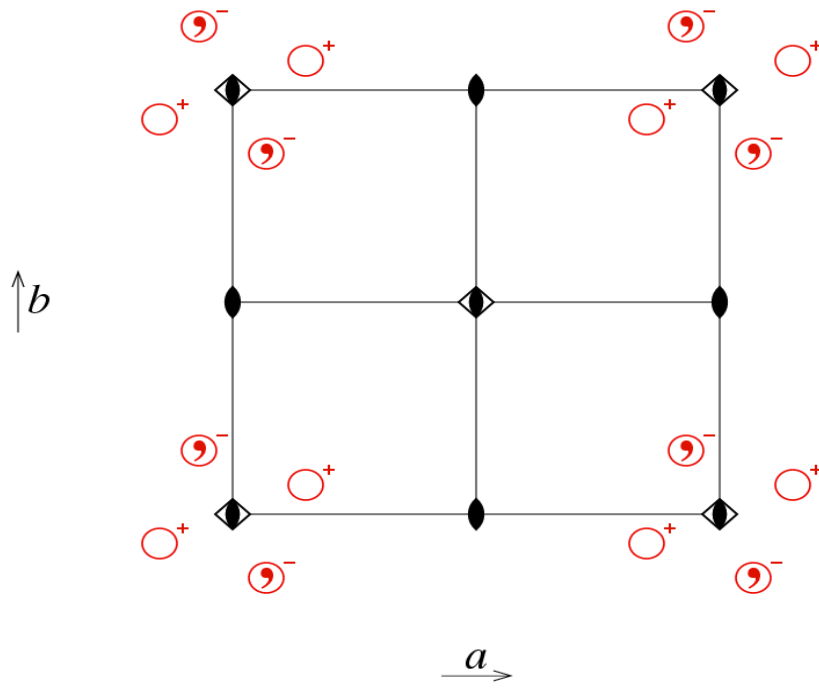
**Figure 1.2:** Image of a quartz single crystal.

The morphological study of crystals goes back to the early description by Nicolaus Steno, 1669. In his book "*De solido intra solidum naturaliter contento*", Steno states that **“the angles between corresponding faces on different crystals of a substance are constant”**. For example, the interfacial angles of quartz crystals (Figure 1.2) are constant, no matter what the shape and size of the crystal and to what extent the faces are developed. This discovery drew the attention to the significance of crystal forms (the sets of symmetry-equivalent faces) and led to the early development of the science of crystallography. Later, the configuration of the vectors normal to the faces gave rise to the first step in the description of crystals by their symmetry properties, namely by the point groups which are the symmetry groups of the face normals. The 32 possible types of point groups were enumerated by Hessel in 1830 (Heesch, H. 1929).

Although for a long time the macroscopic shape and the microscopic three-dimensional periodicity served as the natural characterisation of a crystal, more recent developments, in particular the discovery of quasicrystals in the 1980's (rewarded by the Nobel Prize for Chemistry in 2011), showed that these features are not sufficient to define a crystal. The modern definition of a crystal, officially adopted by the International Union of Crystallography (IUCr) after extensive discussions between leading experts, is based on its nanoscopic atomic arrangement which is observed in diffraction experiments. According to this definition, a material is called a crystal if it has essentially a sharp diffraction pattern. The word essentially means that most of the intensity of the diffraction is concentrated in relatively sharp Bragg peaks, besides the always present diffuse scattering. The positions of the diffraction peaks can be indexed by  $n \geq 3$  integers with respect to a system of  $n$  rationally independent vectors in 3-dimensional space. The conventional crystals are covered as the special case for which  $n = 3$ , the quasicrystals, as well as co-crystals and incommensurately modulated crystal structures, require  $n > 3$ .

In this thesis, we restrict ourselves to conventional crystals. These are classified according to their symmetry properties. From the periodic arrangement of the atoms in space on the one hand, and the discreteness of the structure on the other hand, one concludes that a crystal structure (crystal pattern) is invariant under the translations by vectors from a lattice, i.e. by all integral linear combinations of three linearly independent vectors. The space group attributed to a crystal structure is the group of isometries of  $\mathbb{R}^n$  (i.e. mappings of  $\mathbb{R}^n$  preserving distances and angles) which leaves the crystal pattern as a whole invariant. Apart from translations, the space group may contain further operations like rotations, screw rotations, reflections, glide reflections, inversions and rotoinversions. An example of a space group (relevant for the melilite twin) is displayed in Figure 1.3. Neglecting the translations, the additional operations correspond to the point group describing the macroscopic symmetry of the crystal.





**Figure 1.3:** Space-group diagram of space group  $P\bar{4}$ , No. 81 ITA: View along the  $c$ -axis of a crystal structure, where the small red circles are symmetrically equivalent points of the general position. The + signs indicate that these atoms are located above the plane generated by the vectors (**a**,**b**).

◈: fourfold rotoinversion      •: twofold rotation

The symmetry description of a crystal is the most relevant for this thesis. However, we have applied the symmetry tools not to the investigation of single crystals, but rather to the analysis of heterogeneous edifices built by two or more crystals related by a mapping which corresponds to a possible crystallographic symmetry operation. Mostly, during the growth of a crystal, or if the crystal is subjected to a phase transition under a change of temperature and/or pressure, or to a mechanical action, two or more inter- or over-grown crystals may be formed in a (quasi-)symmetrical shape. These (quasi-)symmetrical inter- or over-growths of crystals are called twinned crystals (twins for short). A classical example of a growth twin is the Japan twin in quartz shown in Figure 1.4.

Having been the subject of research for many eminent crystallographers, the study of twins can be considered as a specialised branch inside crystallography which has been called “geminography” by J. D. H. Donnay (Nespolo and Ferraris, 2005). The development of X-ray diffraction equipments and crystallographic software packages gives the possibility to analyse simple cases of twinning and obtain structural data from twinned crystals almost automatically. However, more complex examples still pose a challenge for the routine investigation.



**Figure 1.4:** Japan twin in quartz.

Our interest to study twins is motivated by two important reasons:

- the rationale for the occurrence of growth twins;
- the effects of twinning on the crystal properties relevant for applied science and technology.

### **1. The problem of twin occurrence**

The heterogeneity of a twin structure presents an important difference to the homogeneity of a single crystal. Moreover, this heterogeneity (twinning) can be produced in two ways:

Naturally: Twins can occur as minerals in different locations. Their occurrence

may be frequent or not. However, based only on the observation, neither the twin's occurrence nor the frequency of its occurrence can always be easily explained. For example, the frequency of the staurolite twins and their crystal structures were regarded as an important issue for mineralogical scientists (Marzouki *et al.*, 2014a). Twins can occur, naturally, by sharing a surface (contact twins) or sharing a volume (penetration twins).

Artificially: Certain compounds have a high tendency to form twins, but it is usually desirable to avoid twinning (see below). Understanding the conditions that favour twinning is therefore a task of fundamental importance.

## **2. The effects of twinning on the properties of a crystal**

Individual crystals in a twin are separated by an interface called composition surface which represents a discontinuity for at least a sub-structure. The heterogeneous character of a twin represents an obstacle to the structural investigation and the technological applications of the material under investigation. In particular:

- The potential technological applications are hindered by the presence of twinning (*e.g.* the piezoelectric effect is reduced or annihilated).
- The presence of twinning reduces the amount of details that can be obtained from a structural study by diffraction experiments, especially for samples with large unit cells (as, for example, for macromolecules) for which the resolution that can be achieved is already limited by the size of the unit cell.

Material scientists growing crystals with targeted properties aim at avoiding the formation of twins. Understanding the conditions under which they are likely to form is an important prerequisite to develop a synthesis protocol capable of reducing, if not eliminating, the occurrence of twins.

Furthermore, as already remarked, even nowadays twinned crystals still form an

obstacle in the automatic solution and refinement of crystal structures.

In this thesis, we take a novel approach to investigate the possible structural basis for the formation of twins. As of today, the only systematic approach to twinning has been through the empirical rules of twinning enunciated by the reticular theory of twinning (“French school”: Friedel, 1904).

From the reticular point of view, twinning can occur when the operation mapping the orientation of the individuals overlaps a substantial amount of the nodes of the individual lattices (restored nodes). As a heuristic rule, at least one sixth of the lattice nodes should be restored in order to make the formation of the twin likely (Friedelian twin). Although the reticular theory ignores the actual contents of the unit cell, a high restoration of lattice nodes indicates the possible existence of a common sub-structure across the interface between separated individuals. The definite criterion, however, is the restoration of the atoms within the structure under a mapping known as the twin operation, which is the object of the structural theory of twinning: its aim is to identify the atomic substructure invariant under the twin operation (restored substructure). The underlying lattice common to both individuals (twin lattice) reduces the analysis to the atoms in a finite volume of the structure. In this thesis, two approaches towards a structural theory of twinning are considered, the *crystallographic orbit approach* and the *layer group approach*.

The crystallographic orbit approach: As its name suggests, the crystallographic orbit approach is based on the analysis of the twin structure via its crystallographic orbits in order to detect the subset of atoms which crosses the interface unperturbed or almost unperturbed. Under the action of the space group  $G$ , each atom in a crystal is repeated in space to form a crystallographic orbit  $O$ , i.e.  $O$  is the set of all atoms obtained from a single atom under the symmetry operations of the space group  $G$ . Each point of a crystallographic orbit defines uniquely a largest subgroup of  $G$  which maps that point onto itself and is called its site-symmetry group (or stabilizer group).

The site-symmetry groups belonging to different points in the same crystallographic orbit are conjugate subgroups of  $G$  and all points  $X$  for which the site-symmetry groups are conjugate subgroups of  $G$  form a single Wyckoff position. Under the action of a subgroup of  $G$ , an orbit  $O$  can be split into suborbits, since positions which are symmetrically equivalent under  $G$  may be no longer equivalent under the subgroup. The common sub-structure across the interface between separated individuals (the composition surface), consists of split suborbits which are invariant under the twin operation  $t$ .

The layer group approach: Due to the periodicity of the twin pattern, it is sufficient to analyse the restoration for a finite part of the structure. In addition, by restricting the structural symmetry analysis to a slice around the composition surface, we can find that such a slice has a symmetry which contains, exactly or approximately, the twin operation.

For a given space group  $G$  of a crystal, the layer group of a section passing through this crystal is the group of symmetries of this section. In particular, the layer group has translational symmetry only in two independent directions. When the composition surface can be considered as a two-dimensional plane and is parallel to the twin plane, the symmetry of the atomic substructure close to this surface can be characterised by a layer group. Looking at the slice containing the twin plane, the part of the common sub-structure across the interface between separated individuals which is close to the interface can be identified as the subset of atoms within this slice which is invariant under the twin operation  $t$ .

This thesis gives – via these two approaches - structural evidence underlying the formation of twins that explains the occurrence and frequency in a number of important examples of twins. Our investigation strategy is based on modern tools provided by contemporary mathematical crystallography. The conclusive conditions

can only be obtained by the pseudo-symmetry analysis of continuous substructures across the interface separating the individuals in a twinned crystal. Such an analysis is still essentially an *a posteriori* study of known twins, but it represents the first step towards a general structural theory of twinning that should allow predicting the structurally necessary conditions explaining the occurrence and frequency of twinned crystals.

## Some examples of twinned crystals

Below, a few important examples of twinned crystals are displayed. The first two, quartz and calcite are very common and form various types of twins. The other three examples are the twins of melilite, staurolite and aragonite which were investigated in the three articles contained in this thesis.

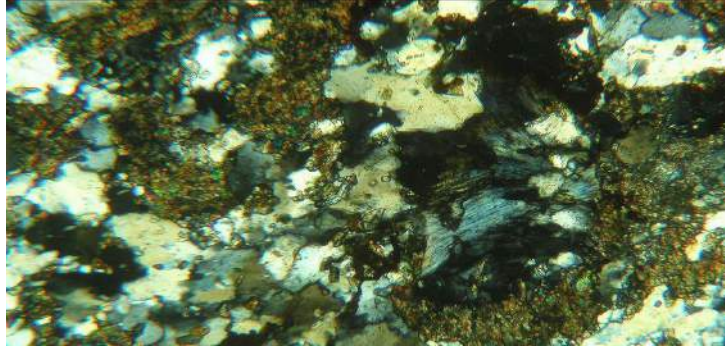
**1) Quartz (Japan Law Twin)** is the most common silicate mineral and the most abundant mineral in the Earth crust. Quartz is found in nearly every geological environment and occurs in practically all but ultramafic rocks.



**2) Calcite (Butterfly Twin)** is a carbonate mineral, the most stable polymorph of calcium carbonate ( $\text{CaCO}_3$ ).



3) **Melilite** is a group of sorosilicate minerals with general formula  $X_2YZ_2O_7$ , it gives reflection twins on (100) and (001). More recently, a further reflection twin, on  $(1\bar{2}0)$ , has been reported by Bindi *et al.* (2003).



4) **Staurolite** gives two rotation twins, which occur with different frequency: the Greek cross twin (lower frequency, with  $90^\circ$  angle) and the Saint Andrews cross twin (higher frequency, with  $60^\circ$  angle). Staurolite has been considered as an enigma because of the frequent twinning and its remarkable pseudosymmetry.



Greek cross.



Saint Andrews cross.



**5) Aragonite** is the high-pressure polymorph of  $\text{CaCO}_3$ , metastable at ambient conditions. It is a reflection twin with frequent twinning on  $\{110\}$ .

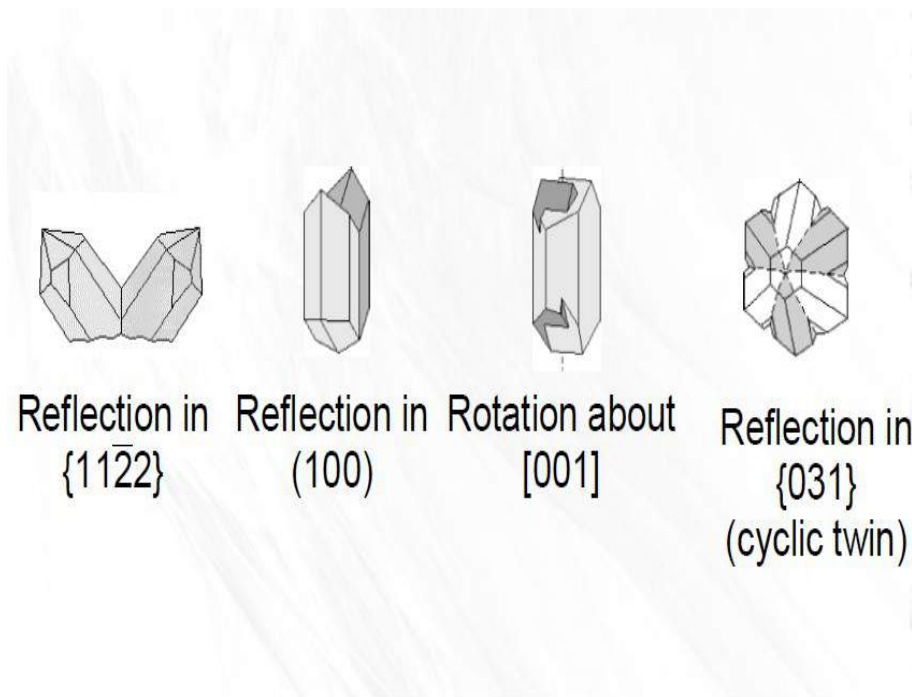


## Chapter II. Description and analysis of twins

### II.1. Basic definitions and classifications of twins

A *twinned crystal* (twin) is a heterogeneous crystalline edifice composed of two or more homogeneous crystals of the same phase with different orientation related by a *twin operation*, i.e. a crystallographic operation mapping the orientation of one individual onto that of the other(s) (Friedel, 1904, 1926, 1933) (Figure 2.1). The atomic structure itself is mapped by a space group operation having the twin operation as its linear part. If we want to emphasize that combining the twin operation with different vector parts gives rise to symmetry operations of different types, we will use the term *restoration operation* for the space group operations. However, it will usually be clear from the context whether a twin operation (mapping the orientation) or a restoration operation (mapping the atom positions) is meant. A *twin element* is the geometric element in direct space (plane, line, centre) about which the twin operation is performed.

The result of a twin operation is an over- or intergrowth of two or more separate crystals sharing a common substructure. This phenomenon is called *crystal twinning*.



**Figure 2.1:** Mapping of individuals in twins. From the left to the right; Japanese Law twin, Swallow Tail twin, Carlsbad Law twin and chrysoberyl cyclic twin (Figures from Stephen A. Nelson webpage at Tulane University: <http://www.tulane.edu/~sanelson/eens211/twinning.htm>).

Several criteria are used to classify twins. Here we give the most common ones.

**Morphology** divides twins in:

- *Contact twins*: separated by a surface;
- *Penetration twins*: sharing a volume;
- *Simple twins*: consisting of two individuals.
- Twins in which the individuals are repeated, subdivided into:
  - *Polysynthetic twins*: where the individuals are repeated in a more or less linear arrangement;
  - *Cyclic twins*: where N individuals are repeated to form a closed edifice where the N-th individual is in contact with the first.

**Dimensionality of the twin lattice**, i.e. the dimension of the subspace in which a common (reasonable) periodicity can be found (Friedel, 1933):

- *Triperiodic twins*, having a common lattice in three dimensions (by far the most common type of twins);
- *Diperiodic twins*, for which the common lattice spans a two-dimensional plane;
- *Monoperiodic twins*, sharing only a lattice row.

According to Mallard's law (Friedel, 1904, 1926) the twin operation is a crystallographic symmetry operation about a direct lattice element. On the basis of **the twin operation**, twins can be divided into three types:

- *Inversion twins*: the symmetry operation can be taken as an inversion;
- *Rotation twins*: the symmetry operation can be taken as a rotation;
- *Reflection twins*: the symmetry operation can be taken as a reflection.

Twins can also be classified from the **genetic viewpoint**, one distinguishes three categories:

- ***Transformation twins***, which form during a phase transition leading to a loss of point symmetry;
- ***Mechanical twins***, which form as the result of a mechanical action (typically, an oriented pressure) on the crystal;
- ***Growth twins***, which form during crystal growth, either at the nucleation stage or by oriented attachment (for a review, see Nespolo and Ferraris, 2004).

For transformation twins, the symmetry relation between the original untwinned crystal and the twin is easily found. The twin operation(s) belong to the group of the parent phase but not to that of the daughter phase. For the two other categories, the symmetry of the twin depends on aleatory factors, like the orientation of the mechanical force or the relative orientation of the individuals during the crystal growth. Therefore, there is no general relation between the symmetry of the untwinned crystal and that of the twin.

The group-subgroup relation gives the number of domain states for transformation twins. This number depends on the mechanism and kinetics of the phase transition.

Based on the atomic mechanism (Buerger, M.J., 1951), Buerger classified phase transitions in two types:

- *reconstructive*: with changes in the pattern of chemical bonds;
- *displacive*: characterised by only small atomic shifts and *order-disorder* of the atomic distribution on given Wyckoff positions<sup>1</sup>.

For details on this classification see Nespolo, 2015.

The heterogeneity of the twinned crystal makes it impossible to provide a space-group description of the twin: there is in fact no structure common to the twinned individuals. However, to the whole twinned edifice a point group can be assigned which describes the symmetry of the twin. Let  $H$  be the point group of the first individual of a twin. For a twin consisting of  $N$  individuals, the point groups  $H_i$ ,  $i = 1 \dots N$  of all the individuals are of the same type (same Hermann-Mauguin symbol) as  $H$ , but they have different orientations in space. The common symmetry  $H^*$  is obtained as the intersection of these groups  $H_i$ , i.e.  $H^* = \bigcap_i H_i$  contains the operations about symmetry elements which are parallel in the  $H_i$  groups. If we assign to each individual a different colour, then the twin operations are *chromatic*, i.e. mappings that permute the colours (identifying the individuals) and the point group describing the symmetry of the twin is a *chromatic point group*,  $K$  (Nespolo, 2004). It is obtained by extending the common point symmetry of the individuals  $H^*$ , in their respective orientations, by the twin operation, in other words:  $K$  is the group generated by  $H^*$  and the twin operation. If  $K$  is decomposed into cosets with respect to  $H^*$ , the single cosets are called *twin laws* (see section II.2) and contain those operations that map a fixed individual to another chosen individual:

$$K = \cup_i t_i H^* = H^* \cup t_1 H^* \cup t_2 H^* \dots \cup t_n H^* \quad (1)$$

---

<sup>1</sup> Müller [8] uses the term *misorder* instead of *disorder* claiming that the phenomenon is not a real disorder but rather “order with faults”.

Let  $K_A$  be the achromatic group isomorphic to  $K$ .  $K_A$  is a supergroup of  $H^*$ ; the different relations between  $K_A$  and  $H$  are:

- If  $H^* = H \Rightarrow K_A \supset H$ .
- When the extension of  $H^*$  by the twin operation  $t$  restores all point group operations which are lost when taking  $H^*$  as intersection of  $H_i \Rightarrow K_A = H$ .
- When  $t$  restores only a subset of the operations of  $H_i$  lost in  $H^* \Rightarrow K_A \subset H$ .
- When  $t$  does not correspond to any of the symmetry operations of  $H$  lost in  $H^* \Rightarrow K_A$  is not directly related to  $H$ .

For the last case, a classical example is that of twins with inclined axes in quartz (Japan, Esterel, Sella, Belowda Beacon, Breithaupt, Wheal Coates, Cornwall, Pierre-Levée, differing in the twin plane and thus the relative inclination of the  $c$  axes; Friedel, 1923), for which  $H = 321$ ,  $H^* = 1$ ,  $K = m'$ ,  $K_A = m$ , the prime indicating the chromatic operation (twin operation).

## II.2. The twinning parameters and the reticular classification

A prerequisite for the formation of a twin is the existence of a common substructure which crosses, more or less unperturbed, the interface physically separating the individuals (Marzouki *et al.*, 2014a). The crystal structure cannot have a symmetry higher than its Bravais lattice, however, it can be the same (holohedral structure) or a lower symmetry (merohedral structure), thus a common lattice or a sublattice is a pre-requisite for the existence of a common substructure. This represents the necessary condition of the reticular theory of twinning developed by the so-called “French school” (Bravais, 1851; Mallard, 1885; Friedel, 1904, 1926). The common (sub-)lattice called the **twin lattice**  $L_T$  (Donnay, 1940) is based on the twin element (twin plane or twin axis) and the lattice element (line or plane) that are mutually (quasi-)perpendicular.  $L_T$  is defined by these two elements, the lattice plane  $(hkl)_T$  and the lattice row  $[uvw]_T$

When the individual lattice  $\mathbf{L}_{\text{ind}}$  or a sublattice of it crosses the composition surface without any perturbation, the lattice plane  $(hkl)_T$  and the lattice row  $[uvw]_T$  are mutually perpendicular and  $\mathbf{L}_T$  coincides precisely with  $\mathbf{L}_{\text{ind}}$  or a sublattice of it. One speaks of Twin Lattice Symmetry or TLS. When  $(hkl)_T$  and  $[uvw]_T$  are quasi-perpendicular, this shows a certain mismatch on the two sides of the composition surface. In this case the common sublattice  $\mathbf{L}_T$  is defined as an idealisation which does not take into account this mismatch and one speaks of Twin Lattice Quasi Symmetry or TLQS (Donnay & Donnay, 1974). In other words, in the TLQS case,  $\mathbf{L}_{\text{ind}}$  or a sublattice of it crosses the composition surface with small perturbation which becomes worse the farther one moves from this surface. As a consequence,  $\mathbf{L}_T$  can be, approximately, defined everywhere with a small change of orientation on the composition surface. The degree of pseudo-symmetry corresponds to the deviation from the perpendicularity condition and is measured by the angle  $\omega$  called the *obliquity*: concretely  $\omega$  is the angle between the direction perpendicular to the twin plane and the rational direction closest to it (or, for rotation twins, between the plane perpendicular to the twin axis and the rational plane closest to it). The obliquity is the first parameter of twinning, the second being the twin index, see below.

A zero-obliquity TLQS may occur for manifold twins, i.e. twins in which the twin operation is of order higher than two. For example, in a pseudo-tetragonal twin lattice  $\mathbf{L}_T$  with cell parameters  $\mathbf{a}$  and  $\mathbf{b}$  numerically close to each other where the twin operation is a fourfold rotation along  $\mathbf{c}$ , the twin axis is exactly perpendicular to the (001) plane, yet the overlap of the lattices of the two individuals is only approximate. In a case like this, a linear, rather than angular, measure of the mismatch is necessary, like the **twin misfit**  $\delta$  defined as the distance between the first nodes along the two shortest directions in the plane of  $\mathbf{L}_T$  perpendicular to the twin axis that are quasi-restored by the twin operation (Nespolo & Ferraris, 2007; Nespolo, 2015). The twin misfit  $\delta$  is computed as:

$$\delta = \langle \Delta u \Delta v \Delta w | \mathbf{G} | \Delta u \Delta v \Delta w \rangle^{1/2}$$

where  $\Delta u \Delta v \Delta w$  is the difference between the  $uvw$  indices in  $\mathbf{L}_T$  of the two nodes quasi-restored by the twin operation (for details of the calculation, see Nespolo & Ferraris, 2007). This twin misfit defines the degree of lattice misorientation for the zero-obliquity TLQS, (for details, see Nespolo, 2015).

### Twin laws and twin operations

In the literature, some confusion exists when the relation between the orientation of the individuals in a twin has to be specified. As shown by Eq. (1), the (left) coset decomposition of  $K$  with respect to  $H^*$  is the union of a number of cosets each of which corresponds to a *twin law*. The length of a coset is equal to  $|H^*|$ , the order of  $H^*$ . Any operation in a coset can be chosen as coset representative and any of these can be equally taken as *twin operation*. This twin operation represents a mapping between the individuals in a twin but not a symmetry operation for the individuals in the twin. For the case of TLS, the twin operation is geometrically equivalent to any other operation in the same coset in the sense that all operations in the coset map the orientation of the individual in the same way.

In the case of non-zero obliquity twins (TLQS), the overlap of the individual lattices only approximately forms the twin lattice  $\mathbf{L}_T$ . Thus, the geometric equivalence of the twin operations is no longer precise but only approximate within the same twin law.

### The calculation of the obliquity

The concept of obliquity was introduced by Friedel in 1920 in order to measure the overlap of the individual lattices in the case of twinning. Let  $(hkl)$  be the Miller indices of the twin plane and  $[uvw]$  the indices of the rational direction close to the normal of the twin plane. For rotation twins,  $[uvw]$  becomes the twin axis and  $(hkl)$  the Miller indices of the lattice plane quasi-perpendicular to it. The obliquity is the



angle between  $[uvw]$  and  $[hkl]^*$  (the latter expressing the normal to  $(hkl)$  as a direction in reciprocal space) and is computed through the following equation (Grimmer & Nespolo, 2006; Nespolo, 2015):

$$\omega = \cos^{-1} \left( \frac{|hu + kv + lw|}{\langle hkl | G^* | hkl \rangle^{1/2} \langle uvw | G | uvw \rangle^{1/2}} \right) \quad (2)$$

where  $\mathbf{G}$  and  $\mathbf{G}^*$  are the direct and reciprocal metric tensors.

If  $\omega = 0$ ,  $[uvw]$  and  $[hkl]^*$  coincide and this means that the expression of  $[hkl]^*$  in direct space is rational. If this condition does not depend on the external conditions like temperature or pressure, one speaks of intrinsic-TLS or *i*-TLS. Conversely, one speaks of extrinsic-TLS or *e*-TLS when this perpendicularity is an accidental feature of the crystal realised only in a certain interval of temperature and pressure (cf. Nespolo & Ferraris, 2006)).

If  $\omega \neq 0$ , the direction  $[uvw]$  quasi-perpendicular to  $(hkl)$  is irrational. To compute the obliquity one has to get the irrational expression of  $[hkl]^*$  in direct space and then find a rational direction close to it. The expression of  $[hkl]^*$  in direct space is obtained by imposing (see Nespolo, 2015):

$h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$  or, in vectorial expression:  $\langle hkl | \mathbf{a}^* \mathbf{b}^* \mathbf{c}^* \rangle = \langle \mathbf{abc} | uvw \rangle$  where  $u$ ,  $v$  and  $w$  are not restricted to integer values.

A straightforward computation (see Nespolo, 2015) using the metric tensor  $\mathbf{G}$  and its inverse, the reciprocal metric tensor  $\mathbf{G}^*$ , yields the solution:

$$(hkl)\mathbf{G}^* = (uvw) \quad (3)$$

The closest integers to the generally irrational values obtained by Eq. (3) give the

lattice direction quasi-perpendicular to the twin plane  $(hkl)$ .

In case of rotation twins, an analogous derivation gives:

$$(uvw)\mathbf{G} = (hkl) \quad (3')$$

and the closest integers to the generally irrational values obtained by Eq. (3') give the lattice plane quasi-perpendicular to the twin axis  $[uvw]$ .

For the Twin Lattice Symmetry (TLS), the twin lattice is defined as the intersection of the lattices of the individuals in their respective orientations:

$$\mathbf{L}_T = \cap_i \mathbf{L}_{ind}(i), \text{ where } \mathbf{L}_{ind}(i) \text{ is the lattice of the } i\text{-th individual.}$$

Let  $\mathbf{L}_{ind}(1)$  be a fixed individual taken as reference, the orientation of each  $\mathbf{L}_{ind}(i)$  is obtained from the multiplication of  $\mathbf{L}_{ind}(1)$  by the twin operation  $t_i$  which is the  $i$ -fold composition of the twin operation  $t$  with itself (Marzouki *et al.*, 2014a):

$$\mathbf{L}_{ind}(i) = t_i \mathbf{L}_{ind}(1)$$

so that  $\mathbf{L}_T$  becomes:

$$\mathbf{L}_T = \cap_i t_i \mathbf{L}_{ind}(1)$$

The inverse of the fraction of lattice nodes restored by the twin operation (nodes of  $\mathbf{L}_{ind}(i)$  belonging to  $\mathbf{L}_T$ ) is called the **twin index  $n$** . It corresponds to the ratio between the volumes of the primitive cells of the twin and the individual (Catti & Ferraris, 1976; Nespolo and Ferraris, 2006)

$$n = V(L_T)/V(L_{ind}).$$

The twin index  $n$  represents the second twinning parameter.

### The calculation of the twin index

Let  $(hkl)$  and  $[uvw]$  be the lattice plane and lattice row defining the cell of the twin lattice, and let us define the quantity  $X = |hu + kv + lw|$ . In the case of a primitive cell,  $X$  gives the number of lattice planes of the  $(hkl)$  family between successive lattice nodes along  $[uvw]$ . In this case, the twin index is given by  $n = X$  or  $n = X/2$  depending on  $X$  being odd or even. In the general case of a possibly centred cell, the twin index is of the form

$$n = X/f$$

where  $f$  depends on the centring type and on the parities of  $X$ ,  $h$ ,  $k$ ,  $l$ ,  $u$ ,  $v$  and  $w$  (see Nespolo & Ferraris, 2007 for the precise computations involved).

In the case of manifold twins, the twin operation is a rotation of higher order about  $[uvw]$  and in general the rotational symmetry of the two-dimensional unit cell in the  $(hkl)$  plane normal to  $[uvw]$  does no longer coincide with that of the twin operation. The above reasoning has to be generalised because for a plane of the family  $(hkl)$  no longer all lattice nodes are restored and because the number of lattice planes of the  $(hkl)$  family between two neighbouring nodes along the  $[uvw]$  direction having non-zero restoration is no longer restricted to 1 or 2. Let  $\xi$  be the number of planes (out of  $N$ ) that are partially restored by the twin operation (the other  $N - \xi$  being not restored at all). If  $\Xi$  is the reciprocal of the relative amount of restored lattice nodes for a plane of the  $(hkl)$  family that is partially restored by the twin operation, the twin index is  $n = N\Xi / \xi$  (for a detailed derivation, see Nespolo & Ferraris, 2007 and Nespolo, 2015).

From the reticular point of view, another important classification of twins distinguishes four categories:

**$n = 1$ :** Twinning by *merohedry*, for which  $H^* = H$  and  $K_A$  is a supergroup of  $H$ . It is subdivided into:

- twinning by *syngonic merohedry*, when the twin operation belongs to the same crystal family as the individual; it is further subdivided into class I when the twin operation can be taken as an inversion, and class IIA when it cannot;
- twinning by *metric merohedry*, or class IIB, when the twin operation belongs to a higher crystal family (this happens in presence of metric specialisations, as for example when an orthorhombic crystal has accidentally  $\mathbf{a} = \mathbf{b}$ ).

**$n > 1$ :**

- twinning by *reticular merohedry*, when  $K_A$  is not isomorphic to  $H$ ;
- twinning by *reticular polyholohedry*, when  $K_A$  is of the same type as  $H$ .

Likewise, for TLQS, the same classification scheme leads, respectively, to twinning by pseudo-merohedry, reticular pseudo-merohedry and reticular pseudo-polyholohedry.

### **II.3. Friedelian and hybrid twins**

The formation of a twin requires the presence of a common substructure across the composition surface. In other words, a subset of atoms of the crystal structure should be able to cross the composition surface more or less undisturbed (Marzouki *et al.*, 2014a). Because the lattice represents the periodicity of the structure, the overlap of a reasonable amount of lattice nodes of the individuals in  $\mathbf{L}_T$  with a limited deviation from perfect restoration is a necessary condition for the existence of this common substructure. As a consequence, the occurrence frequency of twinning depends on the twin index and the obliquity, which precisely measure the degree of lattice

restoration. Friedel gave as empirical limits for the occurrence of twins  $n \leq 6$  and  $\omega \leq 6$ . Twins falling within these limits are called *Friedelian* twins. Nevertheless some twins with higher index are known that violate the empirical limits: they are called non-Friedelian twins (Nespolo and Ferraris, 2005).

The classical reticular theory cannot explain the occurrence of the non-Friedelian twins and their presence represents an apparent contradiction to the general conclusion that a high degree of lattice restoration is a necessary condition for a twin to form. However, in most cases these twins contain, within the empirical limit on the obliquity, two or more sublattices based on the identified twin element. The classical reticular theory considers only one quasi-restored sublattice, whereas the consideration of multiple sublattices is necessary to obtain a good estimation of the degree of quasi-restoration. When all the concurrent sublattices are taken into account, the necessary conditions are no longer contradicted. The interpretation of the occurrence of this kind of twins, which are called *hybrid twins*, is done within the hybrid theory of twinning (Nespolo and Ferraris, 2005). This theory represents an extension of the reticular theory and measures the lattice quasi-restoration in terms of a twin index  $n_E$  (Nespolo, M. and Ferraris, G., 2006), called the *effective twin index*, which corresponds to the ratio of the total number of nodes inside  $\mathbf{L}_T$  and the number of nodes inside  $\mathbf{L}_T$  belonging to any of the sub-lattices  $\mathbf{L}_j$  (the theory of hybrid twins is developed in detail in Nespolo and Ferraris, 2005; 2006). In the hybrid theory, twins can be classified into four categories (for more details, see Nespolo and Ferraris, 2009):

1. **Friedelian non-hybrid twins**: only one sublattice exists, the twin index and twin obliquity are within the empirical limits  $n \leq 6$  and  $\omega \leq 6$ ;
2. **Friedelian hybrid twins**: two or more concurrent sublattices exist, which give an effective twin index lower than the classical twin index, the latter being nevertheless within the empirical limit of  $n \leq 6$ ;
3. **Non-Friedelian hybrid twins**: more than one concurrent sublattices exist,

which give an effective twin index  $n_E \leq 6$ , whereas the classical twin index is outside the empirical limit of 6;

4. **Non-Friedelian non-hybrid twins:** only one sublattice (the twin lattice) exists, which gives a twin index outside the empirical limit of 6.

The hybrid theory explains the occurrence of twins belonging to the first three categories. The few examples in the category No. 4 cannot be explained even by the hybrid theory but the possibility of a wrong choice of the twin element has to be considered (reflection twins in place of rotation twins or vice versa). This indeed resolves the apparent contradiction of a higher frequency of twins with higher index than twins with a lower index observed in some cases like the staurolite twins. The Saint Andrews cross twin of staurolite, with index  $n = 12$ , is more frequent than the Greek cross twin with index  $n = 6$  (Nespolo and Ferraris, 2007). These twins are often reported as reflection twins on (031) and (231), respectively, but experimental studies (Hurst, et al., 1956) have shown that this interpretation is incorrect and that they actually are rotation twins. For the Saint Andrews cross twin ( $n = 12$ ), the correct choice of the twin element as a line shows the existence of two lattice planes quasi-perpendicular to it and correspondingly two sublattices are quasi-restored by the twin operation. This gives an effective index  $n_E = 6.0$  and as a consequence the Saint Andrews twin is brought back into the Friedelian limits. The occurrence frequency no longer contradicts the necessary condition of a good lattice restoration (Nespolo and Ferraris, 2009).

#### **II.4. *Towards a structural theory of twinning***

The reticular theory of twinning can only provide partial prerequisites for the formation of twins, which are governed by the structure. More conclusive conditions can only be obtained via an analysis of the atomic contents of the unit cells. Under the action of the space group  $G$  of a crystal, each atom in the crystal is repeated in space to form a crystallographic orbit  $O$ , i.e.  $O$  is the set of all atoms obtained from a

single atom under the symmetry operations of the space group  $G$ . The eigensymmetry  $\mathcal{E}(O)$  of the orbit may be a supergroup of  $G$  or coincide with it. Accordingly, crystallographic orbits are classified into three types depending on the relation between  $G$  and  $\mathcal{E}$ :

*Characteristic orbit:*  $G = \mathcal{E}$ .

*Non-characteristic orbit:*  $G < \mathcal{E}$  but  $T_G = T_{\mathcal{E}}$ .

*Extraordinary orbit:*  $T_G < T_{\mathcal{E}}$ , a special case of a non-characteristic orbit defining a superlattice (smaller unit cell).

Here,  $T_{\mathcal{E}}$  and  $T_G$  are the translation subgroups of  $\mathcal{E}$  and  $G$ , respectively. When  $G < \mathcal{E}$ , an operation  $t$  belonging to  $\mathcal{E}$  but not to  $G$  may map the orientation of crystal 1 onto that of crystal 2 while preserving  $O$  and may thus serve as twin operation which fixes the orbit  $O$  as a common substructure. As we will see, the symmetry analysis will mainly be applied to orbits under a particular subgroup  $\mathcal{H}$  of  $G$ , namely the largest subgroup of  $G$  compatible with the twin lattice  $L_T$ . With respect to the twin lattice, the continuous substructure across the interface is then given by the split orbits  $O_{ij}$  or the union of them: it is this substructure which is restored by the twin operation  $t$ :

- a split orbit  $O_{ij}$  (obtained under the action of  $\mathcal{H}$ ) is restored by the twin operation  $t$  if and only if its eigensymmetry  $\mathcal{E}(O_{ij})$  contains  $t$ ;
- the union  $\cup_{ij} O_{ij}$  is restored by  $t$  if and only if its eigensymmetry  $\mathcal{E}(\cup_{ij} O_{ij})$  contains  $t$ .

For twins in which the composition surface is planar and parallel to the twin plane or, for rotation twins, to the plane (quasi-)perpendicular to the twin axis, one can obtain additional information by restricting the symmetry analysis locally, information which is not independent but complements the evidence derived from the restoration of crystallographic orbits. Let  $K$  be a slice through the crystal structure taken around the composition plane of the twin and let  $\mathcal{L}$  be the symmetry group of  $K$  (layer

group). The two individual crystals have space groups  $G_1$  and  $G_2$  (of the same type but with different orientation) and induce layer groups  $\mathcal{L}_1$  and  $\mathcal{L}_2$  of the slice  $K$ , the intersection of which is included in  $\mathcal{L}$ , i.e.  $\mathcal{L}_1 \cap \mathcal{L}_2 \subset \mathcal{L}$ . If  $\mathcal{L}$  contains any operation that maps the orientation of  $G_1$  onto that of  $G_2$ , this operation can explain the formation of the twin. In order to find the twin operation as an element of a layer group, it may be necessary to exclude some atoms from the slice which are not restored by the twin operation. This is analogous to the fact that not all crystallographic orbits under  $G$  are invariant under the twin operation, but that only some of the split orbits under  $\mathcal{H}$  are restored.

It is worthwhile to note that the two approaches just sketched have useful interrelations. On the one hand, having a crystallographic orbit (or split orbit) which is restored by the twin operation, restricting it to the slice around the composition plane yields a substructure within the slice which is invariant under the twin operation (note that the twin operation fixes the composition plane). On the other hand, finding the twin operation as an element of a layer group shows which (split) orbits are related by the twin operation by identifying to which orbits the atoms in the slice belong.

## Crystallographic orbit approach

The formation of a twin requires a structural continuity through the composition interface. Such a structural continuity can be realised by a substructure which is invariant under the twin operation  $t$ . To find such an invariant substructure, one may apply three different types of pseudo-symmetry analysis with respect to crystallographic orbits:

- orbits under the full space group  $G$  of the individual ( $G$ -description);
- orbits under the translation group  $T_T$  of the twin lattice ( $T$ -description);
- orbits under the intersection  $\mathcal{H}$  of the space groups of the individuals ( $\mathcal{H}$ -

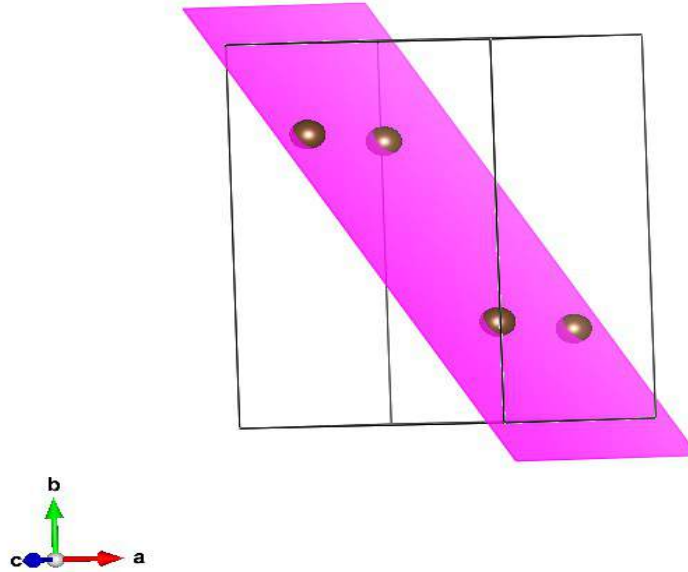


description).

**Crystallographic orbit approach under  $G$  ( $G$ -description)**: The symmetry of a crystal structure is described by a space group  $G$  and the atomic positions and the symmetry operations are typically given with respect to a conventional basis of the individual crystal. However, the description of the twin operation with respect to this basis is usually complex because, with the exception of twinning by (pseudo-)merohedry, the twin element is not aligned with the symmetry directions of the individual. It is clear that not all orbits  $O_i$  under  $G$  can be fully restored by the twin operation  $t$ , otherwise  $t$  would belong to  $G$  and the crystal would in fact be a single crystal and not a twinned crystal. For the full orbits under  $G$ , we find the following two cases of quasi-restoration:

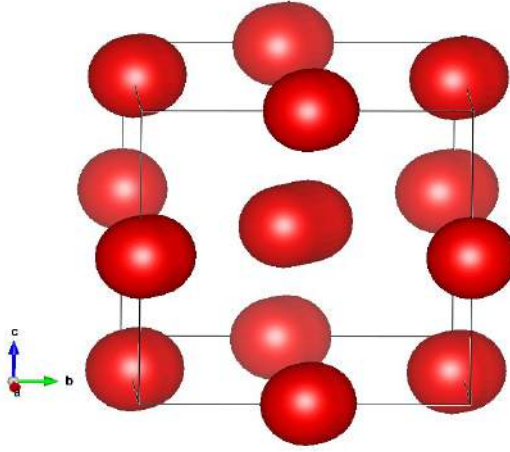
1. An orbit  $O_i$  is quasi-restored by  $t$ , i.e. the twin operation  $t$  maps each atom of  $O_i$  to a position close to an atom belonging to  $O_i$ .
2. A union of orbits under  $G$  is quasi-restored by  $t$ .

An example for the first case is found in the aragonite twin, the carbon atoms are located on the (011) plane which is the twin plane (Figure 2.2). Thus, the carbon orbit is quasi-restored by the mirror (011), since all the atoms in this orbit are actually fixed by the twin operation.



**Figure 2.2:** The position of the carbon atoms (brown color) on the twin plane (pink plane) (Figures of atomic structures are drawn with VESTA: Momma & Izumi, 2011).

The staurolite twins provide examples for the restoration of a union of orbits. The union of all oxygen orbits is fully restored, although with a small perturbation, in these twins (Figure 2.3), whereas this is not the case for single orbits of oxygen atoms, since the twin operation maps one orbit to parts of several other oxygen orbits. Actually, it has long been known that the structure of staurolite is based on a pseudo-*fcc* packing of 48 oxygen atoms in the unit cell (Náray-Szabó, 1929) and this pseudo-cubic symmetry is confirmed by the symmetry analysis of the union of oxygen orbits. The eigensymmetry of the union of oxygen is  $Fm\bar{3}m$  (No. 225). The latter contains all twin operations which explains the restoration of the oxygen union by these operations for the staurolite twins (Marzouki *et al.*, 2014b).



**Figure 2.3:** Pseudo-cubic symmetry of the oxygen union; the red balls represent the union of the oxygen atoms.

As a consequence, the structural analysis of full orbits under  $\mathcal{G}$  will be unable to identify the substructure invariant under the twin operation in the case that only part of an orbit under  $\mathcal{G}$  is restored.

**Crystallographic orbit approach under  $T_T$  (T-description):** Noticing that the orbits under  $\mathcal{G}$  are too large to identify the substructure invariant under  $t$ , one may consider instead the opposite extreme of orbits which are as small as possible (in a natural sense), namely the orbits under the translation subgroup  $T_T$  of the twin; this translation subgroup consists of the translations by vectors in the twin lattice  $L_T$  and is the intersection of the translation subgroups of the individuals. Then, each atom in the cell of the twin lattice represents a different orbit with respect to  $T_T$ . To search the invariant subset of atoms under the twin operation  $t$ , one only has to check whether a chosen atom in the twin cell is restored or not by  $t$ . Due to the periodicity of the crystal structure, if one atom is restored by the twin operation (i.e. a single atom is fixed under the twin operation or a pair of atoms is associated to each other) the whole set of atoms equivalent under the translations of the twin lattice will be restored. Thus, it is sufficient to look at the atoms in the twin cell.

The symmetry analysis under  $T_T$  identifies the restored subset of atoms through a

case-by-case checking of the atoms in the twin cell, but such an analysis is not recommended for a twin structure with a large number of atoms in the twin cell. The natural question is then, which atoms are restored with the same accuracy. To this end, instead of looking at single atoms, one can now invert the point of view and look for subgroups  $\mathcal{H}$  of  $\mathcal{G}$  such that atoms in the same orbit under  $\mathcal{H}$  are restored with the same accuracy. From the above discussion it is clear that  $T_T$  already has this property, hence one will look at subgroups  $\mathcal{H}$  of  $\mathcal{G}$  with  $T_{\mathcal{H}} = T_T$ .

### **Crystallographic orbit approach under $\mathcal{H}$ ( $\mathcal{H}$ -description):**

Let  $\mathcal{G}$  be the space group of one of the individuals of a twinned crystal. The twin operation  $t$  maps the first individual to the second individual and the space group of the second individual is the conjugate group  $t\mathcal{G}t^{-1}$ . In addition, the twin operation  $t$  maps the lattice  $\mathbf{L}_{\text{ind}}$  of the first individual to the lattice  $t\mathbf{L}_{\text{ind}}$  of the other individual and the intersection  $\mathbf{L}_T := \mathbf{L}_{\text{ind}} \cap t\mathbf{L}_{\text{ind}}$  is the twin lattice. Since  $t\mathbf{L}_T = t\mathbf{L}_{\text{ind}} \cap t^2\mathbf{L}_{\text{ind}} = t\mathbf{L}_{\text{ind}} \cap \mathbf{L}_{\text{ind}} = \mathbf{L}_T$ , the twin operation fixes the twin lattice (assuming a twofold twin for the sake of simplicity: the generalisation to a higher-degree twin is self-evident).

Under the twin operation, the atoms of the first individual are mapped onto positions close to the atoms of the second individual (with small deviations due to the obliquity). But in order to explain the formation of the twin, at least part of the atoms should be mapped onto positions belonging also to the first individual, i.e. the atoms should be restored within the first individual. These restored atoms can be interpreted as common to both individuals and therefore provide a continuation across the interface between the individuals. In order to investigate the restored atoms, a subgroup  $\mathcal{H}$  of  $\mathcal{G}$  which is compatible with the twin lattice  $\mathbf{L}_T$  is of interest. The intersection of the groups of the two individuals,  $\mathcal{G}$  and its conjugate  $t\mathcal{G}t^{-1}$ , clearly has the correct translation subgroup by construction. Therefore, the intersection subgroup of  $\mathcal{G}$  compatible with the twin lattice is  $\mathcal{H} = \mathcal{G} \cap t\mathcal{G}t^{-1}$ . Since the basis of the twin lattice  $\mathbf{L}_T$  is built from the twin plane  $(hkl)$  and its quasi-normal  $[uvw]$  (or the twin

axis  $[uvw]$  and the quasi-perpendicular plane  $(hkl)$  for a rotation twin), the twin operation has a simple description with respect to the twin basis. On the other hand, the orbits generated under  $\mathcal{G}$  are split into sub-orbits under the action of  $\mathcal{H}$ , these sub-orbits are called split orbits and the components of a full orbit  $O_i$  are denoted by  $O_{ij}$ . The restoration conditions for a split orbit  $O_{ij}$  under  $\mathcal{H}$  are:  $O_{ij}$  is restored to itself, restored to another orbit  $O_{ij'}$  or not restored at all. The crucial difference between a full orbit under  $\mathcal{G}$  and a split orbit under  $\mathcal{H}$  is, that it can not happen that different atoms from a single split orbit are restored to atoms from more than one split orbit (as is found for the full oxygen orbits in staurolite), or that some atoms from a single split orbit are restored while others are not (as is found for the full calcium orbits in melilite). This property is, amongst others, demonstrated in the theorem below.

As a consequence, the substructure invariant under  $t$  is the set of all split orbits under  $\mathcal{H}$  which are restored by  $t$ . The idea of using the intersection subgroup  $\mathcal{H}$  and the properties of the split orbits under  $\mathcal{H}$  are a core result of this PhD thesis. Using  $\mathcal{H}$  has two main advantages:

- It reduces the number of atoms in the twin cell to check for restoration.
- The symmetry analysis is performed in terms of the minimal supergroup of  $\mathcal{H}$  which is generated by  $\mathcal{H}$  and the twin operation. The pseudo-eigensymmetry  $\mathcal{E}$  of a split orbit (or union of split orbits) may be larger than this minimal group, but as for the orbits under  $\mathcal{G}$  different atoms in a single orbit under  $\mathcal{E}$  may be restored with different accuracy.

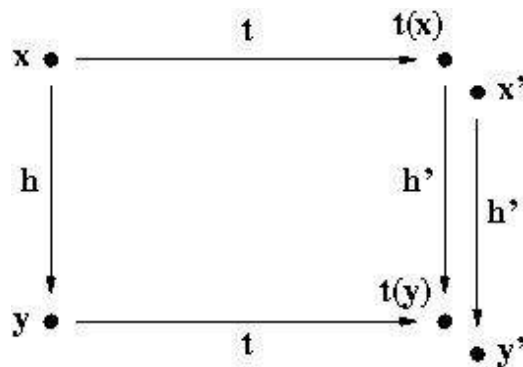
The following theorem summarises the properties of the split orbits under the intersection group  $\mathcal{H}$  which are used in order to identify all the split orbits restored by the twin operation  $t$  and thus allows to find the substructure explaining the formation of the twin.

**Theorem (Marzouki *et al.*, 2014 a).** Assume that  $t$  is a twofold twin operation, i.e.  $t^2$  is an element of  $\mathcal{G}$ . Let  $O_{ij}$  be a split orbit under the intersection group  $\mathcal{H} = \mathcal{G} \cap t\mathcal{G}t$

<sup>1</sup> and let  $\mathbf{x}$  be the position of an atom in  $O_{ij}$ . Let  $\mathbf{x}'$  be the position of the atom in the structure closest to the mapped position  $t(\mathbf{x})$  of  $\mathbf{x}$  under the twin operation, thus  $d_{\min} = \| t(\mathbf{x}) - \mathbf{x}' \|$ . Then the value of  $d_{\min}$  is the same for every atom in  $O_{ij}$ , i.e. the distance of the image of any atom in  $O_{ij}$  under  $t$  to the closest atom position in the structure is always  $d_{\min}$ .

Moreover, if the position  $\mathbf{x}'$  belongs to the split orbit  $O_{ij'}$ , then the closest atoms to the mapped split orbit  $t(O_{ij})$  all belong to  $O_{ij'}$ . In particular, if one atom of  $O_{ij}$  is exactly restored to an atom in  $O_{ij'}$ , then the full split orbit  $O_{ij}$  is mapped to the full split orbit  $O_{ij'}$  under the twin operation.

**Proof:** Let  $\mathbf{x}$  be the position of an atom in  $O_{ij}$ , let  $\mathbf{x}'$  be the position of the atom in the structure closest to  $t(\mathbf{x})$  and assume that  $\mathbf{x}'$  belongs to the split orbit  $O_{ij'}$ . If  $\mathbf{y}$  is the position of another atom in  $O_{ij}$ , then there is a symmetry operation  $h$  in  $\mathcal{H}$  mapping  $\mathbf{x}$  to  $\mathbf{y}$ . Since  $t$  is a twofold twin operation, one has  $tht^{-1} \in t\mathcal{G}t^{-1} \cap t^2\mathcal{G}t^{-2} = t\mathcal{G}t^{-1} \cap \mathcal{G} = \mathcal{H}$  and hence  $tht^{-1} = h' \in \mathcal{H}$ . This means that  $th = h't$ , thus mapping  $\mathbf{y} = h(\mathbf{x})$  by the twin operation  $t$  gives  $t(\mathbf{y}) = th(\mathbf{x}) = h't(\mathbf{x})$ . If one defines  $\mathbf{y}' = h'(\mathbf{x}')$ , then from the fact that  $h'$  is an isometry and thus preserves distances, it follows that  $\| t(\mathbf{y}) - \mathbf{y}' \| = \| h't(\mathbf{x}) - h'(\mathbf{x}') \| = \| h'(t(\mathbf{x}) - \mathbf{x}') \| = \| t(\mathbf{x}) - \mathbf{x}' \| = d_{\min}$ . Since  $h'$  is an element of  $\mathcal{H}$ , it follows that  $O_{ij'}$  contains an atom with distance  $d_{\min}$  to  $\mathbf{y}$ . The same argument applied with the roles of  $O_{ij}$  and  $O_{ij'}$  interchanged now shows that the structure cannot contain an atom closer to  $t(\mathbf{y})$  than  $\mathbf{y}'$ , because that would result in an atom with a distance smaller than  $d_{\min}$  to  $t(\mathbf{x})$ .



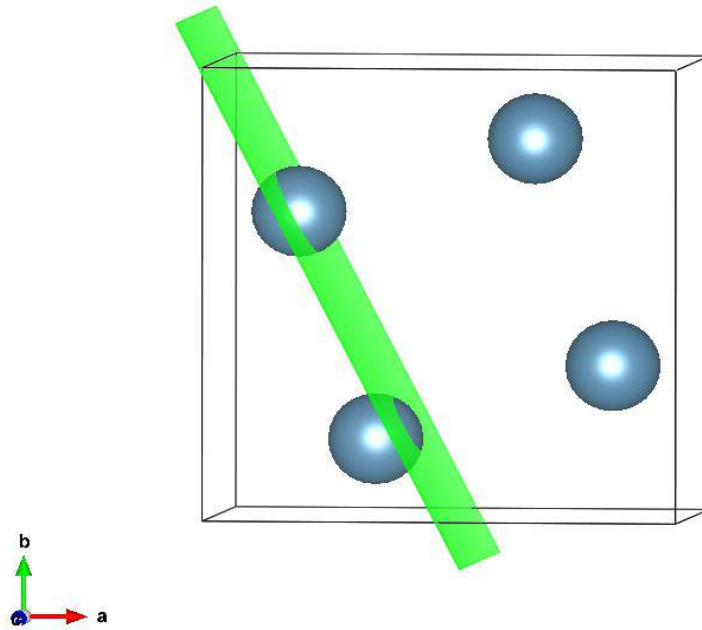
**Remark:** The above proof is easily generalised to a  $k$ -fold twin operation. In this case, the intersection subgroup has to be chosen as  $\mathcal{H} = \mathcal{G} \cap t\mathcal{G}t^{-1} \cap t^2\mathcal{G}t^{-2} \cap \dots \cap t^k\mathcal{G}t^{-(k-1)}$ . Then, the crucial argument in the proof that  $tht^{-1} = h' \in \mathcal{H}$  remains valid.

As an illustrative example we discuss the case of the calcium orbit X in the melilite twin. The analysis of this orbit gave a guideline for developing the pseudo-symmetry analysis in a general way.

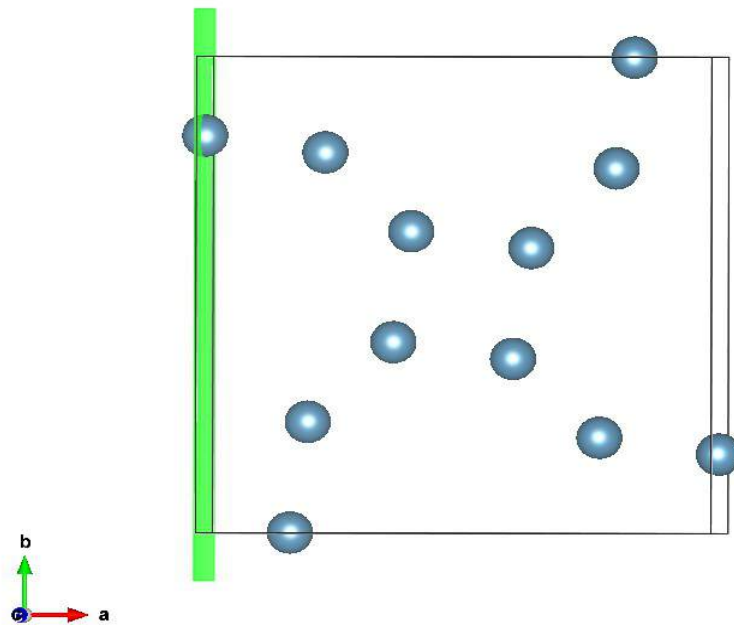
Melilite crystallises in space group  $\mathcal{G} = P\bar{4}_2m$  (no. 113); Bindi *et al.* (2003) have reported a reflection twin on  $(1\bar{2}0)$ .

- The  $\mathcal{G}$ -description of the calcium orbit X.

In the individual basis  $(abc)_I$ , the calcium orbit is represented by the position (0.3316, 0.1684, 0.5065) on Wyckoff position 4e. Therefore, the unit cell contains four atoms from the orbit X (see Figure 2.4), with coordinates (in the individual basis)  $\{ (0.3316, 0.1684, 0.5065); (0.6684, 0.8316, 0.5065); (0.1684, 0.6684, 0.4935); (0.8316, 0.3316, 0.4935) \}$ . By using the PSEUDO program (Capillas *et al.*, 2011) at the Bilbao Crystallographic Server (Aroyo *et al.*, 2006), one checks that the eigensymmetry of this orbit is  $E = P4/mbm$  (no. 127). However, this space group does not contain a symmetry operation with the reflection on  $(1\bar{2}0)$  as linear part (Marzouki *et al.*, 2014a). The  $\mathcal{G}$ -description shows that the calcium orbit is not restored by the twin operation  $t$  - the reflection on  $(1\bar{2}0)$ . One concludes that not all calcium atoms belong to the subset invariant under  $t$ . However, a subset of these atoms is restored by  $t$  (see Figure 2.4).



**Figure 2.4:** View of the calcium orbit (blue color) in the individual basis, along the  $c$ -axis where the green plane is the twin element of the twin operation - reflection in  $(1\bar{2}0)$ .



**Figure 2.5:** View of the restored calcium atoms (blue color) in the twin basis, along the  $c$ -axis where the green plane is the twin element of the twin operation - reflection in  $(100)$ .

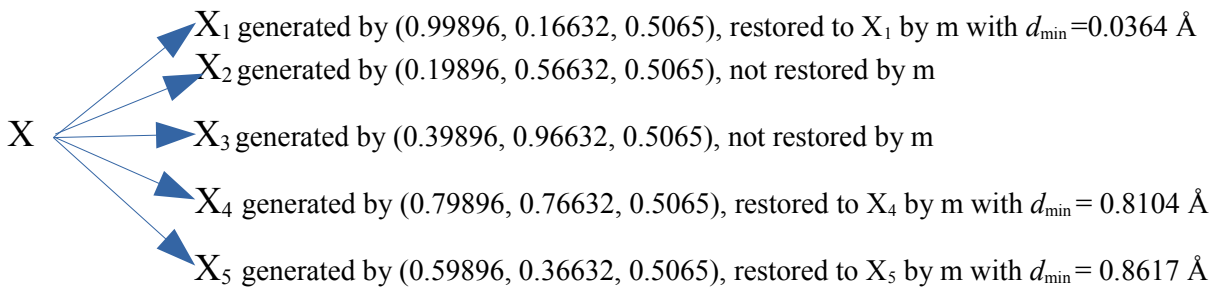


- The  $\mathcal{H}$ -description of the calcium orbit X.

Let  $(abc)_T$  be the twin basis, related to the individual basis  $(abc)_I$  by  $(abc)_I P = (abc)_T$ ,

with  $P = \begin{pmatrix} 1 & 1 & 0 \\ 2 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ . The X orbit under  $\mathcal{G}$  has four atoms in the unit cell of the individual, which give rise to 20 calcium atoms in the twin cell, since the twin index is 5 in this case. For the melilite case,  $\mathcal{H} = \mathcal{G} \cap t\mathcal{G}t^{-1} = P\bar{4}$  (no. 81), and since all atoms are in general position with respect to  $P\bar{4}$ , these 20 atoms are regrouped under H in five split orbits  $X_1 X_2 X_3 X_4$  and  $X_5$ . Note that with respect to the twin basis, the twin operation  $m_{[1\bar{2}0]_I}$  becomes  $m_{[100]_T}$ . In order to check the restoration of a split calcium orbit, it is sufficient to check whether its eigensymmetry contains a symmetry operation with the mirror  $m_{[100]_T}$  as linear part. The minimal supergroups of  $P\bar{4}$  containing such an operation are  $P\bar{4}m2$  (no. 115),  $P\bar{4}c2$  (no. 116),  $P\bar{4}b2$  (no. 117) and  $P\bar{4}n2$  (no. 118). By using the PSEUDO program again, one shows that of these groups only  $P\bar{4}m2$  occurs as the eigensymmetry for a split orbit. More precisely, three split orbits out of five are quasi-restored by  $t$  (see Schema 2.1). Thus, 12 out of these 20 atoms are quasi-restored and at the same time it is shown that the restoration operation having the twin operation  $m_{[100]_T}$  as its linear part must be the reflection located at  $x = 0$ .

The example of calcium leads us the way to a general procedure in order to analyse the other orbits of melilite and more generally other twin examples.



**Schema 2.1:**  $X_j$  stemming from X under  $\mathcal{H} = P\bar{4}$ . A split orbit  $X_j$  is quasi-restored to itself by a twin operation (with  $d_{\min}$  within the accepted tolerance) with

eigensymmetry  $E=P\bar{4}m2$ .

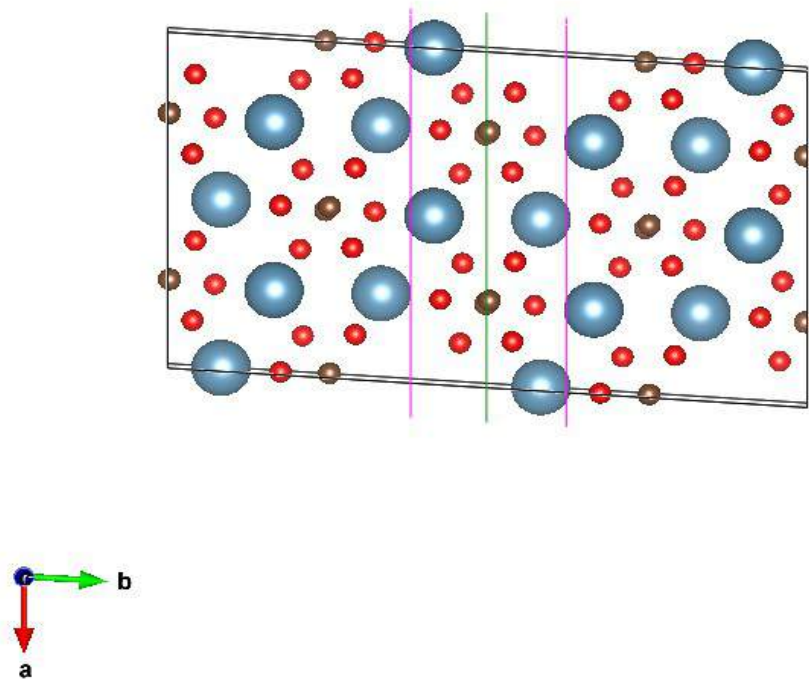
The twins investigated in the course of this PhD project are analysed, mainly, via the subgroup  $\mathcal{H}$ -description of their crystal structure in order to find the substructure of atoms invariant under the twin operation. As a quantitative measure describing this restored subset, the relative amount of restored atoms is given as restoration percentage. This restoration percentage served well for explaining the occurrence of the investigated twins: melilite, staurolite and aragonite.

## Layer group approach

The layer group approach takes an alternative perspective on identifying the invariant subset of atoms which is responsible for the structural continuity across the composition surface. For that, instead of looking at the entire set of atoms, it might be sufficient to analyse the symmetry of the atoms close to the composition interface.

For twins having a plane as composition interface, the symmetry group of a thin slice around this plane may contain an operation relating the orientations of the individuals (Holser, 1958). The restriction to a slice around the composition plane gives rise to a layer group  $\mathcal{L}$  as symmetry group, which contains (at least) the subgroup of the space group  $\mathcal{G}$  of the crystal pattern that leaves the composition plane invariant as a whole. Abstractly, the composition plane is a 2-dimensional plane intersecting the crystal structure and is called a *section plane*. However, since a crystal structure is built from physical objects, it makes sense to replace the abstract plane of thickness 0 by a slice of finite (usually small) width. The width of the slice should be chosen small enough to increase the chance that its symmetry group contains the twin operation, but large enough to be meaningful for the growth process of the crystal (Marzouki *et al.*, 2015). This slice extends symmetrically around the section plane and contains the atoms close to it. The symmetry group of such a slice has a translation subgroup with translations along two independent directions and is therefore a subperiodic group,

called a *sectional layer group*. Let  $K$  be a slice around the section plane at a position  $z=s$  (assuming the  $c$ -axis being normal to the slice), then a straightforward option is to choose the thickness of  $K$  such that for every type of atoms it contains the atoms closest to the geometric element of the twin operation located at  $z = s$  (Figure 2.6). Depending on the type of structure, one might also consider choosing the thickness such that coordination polyhedra close to the twin plane are contained in the slice.



**Figure 2.6:** View along the  $c$ -axis of the slice enclosed by the two pink planes extending around the twin plane (green plane) located at  $y=b/2$ .

In contrast to the crystallographic orbit approach, the layer group approach is a local analysis which deals only with the part of the structure within the slice. For a twinned crystal, the twin operation  $t$  restores a subset of the split orbits. Restricting these restored orbits to a region geometrically close to the geometric element of the twin operation already gives a substructure in the slice that is invariant under the twin operation. On the other hand, a split orbit may be prevented from being restored by non-restored atoms which are far away from the composition interface and which are

thus of little relevance for the growth process of the twin. In this case, atoms within the slice may still be restored. For instance, if the twin operation is a reflection, atoms on the twin plane will be fixed. Therefore, the slice containing the twin plane may be fully-restored by  $t$  even if not all split orbits intersecting it are restored. In such a situation, the symmetry of the slice is generated by the layer group  $\mathcal{L}$  (induced by the space group  $G$  of the individual) and the twin operation  $t$ .

The layer group approach was successfully applied in the case of the aragonite twin and provided additional evidence for the formation of this twin:

- The chosen slice - meaningful for the growth process of the crystal - has a width of 4.22 Å and contains the twin operation in its eigensymmetry and is thus fully restored. On the one hand, the slice is chosen such that it contains the atoms closest to the twin plane, but on the other hand the slices at different locations precisely cover the entire structure. Thus, in any phase of the growth process the invariance of the slice under the twin operation allows for the formation of the twin.
- The local analysis at the intermediate position  $y=1/8$  shows the existence of a partial symmetry operation mapping one half of a slice to the other half but not vice versa. This observation demonstrates a certain amount of structural continuity of the aragonite twin across the composition plane at additional locations of the plane.

The crystallographic orbit approach shows the existence of a substructure invariant under the twin operation. Furthermore, the local analysis of the composition plane in the structure, via layer groups, indicates the location of the slices which are fixed by the twin operation. In fact, these two approaches are not independent of each other, but give complementary information. They both contribute to the explanation of the high frequency of twinning observed in known twins which have been investigated in this PhD work.

## Chapter III. Summaries of articles

In this chapter we give brief summaries of the three articles which were written in the course of this PhD project and which are already published in refereed journals:

- Marzouki, M.A; Souvignier, B; Nespolo, M. (2014a) Analysis of the structural continuity in twinned crystals in terms of pseudo-eigensymmetry of crystallographic orbits. *IUCrJ*, **1**, 39-48.
- Marzouki, M.A; Souvignier, B; Nespolo, M. (2014b) The staurolite enigma solved. *Acta Cryst.*, **A70**, 348-353.
- Marzouki, M.A.; Souvignier, B; Nespolo, M. (2015). Twinning of aragonite – the crystallographic orbit and sectional layer group approach. *Acta Cryst.*, **A71**, 195-202.

All three articles are reproduced at the end of this thesis.

### **III.1. Summary of the article 'Analysis of the structural continuity in twinned crystals in terms of pseudo-eigensymmetry of crystallographic orbits'**

This article is the first one in the series of articles introducing the new methods for the analysis of twins which were developed in the course of this research project. It therefore has an elaborate theoretical part in which the concepts of the pseudo-eigensymmetry analysis are explained and the techniques used to perform the actual analysis are described. This analysis has been performed with the PSEUDO program (Capillas et al., 2011) at the Bilbao Crystallographic Server (Aroyo et al., 2006). The new approach is validated by applying it to the melilite silicate.

In the first part of the article, the current description of twinned crystals by the reticular theory is summarised, because the new approach via the eigensymmetry analysis of crystallographic orbits aims at providing additional conditions explaining the formation of twins which go beyond the lattice point-of-view taken in the

reticular theory. These additional conditions are termed *structurally necessary* conditions, to distinguish them from the necessary conditions on the lattice level.

The main theoretical part of the article explains the concepts of the twin lattice and twin cell, which are inherited from the reticular theory. It is shown how the construction of the twin lattice as the intersection of the lattice of one of the individuals and its transformation by the twin operation leads to an analogous construction on the level of the space groups of the individuals: there, the intersection of the space group  $G$  of one of the individuals and its conjugate by the twin operation (taken as space group operations with trivial vector part) yields the largest subgroup of the two space groups which is compatible with the twin lattice. It is at the same time the intersection of the space groups of the individuals. The significance of this intersection group  $\mathcal{H}$  is its role in the analysis of the restoration accuracy of the atoms: atoms which are related by a translation of the twin lattice are restored with the same accuracy, but this is in general no longer true for atoms in the same orbit under  $G$ . The largest group for which this property holds is just the intersection group  $\mathcal{H}$  and this allows to restrict the restoration analysis to representatives of the orbits under  $\mathcal{H}$  (which are suborbits of the full orbits under  $G$ ). This crucial property of the intersection group  $\mathcal{H}$  is formulated as a theorem and proved in the appendix of the article.

After a brief summary of how crystallographic orbits split into suborbits (which we term *split orbits*) under the action of a subgroup, the different possibilities for the restoration of orbits and suborbits by the twin operation are discussed. Furthermore, it is explained how the actual restoration analysis can be performed by computing the (pseudo-)eigensymmetry of the crystallographic orbits and split orbits and of unions thereof. An important concept introduced is that of a *restoration operation*: the twin operation itself is a point group operation, mapping the orientation of the individual crystals. It is the linear part of the space group operation which actually maps the atoms in the structure. To clearly distinguish these two levels, the space group

operation is termed *restoration operation*<sup>2</sup>. Since the twin operation only determines the linear part of the restoration operation, different vector parts of the restoration operation may alter its type (e.g. turning a reflection into a glide reflection) and the location of its geometric element (the position of the plane or axis).

In the final part of this paper, we present the application of the crystallographic orbit approach to the melilite twins in order to explain their natural occurrence during crystal growth, thus validating the new method.

The case of the melilite silicate is interesting since it displays three different known twins – reflection twins on the planes (100), (001) and  $(1\bar{2}0)$  – which are analysed with respect to their quasi-restored orbits. In particular, it is shown that the first two twins, which are indistinguishable from a lattice viewpoint, being twins by merohedry, show a fairly good degree of structure restoration, but with twin elements in different locations. Since for twins by merohedry the lattices are fully restored by the twin operation, in these two cases the intersection group  $\mathcal{H}$  actually coincides with the space group  $\mathcal{G}$  of the individual. For the case of the  $(1\bar{2}0)$  twin in melilite, the restoration analysis of the split orbits under the intersection group  $\mathcal{H}$  is performed in full detail. It is found that for a suitable restoration operation 68% of the cations and 37% of the oxygen atoms are (approximately) restored, which provides a good explanation for the formation of this twin.

### **III.2. Summary of the article 'The staurolite enigma solved'**

This article is the second one in the series of articles and continues to explain the new methods for the analysis of twins. Based on the pseudo-eigensymmetry analysis, developed in the previous chapter, the full power of the crystallographic orbit approach is demonstrated in its application to the two famous types of twins of the staurolite silicate. In particular, the new methods give the first clear explanation for the different occurrence frequencies of these twins.

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2 Note that in Chapter II we have not explicitly distinguished between the concepts of a twin and a restoration operation, in order to keep the description of the main concepts as simple as possible. It should always be clear from the context whether – in the terminology introduced here - a twin or a restoration operation is meant.

In the first part of the article, we start by summarising the historical description of the staurolite structure; from Cardoso (1928), who suggested the space-group type  $Ccmm$  up to Naray-Szabo & Sasvari (1958) who confirmed  $C2/m$  as the correct space group. Staurolite forms two well-known types of twins with different occurrence frequency, the Greek cross twin (lower frequency), with twin index 6, and the Saint Andrews cross twin (higher frequency) with twin index 12. The hybrid theory of twinning showed that the Greek cross is actually a hybrid twin with two concurrent sub-lattices and effective twin index 6.0 (Nespolo & Ferraris, 2007), which removes the apparent contradiction of having a higher-index twin with higher occurrence frequency. However, the hybrid theory is still not sufficient to explain the different occurrence frequency. In order to explain this frequency issue, one has to analyse the crystallographic orbits of this twin, in terms of their eigensymmetry.

For this purpose, the main part of the article consists of applying the pseudo-eigensymmetry analysis to the staurolite structure. It starts by recalling the Náray-Szabó (1929) statement that the 48 oxygen atoms in the unit cell form a pseudo- $fcc$  packing. The pseudo-eigensymmetry analysis of the union of oxygen orbits shows a cubic eigensymmetry ( $Fm\bar{3}m$ , No. 225 ITA) of this union which confirms the previous statement. Moreover, this eigensymmetry contains all restoration operations of both twins. This implies that the oxygen union is equally and fully-restored by the twin operations of both types of twins. This equal-restoration of the anions justifies the high frequency of twinning of this mineral but cannot explain the different occurrence frequencies of these two twins.

In the next step, we determine for the Greek cross twin (Gc) and the Saint Andrews cross twin (SA) the intersection space groups  $\mathcal{H}_{Gc}$ ,  $\mathcal{H}_{SA}$  through the twin operations  $t_{Gc}$  and  $t_{SA}$ , respectively. The minimal supergroup  $\mathcal{E}$  of the intersection subgroup containing the twin operation 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. We then apply the pseudo-eigensymmetry analysis to the cation sites, and the results are the following :



- A subset of cations in tetrahedral coordination has an eigensymmetry that contains a restoration operation corresponding to the Saint Andrews cross, but no such subset can be found for the Greek cross.
- A subset of octahedral cations has an eigensymmetry that contains a restoration operation for the Greek cross twin, but a larger subset has an eigensymmetry that contains a restoration operation for the Saint Andrews cross twin.

In the final part of this paper, after giving a precise description of the restored orbits of cations, we summarise the pseudo-eigensymmetry analysis outcomes in terms of percentages.

In addition to the oxygen atoms, which are fully restored for both twins, in the Greek cross twin 19% of the cations are (quasi-)restored against 45% for the Saint Andrews cross twin. Consequently, a larger substructure is (quasi-)restored for the Saint Andrews cross twin, which justifies its higher occurrence frequency.

### **III.3. *Summary of the article 'Twinning of aragonite – the crystallographic orbit and sectional layer group approach'***

This article is the third (and in the course of this thesis the last) one in the series of articles introducing the new methods for the structural analysis of twins. In this paper we confirm the strength of the new approach by applying the pseudo-eigensymmetry analysis to the aragonite mineral. Moreover, we introduce the layer group approach described in section II.4.

In the first part of the article, we present aragonite as the high-temperature / high-pressure phase of calcium carbonate  $\text{CaCO}_3$ . It crystallises in a space group of type *Pmcn* (non-standard setting of *Pnma*, No. 62 ITA). It frequently gives twins on  $\{110\}$ , with twin index  $n = 2$  and obliquity  $\omega = 3.74^\circ$  (structural data taken from Caspi *et al.*, 2005). Therefore, this twin falls within the Friedelian empirical limits for the occurrence of twins (i.e. the twin index  $n \leq 6$  and the obliquity  $\omega \leq 6^\circ$ ) and its

formation is justified from the reticular point of view. After a brief summary of the principles of pseudo-eigensymmetry analysis (Marzouki *et al.*, 2014a,b), we discuss the physical meaning of the pseudo-eigensymmetry and tolerance on the atomic quasi-restoration. In this subsection, the physical meaning of the pseudo-eigensymmetry is explained in that it identifies a subset of restored orbits which cross the composition surface, more or less unperturbed, in order to build the common substructure between the individuals. To identify this substructure, we have rationalised the definition of the tolerance on the atomic quasi-restoration (denoted by  $d_{min}$ ). The latter is limited with respect to the radius (ionic or covalent, depending on the type of bond).

The main part of the article carries out the pseudo-eigensymmetry analysis of the aragonite crystallographic orbits. With respect to the full orbits under the space group of the individual, we show that the calcium orbit has a pseudo-hexagonal eigensymmetry ( $P6_3/mmc$ , No. 194) which contains a restoration operation. With respect to the split orbits under the intersection group, we find the following:

- The existence of an important substructure (60% of the atoms) restored by two restoration operations, a  $c$ -glide reflection and an  $n$ -glide, with only minor perturbation.
- The two restoration operations alternate with respect to restored and non-restored atoms every  $b/4$  along the **b**-axis.

In the final part of this paper, we introduce the layer group approach which is based on a local pseudo-eigensymmetry analysis of the slice containing the geometric element of the twin operation (in this case a mirror plane). This local analysis leads to two important results:

- The local analysis of the composition surface in the aragonite structure shows that the twin cell is subdivided into 4 slices of width 4.22 Å and the pseudo-eigensymmetry of each slice is a layer group containing the restoration operation.

- The twin operation restores the slices each  $1/4$  along the **b**-axis, but in addition at the  $1/8$  position in between there is a partial symmetry operation mapping one half of a slice to the other half but not vice versa.

On the one hand, the crystallographic orbit approach shows the existence of a common substructure in aragonite, whose  $C2/c$  pseudo-eigensymmetry contains  $c$ -glide and  $n$ -glide reflections. On the other hand, the local analysis of such a composition surface, via layer groups, shows that the structure is built from slices which are fixed by the twin operation. This explains why the  $\{110\}$  aragonite twin has a high occurrence frequency.

## Chapter IV. Discussion

The occurrence of twins has as a pre-requisite the continuation of a substructure across the composition surface. The analysis of this structural continuity is obtained via the crystallographic orbit approach, which exploits the analysis of the eigensymmetry of each crystallographic orbit corresponding to an occupied Wyckoff position in the crystal. The structural continuity is obtained when this eigensymmetry contains, exactly or approximately, an operation whose linear part coincides with the twin operation  $t$ . Such an operation is called a restoration operation.

Although the occurrence frequency of twins certainly takes values on a continuous scale, it is useful to distinguish two categories of twins:

- 1) frequent twins: twins of a given chemical compound for which twinning has been observed frequently;
- 2) rare twins: these are examples which have been found in a limited number of cases, but for which the chemical compound usually occurs as non-twinned crystal or as a different type of twin.

As shown in chapter II, the application of the pseudo-symmetry analysis of orbits is based on the assumption that a 'good structure restoration' will provide a structurally necessary condition for the formation of twins. Two important parameters are considered in the evaluation of the quality of structural restoration: i) the tolerance limit on the structural pseudosymmetry, i.e. the accepted deviation of the quasi-restoration by a pseudo-eigensymmetry from perfect restoration, and ii) the restoration percentage, i.e. the percentage of atoms restored or quasi-restored by the twin operation.

The discussion in this chapter will focus on the interpretation of the percentage results for the studied twins, with indications for future extensions to other examples, including rare twins which we expect to have a lower degree of structural restoration.

#### **IV.1. *The restoration percentage and twinning frequency***

The reticular (classical and hybrid) approach to twinning gives necessary conditions for the occurrence of twins on the lattice level via two parameters; the twin index  $n$  and the obliquity  $\omega$ . However, these two parameters take into account only the restoration of lattice nodes, but ignore the content of the unit cells. Of course, a good lattice restoration is a prerequisite for the restoration of a substantial substructure, but the reticular theory is not sufficient to differentiate between twins showing a different occurrence frequency despite a close, or even identical, lattice restoration. A striking example are the staurolite twins, where both the St Andrews cross and Greek cross have the same degree of lattice restoration, yet their occurrence frequency is different.

We have shown that the crystallographic orbit approach, thanks to its analysis at the atomic level, is indeed able to explain such different occurrence frequencies, even in a difficult case like that of the staurolite twins, which for this reason have been considered an “enigma” for a long time. In fact, our analysis provides a global, quantitative, analysis of the structural continuity across the composition surface in terms of the (pseudo-)eigensymmetry of the orbits forming the crystal structure. The results of this analysis are expressed in the form of percentages of the atoms in the structure of the individual crystal which are restored or quasi-restored by the twin operation within the accepted tolerance and thus are shared by the individual crystals. This percentage is expected to be a simple indicator which is directly related to the occurrence probability of the twin. It may be enhanced by taking into consideration its dependency on the tolerance limit. Having a good restoration percentage for a low tolerance (and thus almost perfect restoration) is a stronger indication than reaching a reasonable restoration only for a higher tolerance limit. However, reducing the restoration of atoms to a single percentage (or a couple of percentages for different types of atoms) clearly results in a loss of information. In a more refined analysis, considering the structure of the restored atoms and their relations (in particular bonds

between them) gives much more detailed information.

#### **IV.2. *Examples of studied twins with a high restoration percentage***

In case of inorganic crystals, the structure consists of electropositive and electronegative atoms (in ionic crystals these become cations and anions, respectively). In general, electronegative atoms have a bigger size than electropositive atoms and span the bulk of the volume of the crystal structure: the electropositive atoms then occupy the cavities. When the difference of the size is relevant, the largest atoms may dominate the topology of the structure. Hence, the restorations of these atoms may be structurally essential to explain the twin formation, provided that the degree of restoration is sufficient.

As a starting point it was natural to assume that the restoration operation will relate atoms of the same type, but it turned out that this restriction is too strong. It is certainly true that the restoration operation must relate atoms with a chemical and structural similar role, but these may be of different types. For example, in an inorganic crystal whose structure is described by coordination polyhedra, atoms at the corner of a polyhedron can only be restored to atoms in a similar position. Also, atoms centring the same type of polyhedron (*e.g.* tetrahedra or octahedra) can be related by the restoration operation even if their chemical species is different. An example of this type is found in the melilite twin, where Al and Mg atoms in tetrahedral coordination are interchanged.

In the present thesis, we have analysed the structure of three minerals, for which the occurrence and frequency of twins has been well known for a long time. Accordingly, the atomic constituents are described as “cations” and “anions” even if the chemical bond is not necessarily purely ionic, and in some cases it is definitely not, *e.g.* in the case of the carbon-oxygen bond in aragonite. The restoration rates for these three examples are summarised in Table 4.3.

The percentage of restored atoms is dependent on the chosen restoration operation,

therefore the existence of different restoration operations for the melilite twins gives rise to different restoration percentages. However, the melilite case also shows how the restoration percentages may help to identify the operation really responsible for the occurrence of the twin, namely as the operation restoring the largest substructure. For the melilite twin, the highest restoration percentage 50% (Table 4.3) identifies the mirror  $m_{0,y,z}$  as the restoration operation and it confirms the pseudo-eigensymmetry analysis for this frequently observed twin.

In the case of staurolite, since the structure of this mineral is based on an *fcc* packing of oxygen atoms with the cations partly occupying the octahedral and tetrahedral cavities, the (pseudo-)eigensymmetry of the crystallographic orbits showed that the whole substructure built on anions is fully restored (with small deviations) by both twin laws. Consequently, the (pseudo-)eigensymmetry explains, via the high restoration percentage of the anions, why twinning is frequent in staurolite. On the other hand, 45% of the polyhedral sites are quasi-restored in the Saint-Andrews cross twin, against only 19% for the Greek cross twin. In conclusion, this difference in the restoration percentage explains the predominance of the Saint-Andrews cross twin. A finer analysis, considering the orientations of coordination-tetrahedra, adds a further level to the explanation of the different occurrence frequencies.

For the aragonite twins, the pseudo-symmetry analysis shows the existence of two restoration operations, a *c*-glide reflection and an *n*-glide reflection, leading to the same restoration percentage. We, therefore, identify them both as being responsible for the occurrence of the aragonite twin with an exchange of the restored and non-restored atoms every  $b/4$  along the **b**-axis.

Again, the pseudo-symmetry analysis confirms, via the restoration percentage, the occurrence of a frequent twin in aragonite and two restoration operations are identified. In this example, further evidence is obtained by the analysis of the layer groups of slices in the structure parallel to the twinning interface.

**Table 4.3.** The different percentages of the restored substructure for the three studied examples

Twin	restoration operation	% cations	% O	% all atoms
Melilite	$m\ 0,y,z$	68	37 (94)	50 (40)
	$c\ 0,y,z$	0	23 (91)	13 (53)
	$b\ \frac{1}{4},y,z$	20	11 (80)	15 (55)
	$n(0,\frac{1}{2},\frac{1}{2})\ \frac{1}{4},y,z$	0	20 (89)	12 (52)
Greek cross	$2_{[100]}$	19	100	59,5
Saint-Andrews cross	$2_{[101]}$	45	100	72,5
Aragonite	$c\ x,0,z$ and $n\ x,\frac{1}{4},z$	75	50	60
	$n\ x,0,z$ and $c\ x,\frac{1}{4},z$	75	50	60

To conclude, the existence of a high percentage of restored atoms confirms the validity of the pseudo-symmetry analysis on the studied observed twins (melilite, staurolite, aragonite). However, since only three cases of frequent twins have been investigated in this study, it is difficult to determine a universal value as lower boundary for the restoration percentage which would correspond to a twin with high occurrence probability. Indeed, at this stage, we are unable to make a definite conclusion about the general applicability of our approach, but we certainly expect it to be valid, possibly with certain extensions and refinements. If this is eventually verified, then the restoration percentage allows to estimate the probability of the occurrence of a twin. With this purpose in mind, one can distinguish the following four cases:

- 1) Frequent twins with a high restoration percentage.**
- 2) Rare twins with a low restoration percentage.**
- 3) Rare twins with a high restoration percentage.**
- 4) Frequent twins with a low restoration percentage.**

The first category comprises the three examples studied and discussed above. The high percentage of restoration agrees with the high frequency of twinning in the



literature.

For the second category, we expect a low percentage of restoration. To confirm that this is the case, one should collect a statistically significant number of examples of rare twins and compute their restoration percentage. Also, a systematic analysis of all reasonably possible (reasonably low  $hkl$  or  $uvw$  values) but never observed twin operations should lead to a low restoration percentage. Clearly, for such a task a semi-automatic procedure has to be developed and implemented to scan a large interval of ( $hkl$ ) or [ $uvw$ ] indices corresponding to possible twin planes or twin axes. As a demonstration of the considerations required, in the next section we discuss a hypothetical twin plane in aragonite, plausible according to the reticular theory, but for which the restoration percentage would be too low, explaining why such a twin has never been observed.

For categories 3 and 4, we expect to find only a very limited number of examples, which would represent exceptions to an otherwise general approach. Should there be a substantial number of exceptions, then the general validity of our approach has to be questioned and the approach itself has to be further extended and refined. For category 3, the approach may still be generally valid but other factors may occur that prevent the formation of twins, because the structural continuity is a necessary but not a sufficient condition. The analysis of examples in this category would allow to refine the approach by adding additional conditions to the restoration percentage. For example, one could think of bonds between the restored atoms or a skeleton of restored atoms which forms the backbone of the twin structure. Category 4, if examples are found, would definitely contradict the assumption that the structural continuity across the composition surface is measured by the restoration percentage. This would indicate that other factors complementing the restoration percentage predominate in these cases. Therefore, the existence of examples in categories 3 and especially 4 may present a challenge to augment the crystallographic orbit approach in order to make it generally applicable to all twin cases.

### IV.3. *Example of a "negative" twin case*

The main goal of the analysis of structures in terms of the (pseudo-)eigensymmetry of crystallographic orbits is to provide positive evidence that the formation of a certain twinned crystal is likely by identifying a substructure which crosses the composition interface more or less unperturbed. One may expect that the restoration percentages of the different types of atoms give a clear indication for the probability of the twin to form. In the few examples investigated in this thesis, it already becomes clear that enhancing the mere restoration percentages by additional structural information gives more profound explanations of the twin formation. But an important additional question has to be faced, namely how the quantitative analysis of the eigensymmetry of crystallographic orbits can be used to distinguish crystals that are likely to form twins from crystals that do *not* form twins. One certainly can not expect a simple threshold from which onwards twinning is likely and below which it is not. However, one still would like to arrive at some criteria which allow to conclude that a certain structure will not form a twin (or at least only rare twins, with very low occurrence probability). A first step would be an analysis of many more known twins by the methods introduced in this thesis, in order to get a good overview of typical restoration percentages for existing twins. For this purpose, the prototype approach developed in this thesis should be turned into a semi-automatic procedure (see section IV.5: Conclusion and outlook). A similar procedure aimed at excluding twin formation is certainly much more complicated than the affirmative analysis performed in this thesis. One would have to identify twin elements which fulfil the requirements of the reticular theory, which typically means that the (effective) twin index and obliquity are within the Friedelian limits. This is in principle not a problem, but the number of candidate directions for a twin axis or the normal to a twin plane is usually fairly large. For a candidate twin operation one would then apply the restoration analysis developed in the current thesis.

To demonstrate that this is a feasible approach, we apply our method to a

hypothetical twin in aragonite, which from the reticular point of view would have similar formation probability as the one actually observed. We have seen that the  $\{110\}$  twin – in the  $Pmcn$  setting – is perfectly justified on a structural basis. We consider again the same compound and we make the hypothesis of a reflection twin on  $\{011\}$ , again in the  $Pmcn$  setting, which is not known but would have twin index 3 (as opposed to twin index 2 for the existing twin) and obliquity  $1.02^\circ$  (as opposed to  $3.74^\circ$ ). The direction quasi-perpendicular to  $(011)$ , which makes  $1.02^\circ$  obliquity with it, is  $[012]$  which can be regarded as the geometric element of  $m_{[012]}$ . The crystallographic orbits approach justifies the absence of this twin, as we are going to show.

The pseudo-symmetry analysis for this hypothetical twin is performed from the standard setting of aragonite,  $Pmcn$ , in which the cell parameters are  $a = 4.96183 \text{ \AA}$ ,  $b = 7.96914 \text{ \AA}$ ,  $c = 5.74285 \text{ \AA}$ . The shortest directions contained in  $(011)$  are  $[100]$  and  $[01\bar{1}]$ . The twin operation  $m_{[012]}$  fixes the lattice spanned by the basis  $[01\bar{1}]$ ,  $[012]$  and  $[100]$  and no additional centring vectors, therefore these vectors define a primitive basis of this aragonite 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) and the transformation matrix takes the form

$$\mathbf{P} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 1 & 0 \\ \bar{1} & 2 & 0 \end{pmatrix}$$

for which  $(abc)_I \mathbf{P} = (abc)_T$  (where  $(abc)_I$  denotes the individual basis and  $(abc)_T$  the twin basis).

The cell parameters for the twin lattice are  $a = 9.82281 \text{ \AA}$ ,  $b = 13.97957 \text{ \AA}$ ,  $c = 4.96183 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 91.02^\circ$  and this setting of  $\mathbf{L}_T$  defines the twin plane as  $(010)$  plane of the twin lattice.

The extension of the point group of  $\mathcal{H}$  by the twin operation results in a point group of type  $2/m$  and the possible space group types are – depending on the actual restoration operation having the twin operation as its linear part –  $P2/m$ ,  $P2_1/m$ ,  $P2/c$  and  $P2_1/c$  (in their standard  $b$ -unique setting). Of these groups, only  $P2/c$  turns out to

be worth considering, the others restore not a single cation within 0.5 Å (and also only very few oxygen atoms).

The Y orbit of  $\mathcal{G}$  (in Wyckoff position 4c) splits into six orbits (all in Wyckoff position 4g) in the standard ( $P\bar{1}$ ) setting of  $\mathcal{H}$  (Table 4.1). Only the split orbit  $Y_6$  is restored by the c-glide with  $d_{\min} = 0.38374\text{\AA}$  (Table 4.2). Likewise, the X orbit of  $\mathcal{G}$  (in Wyckoff position 4c) splits into six orbits (all in Wyckoff position 4g) in the standard ( $P\bar{1}$ ) setting of  $\mathcal{H}$  (Table 4.1). The split orbit  $X_3$  is restored with  $d_{\min} = 0.45937\text{\AA}$  (Table 4.2). The oxygen atoms OA (in Wyckoff position 4c) and OB (in Wyckoff position 8d) split into six and twelve orbits (all in Wyckoff position 4g), respectively, (Table 4.1). The c-glide restores  $OA_4$  with  $d_{\min} = 0.39750\text{\AA}$  and the union  $OB_1 \cup OB_3$  with  $d_{\min} = 0.34412\text{\AA}$  (Table 4.2). As a consequence, for a tolerance limit of 0.5 Å for both the cation and the oxygen atoms only 1/6 atoms are restored. Therefore, this twin case of aragonite has a very low restoration percentage of 16.66% (Table 4.2). By relaxing  $d_{\min}$  up to 1 Å, the twin operation restores a few more split orbits:

- $Y_1$  with  $d_{\min} = 0.69545\text{\AA}$ .
- $X_6$  with  $d_{\min} = 0.58871\text{\AA}$  and the union  $X_2 \cup X_4$  with  $d_{\min} = 0.79598\text{\AA}$ .
- The union  $OB_5 \cup OB_9$  with  $d_{\min} = 0.90065\text{\AA}$ .

These additional restored orbits extend the substructure restored by the c-glide to 11/30, thus the restoration percentage rises to 36.66%. This percentage is still fairly low, moreover it is doubtful whether deviations around 0.8 or 0.9 Å are still physically meaningful. Recalling that for the studied twin of aragonite (Marzouki *et al.*, 2015) the restoration analysis yielded:

- full restoration of the X-site with  $d_{\min} = 0.1155\text{\AA}$
- 50% of the Y-site is restored with  $d_{\min} = 0.1680\text{\AA}$
- 60% of the oxygen atoms are restored with  $d_{\min} = 0.2154\text{\AA}$

one sees that the worst degree of restoration for the existing (110) twin is lower than the best degree of restoration for the hypothetical (011) twin of aragonite.

Summarising, the pseudo-symmetry analysis shows that for the hypothetical (011) twin the only eigensymmetry containing a restoration operation whose linear part coincides with the twin operation and with at least a minimal restoration quality is  $P2/c$ , but only 16.66% of the structure is restored by the  $c$ -glide reflection, and for none of the atoms the restoration is excellent (the smallest deviation being 0.34412 Å). This low restoration percentage is a strong indicator for the non-occurrence of this twin which can thus be considered as a "negative" case of twinning in aragonite. A closer analysis of the restoration yields additional evidence. Firstly, the locations of the restored atoms in the unit cell are not close to the twin plane which one would expect in a growth twin. Furthermore, none of the restored cations is bonded to any of the restored oxygens (see Figure 4.1). This contradicts the postulated structural continuity, the restored atoms do not form a meaningful substructure common to both individuals in the twin which could form the basis for crystal growth in two different orientations.

Comparing the analysis for this hypothetical twin and the existing twin of aragonite is convincing what concerns working towards a distinction between likely and unlikely twins on the basis of the eigensymmetry analysis developed in this thesis.

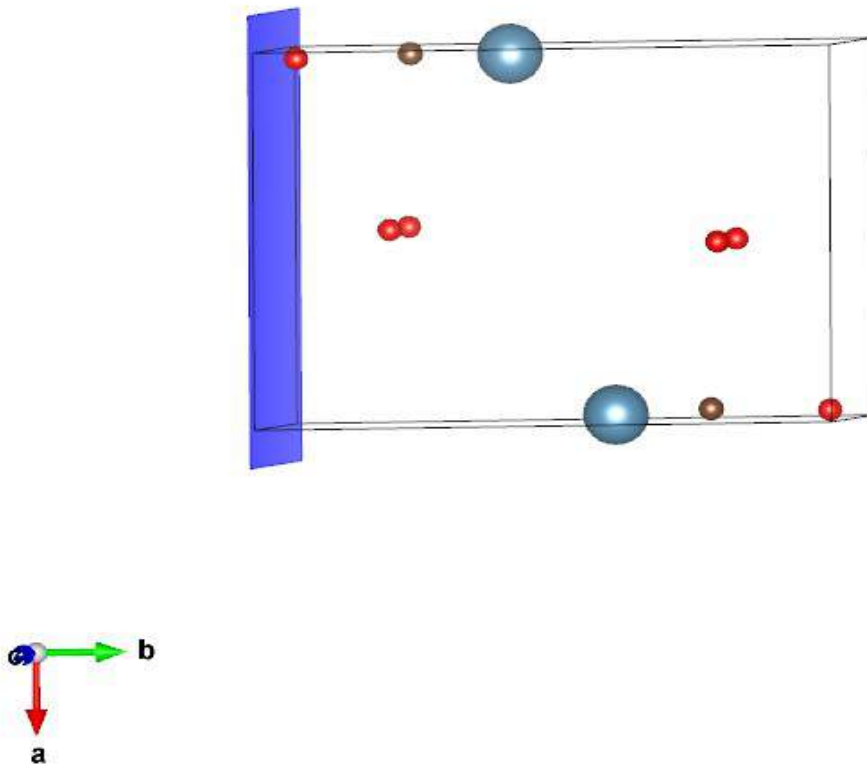
**Table 4.1.** The Split orbits  $X_i$ ,  $Y_i$ ,  $OA_i$  and  $OB_i$  stemming from atomic sites  $X$ ,  $Y$ ,  $OA$  and  $OB$  ( see, Marzouki *et al.*, 2015) under the action of  $\mathcal{H} = P\bar{1}$ . All orbits are in general position, with Wyckoff position 4g.

Split cations	Split orbits stemming from the Y-site	$Y_1$	$Y_2$	$Y_3$	$Y_4$	$Y_5$	$Y_6$
		0.53540	0.68620	0.20207	0.13127	0.35287	0.019533
		0.22650	0.051900	0.55983	0.10683	0.38523	0.71857
		0.25	0.25	0.25	0.75	0.25	0.25
	Split orbits stemming from the X-site	$X_1$	$X_2$	$X_3$	$X_4$	$X_5$	$X_6$
		0.35673	0.69663	0.023400	0.30997	0.36330	0.029967
		0.058267	0.21837	0.39160	0.27503	0.55170	0.88503
		0.25	0.75	0.25	0.75	0.75	0.75
Split anions	Split orbits	$OA_1$	$OA_2$	$OA_3$	$OA_4$	$OA_5$	$OA_6$

	stemming from the OA-site	0.64643	0.41677	0.31310	0.020233	0.24990	0.083433
		0.27597	0.005633	0.60930	0.057367	0.32770	0.33897
		0.25	0.75	0.25	0.75	0.25	0.75
	Split orbits stemming from the OB-site	OB <sub>1</sub>	OB <sub>2</sub>	OB <sub>3</sub>	OB <sub>4</sub>	OB <sub>5</sub>	OB <sub>6</sub>
		0.48247	0.74237	0.48247	0.74237	0.14913	0.18417
		0.19763	0.077533	0.19763	0.077533	0.53097	0.13573
		0.4750	0.0250	0.0250	0.4750	0.4750	0.5250
		OB <sub>7</sub>	OB <sub>8</sub>	OB <sub>9</sub>	OB <sub>10</sub>	OB <sub>11</sub>	OB <sub>12</sub>
		0.40903	0.18417	0.14913	0.40903	0.075700	0.075700
		0.41087	0.13573	0.53097	0.41087	0.74420	0.74420
		0.0250	0.9750	0.0250	0.4750	0.0250	0.4750

**Table 4.2.** Degree of quasi-restoration of split orbits. In all cases the (pseudo-)eigensymmetry is  $P2/c$ .

Orbit or union of orbits	$d_{\min}$ in Å	Restoration percentage of all atoms.
Y <sub>6</sub>	0.38374	16.66%
X <sub>3</sub>	0.45937	
OB <sub>1</sub> ∪OB <sub>3</sub>	0.34412	
OA <sub>4</sub>	0.39750	



**Figure 4.1:** View along (111) of the (quasi-)restored atoms by the  $c$ -glide reflection for the hypothetical aragonite twin with (011) as twin plane.

#### IV.4. "Necessary" vs. "Sufficient" conditions

As shown above, the reticular theory of twinning makes abstraction from the atomic structure and estimates the lattice restoration by the twin operation in terms of the twin index and the obliquity. This estimation gives the necessary conditions for the formation of twins at the lattice level. In fact, the lattice represents the periodicity of the crystal pattern and the continuity of a sublattice is a necessary condition for the continuity of a substructure on the atomic level. A good restoration of the lattice is necessary but not sufficient for the formation of the twins. On the other hand, if we have the "necessary" condition, then it seems quite natural to wonder about "sufficient" conditions.

In mathematics, the terms "necessary" and "sufficient" condition have the

following meaning; related to the implication  $A \Rightarrow B$ :

- A is called a *sufficient condition* for B if B happens in case that A happens, i.e. if A implies B.

- A is called a *necessary condition* for B if B can only happen in case that A happens, in other words B cannot happen if A does not happen. In this case, not-A implies not-B, which, as a logical statement, is equivalent to B implies A.

Clearly, crystallography (even theoretical crystallography) is not pure mathematics, so one may accept notions of the terms "necessary" and "sufficient" which are less strict than the logical statements given above. Allowing for a possibly weekend interpretation of "sufficient", one still has to face the question:

*Does the crystallographic orbit approach provide "sufficient" conditions for twinning?*

The crystallographic orbit approach considers the atoms of the structure as geometric points distributed in the crystal space. Such an idealisation ignores the physico-chemical nature of the crystals as well as the thermodynamic and kinetic conditions. The latter are certainly of fundamental importance because for growth twins the single crystal always corresponds to a thermodynamically more stable (lower energy) state than a twin. The fact that a twin forms instead shows that kinetic effects must become of primary importance. The composition surface is a region of partial structural discontinuity, but a few atomic layers away from it the structure is again the same as in the original crystal, albeit with a different orientation in space. Therefore, the change in orientation that occurs at the composition surface must represent a sort of compromise between the most stable situation, corresponding to the untwinned crystal, which is not realised possibly because of a perturbation (defects, impurities, chemical heterogeneities), and the complete arrest of the growth due to this perturbation. These considerations would be necessary to move from the structurally necessary conditions we have developed to the estimation of possible sufficient conditions. Ultimately, a valid statement about sufficient conditions would require detailed knowledge about the perturbations at the composition surface, which



in practice is not accessible. The best one can conclude from the structurally necessary conditions is that there is no obstacle that prevents a twin from being formed.

#### **IV.5. *Conclusion and outlook***

The well-known reticular theory of twinning gives general necessary conditions for the formation of twins but, dealing only with lattices, it cannot predict the structural conditions. These can be obtained by the analysis of the structural coherence at the interface. This analysis is based on the search for non-characteristic crystallographic orbits whose eigensymmetry contains the twin operation and on sections parallel to the twin interface whose layer groups can be extended by the twin operation.

The pseudo-symmetry analysis of the twins of melilite, staurolite and aragonite presented in this thesis, based on the atomic coordinates and a known twin operation, shows the existence of an important common substructure (consisting of restored atoms) in the twinned crystal.

The crystallographic orbits approach, the layer group approach and in particular the combination of these two approaches represent a general model for the symmetry analysis of the structural continuity of the twins. The goal of this approach is to predict the necessary structural conditions for the formation of twins in a general way through an algebraic algorithm.

In order to meet this challenge, one has to examine a sufficient number of cases and develop a new semi-automatic computing procedure implementing the pseudo-symmetry analysis. The analysis of the examples presented in this thesis already indicates that the mere percentages of the restored atoms are insufficient for explaining the twin formation and that further structural information has to be considered, such as the amount of restored cations and anions, of fully restored coordination polyhedra or of substructures which are close to the twinning interface.

1. In the case of the melilite example, it was indeed the case that the amount of

restored cations and anions was sufficient to give a satisfactory explanation for the formation of this twin. However, in addition to this numerical data, the visualisations in the corresponding article illustrate that the restored atoms form a substructure which is substantial enough to provide the backbone for the twin formation, i.e. from the common substructure crystal growth is plausible in both orientations of the individuals involved.

2. For the two types of staurolite twins (Greek cross and St Andrews cross), the oxygen atoms are fully restored (with high accuracy) which already gives a strong indication that twinning may occur. It is remarkable that in this case one either has to restrict oneself to the split orbits under the intersection group or immediately look at the full union of all orbits of oxygen atoms, since oxygen atoms within one orbit under the full space group of the individual are restored to atoms in different orbits. The analysis of the cation restoration explains in this case the different occurrence frequencies of the two types of twins. Looking at the coordination polyhedra is instructive, since it provides a further explanation for the lack of restoration for part of the cations: the twin operation would map occupied coordination tetrahedra to empty ones and vice versa.
3. In the example of the aragonite twin, it is demonstrated how the layer group approach complements the analysis by crystallographic orbits. Sections containing for each atom type the closest atoms to a plane parallel to the composition surface are restored by the restoration operation, so that the layer group of this section has in fact as its point group an extension of the point group induced by the space group and the twin operation. The restoration of the atoms in these sections also determines the mapping between the split orbits by the restoration operation as analysed in the crystallographic orbit approach.

A general algorithm assessing (and ideally predicting) the probability of twin formation would take as input the crystal structure data, the known or expected twin operation – or an interval of indices specifying possible twin elements to scan – and

possibly a tolerance limit on the structural pseudo-symmetry. As shown in chapter II, this tolerance can be chosen by default as the ionic or the covalent radii of the atoms of the input structure unless specified otherwise by the user. The required data for the structure consists of its space group (e.g. specified by its number in the International Tables for Crystallography or its Hermann-Mauguin symbol), the cell parameters and the types and atomic positions of the atoms in the asymmetric unit. A sub-structure is considered as (pseudo-)restored by a symmetry operation if under the action of this operation all atoms in this sub-structure deviate from their ideal positions by an amount not larger than the tolerance limit on the structural pseudo-symmetry. Taking a symmetry operation having the twin operation as its linear part, the pseudo-symmetry of the sub-structure directly translates into the mapping of this sub-structure on the corresponding orientation in the second individual.

In the search of possible reflection twins, the program would iterate over different ( $hkl$ ) Miller indices of candidate twin planes, computing the percentages of restored atoms and the restoration of further relevant substructures by the corresponding reflections. Likewise, possible rotation twins would be analysed by considering different candidate twin axes  $[uvw]$ .

The output of the program would then consist of a list of candidates for twin operations, together with the percentages of restored atoms (within the accepted tolerance) and further information on the restoration supporting the hypothesis of twin formation with these twin operations. Ultimately, the restoration information determined should lead to a ranking of the different twin operations, explaining and predicting the probability of the formation of twinned crystals.

To validate the algorithm, in a first step the twin operation(s) found in this way have to be compared with known twin operations. When no restoration operation is found for a given set of ( $hkl$ ) or  $[uvw]$  indices, or when the corresponding restoration quality is too low, the corresponding operation should not correspond to any known twin operation, or at least should correspond to rare twins occurring only occasionally in the literature.

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**IUCrJ** (2014). **1**, 39–48



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# Analysis of the structural continuity in twinned crystals in terms of pseudo-eigensymmetry of crystallographic orbits

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Received 3 July 2013

Accepted 25 September 2013

Edited by Y. Murakami, KEK, Japan

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**Keywords:** melilite; structural continuity; twinned crystals

The reticular theory of twinning gives the necessary conditions on the lattice level for the formation of twins. The latter are based on the continuation, more or less approximate, of a substructure through the composition surface. The analysis of this structural continuity can be performed in terms of the eigensymmetry of the crystallographic orbits corresponding to occupied Wyckoff positions in the structure. If  $\mathcal{G}$  is the space group of the individual and  $\mathcal{H}$  a space group which fixes the twin lattice obtained as an intersection of the space groups of the individuals in their respective orientations, then a structural continuity is obtained if (1) the eigensymmetry of an orbit under  $\mathcal{G}$  contains the twin operation; (2) the eigensymmetry of a union of orbits under  $\mathcal{G}$  contains the twin operation; (3) the eigensymmetry of a split orbit under  $\mathcal{H}$  contains the twin operation; or (4) the eigensymmetry of a union of split orbits under  $\mathcal{H}$  contains the twin operation. The case of the twins in melilite is analysed: the (approximate) restoration of some of the orbits explains the formation of these twins.

## 1. Symbols

(**a**, **b**, **c**): basis vectors of the unit cell.

*a*, *b*, *c*: length of basis vectors.

$r_i = \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}$ : coordinates of the *i*th crystallographically independent atom  $A_i$ .

$\mathcal{G}$ : space group of the individual,  $\mathcal{G} = \{g_1, g_2, \dots\}$ , with  $g_1 = 1$  the identity element of  $\mathcal{G}$ .

$O_i$ : orbit of  $r_i$  under  $\mathcal{G}$ ,  $O_i = \{r_i, g_2 r_i, \dots\} = \{r_i^1, r_i^2, \dots\}$  with  $r_i^k = g_k r_i$  for  $g_k \in \mathcal{G}$ .

$O_{ij}$ : splitting of the orbit  $O_i$  under the action of a subgroup of  $\mathcal{G}$ .

$m(O_i)$ : multiplicity of the orbit  $O_i$ , defined as the number of equivalent points in the conventional unit cell of  $\mathcal{G}$ .

(**P**, **p**): matrix-column pair representing a change of basis; composed of a  $3 \times 3$  matrix **P** and a  $3 \times 1$  column **p**.

*T*: matrix representation of the twin operation in the basis of the twin.

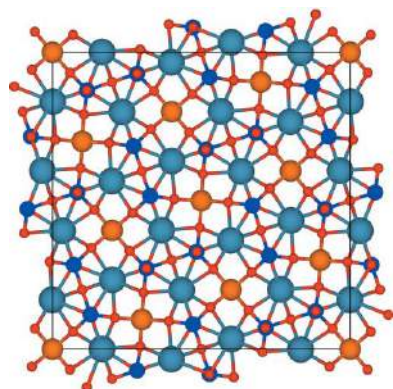
$\mathcal{S}_i$ : site-symmetry group of  $r_i$ .

$\mathcal{H}$ : space group associated with the structure of the twin.

$\mathcal{E}(O_i)$ : eigensymmetry of the orbit  $O_i$ .

## 2. Introduction

A twin is a heterogeneous crystalline edifice composed of two or more homogeneous crystals of the same phase with



different orientation related by a twin operation, *i.e.* a crystallographic operation mapping the orientation of one individual onto that of the other(s) (Friedel, 1904, 1926, 1933). A twin element is the geometric element in direct space (plane, line, centre) about which the twin operation is performed.

Twins can be classified from the genetic viewpoint in three categories:

(1) Transformation twins, which form during a phase transition leading to a loss of point symmetry.

(2) Mechanical twins, which form as the result of a mechanical action (typically, an oriented pressure) on the crystal.

(3) Growth twins, which form during crystal growth, either at the nucleation stage or by oriented attachment (for a review, see Nespolo & Ferraris, 2004a).

For cases (1) and (2), the cause of the formation of the twin is known. For the growth twins the formation can be a response to a mistake in the normal crystal growth of the individual or the random association of two or more crystals with different orientation (non-equivalent under the symmetry group of the crystal). This category of twins appears not only during the formation of a natural crystal but also during the synthesis of artificial crystals.

The interface that separates the individuals represents a discontinuity for at least a sub-structure. This heterogeneity gives rise to serious problems in the structural study of materials and biomaterials and it represents an obstacle for structural investigations as well as for crystal engineering and material design. For example:

(a) The potential technological applications are hindered by the presence of twinning (*e.g.* the piezoelectric effect is reduced or annihilated).

(b) The presence of twinning reduces the amount of details that can be obtained from a structural study, especially for samples with large unit cells (for example, macromolecules) for which the resolution that can be achieved is already limited by the size of the unit cell.

From the viewpoint of the material scientist and of the crystal grower, the development of a synthesis protocol capable of reducing, if not suppressing, the formation of twins is an important goal. To reach this aim a detailed understanding of the formation mechanism of twins is of paramount importance.

A prerequisite for the formation of a twin is a partial structural continuity through the interface. In fact, without any structural continuity the edifice built by the individual crystals would be unstable or simply not form at all; a complete structural continuity is the feature of a single crystal; in a twin a part of the structure has to continue, more or less unperturbed, across the interface. This atomic continuity implies the continuity of a sub-lattice. In fact, the lattice represents the periodicity of the crystal pattern and the continuity of a sub-lattice is a necessary condition for the continuity of a sub-structure. The reticular approach abstracts from the structure and estimates the lattice restoration by the twin operation in terms of the twin index and the obliquity. A good restoration of the lattice is a necessary but not sufficient condition to

obtain a good structure restoration. The latter would enhance the reticular theory to conditions which are *structurally necessary* for the formation of twinned crystals. A general theory on this has not been developed yet.

Extensive research from the lattice viewpoint during more than a century led to the reticular theory developed by Bravais (1851), Mallard (1885) and Friedel (1904, 1926), based on the existence of a common (sub)-lattice in the three dimensions of the crystallographic point space (note however the special case of monoperiodic twins reported by Friedel, 1933). The common (sub)-lattice, called the twin lattice (Donnay, 1940), is based on the twin element (twin plane or twin axis) and the lattice element (line or plane) that are mutually (quasi)-perpendicular. The twin lattice  $\mathbf{L}_T$  is defined by these two elements  $(hkl)_T$  and  $[uvw]_T$ . When the two elements are reciprocally perpendicular one speaks of twin lattice symmetry (TLS: Donnay & Donnay, 1974) and the two elements are symmetry elements for  $\mathbf{L}_T$ . Otherwise one speaks of twin lattice quasi symmetry (TLQS: Donnay & Donnay, 1974); the two elements are only pseudo-symmetry elements for  $\mathbf{L}_T$ . The degree of pseudo-symmetry corresponds to the deviation from the perpendicularity condition and is measured by the angle  $\omega$  called the *obliquity*.<sup>1</sup> The twin index  $n$  is the inverse of the fraction of lattice nodes restored by the twin operation and corresponds to the ratio between the volumes of the primitive cells of the twin and the individual,  $n = V(\mathbf{L}_T)/V(\mathbf{L}_{ind})$ . Friedel gave as empirical limits for the occurrence of twins  $n \leq 6$  and  $\omega \leq 6$ . Twins falling within these limits are called *Friedelian twins* (Nespolo & Ferraris, 2005). The frequency of occurrence of a twin depends on the degree of lattice restoration: the lower the twin index and the obliquity, the better is the lattice restoration and the higher is the probability that the twin actually occurs. This relation between the occurrence frequency of twins and the values of  $n$  and  $\omega$  is an empirical observation, based, however, on the extensive study of twins over more than a century. It shows the necessary (not sufficient) character of the lattice restoration. Nevertheless some twins with higher index are known that violate the empirical limits: they are called non-Friedelian twins (Nespolo & Ferraris, 2005). These twins seem to contradict the general conclusion that a high degree of lattice restoration is a necessary condition for a twin to form. However, in most cases they can be explained by the fact that two or more sublattices contribute to the lattice quasi-restoration. When all the concurrent sublattices are taken into account, the necessary conditions are no longer contradicted. The interpretation of the occurrence of this kind of twins is the object of the hybrid theory of twinning (Nespolo & Ferraris, 2005), which represents an extension of the reticular theory and measures the lattice quasi-restoration in terms of an *effective twin index*  $n_E$  (Nespolo & Ferraris, 2006), a real number defined as the ratio between the lattice nodes of the individual and the lattice nodes belonging to any of the quasi-restored sublattices. In the

<sup>1</sup> For manifold twins (*i.e.* twins in which the twin operation is higher than twofold), a zero-obliquity TLS 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).

case of a single quasi-restored sublattice, this coincides with the classical twin index; otherwise it is lower. In the few examples which are neither explained by the classical reticular nor by the hybrid theory of twinning, the possibility of a wrong choice of the twin element has to be considered (reflection twins in place of rotation twins or *vice versa*). This indeed resolves the apparent contradiction of a higher frequency of twins with higher index than twins with a lower index observed in some cases like the staurolite twins. The Saint Andrews cross twin of staurolite, with index  $n = 12$ , is more frequent than the Greek cross twin with index  $n = 6$  (Nespolo & Ferraris, 2007). These twins are often reported as reflection twins on (031) and (231), respectively, but experimental studies have shown (Hurst *et al.*, 1956) that this interpretation is incorrect and that they actually are rotation twins. For the Saint Andrews cross twin ( $n = 12$ ), the correct choice of the twin element as a line shows the existence of two lattice planes quasi-perpendicular to it and correspondingly two sublattices are quasi-restored by the twin operation. This gives an effective index  $n_E = 6.0$  and as a consequence the Saint Andrews twin is brought back into the Friedelian limits. The occurrence frequency no longer contradicts the necessary condition of a good lattice restoration (Nespolo & Ferraris, 2009).

The reticular theory of twinning can only provide partial prerequisites for the formation of twins, which are governed by the structure. More conclusive conditions can only be obtained by the analysis of the structural coherence at the interface, but such an analysis reduces to a case-by-case *a posteriori* study of known twins. Our purpose is to develop a general structural theory of twinning to predict the structurally necessary conditions for the formation of twins in a general way through an algebraic algorithm. A twin fulfilling these conditions *can* form (and may even be likely to form), but does not necessarily have to form. Indeed, a growth twin is a 'mistake' originated by defects or perturbation of growth conditions and does not correspond to the thermodynamically most stable situation (Buerger, 1945). Donnay & Curien (1960) were the first to suggest the application of the analysis of the eigensymmetry of crystallographic orbits, in the case of pyrite and digenite, which led to the introduction of a restoration index for a subset of atoms (Takeda *et al.*, 1967). This subset must be quasi-continuous across the interface, otherwise the interface would be incoherent, the contact between the individuals would be unstable and the twin would not form. Under the action of the space group  $\mathcal{G}$ , each atom in a crystal is repeated in space to form a crystallographic orbit  $O$ , *i.e.*  $O$  is the set of all atoms obtained under the symmetry operations of the space group  $\mathcal{G}$ . The eigensymmetry  $\mathcal{E}(O)$  of the orbit may be a supergroup of  $\mathcal{G}$  or coincide with it; accordingly, crystallographic orbits are classified in three types according to the relation between  $\mathcal{G}$  and  $\mathcal{E}$ :

*Characteristic orbit:*  $\mathcal{G} = \mathcal{E}$ .

*Non-characteristic orbit:*  $\mathcal{G} \subset \mathcal{E}$  but  $T_{\mathcal{G}} = T_{\mathcal{E}}$ .

*Extraordinary orbit:*  $T_{\mathcal{G}} \subset T_{\mathcal{E}}$ , a special case of non-characteristic orbit defining a superlattice (smaller unit cell) with respect to  $\mathcal{G}$ .

Here  $T_{\mathcal{E}}$  and  $T_{\mathcal{G}}$  are the translation subgroups of  $\mathcal{E}$  and  $\mathcal{G}$ , respectively. When  $\mathcal{G} \subset \mathcal{E}$ , an operation  $t$  belonging to  $\mathcal{E}$  but not to  $\mathcal{G}$  may map the orientation of crystal 1 onto that of crystal 2 and may thus serve as twin operation.

### 3. Crystallographic orbit approach to the analysis of structural continuity in twins

Depending on the nature of the twin operation, twins can be classified into three categories:

- (1) twins by reflection;
- (2) twins by rotation;
- (3) twins by inversion.

An inversion twin is always by (pseudo)-merohedry, *i.e.* it corresponds to twin index  $n = 1$  and does not give rise to a sublattice, because the whole lattice of the individual is (quasi)-restored. For a twin with index  $n > 1$ , the twin operation is not about a lattice direction, which makes its matrix representation non-integral with respect to the basis of the individual. By expressing the twin operation in the basis of the twin, its representation becomes integral again.

The reticular theory of twinning shows that an exact restoration of the lattice is not an absolute condition for the twin to form, a limited departure from the restoration, measured by the obliquity or the twin misfit, being the rule rather than the exception. In the same way, we can expect that a limited departure from structural continuity at the interface does not represent a hindrance to twin formation. In the following, all the occurrences of 'restoration' should thus be read as 'restoration or quasi-restoration'. As a consequence, the eigensymmetry of an orbit has to be taken with some degree of tolerance: a pseudo-eigensymmetry will result in quasi-restoration. The choice of this tolerance has clearly important consequences on the conclusions one may draw about the structural quasi-continuity. Choosing a too small tolerance may lead to a relatively good coherence at the interface being overlooked; a too large tolerance would have no real physical meaning. Clearly, the tolerance has to be chosen keeping in mind the atomic size: it is greater for a large atom than that for a small one. As a rule of the thumb, about 50% of the atomic diameter (*i.e.* the radius: ionic, covalent or atomic depending on the type of bond) seems a reasonable figure.

Let  $(hkl)_T$  and  $[uvw]_T$  be the mutually (quasi)-perpendicular plane and direction which define the cell of the twin lattice. Let  $\mathbf{v}_1$  and  $\mathbf{v}_2$  be 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 twin basis, denoted by  $(\mathbf{abc})_T$ , which is related to the basis  $(\mathbf{abc})_I$  of the individual by the basis transformation  $\mathbf{P}$ :

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

$\mathbf{L}_{\text{ind}}$  and  $\mathbf{L}_T$  have a common origin: there is thus no vector part in the relation between the two references. Given the coordinates  $(xyz)_I$  of an atom in the individual basis, the new coordinates  $(xyz)_T$  of this atom in the twin basis are obtained by the relation:

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

Each atom with coordinates  $r_i$  generates a crystallographic orbit  $O_i$  with eigensymmetry  $\mathcal{E}(O_i)$  under the action of the symmetry operations of the space group  $\mathcal{G}$ . If the orbit is non-characteristic, its eigensymmetry group  $\mathcal{E}(O_i)$  may contain the twin operation  $t$ , in which case the orbit is restored by the twin operation. This cannot be true for all the orbits, otherwise  $t$  would belong to the space group of the individual and the structure would be a single individual and not a twin. When the orbit is not fully restored, a subset of atoms belonging to the orbit can instead be restored. This subset is defined by a subgroup  $\mathcal{H}$  of  $\mathcal{G}$  obtained by intersecting the space groups of the individuals. Since the twin index is  $n > 1$ ,  $\mathcal{H}$  is a proper subgroup of  $\mathcal{G}$ , the translation subgroup of  $\mathcal{H}$  is a subgroup of index  $n$  in the translation subgroup of  $\mathcal{G}$ .

Let  $\mathcal{G}$  be the space group of one of the individuals of a twinned crystal. The twin operation  $t$  maps the first individual to the second individual (assuming, for ease of description, the case of a twofold twin) and the space group of the second individual is the conjugate group  $t\mathcal{G}t^{-1}$ . In addition, the twin operation  $t$  maps the lattice  $\mathbf{L}$  of the first individual to the lattice  $t\mathbf{L}$  of the other individual and the intersection  $\mathbf{L}_T := \mathbf{L} \cap t\mathbf{L}$  is the twin lattice. Since  $t\mathbf{L}_T = t\mathbf{L} \cap t^2\mathbf{L} = t\mathbf{L} \cap \mathbf{L} = \mathbf{L}_T$ , the twin operation fixes the twin lattice. The space group  $\mathcal{H}$  compatible with the twin lattice is the intersection of the space groups of the two individuals, written with respect to the twin basis, *i.e.*  $\mathcal{H} = \mathcal{G} \cap t\mathcal{G}t^{-1}$ . The subgroup  $\mathcal{H}$  is uniquely determined; it consists of those isometries which fix both individuals separately. In particular, its translation subgroup  $\mathcal{T}_{\mathcal{H}}$  consists of the translations by vectors from the twin lattice  $\mathbf{L}_T$ . The above relation is easily generalized to twin operations higher than twofold by replacing  $\mathbf{L}_1 \cap \mathbf{L}_2 = \mathbf{L} \cap t\mathbf{L}$  with  $\cap_i t_i \mathbf{L}_1$ .

To find the elements of  $\mathcal{H}$ , let  $W_i, w_i$  be the linear and translation parts of a symmetry operation of the first individual, written with respect to the twin basis, *i.e.*  $(W_i, w_i) \in \mathbf{P}^{-1}\mathcal{G}\mathbf{P}$ . Since the linear parts of a space group act on its translation lattice, the elements belonging to  $\mathcal{H}$  necessarily have an integral linear part  $W_i$ . Moreover, if  $(W_i, w_i)$  belongs to the intersection, the conjugate  $(W_j, w_j) = \mathcal{T}(W_i, w_i)\mathcal{T}^{-1}$  must be an element of the form  $(W'_i, w'_i) \in \mathbf{P}^{-1}\mathcal{G}\mathbf{P}$ . Choosing an element  $(W'_i, w'_i)$  with  $W'_i = W_j$ , one finally has to check whether  $w_j - w'_i \in \mathbf{L}_T$ . Since the translations in  $\mathcal{H}$  are by vectors in  $\mathbf{L}_T$ , two elements  $(W_i, w_i)$  and  $(W_i, w'_i)$  with the same linear part can only belong to  $\mathcal{H}$  if  $w_i - w'_i \in \mathbf{L}_T$ . This means that for a given element  $(W_i, w_i)$  of  $\mathbf{P}^{-1}\mathcal{G}\mathbf{P}$  one has to check elements of the form  $(W_i, w_i + v)$  for coset representatives  $v$  of  $\mathbf{L}$  with respect to  $\mathbf{L}_T$ .

The study of the orbit behaviour in the twin basis is characterized by the subgroup  $\mathcal{H}$  and the matrix  $\mathbf{P}$ . Considering the group-subgroup related space groups  $\mathcal{G} \supset \mathcal{H}$ , atoms which are symmetrically equivalent under  $\mathcal{G}$ , *i.e.* belong to the same orbit of  $\mathcal{G}$ , may become non equivalent under  $\mathcal{H}$  (splitting of crystallographic orbits), and/or their site-symmetry group  $\mathcal{S}$  can be

reduced (Wondratschek, 1993). Let  $O_i$  be an orbit under  $\mathcal{G}$ ,  $[\mathcal{S}_i, m(O_i)]$  the site symmetry group and the multiplicity of the orbit with respect to the conventional cell of  $\mathcal{G}$ , and let  $[\mathcal{S}_{ij}, m(O_{ij})]$  be defined correspondingly for a split orbit  $O_{ij}$  under  $\mathcal{H}$ , the double index indicating the original orbit under  $\mathcal{G}$  (index  $i$ ) as well as the number of split orbits stemming from it under restriction to  $\mathcal{H}$  (index  $j$ ).

In the case of splitting, the orbit  $O_i = \{\mathbf{g}_k r_i, \mathbf{g}_k \in \mathcal{G}\}$  is divided into two or more orbits of  $\mathcal{H}$ , with the same/or reduced site symmetry group  $\mathcal{S}$  and a multiplicity equal or lower than  $m(O_i)$ . The atoms belonging to  $O_i$  have  $\mathbf{P}^{-1} \cdot \mathbf{g}_k \cdot r_i$  as coordinates in the twin basis. The possibilities of the splitting of the orbit  $O_i$  are described by the following relations:

$$[i] = \sum_{j=1}^k R_j, \quad R_j = \frac{|S(O_i)|}{|S(O_{ij})|} \quad (2)$$

where  $[i]$  is the finite index of  $\mathcal{H}$  in  $\mathcal{G}$ ,  $R_j$  is the ratio of the order of the site-symmetry groups of the orbits  $O_i$  and  $O_{ij}$  in  $\mathcal{G}$  and in  $\mathcal{H}$ , respectively, and  $k$  is the number of orbits in  $\mathcal{H}$  stemming from  $O_i$  in  $\mathcal{H}$  (Wondratschek, 1993).

The atomic restoration by the twin operation can finally be realised in four cases.

(1) The orbit  $O_i$  is non-characteristic and its eigensymmetry  $\mathcal{E}(O_i)$  contains the twin operation  $t$ . In this case,  $\mathbf{P} = \mathbf{I}$ , where  $\mathbf{I}$  is the identity matrix.

(2) The union of two or more orbits has an eigensymmetry which is higher than that of any of the orbits of the union. This may in particular happen in presence of a specialized metric corresponding, exactly or approximately, to a higher crystal family. In this case, if the twin operation is included in this higher eigensymmetry the set of atoms belonging to the union is restored although each orbit, taken separately, is not. The union can obviously be formed only from atoms with interchangeable roles in the structure. For example, the union of orbits defined by crystallographically different types of oxygen, or of atoms having the same coordination environment although a different chemical species. Clearly, the fact that a different atom occurs in the same coordination on the opposite sides of the interface does not affect the structural continuity, especially if the atomic size is not extremely different. The choice of the orbits to be considered in the union must thus rely on the analysis of the structural roles of these orbits. From a formal viewpoint, the restoration occurs if  $t$  belongs to  $\mathcal{E}(U_{\mathcal{G}})$  where  $U_{\mathcal{G}} = \cup_i O_i$  and  $i$  spans the orbits which are not restored by  $t$  and are occupied by atoms with similar structural role. Here again,  $\mathbf{P} = \mathbf{I}$ .

(3) When neither the orbits  $O_i$  nor their union  $U_{\mathcal{G}}$  is restored, a split orbit  $O_{ij}$  under  $\mathcal{H}$  may be restored by the twin operation  $t$  if its eigensymmetry  $\mathcal{E}(O_{ij})$  contains  $t$ .

(4) As in case (2) above, for orbits  $O_{ij}$  whose  $\mathcal{E}(O_{ij})$  does not contain the twin operation  $t$ , the union  $U_{\mathcal{H}} = \cup_{ij} O_{ij}$ , defined on the same criteria as  $U_{\mathcal{G}}$ , has to be considered. The restoration of a union of orbits under  $\mathcal{H}$  may in particular happen when the sublattice fixed by  $\mathcal{H}$  has a specialized metric corresponding, exactly or approximately, to a higher crystal family.



Cases (1) and (3) could of course be subsumed under cases (2) and (4) as unions of a single orbit or split orbit, but we emphasize the importance of these cases by discussing them separately.

The actual analysis performed is exactly the same no matter whether the group considered is  $\mathcal{G}$  or  $\mathcal{H}$  and whether we work on a single orbit or a union of orbits. Let  $\mathcal{K}$  be a general notation for either  $\mathcal{G}$  or  $\mathcal{H}$  and  $O$  a general notation for one of  $O_i$ ,  $O_{ij}$ ,  $U_{\mathcal{G}}$  or  $U_{\mathcal{H}}$ . If  $O$  is restored by the twin operation  $t$ , then the eigensymmetry  $\mathcal{E}(O)$  is a supergroup of  $\mathcal{K}$  containing  $t$ . Such an orbit which belongs to the substructure continuing across the interface of the twin structure that is invariant under the twin operation explains (in part) the formation of the twin.

Because the eigensymmetry of (split) orbits or unions thereof is often approximate and as a consequence the restoration is imperfect, we need a quantitative measure for the degree of restoration. Let  $d_{\min}$  be the minimal distance between the position to which a chosen atom in  $O$  is mapped under the twin operation  $t$  and the atoms in  $O$ . If  $t \in \mathcal{E}(O)$ , then  $d_{\min} = 0$  for all atoms in  $O$ . If  $t$  is only a pseudo-symmetry of  $O$ , then  $d_{\min} > 0$  and its value is a measure for the degree of quasi-restoration.

The advantage of dealing with split orbits under the intersection group  $\mathcal{H} = \mathcal{G} \cap t\mathcal{G}t^{-1}$  is that the value of  $d_{\min}$  is the same for all atoms in a split orbit under  $\mathcal{H}$ , as is shown by the theorem in the Appendix A.

Let  $O^1$  be an orbit  $O$  in the first individual,  $O^2$  the corresponding orbit generated by the twin operation  $t$  in the second individual. The application of the twin operation  $t$  to  $O^1$  generates  $O^2$ . For a fixed *orientation* of the twin element, the formation of a twin may result in a variable degree of atomic restoration depending on the *position* of the twin element in the unit cell, *i.e.* depending on which atoms are exposed to the surface or close to it. Since twinning is a point group phenomenon that occurs at a macroscopic level, the orientation of a twin element only determines the linear part of the twin operation, but not its translational part, corresponding to the position of the twin element. On the other hand, the operation which restores an orbit acts on the structure, at the microscopic (atomic) level and may well also contain an intrinsic translational part (glide or screw component). In other words, the twin operation one observes macroscopically as well as in the diffraction pattern as the overlap of differently oriented reciprocal lattices, can be realised at the atomic levels at different locations and with or without an intrinsic translation. This realisation of the twin operation is hereafter called a *restoration operation*. In order to find the possible restoration operations, one starts with the intersection group  $\mathcal{H}$  and determines its minimal supergroups which contain an operation with the required linear part. However, dealing with split orbits for the intersection subgroup  $\mathcal{H}$  simplifies the analysis drastically. For a single split orbit and pairs of split orbits one simply checks whether the (pseudo-) eigensymmetry contains an operation of the same type as the twin operation and with its geometric element parallel to that of the twin element. The eigensymmetry analysis then provides the

location of the twin element and the nature of the restoration operation.

$O^1$  is restored if  $t \in \mathcal{E}(O^1)$  or if  $d_{\min}$  is lower than a certain threshold which depends on the atomic size (being smaller for smaller atoms). When comparable degrees of restoration are obtained for different locations of the twin element, the probability of twin formation is higher because the twin can form at different stages of crystal growth, corresponding to different atomic surfaces exposed when the twin formation starts. In the opposite case, a higher probability of formation corresponds to the occurrence of a stacking defect, during crystal growth, on a surface corresponding to more restricted, possibly unique, locations of the twin element.

#### 4. Case study: the melilite twins

Melilite is a group of sorosilicate minerals with general formula  $X_2YZ_2O_7$  with  $X = \text{Ca, Na, Sr, K}$  in octahedral coordination,  $Y = \text{Mg, Al, Fe, B}$  in tetrahedral coordination and  $Z = \text{Si, Al}$  again in tetrahedral coordination. These minerals crystallize in space groups of type  $P\bar{4}_21m$  with  $X$  and  $Z$  in Wyckoff positions  $4e$ ,  $Y$  in Wyckoff position  $2a$  and oxygen atoms distributed over three different Wyckoff positions,  $2c$ ,  $4e$  and  $8f$ , respectively. We have analysed the structure reported by Bindi & Bonazzi (2005) for which  $a = 7.826$  (1),  $c = 5.004$  (1) Å. The atomic coordinates are given in Table 1, together with an analysis of the quasi-restoration of each orbit. This analysis has been performed with the *PSEUDO* program (Capillas *et al.*, 2011) at the Bilbao Crystallographic Server (Aroyo *et al.*, 2006). Given the difference in the dimensions of the cations and the anions, a tolerance of 1 Å for the former and 1.5 Å for the latter has been used to evaluate the pseudo-eigensymmetry.

Two twins in melilite are reported by Deer *et al.* (1997), with reflections in  $\{001\}$  and  $\{100\}$  as twin operations: both are twins by merohedry so that  $\mathbf{L}_T$  coincides with  $\mathbf{L}_{\text{ind}}$ . The analysis has to be performed on planes, not on forms, and for this reason in the following the planes (001) and (100) are used; the result is obviously exactly the same if another plane from the same form is used. Since the twins are by merohedry, the intersection group  $\mathcal{H} = \mathcal{G} \cap t\mathcal{G}t^{-1}$  coincides with the group  $\mathcal{G}$  of the individual which is of type  $P\bar{4}_21m$  (No. 113). The minimal supergroups containing symmetry operations with the required linear parts are (all symmetry operations are expressed with respect to the standard setting of  $P\bar{4}_21m$ ):

(1)  $P4/mbm$  (No. 127), with the symmetry operation  $m_{x,y,0}$  for the (001) twin and  $b_{\frac{1}{2},y,z}$  for the (100) twin;

(2)  $P4/nmm$  (No. 129), with  $n_{(\frac{1}{2},\frac{1}{2},0)} x,y,0$  for the (001) twin and  $m_{0,y,z}$  for the (100) twin;

(3)  $P4_2/mnm$  (No. 136), with  $m_{x,y,\frac{1}{4}}$  for the (001) twin and  $n_{(0,\frac{1}{2},\frac{1}{2})} \frac{1}{4},y,z$  for the (100) twin;

(4)  $P4_2/ncm$  (No. 138), with  $n_{(\frac{1}{2},\frac{1}{2},0)} x,y,\frac{1}{4}$  for the (001) twin and  $c_{0,y,z}$  for the (100) twin.

The last two columns in Table 1 give the respective restoration operations contained in the eigensymmetry of the different orbits.

Both (001) and (100) twins are by merohedry, with the whole lattice restored by the twin operations. The degree of

Table 1

Atomic coordinates of melilite (after Bindi & Bonazzi, 2005) and analysis of the quasi-restoration of each orbit.

The orbit (pseudo)-eigensymmetry is given as the minimal distance between atoms quasi-restored by the twin operations. This distance coincides with the degree of pseudo-symmetry ( $\Delta_{\max}$ ) obtained by *PSEUDO* (Capillas *et al.*, 2011) as the maximal distance between atoms produced by the additional symmetry operations of  $\mathcal{E}(O)$ . ( $\mathbf{P}, \mathbf{p}$ ) is the matrix-column pair relating the coordinate system of  $\mathcal{G}$  to that of  $\mathcal{E}(O)$ . The restoration operations are given with respect to the coordinate system of  $\mathcal{G}$ .

Site	Wyckoff position	Coordinates	$\mathcal{E}(O)$	( $\mathbf{P}, \mathbf{p}$ )	$d_{\min}$ (Å)	Restoration operations for (001) twin	Restoration operations for (100) twin
X	4e	0.3316(1) 0.1684(1) 0.5065(2)	$P4/mbm$	(I   000)	0.0651	$m\ x,y,0$	$b\ \frac{1}{4}y,z$
Y	2a	0 0 0	$P4/mmm$	$\begin{pmatrix} 1 & 1 & 0 &   & 0 \\ \bar{1} & 1 & 0 &   & 0 \\ 0 & 0 & 1 &   & 0 \end{pmatrix}$	0	$m\ x,y,0$ $n(\frac{1}{2},\frac{1}{2},0)\ x,y,0$	$b\ \frac{1}{4}y,z$ $m\ 0,y,z$
Z	4e	0.1399(2) 0.3601(1) 0.9359(3)	$P4/mbm$	(I   000)	0.6415	$m\ x,y,0$	$b\ \frac{1}{4}y,z$
O1	2c	0.5 0	$P4/nmm$	(I   $\frac{13}{44}0$ )	0	$n(\frac{1}{2},\frac{1}{2},0)\ x,y,0$	$m\ 0,y,z$
O2	4e	0.1805(9) 0.1408(5) 0.3592(5) 0.2558(9)	$I4/mmm$ $P4_2/nmm$	(I   $0\frac{11}{24}$ ) (I   $0\frac{11}{24}$ )	0.6956 0.0580	$m\ x,y,\frac{1}{4}\ n(\frac{1}{2},\frac{1}{2},0)\ x,y,0$ $m\ x,y,\frac{1}{4}$	$n(0,\frac{1}{2},\frac{1}{2})\ \frac{1}{4}y,z\ m\ 0,y,z$ $n(0,\frac{1}{2},\frac{1}{2})\ \frac{1}{4}y,z$
O3	8f	0.0795(6) 0.1868(5) 0.7864(6)	$P4_2/nmm$ $P4_2/ncm$ $P4/nmm$	(I   $0\frac{11}{24}$ ) (I   $\frac{131}{444}$ ) (I   $\frac{13}{44}0$ )	0.3643 1.2422 1.2443	$m\ x,y,\frac{1}{4}\ n(\frac{1}{2},\frac{1}{2},0)\ x,y,\frac{1}{4}$ $n(\frac{1}{2},\frac{1}{2},0)\ x,y,0$	$n(0,\frac{1}{2},\frac{1}{2})\ \frac{1}{4}y,z$ $c\ 0,y,z$ $m\ 0,y,z$

structural restoration is the same for both twins, since the minimal supergroups of  $P\bar{4}2_1m$  containing a restoration operation for one of the twins also contain one for the other twin. All cation orbits are approximately restored by a reflection located at the origin for the (001) twin and by a  $b$ -glide reflection shifted  $\frac{1}{4}$  from the origin for the (100) twin, with displacements ranging from 0 (perfect restoration) to 0.6415 Å. On the other hand, all anions are quasi-restored by a reflection shifted  $\frac{1}{4}$  from the origin for the (001) twin and by an  $n$ -glide reflection shifted  $\frac{1}{4}$  from the origin for the (100) twin, with displacements between 0.0580 and 0.6956 Å. The two further possible restorations for O<sub>3</sub> correspond to different pseudo-eigensymmetries but the much higher value of  $d_{\min}$  makes their contribution hardly significant.

More recently, a further reflection twin, on (1 $\bar{2}0$ ), has been reported in melilite by Bindi *et al.* (2003). The restoration under the action of the twin operation has to be checked in  $\mathcal{G} = P\bar{4}2_1m$  for each orbit  $O_i$  [this is easily done by inspecting Table 1:  $\mathcal{E}(O)$  never contains  $m_{[1\bar{2}0]}$ ] as well as for the union  $\mathcal{U}_{\mathcal{G}}$  of atoms with similar structural role, *i.e.* Y and Z, which are both in tetrahedral coordination, and the three types of oxygen atoms (Table 2). Neither  $\mathcal{E}(O_i)$  nor  $\mathcal{E}(\mathcal{U}_{\mathcal{G}})$  contain  $m_{[1\bar{2}0]}$  as a proper or pseudo-symmetry which therefore does not restore any orbit or union of orbits under  $\mathcal{G}$ . The next step is to check for the restoration of split orbits under  $\mathcal{H}$ .

In a tetragonal lattice, a plane ( $hk0$ ) is exactly perpendicular to the direction with the same indices [ $h\bar{k}0$ ]; the direction [1 $\bar{2}0$ ] is therefore exactly perpendicular to the twin plane, which can thus also be indicated as  $m_{[1\bar{2}0]}$ . This perpendicularity imposed by the metric of the lattice is known as intrinsic TLS or iTLS (Nespolo & Ferraris, 2006). Twinning is by reticular polyhohedry, with twin index  $n = 5$  (for details, see Nespolo & Ferraris, 2004b). The two shortest in-plane directions are [210]

and [001] so that the transformation from the basis of the individual to that of the twin, see equation (1), is immediately obtained as follows:

$$(\mathbf{abc})_I \begin{pmatrix} 1 & 2 & 0 \\ \bar{2} & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = (\mathbf{abc})_T.$$

Applying the inverse transformation, the twin plane in the basis of the twin lattice becomes (100) or  $m_{[100]}$ , equation (1'):

$$\mathbf{P}^{-1} \begin{pmatrix} 1 \\ \bar{2} \\ 0 \end{pmatrix}_I = \begin{pmatrix} 1/5 & \bar{2}/5 & 0 \\ 2/5 & 1/5 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ \bar{2} \\ 0 \end{pmatrix}_I = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}_T$$

so that the matrix representation  $\mathbf{T}$  of the twin operation  $t$  in the twin basis is simply:

$$\mathbf{T} = \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

In our case,  $\mathcal{H} = \mathcal{G} \cap t\mathcal{G}t^{-1} = P\bar{4}$ ,  $a = 17.4995$ ,  $c = 5.0040$  Å: in fact, neither the 2-fold axis nor the reflection plane contained in  $\mathcal{G}$  fix the twin lattice, whereas the  $\bar{4}$  axis does fix it and is common to  $\mathcal{G}$  and  $t\mathcal{G}t^{-1}$ .

Table 2

Analysis of the eigensymmetry of  $U_{\mathcal{G}}$ ,  $\mathcal{G} = P\bar{4}2_1m$ .

$U_{\mathcal{G}}$	$\mathcal{E}(U_{\mathcal{G}})$	( $\mathbf{P}'_{ij}, \mathbf{P}'_{ij}$ ) <sup>-1</sup>	[1 $\bar{2}0$ ] <sub><math>\mathcal{E}(U_{\mathcal{G}})</math></sub>
YUZ	$P4/mbm$	(I   000)	[1 $\bar{2}0$ ], $\notin$
O <sub>1</sub> UO <sub>2</sub>	$P4_2/nmm$	(I   $0\frac{11}{24}$ )	[1 $\bar{2}0$ ], $\notin$
O <sub>1</sub> UO <sub>3</sub>	$P4_2/nmm$	(I   $0\frac{11}{24}$ )	[1 $\bar{2}0$ ], $\notin$
O <sub>2</sub> UO <sub>3</sub>	$P4_2/nmm$	(I   $0\frac{11}{24}$ )	[1 $\bar{2}0$ ], $\notin$
O <sub>1</sub> UO <sub>2</sub> UO <sub>3</sub>	$P4_2/nmm$	(I   $0\frac{11}{24}$ )	[1 $\bar{2}0$ ], $\notin$

Let  $m(O_i)$  be the multiplicity of each orbit  $O_i$  in  $\mathcal{G}$ ,  $i \in \{1, 2, \dots, 6\}$ , and let  $n_i$  be the number of the atoms of the orbit  $O_i$  in the unit cell of the twin lattice. Then:

$$n_i = |\mathbf{P}| \cdot m(O_i)$$

where  $|\mathbf{P}|$  is the determinant of the transformation matrix  $\mathbf{P}$ . The number of atoms  $n_i$ , equivalent under  $\mathcal{G}$ , is divided in the twin basis on  $s$  non-equivalent subsets of atoms under the subgroup  $\mathcal{H}$ : each subset corresponds to a split orbit  $O_{ij}$  indexed by  $s$  and such that:

$$\sum_{j=1}^s m(O_{ij}) = |\mathbf{P}| m(O_i) = n_i.$$

The restoration of a split orbit  $O_{ij}$  is realised when  $\mathcal{E}(O_{ij})$  contains a restoration operation with linear part  $m_{[100]_T}$ . The extensions of  $P\bar{4}$  (No. 81) containing such an operation are  $P\bar{4}m2$  (No. 115),  $P\bar{4}c2$  (No. 116),  $P4b2$  (No. 117) and  $P\bar{4}n2$  (No. 118); the corresponding restoration operations are  $m$   $0,y,z$ ,  $c$   $0,y,z$ ,  $b$   $\frac{1}{4},y,z$  and  $n(0,\frac{1}{2},\frac{1}{2})$   $\frac{1}{4},y,z$ , respectively. To evaluate whether a split orbit under  $\mathcal{H} = P\bar{4}$  is quasi-restored by the operation in  $\mathcal{G}$ , one checks whether one of these four operations maps a split orbit either to itself or to another split orbit of the same type (within the accepted tolerance). This is what is displayed in Tables 3–8. It turns out that the reflection located in the origin gives by far the best restoration results, therefore we will only discuss the restoration by the operation  $m$   $0,y,z$ .

The atoms of type  $X$  in Wyckoff position  $4e$  for  $\mathcal{G} = P\bar{4}2_1m$  fall under the action of the subgroup  $\mathcal{H}$  into five split orbits in Wyckoff position  $4h$  for  $\mathcal{H} = P\bar{4}$ , each having four atoms in the unit cell of the twin lattice. The split orbit  $X_1$  is almost perfectly restored (with a deviation of  $0.03764 \text{ \AA}$ ),  $X_4$  and  $X_5$  are also quasi-restored with a much larger but still acceptable deviation ( $0.8617 \text{ \AA}$ ).

The atoms of type  $Y$  in Wyckoff position  $2a$  fall into four split orbits, two of which have four atoms in the twin cell and the other two a single atom. The two split orbits with a single atom in the twin cell are perfectly restored; the split orbit  $Y_4$  is quasi-restored to the split orbit  $Z_3$  with a deviation of  $0.6493 \text{ \AA}$ . This is an admissible replacement, since both the  $Y$  and the  $Z$  atoms are in tetrahedral coordination.

The atoms of type  $Z$  in Wyckoff position  $4e$  fall again into five split orbits each having four atoms in the twin cell. Besides the split orbit  $Z_3$  which is interchanged with  $Y_4$ , three more split orbits are approximately restored (with deviations between  $0.5621$  and  $0.9793 \text{ \AA}$ ).

The oxygen atoms in Wyckoff position  $2c$  fall into two orbits with four atoms in the twin cell and one orbit with two atoms in the twin cell. The split orbit with two atoms is exactly restored, the other two split orbits are only quasi-restored when the threshold for anions is relaxed to  $1.5 \text{ \AA}$  (deviations  $1.1740$  and  $1.3402 \text{ \AA}$ ) and one may doubt whether these are still meaningful for the formation of the twin. The oxygen atoms in Wyckoff position  $4e$  fall into five split orbits (each having four atoms in the twin cell). The split orbits  $O_{25}$  and  $O_{22}$  are approximately restored to themselves (with deviations of  $0.5432$  and  $0.9856 \text{ \AA}$ ), the orbit  $O_{24}$  is quasi-restored to the split orbit  $O_{34}$  belonging to the oxygen atoms in Wyckoff

**Table 3**

Analysis of the split orbits  $X_j$  stemming from  $X$  under  $\mathcal{H} = P\bar{4}$ .

A split orbit  $X_j$  is quasi-restored to a split orbit  $X_k$  (which may be the same as  $X_j$ ) by a twin operation if the approximate eigensymmetry  $\mathcal{E}$  of the union  $X_j \cup X_k$  contains (with  $d_{\min}$  within the accepted tolerance) one of  $P\bar{4}m2$ ,  $P\bar{4}c2$ ,  $P4b2$  or  $P\bar{4}n2$ , corresponding to the admissible restoration operations  $m$   $0,y,z$ ,  $c$   $0,y,z$ ,  $b$   $\frac{1}{4},y,z$  and  $n(0,\frac{1}{2},\frac{1}{2})$   $\frac{1}{4},y,z$ , which are abbreviated as  $m$ ,  $c$ ,  $b$  and  $n$  in the tables.

Orbit	Coordinates	Wyckoff positions	Restoration operation	Restored to	$d_{\min}$ (Å)
$X_1$	0.99896, 0.16632, 0.5065	$4h$	$m$	$X_1$	0.0364
$X_2$	0.19896, 0.56632, 0.5065	$4h$		–	
$X_3$	0.39896, 0.96632, 0.5065	$4h$		–	
$X_4$	0.79896, 0.76632, 0.5065	$4h$	$m$	$X_4$	0.8104
$X_5$	0.59896, 0.36632, 0.5065	$4h$	$m$	$X_5$	0.8617

**Table 4**

Analysis of the split orbits  $Y_j$  stemming from  $Y$  under  $\mathcal{H} = P\bar{4}$ .

Same conventions as in Table 3.

Orbit	Coordinates	Wyckoff positions	Restoration operation	Restored to	$d_{\min}$ (Å)
$Y_1$	0, 0, 0	$1a$	$m$	$Y_1$	0
			$b$	$Y_2$	0
$Y_2$	0.5, 0.5, 0	$1c$	$m$	$Y_2$	0
			$b$	$Y_1$	0
$Y_3$	0.2, 0.4, 0	$4h$	$b$	$Z_3$	0.6493
$Y_4$	0.9, 0.3, 0	$4h$	$m$	$Z_3$	0.6493

**Table 5**

Analysis of the split orbits  $Z_j$  stemming from  $Z$  under  $\mathcal{H} = P\bar{4}$ .

Same conventions as in Table 3.

Orbit	Coordinates	Wyckoff positions	Restoration operation	Restored to	$d_{\min}$ (Å)
$Z_1$	0.88394, 0.12798, 0.9359	$4h$	$m$	$Z_1$	0.7061
$Z_2$	0.08394, 0.52798, 0.9359	$4h$	$m$	$Z_2$	0.9793
$Z_3$	0.28394, 0.92798, 0.9359	$4h$	$m$	$Y_4$	0.6493
			$b$	$Y_3$	0.6493
$Z_4$	0.68394, 0.72798, 0.9359	$4h$		–	
$Z_5$	0.48394, 0.32798, 0.9359	$4h$	$m$	$Z_5$	0.5621

**Table 6**

Analysis of the split orbits  $O_{ij}$  stemming from  $O_i$  under  $\mathcal{H} = P\bar{4}$ .

Same conventions as in Table 3. The restorations with  $d_{\min}$  below  $1 \text{ \AA}$  are highlighted in bold.

Orbit	Coordinates	Wyckoff positions	Restoration operation	Restored to	$d_{\min}$ (Å)
$O_{11}$	0.5, 0, 0.1805	$2g$	$m$	$O_{11}$	<b>0</b>
			$n$	$O_{11}$	<b>0.6956</b>
$O_{12}$	0.1, 0.2, 0.1805	$4h$	$m$	$O_{21}$	1.3402
			$c$	$O_{36}$	<b>0.5632</b>
			$b$	$O_{34}$	1.4183
			$n$	$O_{35}$	1.2773
$O_{13}$	0.3, 0.6, 0.1805	$4h$	$m$	$O_{35}$	1.1740
			$b$	$O_{36}$	<b>0.2527</b>
			$n$	$O_{21}$	1.3251

position  $8f$  (with deviation  $0.4103 \text{ \AA}$ ) and the remaining two orbits are quasi-restored to different split orbits with deviations between  $1$  and  $1.5 \text{ \AA}$ . Finally, the oxygen atoms in Wyckoff position  $8f$  fall into ten split orbits with four atoms

**Table 7**  
Analysis of the split orbits  $O_{2j}$  stemming from  $O_2$  under  $\mathcal{H} = P\bar{4}$ .

Same conventions as in Table 3.

Orbit	Coordinates	Wyckoff positions	Restoration operation	Restored to	$d_{\min}$ (Å)
$O_{21}$	0.88448, 0.12816, 0.2558	$4h$	$m$	$O_{12}$	1.3402
			$m$	$O_{31}$	1.4748
			$c$	$O_{21}$	<b>0.3182</b>
			$n$	$O_{13}$	1.3251
$O_{22}$	0.08448, 0.52816, 0.2558	$4h$	$m$	$O_{22}$	<b>0.9856</b>
			$c$	$O_{32}$	1.0051
			$b$	$O_{37}$	1.2569
			$n$	$O_{22}$	1.3950
$O_{23}$	0.28448, 0.92816, 0.2558	$4h$	$m$	$O_{36}$	1.4560
			$c$	$O_{38}$	1.1174
			$b$	$O_{35}$	1.1016
			$n$	$O_{32}$	1.4935
$O_{24}$	0.68448, 0.72816, 0.2558	$4h$	$m$	$O_{34}$	<b>0.4103</b>
			$c$	$O_{24}$	1.0825
			$b$	$O_{39}$	1.3750
			$n$	$O_{36}$	1.4279
$O_{25}$	0.48448, 0.32816, 0.2558	$4h$	$m$	$O_{25}$	<b>0.5432</b>
			$c$	$O_{35}$	1.1363
			$c$	$O_{310}$	1.4764

**Table 8**  
Analysis of the split orbits  $O_{3j}$  stemming from  $O_3$  under  $\mathcal{H} = P\bar{4}$ .

Same conventions as in Table 3.

Orbit	Coordinates	Wyckoff positions	Restoration operation	Restored to	$d_{\min}$ (Å)
$O_{31}$	0.94118, 0.06916, 0.7864	$4h$	$m$	$O_{21}$	1.4748
			$c$	$O_{31}$	<b>0.4452</b>
			$b$	$O_{310}$	1.0048
			$n$	$O_{310}$	1.4670
$O_{32}$	0.14118, 0.46916, 0.7864	$4h$	$m$	$O_{32}$	1.0794
			$c$	$O_{22}$	1.0051
			$b$	$O_{38}$	1.3284
			$n$	$O_{23}$	1.4935
$O_{33}$	0.34118, 0.86916, 0.7864	$4h$	$m$	$O_{39}$	1.2177
			$c$	$O_{37}$	1.1345
			$n$	$O_{33}$	<b>0.7824</b>
			$m$	$O_{24}$	<b>0.4103</b>
$O_{34}$	0.74118, 0.66916, 0.7864	$4h$	$c$	$O_{39}$	1.3239
			$b$	$O_{12}$	1.4183
			$m$	$O_{13}$	1.1740
			$m$	$O_{35}$	1.4413
$O_{35}$	0.54118, 0.26916, 0.7864	$4h$	$c$	$O_{25}$	1.1363
			$b$	$O_{23}$	1.1016
			$n$	$O_{12}$	1.2773
			$n$	$O_{38}$	1.4677
$O_{36}$	0.89444, 0.20938, 0.7864	$4h$	$m$	$O_{23}$	1.4560
			$c$	$O_{12}$	<b>0.5632</b>
			$b$	$O_{13}$	<b>0.2527</b>
			$n$	$O_{24}$	1.4279
$O_{37}$	0.09444, 0.60938, 0.7864	$4h$	$c$	$O_{33}$	1.1345
			$b$	$O_{22}$	1.2569
			$n$	$O_{37}$	<b>0.5190</b>
			$m$	$O_{38}$	<b>0.3283</b>
$O_{38}$	0.29444, 0.00938, 0.7864	$4h$	$c$	$O_{23}$	1.1174
			$b$	$O_{32}$	1.3284
			$n$	$O_{35}$	1.4677
			$m$	$O_{33}$	1.2177
$O_{39}$	0.69444, 0.80938, 0.7864	$4h$	$c$	$O_{34}$	1.3239
			$b$	$O_{24}$	1.3750
			$n$	$O_{39}$	<b>0.3764</b>
			$m$	$O_{310}$	<b>0.1946</b>
$O_{310}$	0.49444, 0.40938, 0.7864	$4h$	$c$	$O_{25}$	1.4764
			$b$	$O_{31}$	1.0048
			$n$	$O_{31}$	1.4670

**Table 9**  
Summary of the percentage of atomic quasi-restoration by the  $(1\bar{2}0)$  twin plane in melilite for the admissible restoration operations (expressed in the basis of the twin).

The values in parentheses are obtained by also taking into account the oxygen atoms restored with a degree of approximation between 1 and 1.5 Å. In the unit cell of the twin lattice, there are 20 cations of type  $X$ , 10 cations of type  $Y$ , 20 cations of type  $Z$  and 70 oxygen atoms, thus in total 120 atoms.

Restoration operation	% $X$	% $Y$	% $Z$	% cations	%O	% all atoms
$m$ 0,y,z	60	60	80	68	37 (94)	50 (83)
$c$ 0,y,z	0	0	0	0	23 (91)	13 (53)
$b$ $\frac{1}{4}$ ,y,z	0	60	20	20	11 (80)	15 (55)
$n$ ( $0, \frac{1}{2}, \frac{1}{2}$ ) $\frac{1}{4}$ ,y,z	0	0	0	0	20 (89)	12 (52)

each. Besides the split orbit  $O_{34}$  that is interchanged with  $O_{24}$ , the two orbits  $O_{310}$  and  $O_{38}$  are quasi-restored to themselves with low deviations (0.1946 and 0.3283 Å). Six more of these split orbits are quasi-restored with higher deviations (between 1 and 1.5 Å).

Table 9 shows a summary of the above analysis, where we see that the percentage of atoms quasi-restored by the reflection is much better than for the three glide reflections. The fact that 68% of the cations and 37% of the anions are restored within 1 Å is a strong justification for the occurrence of this twin.

In Figs. 1 and 2 we display views of the twin cell. Figs. 1(a) and 2(a) show all atoms, and Figs. 1(b) and 2(b) the quasi-restored atoms. Fig. 1 is a view along the  $c$  axis, *i.e.* the direction of the fourfold rotoinversion axis contained in the subgroup  $\mathcal{H}$ ; Fig. 2 is along the normal of the (111) plane.

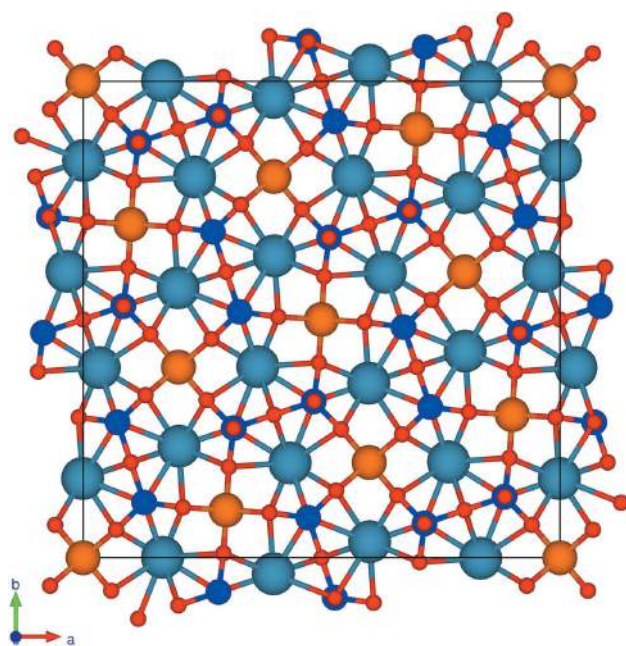
## 5. Conclusions

The reticular theory of twinning represents an elegant and general approach for estimating the probability of the occurrence of a twin. However, because it provides a necessary condition only on the lattice level, its application as an *a priori* predictive tool is limited: while a low lattice restoration clearly indicates low probability of formation, a high lattice restoration is indicative, but not conclusive, of a probable occurrence.

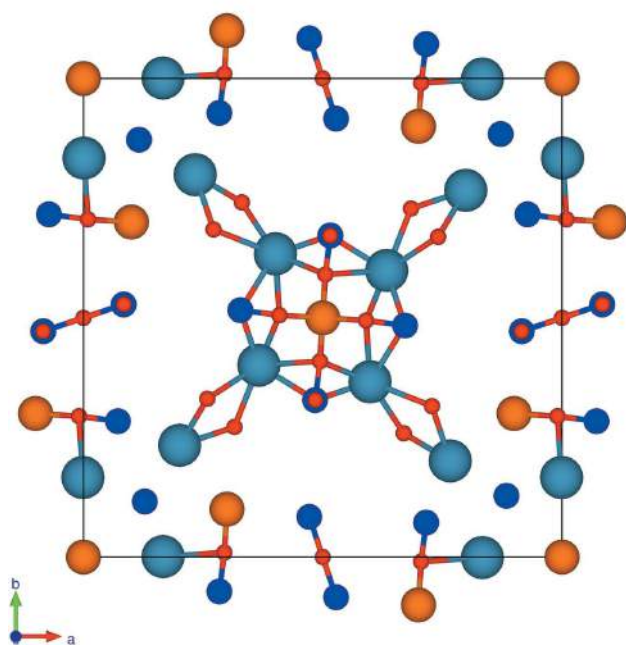
The analysis of the eigensymmetry of the crystallographic orbits corresponding to occupied Wyckoff positions is the key for obtaining a quantitative estimation of the structural restoration realised by the twin operation(s) and for obtaining structurally necessary conditions enhancing the reticular conditions for the twin formation. The example of melilite is particularly instructive. The (001) and (100) twins are both twins by merohedry and from the reticular viewpoint both twins should have a high probability of occurrence. As a matter of fact, the structural restoration is also fairly good, although the cations and anions require different locations of the twin element. The  $(1\bar{2}0)$  twin, despite a twin index of 5, also leads to a relatively high degree of atomic restoration, which explains the occurrence of this twin.

The approach we have developed in this article opens new perspectives in the study of twins and is currently being applied to other known examples.





(a)



(b)

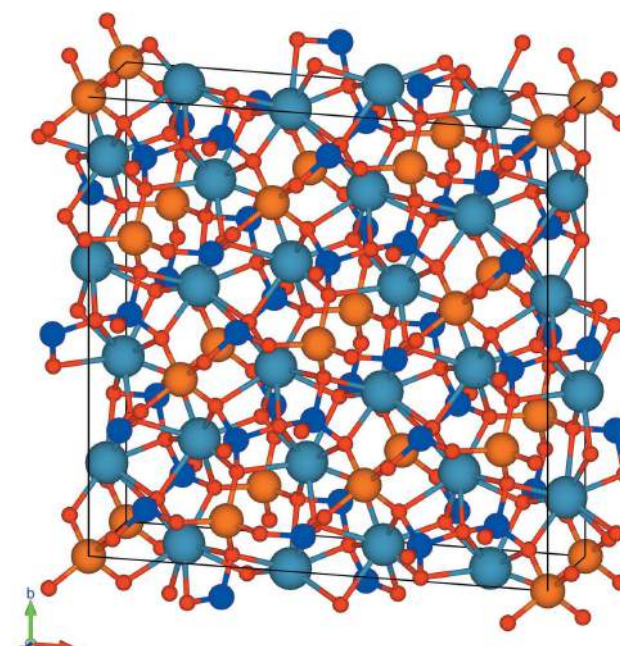
**Figure 1**

View of the unit cell of the twin lattice of melilite along the  $c$  axis. The atoms of type  $X$  (mainly calcium in our example) are coloured light blue, the atoms of type  $Y$  (mostly magnesium) in orange, the atoms of type  $Z$  (mainly silicon) dark blue and the oxygen atoms are in red. (a) View of all atoms in the cell and (b) the quasi-restored atoms.

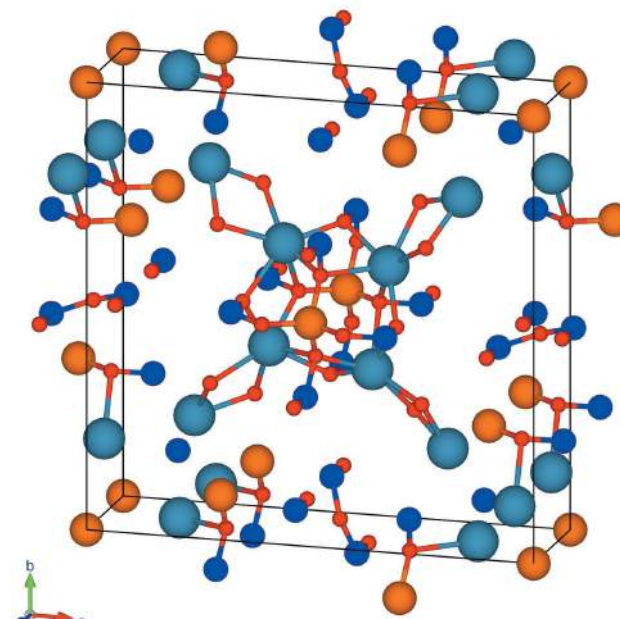
## APPENDIX A

**Theorem.** Assume<sup>2</sup> that  $t$  is the twin operation such that  $t^2$  is an element of  $\mathcal{G}$ . Let  $O_{ij}$  be a split orbit under the intersection

<sup>2</sup> This includes the twin operation of a twofold twin as well as twin operations of higher order about symmetry elements for the individual, like a fourfold rotation about a twofold symmetry axis or a sixfold rotation about a threefold symmetry axis. For details, see Nespolo (2004).



(a)



(b)

**Figure 2**

View of the unit cell of the twin lattice of melilite along to the (111) plane: (a) all atoms in the cell, (b) the quasi-restored atoms.

group  $\mathcal{H} = \mathcal{G} \cap t\mathcal{G}t^{-1}$  and let  $\mathbf{x}$  be the position of an atom in  $O_{ij}$ . Let  $\mathbf{x}'$  be the position of the atom in the structure closest to the mapped position  $t(\mathbf{x})$  of  $\mathbf{x}$  under the twin operation, thus  $d_{\min} = \|t(\mathbf{x}) - \mathbf{x}'\|$ . Then the value of  $d_{\min}$  is the same for every atom in  $O_{ij}$ , i.e. the distance of the image of any atom in  $O_{ij}$  under  $t$  to the closest atom position in the structure is always  $d_{\min}$ .

Moreover, if the position  $\mathbf{x}'$  belongs to the split orbit  $O_{i'j'}$ , then the closest atoms to the mapped split orbit  $t(O_{ij})$  all belong to  $O_{i'j'}$ . In particular, if one atom of  $O_{ij}$  is exactly

restored to an atom in  $O_{ij}$ , then the full split orbit  $O_{ij}$  is mapped to the full split orbit  $O_{ij'}$  under the twin operation.

**Proof:** Let  $\mathbf{x}$  be the position of an atom in  $O_{ij}$ , let  $\mathbf{x}'$  be the position of the atom in the structure closest to  $t(\mathbf{x})$  and let the split orbit to which  $\mathbf{x}'$  belongs be  $O_{ij'}$ . If  $\mathbf{y}$  is the position of another atom in  $O_{ij}$ , then there is a symmetry operation  $h$  in  $\mathcal{H}$  mapping  $\mathbf{x}$  to  $\mathbf{y}$ . Since  $t$  is a twofold twin operation, one has  $tht^{-1} \in t\mathcal{G}t^{-1} \cap t^2\mathcal{G}t^{-2} = t\mathcal{G}t^{-1} \cap \mathcal{G} = \mathcal{H}$  and hence  $tht^{-1} = h' \in \mathcal{H}$ . This means that  $th = h't$  and thus mapping  $\mathbf{y} = h(\mathbf{x})$  by the twin operation  $t$  gives  $t(\mathbf{y}) = th(\mathbf{x}) = h't(\mathbf{x})$ . If one defines  $\mathbf{y}' = h'(\mathbf{x}')$ , then from the fact that  $h'$  is an isometry and thus preserves distances, it follows that  $\|t(\mathbf{y}) - \mathbf{y}'\| = \|h't(\mathbf{x}) - h'(\mathbf{x}')\| = \|h'[t(\mathbf{x}) - \mathbf{x}']\| = \|t(\mathbf{x}) - \mathbf{x}'\| = d_{\min}$ . Since  $h'$  is an element of  $\mathcal{H}$ , it follows that  $O_{ij'}$  contains an atom with distance  $d_{\min}$  to  $\mathbf{y}$ . The same argument applied with the roles of  $O_{ij}$  and  $O_{ij'}$  interchanged now shows that the structure can not contain an atom closer to  $t(\mathbf{y})$  than  $\mathbf{y}'$ , because that would result in an atom with distance less than  $d_{\min}$  to  $t(\mathbf{x})$ .

**Remark:** The above proof is easily generalized to the case of a  $k$ -fold twin. In this case, the intersection subgroup has to be chosen as  $\mathcal{H} = \mathcal{G} \cap t\mathcal{G}t^{-1} \cap t^2\mathcal{G}t^{-2} \cap \dots \cap t^{k-1}\mathcal{G}t^{-(k-1)}$ . Then the crucial argument in the proof that  $tht^{-1} = h' \in \mathcal{H}$  remains valid.

## Acknowledgements

We would like to thank two anonymous referees for their valuable remarks which helped to significantly improve the manuscript.

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Acta Crystallographica Section A

**Foundations and  
Advances**

ISSN 2053-2733

## The staurolite enigma solved

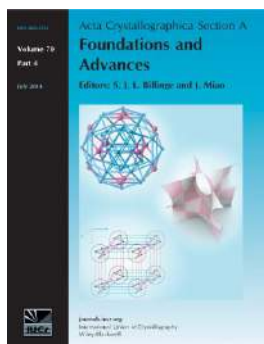
Mohamed Amine Marzouki, Bernd Souvignier and Massimo Nespolo

*Acta Cryst.* (2014). **A70**, 348–353

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## 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 *C222*<sub>1</sub> 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  $90^\circ$  twin or *Greek cross* twin and the  $60^\circ$  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  $\omega$ , which measures deviation



**Table 1**

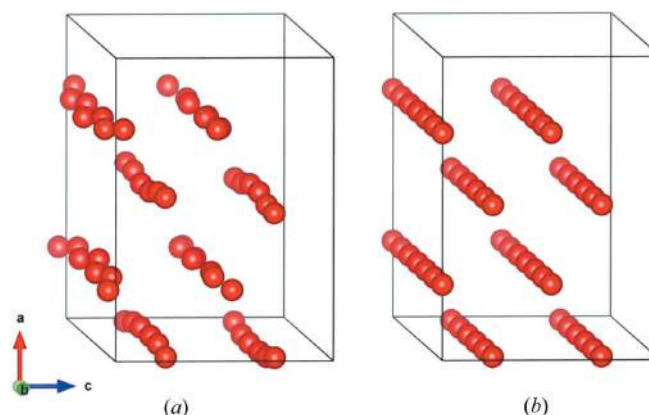
Atomic coordinates of cations in staurolite in the setting of the individual.

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).<sup>1</sup> 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

<sup>1</sup> 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, Náray-Szabó (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 *Fm3m* (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 *Fm3m*. 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 Náray-Szabó (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.

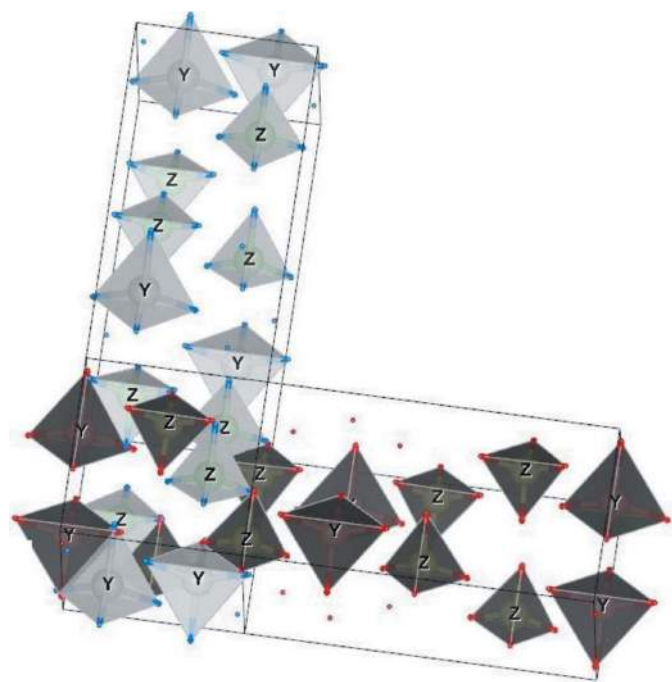
In all cases, the (pseudo)-eigensymmetry is  $P2/m$ .

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  $[1\bar{1}1]$ ,  $[10\bar{2}]$  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,  $\alpha = \beta = 90.001^\circ$ ,  $\gamma = 88.772^\circ$  for the Greek cross twin and  $a = 13.7796$ ,  $b = 33.4821$ ,  $c = 19.2283$  Å,  $\alpha$



**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  $1 \text{ \AA}$ , as in our previous analysis of melilite twins (Marzouki *et al.*, 2014). Tables S1, S2 and S3 (available in the supporting information<sup>2</sup>) 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.

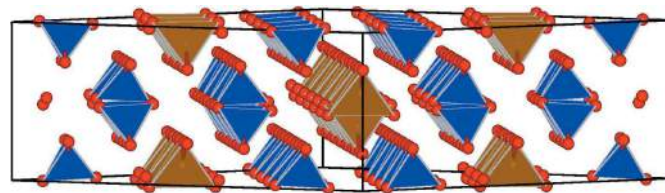
Twin	Octahedral sites restored (%)	Tetrahedral sites restored (%)	Cation sites restored (%)
Greek cross	30	0	19
Saint Andrews cross	56	25	45

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.

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



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# Twining of aragonite – the crystallographic orbit and sectional layer group approach

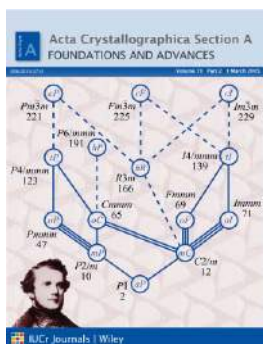
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*Acta Cryst.* (2015). **A71**, 195–202

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# Twinning of aragonite – the crystallographic orbit and sectional layer group approach

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Received 29 July 2014

Accepted 11 December 2014

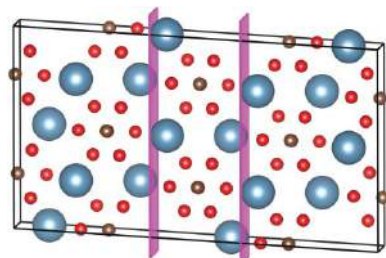
**Keywords:** aragonite; crystallographic orbits; eigensymmetry; sectional layer group; twinning.

The occurrence frequency of the {110} twin in aragonite is explained by the existence of an important substructure (60% of the atoms) which crosses the composition surface with only minor perturbation (about 0.2 Å) and constitutes a common atomic network facilitating the formation of the twin. The existence of such a common substructure is shown by the  $C2/c$  pseudo-eigensymmetry of the crystallographic orbits, which contains restoration operations whose linear part coincides with the twin operation. Furthermore, the local analysis of the composition surface in the aragonite structure shows that the structure is built from slices which are fixed by the twin operation, confirming and reinforcing the crystallographic orbit analysis of the structural continuity across the composition surface.

## 1. Introduction

Aragonite is the high-pressure polymorph of  $\text{CaCO}_3$ , metastable at ambient conditions, which occurs also as an important component of coral skeletons (Higuchi *et al.*, 2014). A salient feature of this mineral is its frequent twinning on {110}. The dihedral angle between (110) and (100) is about  $58^\circ$ : this favours the frequent occurrence of {110} twins as ‘thrillings’, whose morphology simulates a hexagonal single crystal. For this reason, it has been called a ‘mimetic twin’ (Tomkeieff, 1925). A second twin, on {103}, is much less common and corresponds to a hybrid twin with two concurrent sublattices (the analysis of this twin is given in Nespolo & Ferraris, 2009).

Symmetry beyond space-group operations plays a crucial role in the aragonite {110} twin. This has been pointed out by Makovicky (2012), who analysed the local symmetry of the aragonite structure and gave an OD [order–disorder, see *e.g.* Āurovič (1997) for a simple introduction or Ferraris *et al.* (2008) for a comprehensive account] interpretation of {110} twinning. Here we emphasize the role of pseudo-symmetry and show that the crystallographic orbits building up the structure of aragonite have an approximate eigensymmetry which explains a high degree of structural restoration across the composition surface.



## 2. Crystallographic orbits approach to the structural study of twins

The general approach of analysing the structure of twins *via* the restoration of crystallographic orbits is described in Marzouki *et al.* (2014*a*), together with the application to the analysis of melilite. The more complex case of staurolite is analysed in Marzouki *et al.* (2014*b*). We therefore restrict

ourselves to presenting the fundamental principles; the reader will find more details in the two quoted articles.

Each atom in the asymmetric unit of a crystal structure represents an infinite set of atoms equivalent by symmetry, called a *crystallographic orbit*. Let  $\mathcal{E}$  be the *eigensymmetry* of this orbit, *i.e.* the group of all motions mapping the orbit to itself. The intersection of the eigensymmetries of all crystallographic orbits in a crystal structure is the space group  $\mathcal{G}$  of that structure:  $\mathcal{G} = \cap_i \mathcal{E}_i$ . The eigensymmetry of each orbit can be equal to or a proper supergroup of the space group of the structure: one speaks of *characteristic* and *non-characteristic* orbits, respectively.

The twin operation does not belong to the point group of the crystal but it may belong, exactly or approximately, to the point group of the eigensymmetry of one or more non-characteristic crystallographic orbits building the structure of that crystal. When this is the case, the corresponding crystallographic orbits cross the composition surface of the twin (almost) unperturbed and define a substructure common to the twinned individuals. If this substructure represents a significant portion of the structure of the crystal, the occurrence probability of the twin is high.

If the twin operation does not belong to the point group of the eigensymmetry of a crystallographic orbit in  $\mathcal{G}$ , it may still belong to that of a sub-orbit. This sub-orbit is obtained by taking the maximal subgroup  $\mathcal{H}$  of  $\mathcal{G}$  which is compatible with the twin lattice. A crystallographic orbit in  $\mathcal{G}$  splits, in general, into two or more orbits under the action of  $\mathcal{H}$  (Wondratschek, 1993) and the twin operation may belong to the point group of the eigensymmetry of one or more of these split orbits.

It is to be emphasized that the twin operation maps the *orientation* of twinned crystals and is therefore a point-group operation. Interpreted as a space-group operation it is only determined up to its translational part. The actual operation that maps the substructures has, however, a specific translational part: it is called *restoration operation* for the sake of clarity, a term reminiscent of the concept of *restoration index* introduced by Takeda *et al.* (1967) as a structural counterpart of the twin index. However, to avoid cumbersome formulations we will occasionally say that the twin operation maps an atom or a substructure, silently implying that some symmetry operation with the twin operation as linear part (*i.e.* a restoration operation) maps the substructure.

## 2.1. Physical meaning of the pseudo-eigensymmetry and tolerance on the atomic quasi-restoration

The composition surface of a twin represents a discontinuity in the atomic structure. As discussed above, for a twin to exist and be physically stable, a substructure common to the individuals should exist. This substructure is expected to cross the composition surface *more or less* unperturbed. This means that some crystallographic orbits, or sub-orbits, experience a limited deviation at the composition surface, *i.e.* that their eigensymmetry is close to a space group which contains a restoration operation whose linear part is the twin operation.

Let  $d_{\min}$  be the minimal distance between the position to which a chosen atom in a crystallographic orbit  $O$  is mapped under the restoration operation  $t$  and the atoms in  $O$ . If  $t \in \mathcal{E}(O)$ , then  $d_{\min} = 0$  for all atoms in  $O$ . If  $t$  is only a pseudo-symmetry of  $O$ , then  $d_{\min} > 0$  and its value is a measure for the degree of quasi-restoration. A question naturally arises about the maximal acceptable value of  $d_{\min}$ : in the previous examples of melilite and staurolite (Marzouki *et al.*, 2014a,b) we have indicated, as a rule of thumb, a value close to the atom radius (ionic or covalent, depending on the type of bond), because if the approximation on the atomic restoration is beyond this limit the atomic separation on the two sides of the composition surfaces seems too large to justify the existence of a common substructure. In the two previous examples, and especially for the case of staurolite, the restoration obtained was significantly better than this intuitive threshold. As we are going to show, the same is true also for aragonite. Clearly, a larger number of cases has to be analysed before a general conclusion can be satisfactorily drawn but a clear trend seems already to be emerging.

A related question arises about the possibility of having sub-orbits with a better restoration than the full orbit. Suppose that an orbit is restored with a tolerance  $d_G$ , and that the sub-orbits obtained by splitting in  $\mathcal{H}$  are restored with tolerances  $d_{\mathcal{H}1}$  through  $d_{\mathcal{H}n}$ , where  $n$  is the number of sub-orbits in which the original orbit splits when going from  $\mathcal{G}$  to  $\mathcal{H}$ . If  $d_{\mathcal{H}i}$  is significantly smaller than  $d_G$  for some of the  $i$ , the atomic restoration is better described by the split orbits even if  $d_G$  is within the accepted tolerance. However, when  $d_G$  is small, the difference between  $d_G$  and  $d_{\mathcal{H}i}$  does not really have a physical meaning and the splitting scheme does not give additional information for the description of the atomic restoration, as we are going to see for the  $X$  atoms in aragonite.

## 3. Analysis of the {110} twin in aragonite via the crystallographic orbits approach

A structure analogous to that of aragonite is found also in the carbonates hosting a cation bigger than calcium: witherite  $\text{BaCO}_3$ , strontianite  $\text{SrCO}_3$  and cerussite  $\text{PbCO}_3$ , as well as in nitre  $\text{KNO}_3$ . The considerations developed in this section apply to all the isotopes; for the sake of generality, we describe the general formula as  $\text{XYO}_3$ , with the big cations (Ca, Ba, Sr, Pb, K) in the  $X$  site and small ones (C, N) in the  $Y$  site. These minerals crystallize in space groups of type  $Pm\bar{c}n$  (non-standard setting of  $Pnma$  No. 62: transformation from  $Pnma$  to  $Pm\bar{c}n$ : **bca** and  $yzx$ ; from  $Pm\bar{c}n$  to  $Pnma$ : **cab** and  $zxy$ ),<sup>1</sup> with  $X$  and  $Y$  in Wyckoff positions 4c, and the oxygen atoms distributed over two different Wyckoff positions: 4c and 8d. We analyse the aragonite structure reported by Caspi *et al.* (2005) for which  $a = 4.96183$ ,  $b = 7.96914$ ,  $c = 5.74285$  Å, whose atomic coordinates are given in Table 1 (coordinates expressed with respect to the standard setting  $Pnma$  of  $\mathcal{G}$ ).

<sup>1</sup> The twin law {110} is expressed with respect to a morphological cell having  $a:b:c \simeq 0.6:1:0.7$  (Barry & Mason, 1959), which corresponds to the  $Pm\bar{c}n$  setting of the space group.

Table 1

Atomic coordinates of aragonite in the *Pnma* setting of the space group.

Atoms	Wyckoff position	Coordinates
X (Ca)	4c	0.75985, $\frac{1}{4}$ , 0.41502
Y (C)	4c	0.91760, $\frac{1}{4}$ , 0.76194
OA	4c	0.90547, $\frac{1}{4}$ , 0.92238
OB	8d	0.91275, 0.47499, 0.68012

### 3.1. The twin lattice of aragonite

We denote by  $(\mathbf{abc})_I$  the basis for an individual and by  $(\mathbf{abc})_T$  the basis of the twin lattice. The direction quasi-normal to the (110) twin plane is [310]; the twin plane can thus also be regarded as the geometric element<sup>2</sup> of  $m_{[310]}$ . The following analysis is performed from the standard setting of the space group, *Pnma*, in which the cell parameters become  $a = 5.74285$ ,  $b = 4.96183$ ,  $c = 7.96914$  Å, the twin plane (011) and the direction quasi-normal to it becomes [031], so that in this setting the twin plane can be regarded as the geometric element of  $m_{[031]}$ . The shortest directions contained in (011) are [100] and  $[0\bar{1}\bar{1}]$ . The twin lattice  $\mathbf{L}_T$  spanned by the twin plane and the direction quasi-normal to it is obtained from the lattice  $\mathbf{L}$  of the individual by the relation  $\mathbf{L}_T = \mathbf{L} \cap t\mathbf{L}$  (Marzouki *et al.*, 2014a), its unit cell is spanned by the three vectors [031],  $[0\bar{1}\bar{1}]$ , [100]. However, the vector  $\frac{1}{2}([031] + [0\bar{1}\bar{1}])$ , which relates the origin and the 020 node of  $\mathbf{L}$ , also belongs to the twin lattice, hence the cell of  $\mathbf{L}_T$  built in this way is *C*-centred (Fig. 1). The twin index is 2 and the obliquity is  $3.74^\circ$  (computation performed with the software *GEMINOGRAPHY*: Nespolo & Ferraris, 2006). Twinning is by reticular pseudo-polyhohedry, meaning that the twin lattice belongs to the same crystal family as the lattice of the individual, within the approximation represented by the obliquity (Nespolo & Ferraris, 2004).

The maximal subgroup  $\mathcal{H}$  of  $\mathcal{G}$  compatible with the twin lattice is  $\mathcal{H} = \mathcal{G} \cap t\mathcal{G}t^{-1} = C\bar{1}$ : indeed, among the symmetry elements of *Pnma*, neither the rotation/screw axes nor the mirror/glide planes are parallel in the two orientations of  $\mathcal{G}$  and  $t\mathcal{G}t^{-1}$  so that none of them is retained in the intersection. Only the inversion centre, being a zero-dimensional point, remains in the intersection. The bases  $(\mathbf{abc})_I$  for  $\mathcal{G}$  and  $(\mathbf{abc})_T$  for  $\mathcal{H}$  are related by the following transformation:

$$(\mathbf{abc})_I \mathbf{P} = (\mathbf{abc})_T, \quad \mathbf{P} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 3 & 0 \\ \bar{1} & 1 & 0 \end{pmatrix}, \quad (1)$$

which results in the cell parameters for the twin lattice  $a = 9.3876$ ,  $b = 16.8845$ ,  $c = 5.74285$  Å,  $\alpha = 90$ ,  $\beta = 90$ ,  $\gamma = 86.26^\circ$  and in this setting the cell of  $\mathbf{L}_T$  is the standard *C*-centred cell. Equation (1) defines the twin plane as the (010) plane of the

<sup>2</sup> A *geometric element* is defined, for any given symmetry operation, as the point, line or plane fixed by the operation after removing any intrinsic translation. The geometric element allows the operation to be located and oriented. It differs from a symmetry element in that the latter is the combination of a geometric element with the set of symmetry operations having this geometric element in common (for details, see de Wolff *et al.*, 1989).

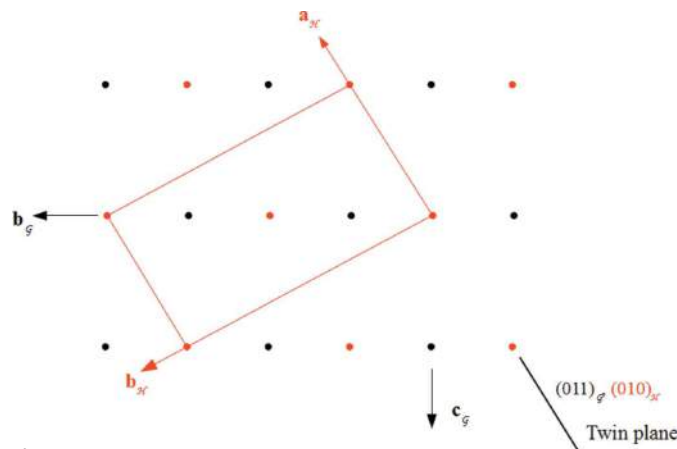


Figure 1

The twin lattice of the aragonite (110) twin – (011) in the standard *Pnma* setting of the space group – seen in projection along the *a* axis of  $\mathcal{G}$ . The  $\mathbf{b}_H$  axis is direction [031] in *Pnma*. Red nodes are (quasi) restored by the twin operation: they represent half of the lattice nodes of  $\mathcal{G}$  so that the twin index is 2.

twin lattice; the axial setting of  $\mathcal{H}$  is therefore the standard monoclinic *b*-unique. However, the cell parameters of  $\mathbf{L}_T$  show that the symmetry-unrestricted angle  $\beta$  is actually  $90^\circ$  whereas the  $\gamma$  angle, which would be symmetry restricted in a truly monoclinic group, actually deviates from  $90^\circ$  by an amount that corresponds precisely to the obliquity and represents a measure of the pseudo-symmetry of the twin lattice.

The extension of the point group of  $\mathcal{H}$  by the twin operation results in a (pseudo)-monoclinic group, either *C2/m* or *C2/c*.

### 3.2. Crystallographic orbits whose eigensymmetry is a supergroup of $\mathcal{G}$

For the crystallographic orbit defined by the Ca cations in the aragonite structure (*X* cations for the isotypes) the minimal supergroup which contains a mirror plane whose linear part coincides with the twin plane is  $\mathcal{E} = P6_3/mmc$  (No. 194). The transformation matrix from  $\mathcal{G}$  to  $\mathcal{E}$  is  $(001/\frac{1}{2}\frac{1}{2}0/\frac{1}{2}\frac{1}{2}0)$  with origin shift  $0\frac{1}{4}\frac{1}{4}$ . The inverse transformation  $(0\bar{1}1/0\bar{1}\bar{1}/100)$  – origin shift  $\frac{1}{2}00$  – applied to [031] gives  $[\bar{1}20]$ , which is a symmetry direction of *P6<sub>3</sub>/mmc* normal to which we have the (010) *c* glide of  $\mathcal{E}$ . This is precisely the restoration operation for the *X* cations whose linear part coincides with the twin operation (once the axial transformation is taken into account).<sup>3</sup> The degree of approximation in the restoration is the minimal distance between atoms quasi-restored by the twin operation. This can be obtained by the *PSEUDO* routine (Capillas *et al.*, 2011) at the Bilbao Crystallographic Server (Aroyo *et al.*, 2006), and coincides with the maximal distance ( $\Delta_{\max}$ ) between atoms produced by the additional symmetry operations of  $\mathcal{E}$  with respect to  $\mathcal{G}$ . For the Ca atoms in aragonite this distance is 0.1155 Å, *i.e.* an excellent degree of quasi-restoration. Considering the relatively large ionic radius

<sup>3</sup> Between  $\mathcal{G}$  and  $\mathcal{E}$  the intermediate minimal supergroup *Cmcm* (No. 63) exists, which however does not contain a symmetry operation with a linear part coinciding with the twin operation. The increase in the translation subgroup is required to turn the original [031] direction of  $\mathcal{G}$  into a symmetry direction of  $\mathcal{E}$ .



Table 2  
Coordinates of the  $Y$  cations in the axial setting of  $\mathcal{H} = C\bar{1}$ .

The rows give the split orbits under  $\mathcal{H}$ . The coordinates in the  $C\bar{1}$  setting are obtained from those in the original  $Pnma$  setting by transforming them with the inverse basis transformation  $\mathbf{P}^{-1} = (0 \frac{1}{4} \frac{3}{4} 0 \frac{1}{4} \frac{1}{4} 1 \ 0 \ 0)$ . The 16  $Y$  cations in the twin cell are obtained from the coordinates given in Table 1 by first expanding the given position to the four positions in the unit cell of the individual equivalent under  $Pnma$  and then adding to each of these positions coset representatives for the (centred) twin lattice with respect to the lattice of the individual. These coset representatives may be chosen as  $(0, 0, 0)$ ,  $(0, 1, 0)$ ,  $(0, 2, 0)$ ,  $(0, 3, 0)$ . Taking the first atom as representative  $Y$ , the other atoms in the split orbit are located at  $-Y$ ,  $Y + (\frac{1}{2}, \frac{1}{2}, 0)$ ,  $-Y + (\frac{1}{2}, \frac{1}{2}, 0)$ . The representatives are chosen with minimal  $y$  in their split orbit.

Orbit	$Y$	$-Y$	$Y + (\frac{1}{2}, \frac{1}{2}, 0)$	$-Y + (\frac{1}{2}, \frac{1}{2}, 0)$
$Y_1$	0.24105, 0.00299, 0.91760	0.75895, 0.99701, 0.08240	0.74105, 0.50299, 0.91760	0.25895, 0.49701, 0.08240
$Y_2$	0.74105, 0.00299, 0.58240	0.25895, 0.99701, 0.41760	0.99105, 0.75299, 0.91760	0.00895, 0.24701, 0.08240
$Y_3$	0.49105, 0.25299, 0.91760	0.50895, 0.74701, 0.08240	0.24105, 0.50299, 0.58240	0.75895, 0.49701, 0.41760
$Y_4$	0.99105, 0.25299, 0.58240	0.00895, 0.74701, 0.41760	0.49105, 0.75299, 0.58240	0.50895, 0.24701, 0.41760

Table 3  
Eigensymmetry of pairs of  $Y_i$  orbits under  $\mathcal{H} = C\bar{1}$ .

The Wyckoff positions are given for the idealized structure having the (pseudo-)eigensymmetry group  $\mathcal{E}$  as proper symmetry group. To obtain the idealized structure, the atoms have to be moved by the given distance  $d_{\min}$ . In some cases, both single orbits in a pair are invariant under the restoration operation. These cases are indicated by giving two Wyckoff positions.

Orbits	$\mathcal{E}$	Wyckoff position for $\mathcal{E}$	$(\mathbf{P}, \mathbf{p})$	$d_{\min}$ (Å)	Restoration operation (with respect to the origin of $\mathcal{H}$ )
$Y_1 \cup Y_2$	$C2/m$	$2 \times 4i$	$(\mathbf{I} \mid 000)$	0.1010	$m \ x0z, a \ x\frac{1}{4}z$
	$C2/c$	$8f$	$(\mathbf{I} \mid 000)$	0.1680	$c \ x0z, n \ x\frac{1}{4}z$
	$C2/m$	$4g + 4h$	$(\mathbf{I} \mid \frac{1}{4}0)$	0.9612	$m \ x\frac{1}{4}z, a \ x0z$
	$C2/c$	$8f$	$(\mathbf{I} \mid \frac{1}{4}0)$	0.9518	$c \ x\frac{1}{4}z, n \ x0z$
$Y_3 \cup Y_4$	$C2/m$	$2 \times 4i$	$(\mathbf{I} \mid \frac{1}{4}0)$	0.1010	$m \ x\frac{1}{4}z, a \ x0z$
	$C2/c$	$8f$	$(\mathbf{I} \mid \frac{1}{4}0)$	0.1680	$c \ x\frac{1}{4}z, n \ x0z$
	$C2/m$	$4g + 4h$	$(\mathbf{I} \mid 000)$	0.9612	$m \ x0z, a \ x\frac{1}{4}z$
	$C2/c$	$8f$	$(\mathbf{I} \mid 000)$	0.9518	$c \ x0z, n \ x\frac{1}{4}z$

of the  $X$  cations (about 1 Å for calcium), the restoration of the whole orbit is realized within about 10% of this radius, which means only a small perturbation in the substructure continuity across the composition surface. As we are going to show in the next section, if one checks the restoration of the sub-orbits into which the  $X$  orbit splits under  $\mathcal{H}$ , one observes an even better restoration for half of the sub-orbits under  $\mathcal{H}$  (0.0233 Å instead of 0.1155 Å), but this does not add further physically meaningful significance to the above analysis because in both cases the degree of approximation is much smaller than the ionic radius.

The same analysis applied to the  $Y$  cations results in exactly the same eigensymmetry with the same transformation matrix. However, the degree of quasi-restoration is much worse – for carbon in aragonite it is 0.9641 Å, which is larger than the covalent radius. The  $Y$  orbit is therefore badly restored by the twin operation. However, for half of the carbon atoms the quasi-restoration is actually much better, as we are going to see by analysing the distribution of  $Y$  cations in terms of the  $\mathcal{H}$  subgroup.

For the oxygen atoms, no supergroup of  $\mathcal{G}$  containing the twin plane as symmetry plane exists within an acceptable approximation and the analysis in terms of split orbits is mandatory.

### 3.3. Crystallographic orbits whose eigensymmetry is a supergroup of $\mathcal{H}$

The  $Y$  orbit of  $\mathcal{G}$  (in Wyckoff position 4c) splits into eight orbits (all in Wyckoff position 2i) in the standard ( $P\bar{1}$ ) setting of  $\mathcal{H}$ . These are however pairwise related by the  $C$ -centring vector so that actually splitting is reduced to four orbits (in Wyckoff position 2i) in the  $C\bar{1}$  setting of  $\mathcal{H}$  (Table 2). The four atoms belonging to the same split orbit in the unit cell of  $C\bar{1}$  correspond to four translationally equivalent atoms in different unit cells of  $\mathcal{G}$ , i.e. atoms related by integer translations in  $\mathcal{G}$ . The pairwise unions  $Y_1 \cup Y_2$  and  $Y_3 \cup Y_4$  possess eigensymmetry  $C2/m$  and  $C2/c$ , which correspond to slightly different restoration (0.1010 and 0.1680 Å, respectively) but the origin is not the same for the two sub-orbits: it coincides with that of  $\mathcal{H}$  for  $Y_1 \cup Y_2$  whereas it is shifted by  $\frac{1}{4} \frac{1}{4} 0$  for  $Y_3 \cup Y_4$  (Table 3). Considering this origin shift, the physical plane  $x0z$  acts as  $m$  mirror or  $c$  glide for  $Y_1 \cup Y_2$  but as  $a$  glide or  $n$  glide for  $Y_3 \cup Y_4$ , whereas the physical plane  $x\frac{1}{4}z$  acts as  $a$  glide or  $n$  glide for  $Y_1 \cup Y_2$  but as  $m$  mirror or  $c$  glide for  $Y_3 \cup Y_4$ . In other words, one of the two unions is well restored (within less than 0.2 Å) by one physical plane, whereas the other union is restored much more poorly (with deviation about 1 Å, larger than the covalent radius and hardly meaningful) by the same physical plane. The role is exchanged every  $b/4$ . When the union of the four split orbits, which corresponds to the unsplit orbit in  $\mathcal{G}$ , is considered, the same eigensymmetry  $C2/m$  or  $C2/c$  is found again but this time the degree of eigensymmetry corresponds to the highest  $\Delta_{\max}$ , 0.9518 or 0.9612 Å, respectively. The latter corresponds precisely to the degree of eigensymmetry found for the  $Y$  orbit of  $\mathcal{G}$ .

Quite obviously, in a case like that of the  $Y$  cations, when the realization of the twin operation in the pseudo-eigensymmetry for an orbit under  $\mathcal{G}$  gives a large deviation from restoration, the analysis of the split orbits in  $\mathcal{H}$  is mandatory to explain the formation of the twin. On the other hand, for the  $X$  cations the excellent restoration of the whole orbit does not require such an analysis. However, one has to check the position of the pseudo-symmetry element responsible for this restoration with respect to the setting of  $\mathcal{H}$ , because it is in this setting that the restoration of half of the  $Y$  cations has been obtained. It may happen that the  $c$  glide belonging to  $\mathcal{E}(X)$  coincides with either of the mirrors

**Table 4**  
Coordinates of representatives for the split orbits of the  $X$  cations under the action of  $\mathcal{H}$ .

The representatives are chosen to have minimal  $y$  coordinate. The full split orbits are obtained as explained in the caption of Table 2.

Orbit	$X_1$	$X_2$	$X_3$	$X_4$
Representative	0.75123, 0.16626, 0.75985	0.25123, 0.16626, 0.74015	0.49877, 0.08375, 0.24015	0.99877, 0.08375, 0.25985

**Table 5**  
Eigensymmetry of pairs of  $X_i$  orbits under  $\mathcal{H} = C\bar{1}$ .

The conventions are the same as those in Table 3.

Orbits	$\mathcal{E}$	Wyckoff position for $\mathcal{E}$	$(\mathbf{P}, \mathbf{p})$	$d_{\min}$ (Å)	Restoration operation (with respect to the origin of $\mathcal{H}$ )
$X_1 \cup X_2$	$C2/c$	$8f$	$(\text{I} \mid 000)$	0.0233	$c \ x0z, n \ x\frac{1}{4}z$
$X_3 \cup X_4$	$C2/c$	$2 \times 4e$	$(\text{I} \mid 000)$	0.1155	$c \ x0z, n \ x\frac{1}{4}z$
$X_1 \cup X_2$	$C2/c$	$2 \times 4e$	$(\text{I} \mid \frac{11}{44}0)$	0.1155	$c \ x\frac{1}{4}z, n \ x0z$
$X_3 \cup X_4$	$C2/c$	$8f$	$(\text{I} \mid \frac{11}{44}0)$	0.0233	$c \ x\frac{1}{4}z, n \ x0z$

belonging to  $\mathcal{E}(Y_i)$ , restoring thus both types of cations, or not, in which case the two types of cations would be restored for different positions of the twin element, *i.e.* at different moments during the crystal growth. To find the answer one has simply to repeat the above analysis in  $\mathcal{H}$  performed for the  $Y$  cations this time for the  $X$  cations. Tables 4 and 5 are the equivalent of Tables 2 and 3. The same conclusions can be drawn for the  $X_i$  orbits as for the  $Y_i$  orbits. However, this time the difference between the degree of restoration of the two pairs of orbits is negligible (0.0233 Å *versus* 0.1155 Å) and justifies considering the union of all four split orbits as restored within the slightly larger approximation, which reproduces the result obtained in the previous section for  $\mathcal{E}(X)$  starting from  $\mathcal{G}$ .

Finally, the analysis of the oxygen orbits leads exactly to the same conclusions as those obtained for the  $Y$  cations (Tables 6, 7 and 8).

The general conclusion that can be drawn about the quasi-restoration in the structure of aragonite by the twin operation is that each  $b/4$  (of the  $H$ -cell) all the  $X$  cations, half of the  $Y$  cations and half of the oxygen atoms are restored, with an exchange of the restored and non-restored atoms every  $b/4$  (Table 9).

Actually, all the restoration rates given do not take into account the deviations from the exact metric of  $\mathcal{E}$ . For the Ca cation, the  $P6_3/mmc$  supergroup of  $\mathcal{G}$  is only approximated because the  $\gamma$  angle is 116.18° instead of 120°. For the other orbits, the monoclinic supergroup of  $\mathcal{H}$  is only approximated because the  $\gamma$  angle is 86.26° instead of 90°. As a consequence, the degree of quasi-restoration is slightly underestimated. To obtain a precise value, this metric deviation should be taken into account. In the adjusted metric, the linear part of the twin operation is no longer a unimodular matrix. However, the correction obtained by using this matrix is within 10% of the minimal distance obtained by *PSEUDO* and does not affect the conclusions drawn from the approximate treatment neglecting this metric deviation. For example, the union of the split oxygen orbit  $OA_2 \cup OB_5$  is quasi-restored with  $d_{\min} = 0.2154$  Å, while this union is quasi-restored with  $d_{\min} = 0.2336$  Å after applying a Gram–Schmidt process (Cheney & Kincaid, 2010) to the aragonite twin basis. Since the effect is minimal, the small angular deviations are neglected throughout this article.

The crystallographic orbits approach, which represents a global analysis of the structure continuity across the composition surface, shows the existence of two pairs of restoration operations for the aragonite (110) twin: the  $c$ -glide reflection

**Table 6**  
Coordinates of representatives for the split orbits of the  $OA$  anions under the action of  $\mathcal{H}$ .

The representatives are chosen to have minimal  $y$  coordinate. The full split orbits are obtained as explained in the caption of Table 2.

Orbit	$OA_1$	$OA_2$	$OA_3$	$OA_4$
Representative	0.12929, 0.20690, 0.09453	0.62071, 0.04310, 0.59453	0.12071, 0.04310, 0.90547	0.62929, 0.20690, 0.40547

**Table 7**  
Coordinates of representatives for the split orbits of the  $OB$  anions under the action of  $\mathcal{H}$ .

The representatives are chosen to have minimal  $y$  coordinate. The full split orbits are obtained as explained in the caption of Table 2.

Orbit	$OB_1$	$OB_2$	$OB_3$	$OB_4$
Representative	0.89135, 0.21122, 0.08725	0.99615, 0.17628, 0.58725	0.75385, 0.07372, 0.08725	0.39135, 0.21122, 0.41275
Orbit	$OB_5$	$OB_6$	$OB_7$	$OB_8$
Representative	0.35865, 0.03878, 0.91275	0.25385, 0.07372, 0.41275	0.49615, 0.17628, 0.91275	0.85865, 0.03878, 0.58725

Table 8

Eigensymmetry of pairs of oxygen orbits under  $\mathcal{H} = C\bar{1}$ .

The conventions are the same as those in Table 3.

Orbits	$\mathcal{E}$	Wyckoff position for $\mathcal{E}$	( $\mathbf{P}, \mathbf{p}$ )	$d_{\min}$ (Å)	Restoration operation (with respect to the origin of $\mathcal{H}$ )
$OA_2 \cup OB_5$	$C2/c$	$8f$	(I   000)	0.2154	$c\ x0z, n\ x\frac{1}{4}z$
$OA_3 \cup OB_8$	$C2/c$	$8f$	(I   000)	0.2154	$c\ x0z, n\ x\frac{1}{4}z$
$OB_6 \cup OB_3$	$C2/c$	$8f$	(I   000)	0.0718	$c\ x0z, n\ x\frac{1}{4}z$
$OA_1 \cup OB_4$	$C2/c$	$8f$	(I   $\frac{1}{4}0$ )	0.2154	$c\ x\frac{1}{4}z, n\ x0z$
$OA_4 \cup OB_1$	$C2/c$	$8f$	(I   $\frac{1}{4}0$ )	0.2154	$c\ x\frac{1}{4}z, n\ x0z$
$OB_2 \cup OB_7$	$C2/c$	$8f$	(I   $\frac{1}{4}0$ )	0.0718	$c\ x\frac{1}{4}z, n\ x0z$

$c_{x,0,z}$  located at  $y = 0$  gives, when being composed with the centring translation  $(\frac{1}{2}, \frac{1}{2}, 0)$ , the  $n$  glide  $n_{(1/2, 0, 1/2)x, 1/4,z}$ , the  $c$  glide  $c_{x,1/4,z}$  located at  $y = \frac{1}{4}$  gives upon composition with the translation  $(\frac{1}{2}, \frac{1}{2}, 0)$  the  $n$  glide  $n_{(1/2,0,1/2)x,0,z}$ . The pairs of restoration operations differing only by the centring translation clearly restore the same subset of the atomic structure.

#### 4. Local analysis via layer groups

The analysis of twins *via* crystallographic orbits investigates the structural continuity across the composition surface. This can take an irregular shape for zero obliquity but is limited to a plane for non-zero obliquity (Friedel, 1904), although in the very rare case of monoperiodic twins the twinned individuals share a single lattice direction (Friedel, 1933). The intrinsic symmetry properties of the composition surface can be described by subperiodic groups: layer groups in the case of a plane and rod groups in the case of a line. In the case of aragonite, the composition surface is a plane (the geometric element of the twin operation) and we will from now on restrict ourselves to the discussion of layer groups (rod groups being analogous, but simpler).

The composition plane is a two-dimensional plane intersecting the crystal structure and is called a *section plane*. However, since a crystal structure is built from physical objects, it makes sense to replace the abstract plane of thickness zero by a slice of finite (usually small) width which extends symmetrically around the section plane and contains the atoms close to it. The symmetry group of such a slice has a translation subgroup with translations along two independent directions and is therefore a sectional layer group. It is clear that this sectional layer group contains all those symmetry operations of the space group  $\mathcal{G}$  which fix the composition plane. But the crucial question in the analysis of twins is whether the layer group is actually larger than this group induced by the space group and contains an additional symmetry operation having the twin operation as linear part. Of course, as in the analysis *via* crystallographic orbits, the twin operation may only be a pseudo-symmetry of the layer and it may be necessary to exclude a (hopefully small) part of the atoms in the chosen slice.

Table 9

Summary of the atomic restoration.

Restoration operation	X	Y	O	All atoms
$c_{x,0,z}$ and $n_{x\frac{1}{4}z}$	16/16 (100%)	8/16 (50%)	24/48 (50%)	48/80 (60%)
$n_{x,0,z}$ and $c_{x\frac{1}{4}z}$	16/16 (100%)	8/16 (50%)	24/48 (50%)	48/80 (60%)

To analyse the layer-group symmetry, let  $\mathbf{d}$  be a vector perpendicular to a section plane  $\mathbf{S}$ . Owing to the periodicity of the crystal pattern along  $\mathbf{d}$ , to find all different types of sectional layer groups for slices perpendicular to  $\mathbf{d}$  it is enough to consider section planes at heights  $s$  with  $0 \leq s < 1$  (fractional coordinate along  $\mathbf{d}$ ). The sectional layer group  $\mathcal{L}$  will always contain translations along two independent directions within the plane, which we assume to form a crystallographic basis for the lattice of translations fixing the section plane. To keep in line with the axial setting (*b*-unique monoclinic) used in the previous section, the in-plane vectors will be taken as  $\mathbf{a}'$  and  $\mathbf{c}'$ ; a point  $\mathbf{p}$  in the section plane at height  $s$  is then given by  $x\mathbf{a}' + s\mathbf{d} + z\mathbf{c}'$ .

Let  $g$  be an operation of a sectional layer group. Then the linear part of  $g$  maps  $\mathbf{d}$  either to  $+\mathbf{d}$  or to  $-\mathbf{d}$ . In the former case,  $g$  is called *side-preserving*, in the latter case it is called *side-reversing* ( $\tau$  and  $\rho$  operations, respectively, in the OD language: Āurovič, 1997). Moreover, since the section plane remains fixed under  $g$ , the vectors  $\mathbf{a}'$  and  $\mathbf{c}'$  are mapped to linear combinations of themselves by the linear part of  $g$ . Therefore, with respect to the (usually non-conventional) basis  $\mathbf{a}', \mathbf{d}, \mathbf{c}'$  (Fig. 2) the linear part of  $g$  is represented by a matrix  $\mathbf{M}'_g$  of the form

$$\mathbf{M}'_g = \begin{pmatrix} \alpha_{11} & 0 & \alpha_{13} \\ 0 & \alpha_{22} & 0 \\ \alpha_{31} & 0 & \alpha_{33} \end{pmatrix}.$$

In order to determine which elements of the space group  $\mathcal{G}$  fix the section plane, *i.e.* belong to the sectional layer group  $\mathcal{L}$ , the elements of  $\mathcal{G}$  are expressed with respect to the coordinate system with basis  $\mathbf{a}', \mathbf{d}, \mathbf{c}'$ , keeping the origin. If  $\mathbf{M}_g$  is the matrix of the linear part of  $g$  with respect to the original basis  $\mathbf{a}, \mathbf{b}, \mathbf{c}$  and  $\mathbf{P}$  is the basis transformation such that  $(\mathbf{a}, \mathbf{b}, \mathbf{c})\mathbf{P} = (\mathbf{a}', \mathbf{d}, \mathbf{c}')$ , the coordinate transformation results in the matrix  $\mathbf{M}'_g = \mathbf{P}^{-1}\mathbf{M}_g\mathbf{P}$  for the linear part and in a vector  $(t_1, t_2, t_3)$  for the translation part.  $\mathbf{M}'_g$  has to be of the form given above, otherwise the section plane is not fixed by  $g$ . Assuming that this is the case, *i.e.* that  $g$  does indeed belong to the layer group  $\mathcal{L}$ ,  $\alpha_{22}$  can only have the values 1 or  $-1$ :

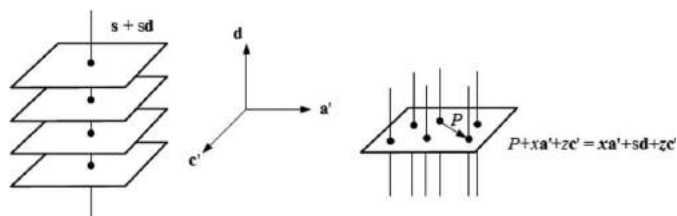


Figure 2

Definition of the axial setting for the layer group.



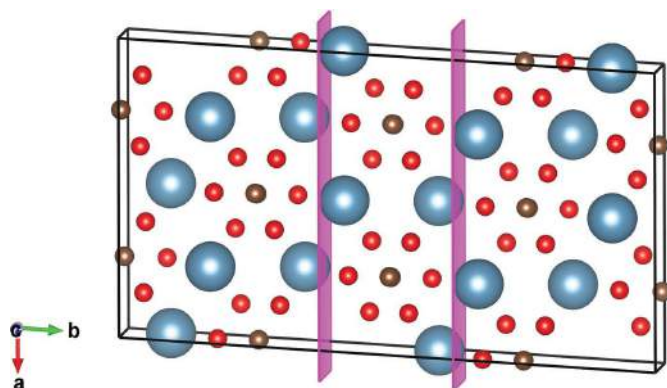


Figure 3

View along the  $c$  axis of the slice defined as the thickness limited by the two pink planes and containing the 12 oxygen atoms (figure drawn with VESTA: Momma & Izumi, 2011).

(a) If  $\alpha_{22} = 1$ ,  $g$  is side-preserving,  $\mathbf{M}'_g \cdot \mathbf{d} = \mathbf{d}$  and  $t_2$  must necessarily be zero, since otherwise the plane is shifted along  $\mathbf{d}$ . Such an element belongs to the layer group at any height  $s$ .

(b) If  $\alpha_{22} = -1$ ,  $g$  is side-reversing,  $\mathbf{M}'_g \cdot \mathbf{d} = -\mathbf{d}$  and a plane situated at height  $s$  along  $\mathbf{d}$  is only fixed if  $t_2 = 2s$ .

In the case of aragonite, the scanning direction  $\mathbf{d}$  is normal to the twin plane and thus  $\mathbf{d} = [031]$ . Since the chosen basis of the twin lattice consists of two vectors in the twin plane and one normal to it (with the slight deviations resulting from the obliquity), the transformation to the basis for the layer group can be taken as

$$\mathbf{P} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 3 & 0 \\ \frac{1}{2} & 1 & 0 \end{pmatrix},$$

which is precisely the transformation to the twin basis. This means that the twin basis  $\mathbf{a}'$ ,  $\mathbf{d}$ ,  $\mathbf{c}'$  with  $\mathbf{d} = [031]$ ,  $\mathbf{a}' = [01\bar{1}]$  and  $\mathbf{c}' = [100]$  is also chosen as the basis for the layer group. The layer groups are found to be as follows:

(a) For  $\alpha_{22} = 1$ , the only side-preserving element of  $\mathcal{G}$  fixing the section layer is the identity and the layer group  $\mathcal{L}$  is of type  $\bar{1}$  [No. 1, *International Tables for Crystallography* Vol. E (ITE): Kopský & Litvin, 2010].

(b) For  $\alpha_{22} = -1$ , the only side-reversing elements of  $\mathcal{G}$  are the inversion for  $y = 0$  and the twofold screw  $c$  axis  $2(0, 0, \frac{1}{2})_{\frac{1}{8}, \frac{1}{8}, z}$  located at  $y = \frac{1}{8}$ . As a consequence, the layer group  $\mathcal{L}$  is of type  $\bar{1}$  (No. 2, ITE) at  $y = 0$  or of type  $2_1$  (No. 9, ITE) at  $y = \frac{1}{8}$ . Owing to the condition  $t_2 = 2s$  equivalent elements are found at  $y = \frac{1}{2}$  and  $y = \frac{5}{8}$ . But due to the  $C$ -centring, the periodicity of the side-reversing elements is actually  $\frac{1}{4}$ .

Summarizing, the layer group  $\mathcal{L}$  induced by the symmetry operations of  $\mathcal{G}$  is of type  $\bar{1}$  (No. 2, ITE) for  $s = 0, \frac{1}{4}, \frac{1}{2}$  and  $\frac{3}{4}$ , of type  $2_1$  (No. 9, ITE) for  $s = \frac{1}{8}, \frac{3}{8}, \frac{5}{8}$  and  $\frac{7}{8}$  and of type  $\bar{1}$  (No. 1, ITE) for all other  $s$ .

The layer groups obtained from the space group  $\mathcal{G}$  are valid for slices of any thickness in one of the individuals of the twin. However, since the twin operation is not contained in the point group of the individuals, a symmetry operation with the twin operation as linear part can only belong to the layer group of a slice of finite width around the composition plane.

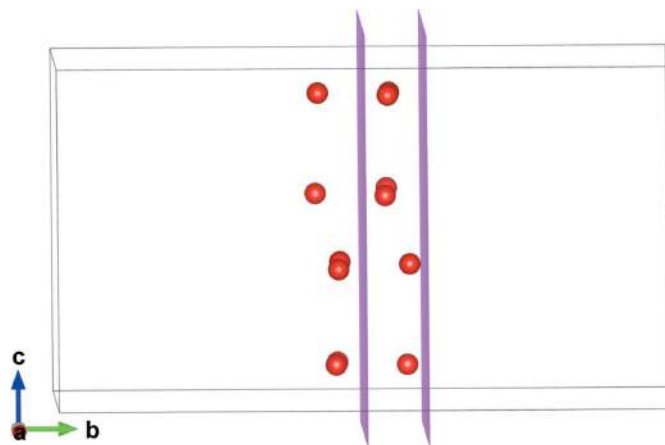


Figure 4

View along the  $a$  axis of the restored 12 oxygen atoms by the  $c$ -glide reflection.

In general, the width of the slice should be chosen small, but large enough to be meaningful for the growth process of the crystal. A typical choice would be to choose the slice such that it contains the coordination polyhedra of the structure closest to the composition plane. In the case of aragonite, a further indication is the periodicity of the layer-group symmetry, which is  $\frac{1}{4}$  along the  $b$  axis.

Looking at the cell of the twin lattice shown in Fig. 3, one sees that subdividing the cell into four slices of width  $4.22 \text{ \AA}$  is a natural choice, since this slice contains the  $X$  cations,  $Y$  cations and oxygen atoms closest to the composition plane (Fig. 4).

The pseudo-eigensymmetry<sup>4</sup>  $\mathcal{E}(K)$  of the slice  $K$  at position  $y = 0$  is found to be a layer group generated by the layer group  $\mathcal{L}$  of type  $\bar{1}$  induced by  $\mathcal{G}$  and the restoration operation, which is a  $c$  glide. The group  $\mathcal{E}(K)$  is of type  $\bar{1}2/c$  (No. 16, ITE, in a non-conventional setting), the restoration accuracy is  $0.2154 \text{ \AA}$ . This deviation from perfect restoration is the maximum of the deviations for the split orbits intersecting the slice. For the  $X$  cations, these are the split orbits  $X_3$  and  $X_4$  with restoration accuracy  $0.1155 \text{ \AA}$ , for the  $Y$  cations the split orbits  $Y_1$  and  $Y_2$  with restoration accuracy  $0.1680 \text{ \AA}$  intersect the slice. For the oxygen atoms, the restoration in the slice actually determines the matching of the split orbits in the crystallographic orbit approach. For example, the slice contains two atoms of the split orbit  $OA_2$  which are mapped to two atoms of the orbit  $OB_5$  with deviation  $0.2154 \text{ \AA}$ . Similarly, two oxygen atoms in the split orbit  $OA_3$  are matched with two oxygen atoms in the split orbit  $OB_8$ , again with deviation  $0.2154 \text{ \AA}$  and two oxygen atoms in  $OB_6$  are matched with two oxygen atoms in  $OB_3$  with deviation  $0.0718 \text{ \AA}$ . Since the cell of the twin lattice is  $C$ -centred, the eigensymmetry  $\mathcal{E}(K)$  of the slice  $K$  at  $y = \frac{1}{4}$  is isomorphic (conjugate by the centring translation). Thus the aragonite structure is built from equivalent slices invariant under the twin operation which are

<sup>4</sup>In analogy with the eigensymmetry of a crystallographic orbit, the eigensymmetry of a slice is defined as the group of motions mapping the set of atoms in the slice to itself.

Table 10

Oxygen atoms restored by the partial symmetry operation  $t' = x + \frac{1}{4}, \bar{y} + \frac{1}{4}, z + \frac{1}{2}$  which is a glide reflection with the plane  $x, \frac{1}{8}, z$  as geometric element and with intrinsic translation vector  $(\frac{1}{4}, 0, \frac{1}{2})$ .

The atoms in the first column are restored to those in the second column (with the given accuracy), but not *vice versa*.

Oxygen atoms to the left of $y = \frac{1}{8}$	Oxygen atoms to the right of $y = \frac{1}{8}$	$d_{\min}$ (Å)
0.12071, 0.04310, 0.90547 (OA <sub>3</sub> )	0.39135, 0.21122, 0.41275 (OB <sub>4</sub> )	0.2154
0.25385, 0.07372, 0.41275 (OB <sub>6</sub> )	0.49615, 0.17628, 0.91275 (OB <sub>7</sub> )	0.0718
0.35865, 0.03878, 0.91275 (OB <sub>5</sub> )	0.62929, 0.20690, 0.40547 (OA <sub>4</sub> )	0.2067
0.62071, 0.04310, 0.59453 (OA <sub>2</sub> )	0.89135, 0.21122, 0.08725 (OB <sub>1</sub> )	0.2154
0.75385, 0.07372, 0.08725 (OB <sub>3</sub> )	0.99615, 0.17628, 0.58725 (OB <sub>2</sub> )	0.0718
0.85865, 0.03878, 0.58725 (OB <sub>8</sub> )	0.12929, 0.20690, 0.09453 (OA <sub>1</sub> )	0.2067

centred at  $y$  values that are multiples of  $\frac{1}{4}$ . Therefore, the composition surface does not impose restrictions on the formation of the twin.

The slice at  $y = \frac{1}{8}$  provides an interesting variation of the above analysis. Considering only the  $X$  cations closest to the composition plane at  $y = \frac{1}{8}$ , the eigensymmetry of the slice contains a translation by  $\frac{1}{2}\mathbf{a}'$  and a glide reflection  $t'$  with the twin operation  $x, \bar{y}, z$  as linear part and translation part  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ . Note that the square of the operation  $t'$  is equivalent to the additional translation by  $\frac{1}{2}\mathbf{a}'$ . Now, extending the slice such that it contains the 12 oxygen atoms closest to the composition plane (*e.g.* by again choosing the width as  $\frac{1}{4}$  of the twin cell in the  $\mathbf{d}$  direction), the operation  $t'$  is no longer a symmetry operation of the slice. This is due to the fact that the translation by  $\frac{1}{2}\mathbf{a}'$  is not a symmetry operation for any of the oxygen atoms in the aragonite structure. However, it is interesting to note that  $t'$  restores the left half of the slice (*i.e.* the half between  $y = 0$  and  $y = \frac{1}{8}$ ) to the right half (between  $y = \frac{1}{8}$  and  $y = \frac{1}{4}$ ) (Table 10) and is therefore only a partial symmetry operation. This partial symmetry actually also holds for the  $Y$  cations, the carbon atoms close to  $y = 0$  are mapped by  $t'$  to those close to  $\frac{1}{4}$ , but not *vice versa*. Although  $t'$  is not a proper symmetry operation of the slice around  $y = \frac{1}{8}$ , the presence of this partial symmetry operation mapping one half of a slice to the other half further increases the probability of the twin to form, since it occurs precisely in the middle between the slices with full restoration.

## 5. Conclusions

The crystallographic orbit approach shows the existence of a common substructure in aragonite, whose  $C2/c$  pseudo-eigensymmetry contains restoration operations having the twin operation as linear part. Furthermore, the local analysis of the composition surface in the aragonite structure, *via* layer

groups, strongly indicates that the {110} aragonite twin has a high probability of occurrence, since the structure is built from slices which are fixed by the twin operation. These two approaches converge to the conclusion that the {110} twin in aragonite is structurally favoured and explain the high frequency of twinning observed in this mineral.

## Acknowledgements

The critical remarks of two anonymous referees allowed us to improve the presentation.

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