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Structural rationale for the occurrence of the elbow twins in cassiterite and rutile

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Elbow twins are a distinct feature of cassiterite and rutile. Their occurrence is justified by the reticular theory of twinning because of the existence of a common sublattice — the twin lattice — formed by the overlap of a large fraction of the lattice nodes of the individuals. Yet, the atomic basis for the existence of twins falls outside the possibilities of the reticular theory. We present here the analysis of the pseudo-eigensymmetry of the crystallographic orbits building the structure of the elbow twins and show that their occurrence is justified by the complete restoration of the structure near the composition surface, with a deviation of less than 0.7 Å.

Keywords: Cassiterite, Crystallographic orbits, Elbow twins, Pseudo-symmetry, Rutile, Twinning

INTRODUCTION

Buerger (1945) classified twins on the basis of their formation mechanism in three categories: transformation twins, mechanical (gliding) twins and growth twins. All the three types occur frequently in minerals: the Swiss (Dauphiné) twin in quartz is a typical example of a transformation twin following the β-α transition during cooling; the mechanical twinning in calcite is a marker of rock collisional events (Rocher et al., 1996); growth twins can form at any stage during crystal growth, due to a perturbation (impurity, dislocation or other defect) during the normal growth process or to the coalescence of nano, micro or macro-crystals (Nespolo and Ferraris, 2004). The growth of a homogeneous, untwinned crystal is evidently thermodynamically favourable with respect to the formation of a twin so that growth twins would not appear if the system were in perfect equilibrium without perturbations. The formation of the twin is therefore the consequence of a sort of mistake during the normal crystal growth process. However, a twin is not necessarily the result of a perturbation of crystal growth: its formation requires a certain degree of structural continuity between the twinned individuals (domains). Until recently, a general theory to estimate the structural continuity in twins was not available and to find an explanation why some twins occur frequently while others are rare if not non-existent we made reference to the reticular theory developed by the so-called French school (Bravais, 1851; Mallard, 1885; Friedel, 1904, 1926). This theory establishes a relation between the degree of lattice overlap produced by the twin operation and the occurrence frequency of the twin. The lattice overlap is measured by the twin index n, which is the inverse of the ratio of the lattice nodes common to the twinned individuals. Furthermore, the twin obliquity ω (or, for twin operations of order higher than two, the twin misfit δ: Nespolo and Ferraris, 2007), measures the deviation from perfect overlap. The lower the twin index and the obliquity, the better the lattice overlap in the twin and the higher the probability that the twin will form.

The reticular approach allowed us to establish a statistically significant correlation between the degree of lat-

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tice overlap and the frequency of twins: indeed, twins that occur in nature have a reasonably high degree of lattice overlap. The reticular theory of twinning cannot, however, explain why hypothetical twins with a satisfactory degree of overlap do not occur or are definitely rarer than one would expect. Furthermore, some twins which should not occur because of a too low degree of lattice overlap actually do occur, although normally with lower frequency. Empirical limits of $n = 6$ and $\omega = 6°$ were given by Friedel (1926) and twins falling within these limits have been called ‘Friedelian twins’ (Nespolo and Ferraris, 2005). Non-Friedelian twins violate what is considered a ‘necessary’ condition for the occurrence of twins. This apparent contradiction was actually removed with the introduction of the hybrid theory of twinning, where two or more concurrent sublattices co-exist and contribute to the overall degree of lattice restoration, measured by an ‘effective twin index’ n_E which counts the contribution of all these sublattices (Nespolo and Ferraris, 2006). Friedelian twins can themselves also occur as hybrid twins: each of the sublattices alone would justify the occurrence of twinning: their coexistence, leading to an even smaller index (larger percentage of common lattice nodes) strengthens the rationale behind the occurrence of these twins (for a review on hybrid twins, see Nespolo and Ferraris, 2009 and Pignatelli et al., 2011).

The reticular approach, even in its hybrid extension, cannot discriminate between the occurrence probability of twins of compounds having unit cells with similar volumes and corresponding to the same twin index and obliquity, because it does not consider the atomic content of the unit cell but just the lattice. Its predictive possibilities are therefore limited. To go beyond this limitation we have introduced a structural theory of twinning, based on the idea that in order to form and be stable a twin must have a common substructure: some of the atoms building the structure must cross the ‘composition surface’ (i.e., the interface separating two twinned individuals) with limited perturbation. The details of the approach have been presented in Marzouki et al. (2014a), together with the analysis of the case of melilite. The application to staurolite, aragonite and marcasite have been presented in Marzouki et al. (2014b, 2015) and Nespolo and Souvignier (2015). Below we give a short summary of the principle and present the application to the so-called elbow twins, which occur as {011} reflection twins in cassiterite and rutile[1]. The terminology specific to twinning has been recently reviewed in Nespolo (2015).

NON-CHARACTERISTIC CRYSTALLOGRAPHIC ORBITS AS THE KEY TO IDENTIFY THE COMMON SUBSTRUCTURE OF TWINS

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 (Engel et al., 1984; Matsumoto, 1985).

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 $\mathcal{E}$ 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. In the case that 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, a term suggested by the concept of restoration index introduced long ago by Takeda et al. (1967) as a structural counterpart of the twin index.

The restoration operation t maps a chosen atom A in a crystallographic orbit (or sub-orbit) O to a position A′. The distance between A′ and the closest atom in O will be called $d_{\min}$. If $t \in \mathcal{E}(O)$ then $d_{\min} = 0$. If t is only a pseudo-symmetry operation of O, then $d_{\min} > 0$ and its

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[1] The term ‘elbow twin’ has been applied also to a twin in zircon (Jocelyn and Pidgeon, 1974): however, the structure, symmetry and twin law are different from the cassiterite and rutile case.

value is a measure for the quality of the quasi-restoration.

THE ELBOW TWINS IN CASSITERITE AND RUTILE

The minerals cassiterite and rutile are isostructural (same type of space group, $P4_2/mnm$, No. 136; same Wyckoff positions: $2a$ for the metal, $4f$ for the oxygen atom) and can be represented by the symmetrical packing symbol A(−−½)B(−−½) (Zoltai and Stout, 1984), which gives the fractional occupation of the independent polyhedra (two tetrahedra and one octahedron) formed by a pair of hexagonal sheets of spheres, representing oxygen atoms in this case. The idealized structure is that of the nickeline, consisting thus of an hcp stacking of oxygen atoms where the tetrahedra between two sheets are empty and the octahedra are alternatively empty or occupied by tin (cassiterite) or titanium (rutile). The angle M–O–M (M = Sn, Ti) would be 70° in the idealized structure: in the real structure the octahedra tilt to achieve an angle of 80° to minimize the M–M repulsion (Fig. 1). Because of the strict similarity of the two structures, the following analysis is performed on cassiterite, but the same conclusions apply to rutile as well, with only very minor differences in the numerical values.

The morphology of cassiterite and rutile typically shows {100} and {110} prisms and {111} and {011} te-

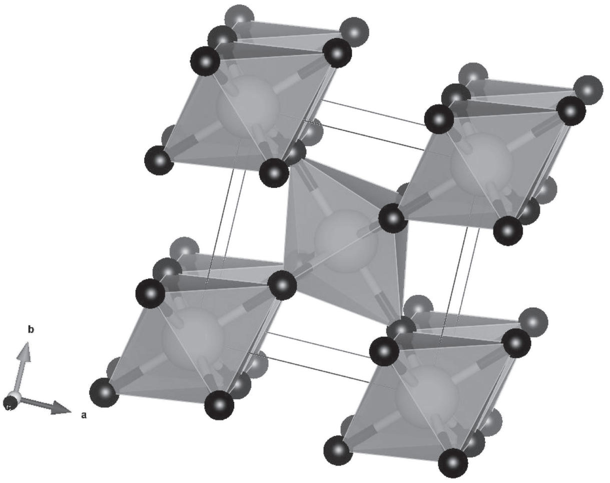

Figure 1. Polyhedral view of the structure of cassiterite and rutile. Large atoms at the centre of the polyhedra are cations (Sn, Ti respectively), small atoms at the corner are oxygen atoms. Figure drawn with VESTA (Momma and Izumi, 2011).

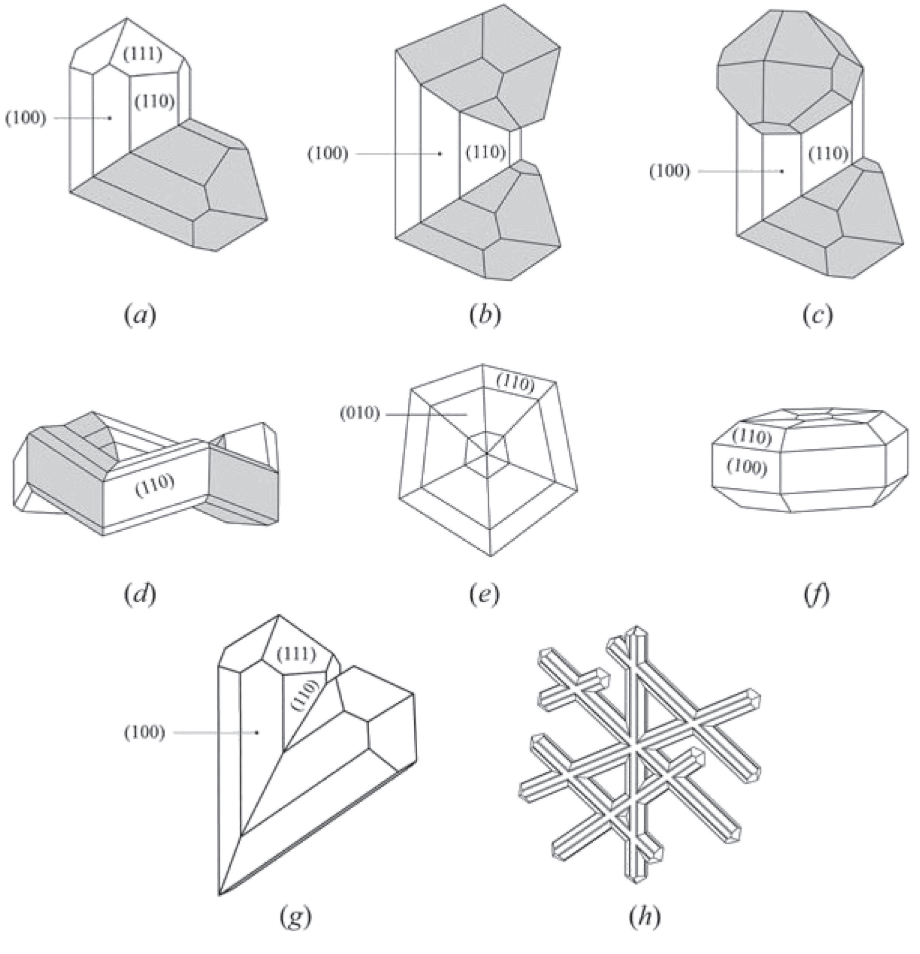

Figure 2. Various forms of rutile twins, with one or several equivalent twin reflection planes {011}. (a) Elbow twin (two orientation states). (b) Triple twin (three orientation states) with twin reflection planes (011) and $(0\bar{1}1)$. (c) Triple twin with twin reflection planes (011) and (101). (d) Cyclic eightfold twin with eight orientation states. (e) Cyclic sixfold twin with six orientation states. Two sectors appear strongly distorted due to the large angular excess of 6 × 5.6° = 33.6°. (f) Perspective view of the cyclic twin of (e). (g) Twin with reflection plane (031) (heart-shaped twin). (h) Sagenite, an intergrowth of (011) twinned rutile (001) prisms. Reproduced after Hahn and Klapper (2014), figure 3.3.6.11 (http://it.iucr.org/) with permission.

tragonal bipyramids, sometimes accompanied by {210} and {320} prisms (Goldschmidt, 1913). The elbow twin is by reflection on {011} so that the composition plane coincides with the twin plane. This twin may occur as a simple twin or repeated: triple or cyclic (Fig. 2). The angle between the [100] directions in the two individuals is 67.8° (cassiterite) and 65.6° (rutile), and that between the [001] directions is 112.2° (cassiterite) and 114.4° (rutile) (computed with TWINY: Nespolo and Iordache, 2013; data for cassiterite from Klementova et al., 2000; for rutile Swope et al., 1995). In case of a cyclic twin (Fig. 2*e*), strong distortion appears between two sectors because of the deviation from 60° between the respective [100] directions — or between the respective (100) faces, which are perpendicular to the faces with the same indices in a tetragonal crystal.

Cassiterite has cell parameters a = 4.7384 Å, c = 3.1865 Å: Sn in position 4a (0,0,0) and O in position 4f (x,x,0) with x = 0.3076. The reticular analysis of this twin has been published by Nespolo and Ferraris (2009), who have shown it is a hybrid twin with two concurrent sublattices: one defined by the unit cell based on (011)/[037] with n = 5 and ω = 1.41°, and the other defined by the unit cell based on (011)/[012] with n = 3 and ω = 2.71°, so that the effective twin index is 2.0. This does not tell much, however, about the structural continuity because no information on the atomic positions is used for analysing the lattice overlap. The following study aims precisely at showing that the occurrence of this twin is justified on the basis of a high structural continuity across the composition surface. The same results are obviously obtained by taking any other plane in the same form, so that in the following we will restrict to (011) as a representative for {011} in order to perform the necessary calculations.

THE TWIN LATTICE OF THE (011) TWIN

In case of hybrid twins, the sublattice corresponding to the lower obliquity defines the twin lattice $\mathbf{L}_\mathrm{T}$; the other sublattices contribute to the twin index within the acceptable limit on the obliquity but the twin index is still computed with respect to the cell of $\mathbf{L}_\mathrm{T}$ (Nespolo and Ferraris, 2006). Accordingly in the case of the elbow twins, $\mathbf{L}_\mathrm{T}$ is based on the pair (011)/[037].

The shortest directions contained in the (011) plane are [0$\bar{1}$1] and [100]. The twin lattice is obtained by the relation $\mathbf{L} \cap \mathrm{t}\mathbf{L} = \mathbf{L}_\mathrm{T}$ (Marzouki et al, 2014a), where **L** is the lattice of the individual, $\mathbf{L}_\mathrm{T}$ is the twin lattice and t is the twin operation. The maximal subgroup $\mathcal{H}$ of $\mathcal{G}$ compatible with the twin lattice is obtained from the same relation applied to the space group: $\mathcal{H} = \mathcal{G} \cap \mathrm{t}\mathcal{G}\mathrm{t}^{-1}$ (Marzouki et al, 2014a)[2]. By conjugating $\mathcal{G} = P4_2/m2_1/n2/m$ with a reflection across (011), the only symmetry direction that remains as symmetry direction in both orientations is [100] so that the symmetry operations which are kept in the intersection are the 2_1 rotation about it, the n-glide reflection perpendicular to it and the inversion. If we take the $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ axes of $\mathbf{L}_\mathrm{T}$ along [037], [100] and [01$\bar{1}$], respectively, in order to obtain a standard b-unique monoclinic setting, the n-glide in the setting of **L** becomes a c-glide in the setting of $\mathbf{L}_\mathrm{T}$. Furthermore, the vectors [01$\bar{1}$] and [037] define a centring vector ½([01$\bar{1}$] + [037]) which relates the origin and the 023 node of **L** and adds an a-glide to the same mirror plane already acting as c-glide, so that it is transformed to an e-glide. The unit cell of $\mathbf{L}_\mathrm{T}$ is thus of type B and $\mathcal{H}$ is of type $B2_1/e$, which is a non-standard setting of $P2_1/c$, the transformation to the standard setting being $(\boldsymbol{a}-\boldsymbol{c})/2,\boldsymbol{b},\boldsymbol{c}$ with the origin in common. In the following, we keep the $B2_1/e$ non-standard setting because the direction (quasi)-normal to the twin plane should be a symmetry direction in the eigensymmetry of the crystallographic orbits and because it keeps the pseudo-orthorhombic metric of the lattice (the standard setting $P2_1/c$ would have a β angle far from 90°, hiding thus the strong pseudo-orthorhombic symmetry of $\mathbf{L}_\mathrm{T}$). The bases $(\boldsymbol{abc})_\mathrm{I}$ for $\mathcal{G}$ and $(\boldsymbol{abc})_\mathrm{T}$ for $\mathcal{H}$ are related by the following transformation:

$$(\boldsymbol{abc})_\mathrm{I}\mathbf{P} = (\boldsymbol{abc})_\mathrm{T},\ \mathbf{P} = \begin{pmatrix} 0 & 1 & 0 \\ 3 & 0 & 1 \\ 7 & 0 & \bar{1} \end{pmatrix} \qquad (1),$$

which results in the cell parameters for the twin lattice a = 26.4501 Å, b = 4.7384 Å, c = 5.7102 Å, β = 91.41°. The determinant of the transformation matrix is 10, i.e., twice the classical twin index defined by this pair of lattice plane/line, because the unit cell of $\mathbf{L}_\mathrm{T}$ is centred. Eq. (1) defines the twin plane as (100) plane of the twin lattice. The extension of the point group of $\mathcal{H}$ by the twin operation results in an orthorhombic holohedral group — within the approximation of the obliquity — as the minimal supergroup of $\mathcal{H}$ containing a restoration operation. Normally, it is not necessary to search for higher super-

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[2] One may object that at this stage the only information available is the twin operation, i.e., a point-group operation, while $\mathcal{G}$ and $\mathcal{H}$ are space groups so that the conjugation relation is formally inconsistent because space group operations include a vector part, while point group operations do not. The above equation is actually a short-hand expression for the computation procedure. The same relation is applied to the point group $\mathcal{P}_\mathcal{G}$ of $\mathcal{G}$, the result being the intersection point group $\mathcal{P}_\cap$. Then, the maximal subgroup of $\mathcal{G}$ having $\mathcal{P}_\cap$ as point group is chosen, and this is $\mathcal{H}$.

Table 1. Atomic coordinates of cassiterite in $\mathcal{H} = B2_1/e$

Atom	Wyckoff position	*x*	*y*	*z*	Atom	Wyckoff position	*x*	*y*	*z*
Sn1	4*a*	0	0	0	O2	8*e*	0.13076	0.19240	0.41532
Sn2	8*e*	0.1	0.5	0.2	O3	8*e*	0.06924	0.80760	0.98468
Sn3	8*e*	0.2	0.5	0.9	O4	8*e*	0.16924	0.80760	0.68468
O1	8*e*	0.03076	0.30760	0.21532	O5	8*e*	0.23076	0.19240	0.11532

groups, although a crystallographic orbit in $\mathcal{H}$, or a union of crystallographic orbits, may possess a higher eigensymmetry than the extension of $\mathcal{H}$ by t. In some cases, however, the orbit idealized in the minimal supergroup of $\mathcal{H}$ possesses a higher eigensymmetry which does not require any further adjustment of the atom positions; in this case, the choice of giving the higher eigensymmetry becomes evident, as it is in the case of the Sn orbits analysed below.

ANALYSIS OF THE RESTORATION OPERATIONS FOR THE CASSITERITE (011) TWIN IN TERMS OF THE PSEUDO-EIGENSYMMETRY OF THE CRYSTALLOGRAPHIC ORBITS

In the $B2_1/e$ setting of space-group type $P2_1/c$ the multiplicity of the Wyckoff positions is doubled because of the *B*-centring vector. The International Tables for Crystallography do not list this setting, so we give here explicitly the positions obtained by the transformation $x/2$, y, $\bar{x}/2+z$ — contravariant with respect to the axial transformation $(\boldsymbol{a}-\boldsymbol{c})/2,\boldsymbol{b},\boldsymbol{c}$ — by keeping the same sequence of Wyckoff letters as in the $P2_1/c$ setting 4*a* (000, ½0½, 0½½, ½½0), 4*b* (¼0¾, ¾0¼, ¼½¼, ¾½¾), 4*c* (00½, ½00, 0½0, ½½½), 4*d* (¼0¼, ¾0¾, ¼½¾, ¾½¼); the general position retains the Wyckoff letter *e* it has in $P2_1/c$ but having double multiplicity it will be indicated as 8*e*.

With the transformation matrix given by Eq. (1) both Sn and O orbits undergo splitting, according to the following scheme - calculations performed by the routine WYCKSPLIT (Kroumova et al., 1998) at the Bilbao Crystallographic Server (Aroyo et al., 2006):

$$\text{Sn: } 2a \rightarrow 4a + 2 \times 8e$$
$$\text{O: } 4f \rightarrow 5 \times 8e.$$

The coordinates of a representative atom of each orbit are reproduced in Table 1 and the pseudo-eigensymmetry of the crystallographic orbits is given in Table 2: the calculations have been performed with the routine PSEUDO (Capillas et al., 2011) at the Bilbao Crystallographic Server. The results are presented in a setting of $\mathcal{E}$ having the same axial orientation as $\mathcal{H}$; this usually non-conventional setting simplifies the identification of the restoration operation, which remains constantly oriented perpendicular to the [100] direction of $\mathbf{L}_\mathrm{T}$. The sequential number of the space-group type in the International Tables for Crystallography is also given in parentheses and the transformation to the standard setting is easily obtained with the Tables or with the Bilbao Crystallographic Server.

The Sn1 orbit corresponds to the invariant lattice complex *F*, whose characteristic Wyckoff position is *Fmmm a* (Fischer and Koch, 2005), in the same axial setting as $\mathbf{L}_\mathrm{T}$ and with the origin in common; this is thus the eigensymmetry $\mathcal{E}$ of Sn1[3]. The restoration operations for Sn1 are thus *m* (0*yz*), *n* (0*yz*), *b* (¼*yz*) and *c* (¼*yz*). The Sn2 and Sn3 orbits possess the same eigensymmetry, although only as pseudo-eigensymmetry (d_min = 0.5710 and 1.1420 Å respectively), and for Sn_2 an origin shift (¼0¼) from $\mathcal{H}$ to $\mathcal{E}$ is necessary: the [100] component of this shift implies that the role of the two planes at $x = 0$ and $x = ¼$ is exchanged. The restoration operations for this orbit are thus *m* (¼*yz*), *n* (¼*yz*), *b* (0*yz*) and *c* (0*yz*) with respect to the origin of $\mathcal{H}$. *Fmmm* is not a minimal supergroup of $B2_1/e$ so that in principle one does not need to go up to *Fmmm* to find a restoration operation. However, the atomic shift corresponding to d_min is realized in the first step from $B2_1/e$ to an intermediate group of type *Bmeb* or *Bbem* (non-standard settings of *Cmce*, No. 64) and proceeding to *Fmmm* does not require any further adjustment of the atomic positions, so that it is quite natural to give this higher eigensymmetry.

The orbits corresponding to the oxygen atoms all possess an eigensymmetry *Bbem* with *b*-glides and *n*-glides as restoration operations alternating every **a**/4, or *Bmbe* with *m* reflections and *c*-glides as restoration operations again alternating every **a**/4, but the degree of approximation varies widely, from 0.1750 Å for O3 to 1.3170 Å for O5. The union of the two orbits O2 and O4 has *Bmbe* eigensymmetry which does not appear

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[3] Lattice complexes can be seen as a coarser classification of crystallographic orbits into types, so that the same lattice complex may occur in different types of space groups of the same crystal family. Lattice complexes are called invariant if they can occupy a parameterless position in a space group. For details, see Fischer and Koch (2005).

Table 2. Eigensymmetry of the crystallographic orbits of cassiterite under $\mathcal{H} = B2_1/e$[4]

Orbit	$\mathcal{E}$	Wyckoff position for $\mathcal{E}$	Origin shift from $\mathcal{H}$ to $\mathcal{E}$	d_{min} (Å)	Restoration operation
Sn1	*Fmmm* (69)	4*a*	000	0	$m(0yz)$, $n(0yz)$, $b(\tfrac{1}{4}yz)$, $c(\tfrac{1}{4}yz)$
Sn2	*Fmmm* (69)	8*g*	¼0¼	0.5710	$m(\tfrac{1}{4}yz)$, $n(\tfrac{1}{4}yz)$, $b(0yz)$, $c(0yz)$
Sn3	*Fmmm* (69)	8*g*	000	1.1420	$m(0yz)$, $n(0yz)$, $b(\tfrac{1}{4}yz)$, $c(\tfrac{1}{4}yz)$
O1	*Bbem* (64)	8*e*	000	0.6744	$b(\tfrac{1}{4}yz)$, $n(0yz)$
		8*f*	¼0¼	0.3961	$b(0yz)$, $n(\tfrac{1}{4}yz)$
O2	*Bbem* (64)	8*f*	000	0.9671	$b(\tfrac{1}{4}yz)$, $n(0yz)$
		8*e*	¼0¼	1.1105	$b(0yz)$, $n(\tfrac{1}{4}yz)$
O3	*Bbem* (64)	8*f*	000	0.1750	$b(\tfrac{1}{4}yz)$, $n(0yz)$
		8*e*	¼0¼	0.5732	$b(0yz)$, $n(\tfrac{1}{4}yz)$
O4	*Bbem* (64)	8*e*	000	0.9244	$b(\tfrac{1}{4}yz)$, $n(0yz)$
		8*f*	¼0¼	0.7460	$b(0yz)$, $n(\tfrac{1}{4}yz)$
O5	*Bbem* (64)	8*f*	000	1.3170	$b(\tfrac{1}{4}yz)$, $n(0yz)$
		8*e*	¼0¼	1.4256	$b(0yz)$, $n(\tfrac{1}{4}yz)$
	Bmeb (64)	8*e*	000	1.1549	$m(0yz)$, $c(\tfrac{1}{4}yz)$
		8*f*	¼0¼	1.0178	$c(0yz)$, $m(\tfrac{1}{4}yz)$
O2∪O4	*Bmeb* (64)	16*g*	000	1.1792	$m(0yz)$, $c(\tfrac{1}{4}yz)$
		16*g*	¼0¼	1.2994	$c(0yz)$, $m(\tfrac{1}{4}yz)$

[4] 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}. Non-conventional settings of $\mathcal{E}$ are given in order to keep the same axial setting as for $\mathcal{H}$, in which the restoration operation is a mirror or glide reflection about a (100) plane.

for each orbit separately: this means that the m reflection and the c-glide exchange atoms of one orbit with those of the other orbit.

The results on the restoration accuracy as given in Table 2 on the basis of d_{min} alone are actually not sufficient to draw a conclusion about the structural continuity across the composition interface, because another important factor has to be taken into account: the distance of the quasi-restored atoms from the composition surface, that as said above in this case is parallel to the twin plane. In fact, during the growth of the crystal, the perturbation (defect, impurity etc.) modifying the normal growth will eventually result in a change of orientation — and thus the formation of a twin — if a significant continuation of the structure occurs at the composition surface, i.e., if the atoms close to it belong to a crystallographic orbit whose eigensymmetry contains, exactly or approximately, a restoration operation. Whether atoms farther from the composition surface are also restored or not can be considered of secondary importance because the decisive point is what happens around the composition surface at the moment when the change of orientation occurs. The corresponding analysis is shown in Table 3, where for each restoration operation the corresponding orbits are listed by increasing value of d_{min} and the distance Δ from the composition surface.

To judge whether the approximate restoration of a crystallographic orbit plays a significant role in the structural continuity across the composition surface we have to set a threshold on d_{min} as well as on Δ. For the former, we follow here the (heuristic) rule already used in our previous studies, where we have chosen a value close to the radius (ionic or covalent, depending on the type of bond), because if the deviation from perfect 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. Considering that the Sn-O bond is predominantly covalent and that the Sn-O bond length in cassiterite is about 2.05-2.06 Å, a threshold of 1 Å seems reasonable. For the distance Δ up to which we consider atoms being close to the composition surface, we note that each Sn atom is surrounded by six oxygen atoms in octahedral coordination. Since the atoms in the Sn1 orbit precisely lie on the planes at $x = 0$ and $x = \tfrac{1}{2}$, the oxygen atoms of the corresponding coordination octahedra must certainly lie within the chosen value of Δ. The x-coordinates of the oxygen atoms bonded to Sn atoms at $x = 0$ lie between -0.07 and 0.07, the next oxygen atoms not bonded to these Sn atoms are at $x = 0.13$, whereas the next Sn atoms are at $x = 0.10$. Recalling that the a-parameter of the twin cell is 26.4501 Å, a slice extending 2 Å to both sides of a plane containing the Sn atoms will contain precisely the atoms of the coordination polyhedra but no further atoms.

Looking only at the amount of atoms restored with $d_{\mathrm{min}} \leq 1$ Å, we conclude from Table 2 that the best restoration is obtained for $n(0yz)$ as restoration operation — or equivalently $b(\tfrac{1}{4}yz)$, with a total of 36 out of 60 atoms (60%, 20% of the Sn atoms and 80% of the O atoms) in the unit cell of $\mathbf{L}_{\mathrm{T}}$ being restored. For $b(0yz)$ as restora-

Table 3. Crystallographic orbits in cassiterite under $\mathcal{H} = B2_1/e$ rearranged according to the restoration operation, in increasing order of $d_{\min}$[5]

Restoration operation	Orbits	$d_{\min}$ (Å)	Δ (Å)	Restoration operation	Orbits	$d_{\min}$ (Å)	Δ (Å)
$m(0yz)$	Sn1	0	0	$m(\frac{1}{4}yz)$	Sn2	0.5710	3.9675
	Sn3	1.1420	5.2900		O5	1.0178	0.5089
	O5	1.1549	6.1036		O2∪O4	1.2994	2.1361-3.1539
	O2∪O4	1.1792	3.4586-4.4764	$n(\frac{1}{4}yz)$	O1	0.3961	5.7989
$n(0yz)$	Sn1	0	0		Sn2	0.5710	3.9675
	O3	0.1750	1.8314		O3	0.5732	4.7811
	O1	0.6744	0.8136		O4	0.7460	2.1361
	O4	0.9244	4.4764		O2	1.1105	3.1539
	O2	0.9671	3.4586		O5	1.4256	0.5089
	Sn3	1.1420	5.2900	$b(\frac{1}{4}yz)$	Sn1	0	6.6125
	O5	1.3170	6.1036		O3	0.1750	4.7811
$b(0yz)$	O1	0.3961	0.8136		O1	0.6744	5.7989
	Sn2	0.5710	2.6450		O4	0.9244	2.1361
	O3	0.5732	1.8314		O2	0.9671	3.1539
	O4	0.7460	4.4764		Sn3	1.1420	1.3225
	O2	1.1105	3.4586		O5	1.3170	0.5089
	O5	1.4256	6.1036	$c(\frac{1}{4}yz)$	Sn1	0	6.6125
$c(0yz)$	Sn2	0.5710	2.6450		Sn3	1.1420	1.3225
	O5	1.0178	6.1036		O5	1.1549	0.5089
	O2∪O4	1.2994	3.4586-4.4764		O2∪O4	1.1792	2.1361-3.1539

[5] Δ is the minimal distance for each orbit to the plane about which the restoration operation is performed. In the restoration of the union O2∪O4, the two orbits have different minimal distances to the plane, therefore two values for Δ are given in this case.

tion operation, 32 atoms are restored, which amounts to a total of 53.3%, 40% for the Sn atoms and 60% of the O atoms. The other two possible restoration operations $m(0yz)$ and $c(0yz)$ do not restore any oxygen atom at all and are therefore of no significance.

Taking now into consideration also the vicinity to the composition surface, the orbits that satisfy both criteria ($d_{\min} \leq 1$ Å and $\Delta \leq 2$ Å) for the plane at $x = 0$ or ½ are Sn1, O1, O3 under the action of $n(0yz)$ as restoration operation. It was already remarked that the atoms in the Sn1 orbit lie precisely on these planes and one checks that the oxygen atoms in the coordination octahedra of these Sn atoms belong to the O1 and O3 orbits. In fact, the atoms in the orbits Sn1, O1 and O3 are precisely the atoms that are close to the planes at $x = 0$ or $x = \frac{1}{2}$, and one concludes that 100% of the atoms close to each of these planes are restored by the $n(0yz)$ operation. Note that starting from O1, an even better restoration would be obtained by taking $b(0yz)$ as restoration operation, which would still produce a good restoration also for O3; however, this operation does not restore Sn1 so that finally $n(0yz)$ should be considered as the operation responsible for the twin formation, because it produces the largest common substructure.

Having found a good restoration for the direct vicinity of the composition surface, it is natural to ask whether the substructure which is restored extends further than the chosen distance Δ from the composition surface. The closest Sn atoms not on the plane $x = 0$ are located at $x = 0.1$ and belong to the orbit Sn2. This orbit is not restored by the $n(0yz)$ operation, but interestingly the oxygen atoms in the coordination octahedra of these atoms (O1, O2, O3 and O4) are still restored with a moderate quality. Half of these oxygen atoms are common to the coordination octahedra around the Sn1 atoms (O3 and O1) and are thus restored with accuracy 0.1750 Å and 0.6744 Å. The other half is restored with deviations between 0.9244 Å (O4) and 0.9671 Å (O2). As already mentioned in the description above, the structure of cassiterite is built from octahedra half of which are occupied by Sn atoms. What happens to the Sn2 atoms under the $n(0yz)$ operation is that they are mapped into the empty octahedra on the other side of the composition surface, and vice-versa. One may be tempted to conclude that the topology of the polyhedra whose corners are occupied by the oxygen atoms is preserved across the $(0yz)$ plane, whereas for the centres of these polyhedra the twin operation of the elbow twin exchanges occupied and empty sites, resulting in a stacking fault at the location around the Sn2 atoms. However, the deviations of the O2 and O4 positions and the larger distance from the $(0yz)$ plane raise doubts whether these additional polyhedra play a

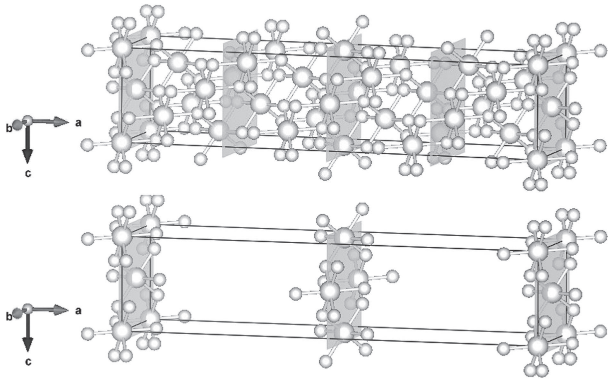

Figure 3. Top: the structure of cassiterite in the $\mathbf{L}_T$ unit cell (large and small spheres are Sn and O atoms, respectively). Shaded (100) planes with intermediate distance **a**/4 represent the candidates for the restoration operations. Bottom: the atoms corresponding to the orbits quasi-restored by an *n*-glide reflection at z = 0 or ½ and close to the glide plane: they represent 33% of the structure of cassiterite but 100% of the region close to the planes. During the crystal growth, when a perturbation resulting in the formation of the elbow twin occurs, the whole substructure close to these planes is quasi-restored, which explains the occurrence frequency of this twin. Figure drawn with VESTA.

significant role for the formation of the twin.

For the planes at x = ¼ or ¾, the Sn atoms close to these planes belong to the orbit Sn3 which is only restored with $d_{\min}$ = 1.1420 Å for *c*(¼*yz*) and *b*(¼*yz*). Moreover, the oxygen atoms in the coordination octahedra of these Sn atoms belong to the orbits O2, O4 and O5 which are restored with accuracy between 1.1549 Å (O5) and 1.1792 Å (O2∪O4) for *c*(¼*yz*) and at 0.9244 Å (O4), 0.9671 Å (O2) and 1.3170 Å (O5) for *b*(¼*yz*). Thus, the role of the planes at x = ¼ and x = ¾ in the formation of the twin is more than doubtful, especially considering the much better restoration produced by the planes at x = 0 and ½.

Figure 3 shows the structure of cassiterite in the unit cell of $\mathbf{L}_T$ as well as the orbits quasi-restored in the elbow twin. Figure 4 shows the superimposition of the (quasi)-restored orbits (Sn, O1 and O3) in the two individuals, where one clearly sees that these orbits define a common substructure close to the composition surface, within the given tolerance of less than 0.7 Å.

The above analysis has been performed on cassiterite but it applies as well to rutile, which is isostructural. The small differences in the cell parameters and fractional coordinates of the oxygen, due to the different atomic size of Sn and Ti, do not lead to any difference in the conclusions.

SUMMARY

Cassiterite and rutile, which are isostructural, show typical twins known as elbow twins, sometimes repeated to give a characteristic morphology. These twins fit well the reticular theory of twinning and their occurrence is even better explained by the hybrid theory, because of the existence of two concurrent sublattices. On a structural basis, however, an explanation of the occurrence of these twins was still missing. We have shown that the substructure close to the twin plane, composed of the Sn1, O1 and O3 crystallographic orbits, is completely quasi-restored, within less than 0.7 Å: therefore, any accidental event occurring during the crystal growth and resulting in a change of orientation corresponding to an elbow twin would only slightly affect the structure in proximity of the composition surface: its main influence is on a region farther from it. The occurrence of this growth twin is therefore perfectly justified from the structural viewpoint.

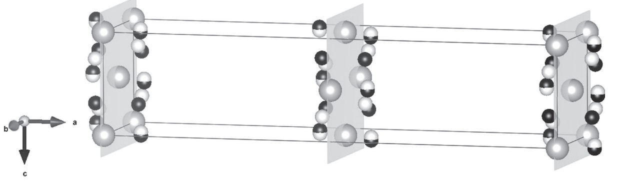

Figure 4. Superimposition of the orbits Sn (large spheres), O1 and O3 (small spheres) in the two individuals (white and black, respectively: for Sn, grey is used because of perfect restoration) as produced by the restoration operation *n*(0*yz*). All the atoms close the (100) plane at x = 0 and x = ½ in the $B2_1/e$ setting of $\mathbf{L}_T$ are restored within a good approximation — the largest displacement between corresponding atoms in the two individuals is 0.6744 Å for O1. The structure of cassiterite undergoes thus only a small perturbation about the composition surface when the crystal forms a twin on (100) at these locations. The same conclusions apply to rutile as well, with minor differences in the numerical values, the two minerals being isostructural. Figure drawn with VESTA.

Actually, the displacements caused by mapping the atoms from the two individuals across the composition surface by the restoration operation, measured by the $d_{\min}$ parameter, is slightly underestimated because in the above analysis the deviation from the orthorhombic metric of the eigensymmetry group $\mathcal{E}$ is not considered. The slight angular deviation coming from the obliquity of the twin lattice (1.41°) results in a β angle of 91.41° instead of 90°. This deviation from the metric symmetry is very small and its influence on the computed value of $d_{\min}$ is negligible.

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