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

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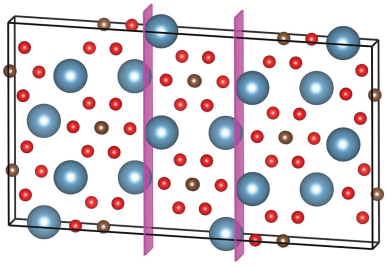
The occurrence frequency of the {110} twin in aragonite is explained by the existence of an important substructure (60% of the atoms) which crosses the composition surface with only minor perturbation (about 0.2 Å) and constitutes a common atomic network facilitating the formation of the twin. The existence of such a common substructure is shown by the *C*2/*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 $CaCO_3$, 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°: 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.* Ďurovič (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.*, 2014*a*,*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 $d_{\mathcal{G}}$, 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 $d_{\mathcal{G}}$ for some of the $i$, the atomic restoration is better described by the split orbits even if $d_{\mathcal{G}}$ is within the accepted tolerance. However, when $d_{\mathcal{G}}$ is small, the difference between $d_{\mathcal{G}}$ 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 $BaCO_3$, strontianite $SrCO_3$ and cerussite $PbCO_3$, as well as in nitre $KNO_3$. The considerations developed in this section apply to all the isotypes; for the sake of generality, we describe the general formula as $XYO_3$, 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 *Pmcn* (non-standard setting of *Pnma* No. 62: transformation from *Pnma* to *Pmcn*: **bca** and *yzx*; from *Pmcn* to *Pnma*: **cab** and *zxy*),[1] with $X$ and $Y$ in Wyckoff positions 4*c*, and the oxygen atoms distributed over two different Wyckoff positions: 4*c* and 8*d*. 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 $\mathcal{G}$).

[1] 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 *Pmcn* 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) | 4*c* | 0.75985, $\frac{1}{4}$, 0.41502 |
| *Y* (C) | 4*c* | 0.91760, $\frac{1}{4}$, 0.76194 |
| O*A* | 4*c* | 0.90547, $\frac{1}{4}$, 0.92238 |
| O*B* | 8*d* | 0.91275, 0.47499, 0.68012 |

### 3.1. The twin lattice of aragonite

We denote by $(\mathbf{abc})_\mathrm{I}$ the basis for an individual and by $(\mathbf{abc})_\mathrm{T}$ 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[2] 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 [01$\bar{1}$]. The twin lattice $\mathbf{L}_\mathrm{T}$ 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 $\mathbf{L}_\mathrm{T} = \mathbf{L} \cap t\mathbf{L}$ (Marzouki *et al.*, 2014*a*), its unit cell is spanned by the three vectors [031], [01$\bar{1}$], [100]. However, the vector $\frac{1}{2}$([031] + [01$\bar{1}$]), which relates the origin and the 020 node of $\mathbf{L}$, also belongs to the twin lattice, hence the cell of $\mathbf{L}_\mathrm{T}$ built in this way is *C*-centred (Fig. 1). The twin index is 2 and the obliquity is 3.74° (computation performed with the software *GEMINOGRAPHY*: Nespolo & Ferraris, 2006). Twinning is by reticular pseudo-polyholohedry, 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 $(\mathbf{abc})_\mathrm{I}$ for $\mathcal{G}$ and $(\mathbf{abc})_\mathrm{T}$ for $\mathcal{H}$ are related by the following transformation:

$$(\mathbf{abc})_\mathrm{I}\mathbf{P} = (\mathbf{abc})_\mathrm{T}, \quad \mathbf{P} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 3 & 0 \\ \bar{1} & 1 & 0 \end{pmatrix}, \qquad (1)$$

which results in the cell parameters for the twin lattice $a = 9.3876$, $b = 16.8845$, $c = 5.74285$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 86.26°$ and in this setting the cell of $\mathbf{L}_\mathrm{T}$ is the standard *C*-centred cell. Equation (1) defines the twin plane as the (010) plane of the twin lattice; the axial setting of $\mathcal{H}$ is therefore the standard monoclinic *b*-unique. However, the cell parameters of $\mathbf{L}_\mathrm{T}$ show that the symmetry-unrestricted angle $\beta$ is actually 90° whereas the $\gamma$ angle, which would be symmetry restricted in a truly monoclinic group, actually deviates from 90° by an amount that corresponds precisely to the obliquity and represents a measure of the pseudo-symmetry of the twin lattice.

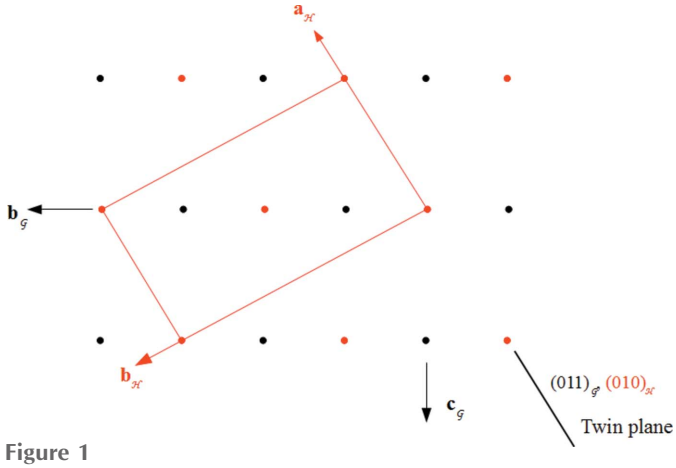



Figure 1
The twin lattice of the aragonite (110) twin – (011) in the standard *Pnma* setting of the space group – seen in projection along the *a* axis of $\mathcal{G}$. The $\mathbf{b}_\mathcal{H}$ axis is direction [031] in *Pnma*. Red nodes are (quasi) restored by the twin operation: they represent half of the lattice nodes of $\mathcal{G}$ so that the twin index is 2.

The extension of the point group of $\mathcal{H}$ by the twin operation results in a (pseudo)-monoclinic group, either *C*2/*m* or *C*2/*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 $(001/\frac{1}{2}\bar{\frac{1}{2}}0/\frac{1}{2}\frac{1}{2}0)$ with origin shift $0\frac{1}{4}\bar{\frac{1}{4}}$. The inverse transformation $(0\bar{1}1/0\bar{1}\bar{1}/100)$ – origin shift $\frac{1}{2}00$ – applied to [031] gives [$\bar{1}\bar{2}0$], which is a symmetry direction of $P6_3/mmc$ 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).[3] 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 ($\Delta_\mathrm{max}$) 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

[2] 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).

[3] 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 $\mathbf{P}^{-1} = (0\ \frac{1}{4}\ \frac{\bar{3}}{4}/0\ \frac{1}{4}\ \frac{1}{4}/1\ 0\ 0)$. 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 $\mathcal{E}$ | (**P**, **p**) | $d_{\min}$ (Å) | Restoration operation (with respect to the origin of $\mathcal{H}$) |
|---|---|---|---|---|---|
| $Y_1 \cup Y_2$ | $C2/m$ | $2 \times 4i$ | (I \| 000) | 0.1010 | $m\ x0z$, $a\ x\frac{1}{4}z$ |
| | $C2/c$ | $8f$ | (I \| 000) | 0.1680 | $c\ x0z$, $n\ x\frac{1}{4}z$ |
| | $C2/m$ | $4g + 4h$ | (I \| $\frac{11}{44}$0) | 0.9612 | $m\ x\frac{1}{4}z$, $a\ x0z$ |
| | $C2/c$ | $8f$ | (I \| $\frac{11}{44}$0) | 0.9518 | $c\ x\frac{1}{4}z$, $n\ x0z$ |
| $Y_3 \cup Y_4$ | $C2/m$ | $2 \times 4i$ | (I \| $\frac{11}{44}$0) | 0.1010 | $m\ x\frac{1}{4}z$, $a\ x0z$ |
| | $C2/c$ | $8f$ | (I \| $\frac{11}{44}$0) | 0.1680 | $c\ x\frac{1}{4}z$, $n\ x0z$ |
| | $C2/m$ | $4g + 4h$ | (I \| 000) | 0.9612 | $m\ x0z$, $a\ x\frac{1}{4}z$ |
| | $C2/c$ | $8f$ | (I \| 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 $\mathcal{H} = C\overline{1}$.

The conventions are the same as those in Table 3.

| Orbits | $\mathcal{E}$ | Wyckoff position for $\mathcal{E}$ | (**P**, **p**) | $d_{\min}$ (Å) | Restoration operation (with respect to the origin of $\mathcal{H}$) |
|---|---|---|---|---|---|
| $X_1 \cup X_2$ | $C2/c$ | $8f$ | (I \| 000) | 0.0233 | $c\ x0z$, $n\ x\frac{1}{4}z$ |
| $X_3 \cup X_4$ | $C2/c$ | $2 \times 4e$ | (I \| 000) | 0.1155 | $c\ x0z$, $n\ x\frac{1}{4}z$ |
| $X_1 \cup X_2$ | $C2/c$ | $2 \times 4e$ | (I \| $\frac{11}{44}$0) | 0.1155 | $c\ x\frac{1}{4}z$, $n\ x0z$ |
| $X_3 \cup X_4$ | $C2/c$ | $8f$ | (I \| $\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 O$A$ 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 O$B$ 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 $\mathcal{E}$ | (**P**, **p**) | $d_{\min}$ (Å) | Restoration operation (with respect to the origin of $\mathcal{H}$) |
|---|---|---|---|---|---|
| $OA_2 \cup OB_5$ | $C2/c$ | 8*f* | (I \| 000) | 0.2154 | $c\ x0z$, $n\ x\frac{1}{4}z$ |
| $OA_3 \cup OB_8$ | $C2/c$ | 8*f* | (I \| 000) | 0.2154 | $c\ x0z$, $n\ x\frac{1}{4}z$ |
| $OB_6 \cup OB_3$ | $C2/c$ | 8*f* | (I \| 000) | 0.0718 | $c\ x0z$, $n\ x\frac{1}{4}z$ |
| $OA_1 \cup OB_4$ | $C2/c$ | 8*f* | (I \|$\frac{11}{44}$0) | 0.2154 | $c\ x\frac{1}{4}z$, $n\ x0z$ |
| $OA_4 \cup OB_1$ | $C2/c$ | 8*f* | (I \|$\frac{11}{44}$0) | 0.2154 | $c\ x\frac{1}{4}z$, $n\ x0z$ |
| $OB_2 \cup OB_7$ | $C2/c$ | 8*f* | (I \|$\frac{11}{44}$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 **d** be a vector perpendicular to a section plane **S**. Owing to the periodicity of the crystal pattern along **d**, to find all different types of sectional layer groups for slices perpendicular to **d** it is enough to consider section planes at heights *s* with $0 \leq s < 1$ (fractional coordinate along **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 **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 **d** either to +**d** or to −**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: Ďurovič, 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 $\mathbf{a}'$, **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 $\mathbf{a}'$, **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 **a**, **b**, **c** and **P** is the basis transformation such that (**a**, **b**, **c**)**P** = ($\mathbf{a}'$, **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:

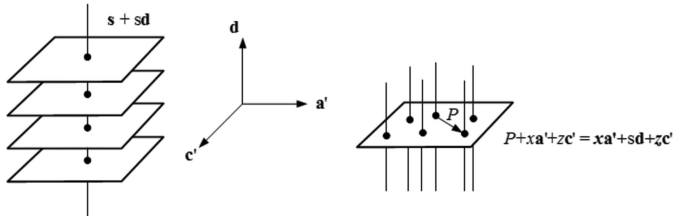



**Figure 2**
Definition of the axial setting for the layer group.

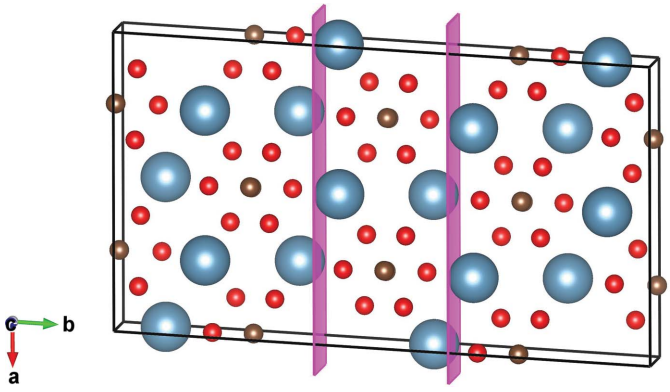



**Figure 3**
View along the *c* axis of the slice defined as the thickness limited by the two pink planes and containing the 12 oxygen atoms (figure drawn with *VESTA*: Momma & Izumi, 2011).

(*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 **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 **d** is only fixed if $t_2 = 2s$.

In the case of aragonite, the scanning direction **d** is normal to the twin plane and thus **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

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

which is precisely the transformation to the twin basis. This means that the twin basis $\mathbf{a}'$, **d**, $\mathbf{c}'$ with **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 $p1$ [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 $p\bar{1}$ (No. 2, ITE) at $y = 0$ or of type $p2_1$ (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 $p\bar{1}$ (No. 2, ITE) for $s = 0, \frac{1}{4}, \frac{1}{2}$ and $\frac{3}{4}$, of type $p2_1$ (No. 9, ITE) for $s = \frac{1}{8}, \frac{3}{8}, \frac{5}{8}$ and $\frac{7}{8}$ and of type $p1$ (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.

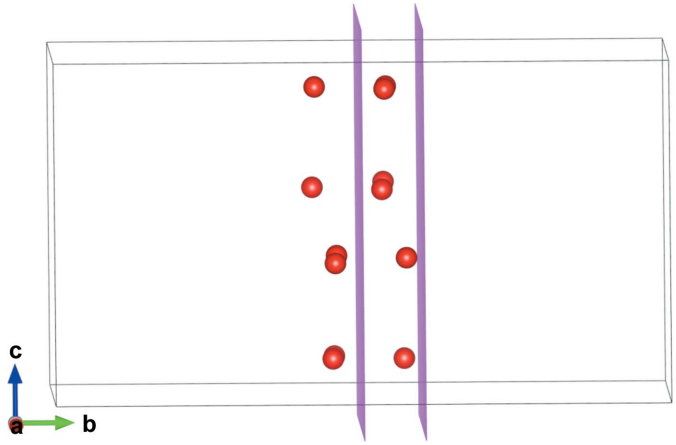



**Figure 4**
View along the *a* axis of the restored 12 oxygen atoms by the *c*-glide reflection.

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 Å 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[4] $\mathcal{E}(K)$ of the slice $K$ at position $y = 0$ is found to be a layer group generated by the layer group $\mathcal{L}$ of type $p\bar{1}$ induced by $\mathcal{G}$ and the restoration operation, which is a $c$ glide. The group $\mathcal{E}(K)$ is of type $p2/c$ (No. 16, ITE, in a non-conventional setting), the restoration accuracy is 0.2154 Å. 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 Å, for the $Y$ cations the split orbits $Y_1$ and $Y_2$ with restoration accuracy 0.1680 Å 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 O$A_2$ which are mapped to two atoms of the orbit O$B_5$ with deviation 0.2154 Å. Similarly, two oxygen atoms in the split orbit O$A_3$ are matched with two oxygen atoms in the split orbit O$B_8$, again with deviation 0.2154 Å and two oxygen atoms in O$B_6$ are matched with two oxygen atoms in O$B_3$ with deviation 0.0718 Å. 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

[4] 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 $t' = x + \frac{1}{4}, \overline{y} + \frac{1}{4}, z + \frac{1}{2}$ 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 ($OA_3$) | 0.39135, 0.21122, 0.41275 ($OB_4$) | 0.2154 |
| 0.25385, 0.07372, 0.41275 ($OB_6$) | 0.49615, 0.17628, 0.91275 ($OB_7$) | 0.0718 |
| 0.35865, 0.03878, 0.91275 ($OB_5$) | 0.62929, 0.20690, 0.40547 ($OA_4$) | 0.2067 |
| 0.62071, 0.04310, 0.59453 ($OA_2$) | 0.89135, 0.21122, 0.08725 ($OB_1$) | 0.2154 |
| 0.75385, 0.07372, 0.08725 ($OB_3$) | 0.99615, 0.17628, 0.58725 ($OB_2$) | 0.0718 |
| 0.85865, 0.03878, 0.58725 ($OB_8$) | 0.12929, 0.20690, 0.09453 ($OA_1$) | 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 $x, \overline{y}, z$ 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 **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.

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