CRYSTAL
Research &Technology

Application of the crystallographic orbit analysis to the study of twinned crystals. The example of marcasite

Massimo Nespolo[1],* and Bernd Souvignier[2]

The continuity of a substructure across the interface is considered a necessary condition for the formation of a twin. The application of the analysis of the eigensymmetry of crystallographic orbits to the derivation of this structural continuity is briefly reviewed and applied to the analysis of the {101} twin in marcasite. This analysis shows that one fourth of the structure, but half of the substructure near the composition surface, is common to the two orientations realized in the twin, the operation mapping the common atoms in the twinned domains being an *n*-glide occurring every one fourth of the period along the direction quasi-perpendicular to the twin plane. The existence of this significant common substructure justifies and explains the formation of the twin.

1 Introduction

From a genetic viewpoint, twins can be divided into three types [1]:

- *Transformation twins*: generated by a solid state phase transition during which some point symmetry operations of the parent phase are lost in the daughter phase but remain in the twinned edifice as twin operations, mapping the orientations of the twinned domains.
- *Mechanical (gliding) twins*: the occurrence of domain states with different orientation is produced by an external force applied to a crystal originally homogeneous.
- *Growth twins*: a perturbation (impurity, dislocation or other defect) during the crystal growth, or the coalescence of nano, micro or macro-crystals with a precise mutual orientation is at the origin of the formation of the twin (about the twin formation by coalescence, see a review in [2]).

While for the first two categories the driving force for the formation of the twin is evident, growth twins would not appear if the system were in perfect equilibrium without perturbations, the growth of an untwinned crystal being the thermodynamically favourable situation. The formation of the twin is therefore the consequence of a sort of mistake during the normal crystal growth process. In order for this mistake to occur, a certain degree of structural continuity between the twinned individuals (domains) is required, otherwise the twin would simply not form. The knowledge of this structural continuity is a pre-requisite towards a route to predict the occurrence probability of twinning: this is an ambitious yet fundamental aim in materials science and drug design. In fact, when frequent twinning occurs as a result of a crystallization process, not only physical properties of technological interest may be severely affected (for instance, the development of an electric field in a piezoelectric material is reduced or suppressed by twinning, because of the different orientation of the fields in the twinned domains), but the quality of the structure refinement is also reduced, because diffractions from the twinned domains overlap without a phase relation, and this effect is particularly critical for compounds crystallizing in large unit cells, like in the case of

* Corresponding author: email: Massimo.Nespolo@crm2.uhp-nancy.fr

[1] Tokyo Institute of Technology, Materials & Structures Laboratory, 4259 Nagatsuta, Midori-ku, Yokohama-city, Kanagawa, 226–8503, Japan**

[2] Radboud University Nijmegen, Faculty of Science, Mathematics and Computing Science, Institute for Mathematics, Astrophysics and Particle Physics. Postbus 9010, 6500 GL, Nijmegen, The Netherlands
**On leave from Université de Lorraine, Faculté des Sciences et Technologies, Institut Jean Barriol FR 2843, CRM2 UMR CNRS 7036, BP 70239, Boulevard des Aiguillettes, F-54506 Vandoeuvre-lès-Nancy cedex France.

Cryst. Res. Technol. **50**, No. 6, 442–450 (2015)

CRYSTAL
Research&Technology

Original Paper

biological macromolecules. A clear understanding of the parameters governing the formation of growth twins is thus a pre-requisite for the development of crystallization protocols capable of reducing the frequency of twinning, for example by acting on the crystal morphology to reduce the development of faces corresponding to possible twin interfaces, called *composition surfaces* in the twin literature.

The so-called French school [3–6] developed a reticular theory of twinning which 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 [7]), measures the deviation from the 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.

This reticular approach has been successfully applied for more than a century to the interpretation of the observed twins, the large majority of which correspond indeed to low values of the index and of the obliquity. Empirical limits of $n = 6$ and $\omega = 6°$ were given by Friedel [6] and twins falling within these limits have been called *Friedelian twins* [8]. Exceptions do exist to this empirical limit, but they are very often *hybrid twins, i.e.* twins in which 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 [9].

The reticular approach, even in its hybrid extension, cannot differentiate 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 with limited perturbation. The details of the approach have been presented in [10], together with the analysis of the case of melilite. The application to staurolite, aragonite and cassiterite have already been presented [11–13]. Below we give a short summary of the principle and present the application to the {101} twin in marcasite. The terminology specific to twinning has been recently reviewed in [14].

2 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.

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. When 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 $\mathcal{H}$ [15] 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 [16] as a structural counterpart of the twin index.

If d_{min} denotes the minimal distance between the position to which a chosen atom in a crystallographic orbit or sub-orbit O is mapped under the restoration operation t and the atoms in O, then $d_{min} = 0$ for all atoms in O in the case that $t \in \mathcal{E}(O)$. If t is only a pseudo-symmetry of O, then $d_{min} > 0$ and its value is a measure for the quality of the quasi-restoration.

3 The {101} twin in marcasite and its twin lattice

Marcasite, FeS$_2$, is a polymorph of pyrite, metastable at ambient conditions. It is a sedimentary, hydrothermal, and secondary mineral, formed also in euxinic oceans, where the oxidation of the reactive organic carbon from sinking marine biomass consumes all of the oxygen, then the available nitrate, to finally produce sulphate reduction leading to accumulation of dissolved sulphide [17]. The structure can be represented by the symmetrical packing symbol A(--½)B(--½) [18], which gives the fractional occupation of the independent polyhedra (two tetrahedra and one octahedron) formed by a pair of hexagonal sheets of spheres representing sulphur atoms in this case. The idealized structure of marcasite consists thus of an *hcp* stacking of sulphur atoms where the tetrahedra between two sheets are empty and the octahedra are alternatively empty or occupied by iron. This alternate occupancy minimizes the Fe-Fe repulsion, which would be significant because octahedra share faces in an *hcp* topology (figure 1). The same topology is found in various sulphides and related minerals crystallising in the same type of space group (*i.e.* ferroselite FeSe$_2$, frohbergite FeTe$_2$, mattagamite CoTe$_2$, kullerudite NiSe$_2$, rammelsbergite NiAs$_2$, lollingite FeAs$_2$) as well as sulphosalts like arsenopyrite, FeAsS, and gudmundite, FeSbS, for which the symmetrical packing symbol is doubled, A(--½)B(--½)A(--½)B(--½), to show the ordering of the non-metal, which reduces the symmetry from orthorhombic to monoclinic. Several of these minerals occur much less frequently than marcasite, yet they too give frequent twinning, a fact that suggests that the common structural topology must favour the occurrence of twins in this group of minerals.

Marcasite crystallises in a space group of type *Pnnm* (standard setting of No. 58). A report claiming that the correct space group would be the non-centrosymmetric subgroup *Pnn*2 was published [19], but was invalidated by the same authors after improvement of the absorption correction [20]. The structural data used in this article are taken from a recent structure report [21]: $a = 4.4446$, $b = 5.4246$, $c = 3.3864$ Å, with Fe in position 2a (0,0,0) and S in position 4g ($x\,y\,0$) with $x = 0.2004$ and $y = 0.3787$.

Marcasite gives frequent twins on {101}, forming "swallowtail" contact twins; this may be repeated to form stellate fivelings [22, 23]. A survey of twins in non-silicate minerals [24] showed that this is a hybrid twin with two concurrent sublattices based on the (101) twin plane, corresponding to two possible quasi-perpendicular
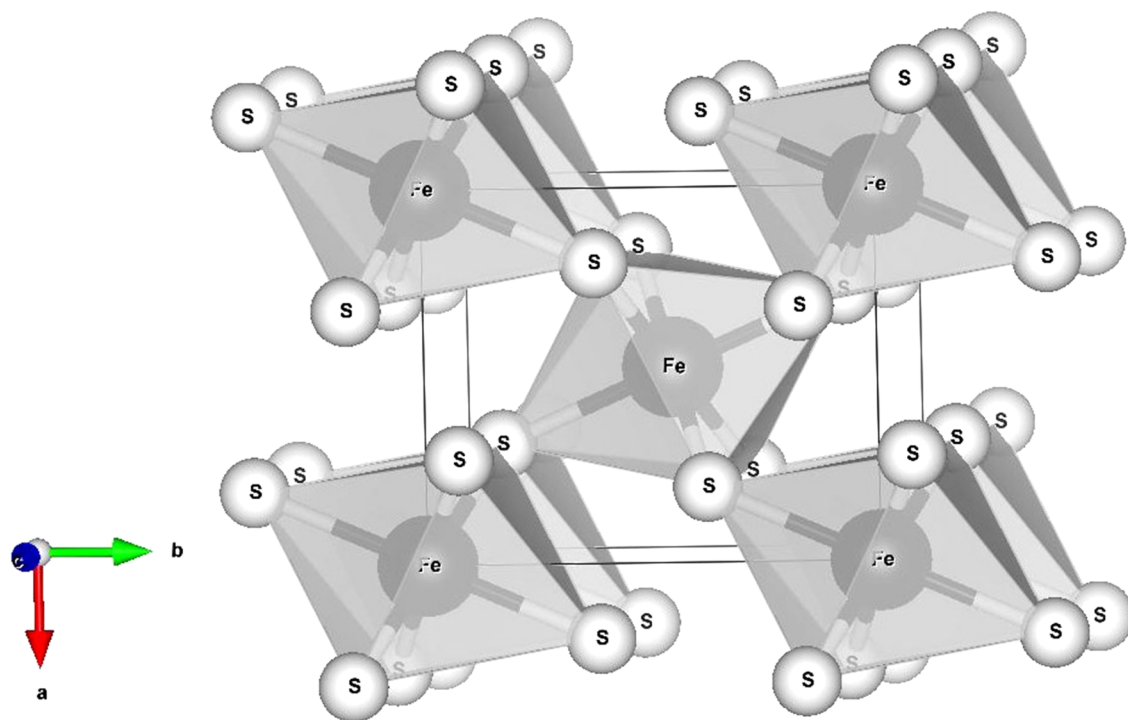

Fig. 1 Polyhedral view of the structure of marcasite drawn in the axial setting of the space group $\mathcal{G} = Pnnm$. Figure drawn with VESTA [29]. The alternation of occupied and empty octahedra reduces the Fe-Fe repulsion that would occur in the face-shared *hcp* topology.

Cryst. Res. Technol. **50**, No. 6, 442–450 (2015)

CRYSTAL
Research&Technology

Original Paper

directions: [305] ($n = 4$, $\omega = 0.89^{\circ}$) and [102] ($n = 3$, $\omega = 4.06^{\circ}$), leading to an effective twin index $n_E = 2.0$. This means that in the cell of the twin lattice defined by the pair of lattice elements (101) and [305], half of the lattice nodes are restored within $\approx 4^{\circ}$, of which an important fraction within less than 1°.

The shortest directions contained in (101) are [010] and [10$\bar{1}$]. The twin lattice is obtained by the relation $\mathbf{L} \cap t\mathbf{L} = \mathbf{L}_T$ (cf. [10]), where $\mathbf{L}$ is the lattice of the individual, $\mathbf{L}_T$ is the twin lattice and t is the twin operation. The unit cell of $\mathbf{L}_T$ is spanned by the three vectors [010], [10$\bar{1}$], [305]. However, also the vector ½([10$\bar{1}$]+[305]), which relates the origin and the 103 node of $\mathbf{L}$, belongs to the twin lattice, hence the cell of $\mathbf{L}_T$ built in this way is S-centred.

The maximal subgroup $\mathcal{H}$ of $\mathcal{G}$ compatible with the twin lattice is $\mathcal{H} = \mathcal{G} \cap t\mathcal{G}\,t^{-1} = S\bar{1}$: indeed, among the symmetry elements of *Pnnm*, 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 ($\boldsymbol{abc}$)$_I$ for $\mathcal{G}$ and ($\boldsymbol{abc}$)$_T$ for $\mathcal{H}$ are related by the following transformation:

$$(\boldsymbol{abc})_I\mathbf{P} = (\boldsymbol{abc})_T, \; \mathbf{P} = \begin{pmatrix} 0 & \bar{1} & 3 \\ 1 & 0 & 0 \\ 0 & 1 & 5 \end{pmatrix} \quad (1)$$

(figure 2) which results in the cell parameters for the twin lattice $a = 5.4246$ Å, $b = 5.5877$ Å, $c = 21.5519$ Å, $\alpha = 90.920^{\circ}$, $\beta = 90^{\circ}$, $\gamma = 90^{\circ}$. For this orientation, the centring vector is A and the space group symbol is $A\bar{1}$, a non-standard setting of $P\bar{1}$ imposed by the orientation of the twin plane with respect to the axes of $\mathcal{G}$. The determinant of the transformation matrix is 8, *i.e.* twice the twin index because of the A centring. $\mathbf{L}_T$ is strongly pseudo-orthorhombic, the deviation being only 0.92° on α. In the following analysis, we will treat it as oA, the small angular deviation on α being of negligible meaning on the orbit pseudo-symmetry and thus on the degree of atomic quasi-restoration produced by the restoration operations. Eq. (1) defines the twin plane as (001) plane of the twin lattice. The extension of the point group of $\mathcal{H}$ by the twin operation results in a monoclinic group (with pseudo-oA lattice), either $A112/m$ (c-unique setting, cell choice 1 of $C2/m$, No. 12) or $A112/a$ (c-unique setting, cell choice 1 of $C2/c$, No. 15). These are the possible minimal supergroups of $\mathcal{H}$ containing a restoration operation. Normally, it is not necessary to search for higher supergroups, although a crystallographic orbit in $\mathcal{H}$, or a union of crystallographic orbits, may possess a higher
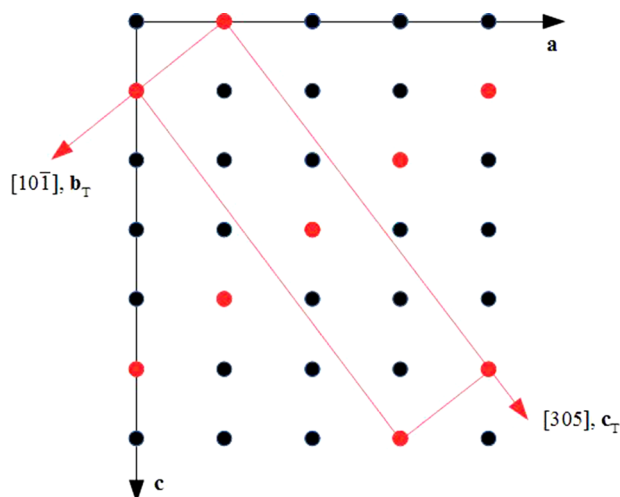

Fig. 2 The (010) plane of the marcasite lattice, showing the projection of the unit cell of the twin lattice $\mathbf{L}_T$., defined by the [10$\bar{1}$] and [305] directions (in red), which become the **b** and **c** axes of $\mathbf{L}_T$. The lattice nodes in red are located at the corners and at the centre of the A face of the unit cell of $\mathbf{L}_T$; they are restored by the reflection about the (101) plane – (001) in the setting of $\mathbf{L}_T$ - and represent one fourth (two out of eight) of the nodes of L contained in the unit cell of $\mathbf{L}_T$. The twin index defined by this sublattice is thus 4.

eigensymmetry than the extension of $\mathcal{H}$ by t. In some cases where a higher symmetry is evident, like in the case of invariant lattice complexes described below, it is nevertheless worth pointing out the existence of higher supergroups.

4 Analysis of the restoration operations for the marcasite {101} twin in terms of the pseudo-eigensymmetry of the crystallographic orbits

In $\mathcal{G} = Pnnm$, a restoration operation for the {101} twin would be a mirror or glide reflection about one of the four planes composing the {101} form in the orthorhombic holohedry. This would be possible only in presence of a (pseudo)-cubic eigensymmetry, which would require a (pseudo)-cubic metric. The axial ratios in marcasite being 0.819:1:0.624, such a (pseudo)-eigensymmetry in $\mathcal{G}$ is excluded *a priori*.

In $P\bar{1}$ with the transformation matrix given by Eq. (1) both Fe and S orbits undergo splitting, according to the following scheme (calculations performed by the Wycksplit routine at the Bilbao Crystallographic Server:

Table 1 Atomic coordinates of marcasite in the $A\bar{1}$ setting of $\mathcal{H}$.

Atoms	Wyckoff position in $P\bar{1}$	x y z	Atoms	Wyckoff position in $P\bar{1}$	x y z
Fe 1	$1a+1g$	0 0 0	S 1	$2\times 2i$	0.3787, 0.87475, 0.02505
Fe 2	$1e+1f$	½ 0 ½	S 2	$2\times 2i$	0.8787, 0.62525, 0.97495
Fe 3	$2i$	½ ¼ ¼	S 3	$2\times 2i$	0.6213, 0.37525, 0.72495
Fe 4	$2i$	0 ¼ ¾	S 4	$2\times 2i$	0.1213, 0.12475, 0.27505
Fe 5	$2\times 2i$	½ ⅞ ⅛	S 5	$2\times 2i$	0.1213, 0.74975, 0.15005
Fe 6	$2\times 2i$	0 ⅛ ⅜	S 6	$2\times 2i$	0.6213, 0.75025, 0.84995
			S 7	$2\times 2i$	0.8787, 0.00025, 0.09995
			S 8	$2\times 2i$	0.3787, 0.49975, 0.90005

Table 2 Eigensymmetry of the crystallographic orbits of marcasite under $\mathcal{H} = A\bar{1}$. 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}. 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 (001) plane.

Orbits	$\mathcal{E}$	Wyckoff position for E	Origin shift from $\mathcal{H}$ to $\mathcal{E}$	d_{min} (Å)	restoration operation (with respect to the origin of $\mathcal{H}$)
Fe$_1\cup$Fe$_2$	$Fmmm$	$4a$	000	0	m (xy0), n (xy0), a (xy¼), b (xy¼)
Fe$_3\cup$Fe$_4$	$Fmmm$	$4a$	0¼¾	0	m (xy¼), n (xy¼), a (xy0), b (xy0)
S$_5\cup$S$_6$	$A112/a$	$8f$	000	0.0028	a (xy0), n (xy¼)
S$_7\cup$S$_8$	$A112/a$	$8f$	¼0¼	0.0028	a (xy¼), n (xy0)

[25, 26]):

$$\text{Fe} : 2a \to 1a + 1e + 1f + 1g + 6 \times 2i$$

$$S : 4g \to 16 \times 2i$$

However, half of the coordinates obtained in this way are related by the A centring vector so that eventually the splitting scheme in $A\bar{1}$ is the one reproduced in Table 1.

The union of the orbits Fe$_1$ and Fe$_2$ corresponds to the invariant lattice complex[1] F, whose characteristic Wyckoff position is $Fmmm\ a$ [27]; this is thus the eigensymmetry $\mathcal{E}$ of Fe$_1 \cup$ Fe$_2$, which has common origin with $\mathcal{H} = A\bar{1}$. The restoration operations for Fe$_1 \cup$ Fe$_2$ are thus m (xy0), n (xy0), a (xy¼) and b (xy¼). The same holds also for the union of the orbits Fe$_3$ and Fe$_4$, but with an origin shift (0¼¾) from $\mathcal{H}$ to $\mathcal{E}$. The restoration operations for Fe$_3 \cup$ Fe$_4$ are thus m (xy¼), n (xy¼), a (xy0) and b (xy0) with respect to the origin of $\mathcal{H}$, *i.e.* the same as for Fe$_1 \cup$ Fe$_2$ but with the role exchanged. In other words, the physical planes (xy0) and (xy¼) restore the whole set of the orbits Fe$_1$, Fe$_2$, Fe$_3$, Fe$_4$, although with a different operation for the two subsets.

The pseudo-eigensymmetry of the orbits in $\mathcal{H} = A\bar{1}$ with an accepted tolerance of 0.5 Å is given in Table 2, obtained with the routine PSEUDO [28] at the Bilbao Crystallographic Server. As predicted in the previous section,

the eigensymmetry is either $A112/m$ or $A112/a$. For the remaining iron orbits, the value of d_{min} is 1.3969 Å (eigensymmetry $A112/m$ with origin shift ¼0¼), definitely too large to be considered meaningful for the structural continuity across the composition surface. For the sulphur orbits, half of the orbits are again restored within a very good approximation (0.0028 Å, see Table 2), while for the other half d_{min} is much larger (1.0798 Å, eigensymmetry $A112/m$: origin shift 000 for S$_1\cup$S$_2$, ¼0¼ for S$_3\cup$S$_4$), so that their contribution to the structural continuity in the twin is negligible. The eigensymmetry of the pairwise restored sulphur orbits is $A112/a$, but for half of these $\mathcal{H}$ and $\mathcal{E}$ have the origin in common, while for the other half an origin shift of ¼0¼ is necessary. Consequently, the physical planes (xy0) and (xy¼) act as a glide and n glide, respectively, for the union of two orbits, the opposite for the other union, similarly to the exchange already observed for the restored iron orbits.

Another important aspect to take into account, besides the restoration accuracy (Table 2), is the distance of the quasi-restored atoms from the composition surface. In fact, for the twin to form, a significant continuation of the structure has to occur at the composition surface: the structural restoration farther from this surface has certainly a minor influence. Table 3 lists the quasi-restored orbits in increasing value of d_{min} and the distance Δ from the composition surface. Considering that the Fe atoms are precisely on the (001) planes at $z = 0$, ¼, ½ and ¾, a physically meaningful value for Δ(S) would correspond to the Fe-S distance (about 2.25 Å).

---

[1] 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 [25].

Cryst. Res. Technol. **50**, No. 6, 442–450 (2015)

CRYSTAL
Research & Technology

Original Paper

Table 3 Quasi-restored crystallographic orbits in marcasite under $\mathcal{H} = A\bar{1}$ rearranged according to the restoration operation, in increasing order of d_{min}. Δ is the minimal distance for each orbit to the plane about which the restoration operation is performed. %1 and %2 are the percentage of atoms in the orbits located at the Δ distance from the planes at z and at $z+\frac{1}{2}$ respectively. For Fe atoms midway the two planes, the percentage is 100; for all the other atoms it is 50, meaning that half of the atoms building the orbit are physically close to the plane and play a physically meaningful role in the substructure common to the individuals building the twin.

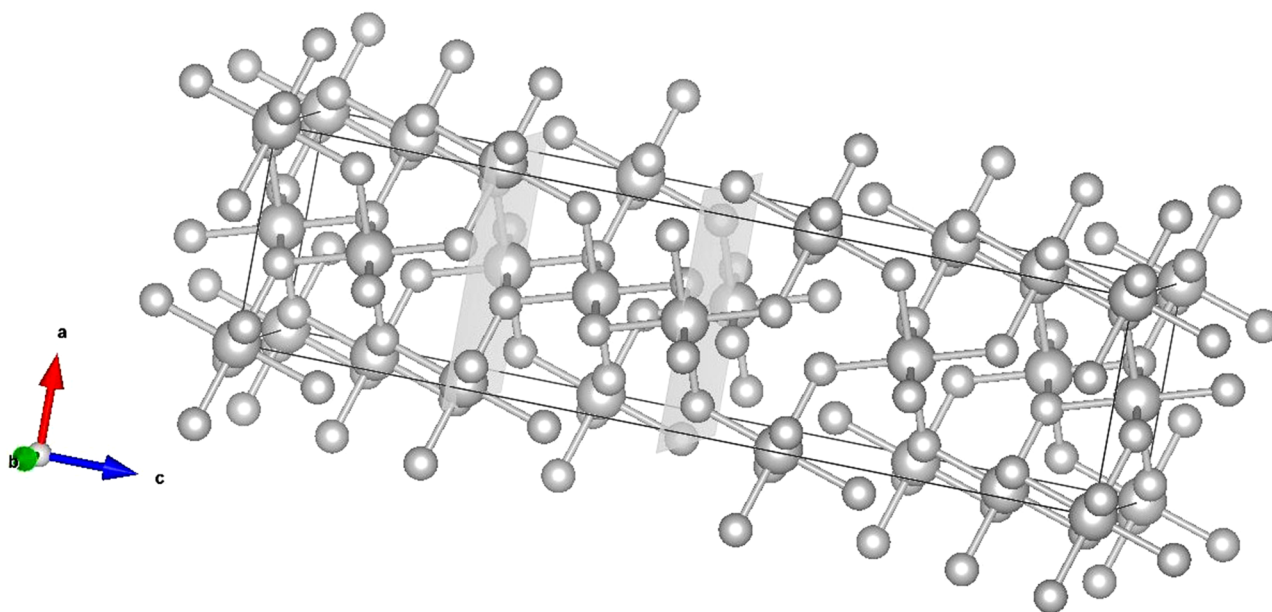| Restoration operation	Orbits	d_{min} (Å)	Δ (Å)	%1	%2	Restoration operation	Orbits	d_{min} (Å)	Δ (Å)	%1	%2
m ($xy0$)	$Fe_1 \cup Fe_2$	0	0	50	50	m ($xy\frac{1}{4}$)	$Fe_3 \cup Fe_4$	0	0	50	50
n ($xy0$)	$Fe_1 \cup Fe_2$	0	0	50	50	n ($xy\frac{1}{4}$)	$Fe_3 \cup Fe_4$	0	0	50	50
	$S_7 \cup S_8$	0.0028	2.1541	50	50		$S_5 \cup S_6$	0.0028	2.1541	50	50
a ($xy0$)	$Fe_3 \cup Fe_4$	0	5.3880	100	100	a ($xy\frac{1}{4}$)	$Fe_1 \cup Fe_2$	0	5.3380	100	100
	$S_5 \cup S_6$	0.0028	3.2339	50	50		$S_7 \cup S_8$	0.0028	3.2339	50	50
b ($xy0$)	$Fe_3 \cup Fe_4$	0	5.3880	100	100	b ($xy\frac{1}{4}$)	$Fe_1 \cup Fe_2$	0	5.3380	100	100

Fig. 3 The structure of marcasite drawn in the axial setting of the {101} twin (see Eq. (1) for the relation between the individual and twin setting). Large and small spheres represent iron and sulphur atoms, respectively. (001) planes of L_T are shown shaded for the two positions $z = \frac{1}{4}$ (equivalent to $z = \frac{3}{4}$) and $z = \frac{1}{2}$ (equivalent to $z = 0$).

Inspection of Tables 2 and 3 shows that there are common restoration operations for both iron and sulphur: these are the a-glide at ($xy0$) as well as the n-glide at ($xy\frac{1}{4}$), or vice versa the n-glide at ($xy0$) as well as the n-glide at ($xy0$): however, only the n glide planes correspond to a Δ(S) value within the Fe-S bond distance. Furthermore, half of the atoms in the restored orbits are physically close to the corresponding planes: in other words, half of the substructure around the composition surface is restored by the twin operations. This is illustrated in figures 3 and 4. Figure 3 is the structure of marcasite in the unit cell of L_T, showing also the location of two planes at $z = \frac{1}{4}$ and $z = \frac{1}{2}$ (the latter is shown instead than that of $z = 0$ for the sake of clearness: every symmetry operation of order two is repeated every half period). Figure 4 is obtained from figure 3 by retaining
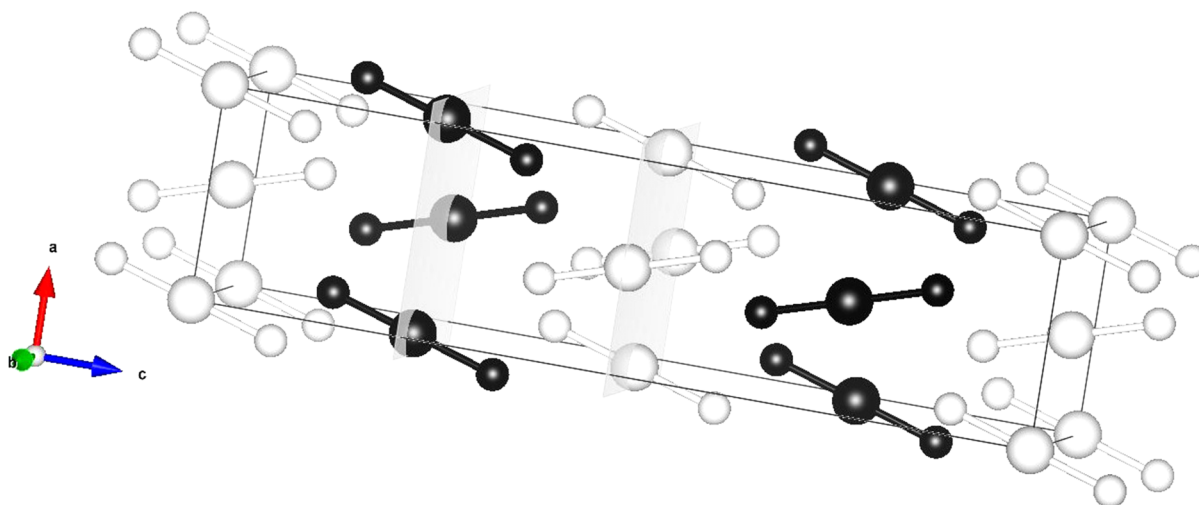
Fig. 4 Part of the structure of marcasite drawn in the axial setting of the {101} twin, showing only the orbits whose eigensymmetry contains a restoration operation, *i.e.* an operation whose linear part coincides with the twin operation. Black atoms are restored by *a* (*xy*0) and *n* (*xy*¼), while white atoms are restored by *a* (*xy*¼) and *n* (*xy*0). See text for details.
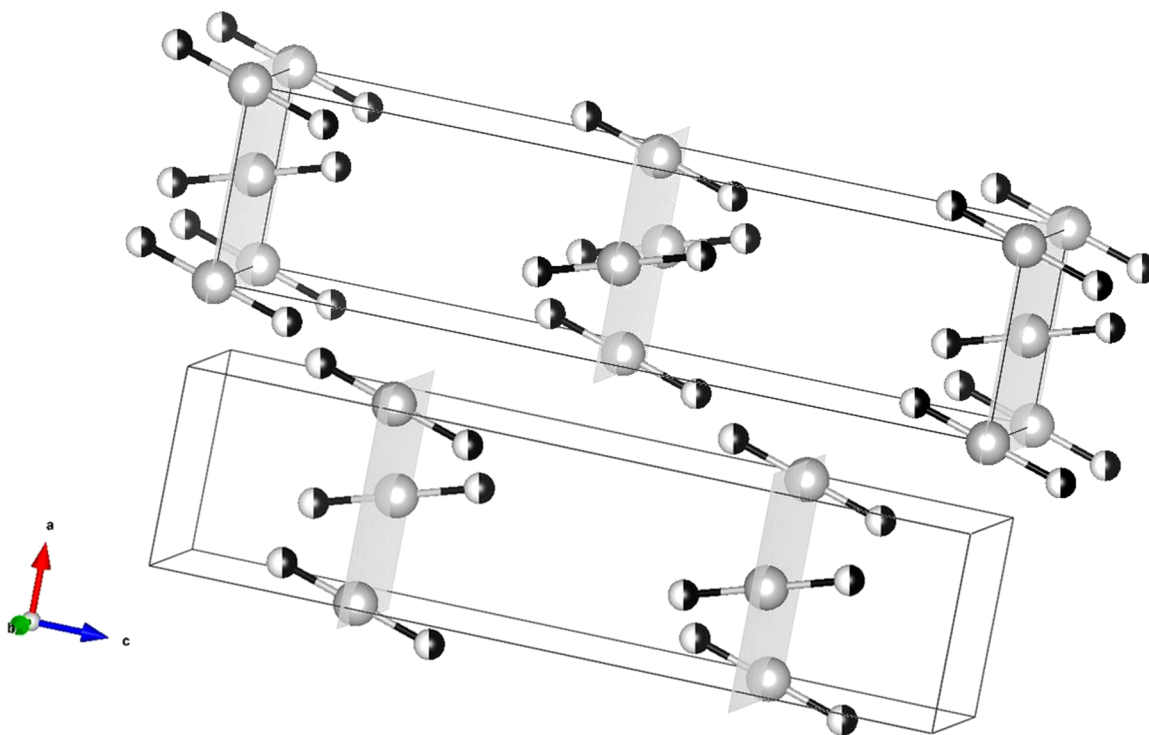

Fig. 5 Common substructure in the marcasite (101) twin for the different positions of the composition surface, shown as shaded rectangle, when the restoration operation is taken as *n* (*xy*0) glide in the setting of L_T. Top: positions at $z = 0$, ½ and 1. Bottom: positions at $z = ¼$ and ¾. Large grey spheres are Fe atoms, exactly restored in the twin. Small spheres are S atoms; white in one individual, black in the other individual. Because of the very small deviation from the exact restoration – 0.0028 Å – in the figure they appear as exactly overlapped, resulting in spheres that are half white and half black. When one of the planes shaded in the figure acts as twin plane, the S atoms on the two sides are of different colour. For the substructure built on these orbits, the twin plane does not represent an obstruction for the continuity so that this substructure crosses the composition surface unperturbed. The existence of this substructure, which represents one fourth of the whole marcasite structure but half of the structure close to the composition surface, explains and justifies the occurrence of the twin.
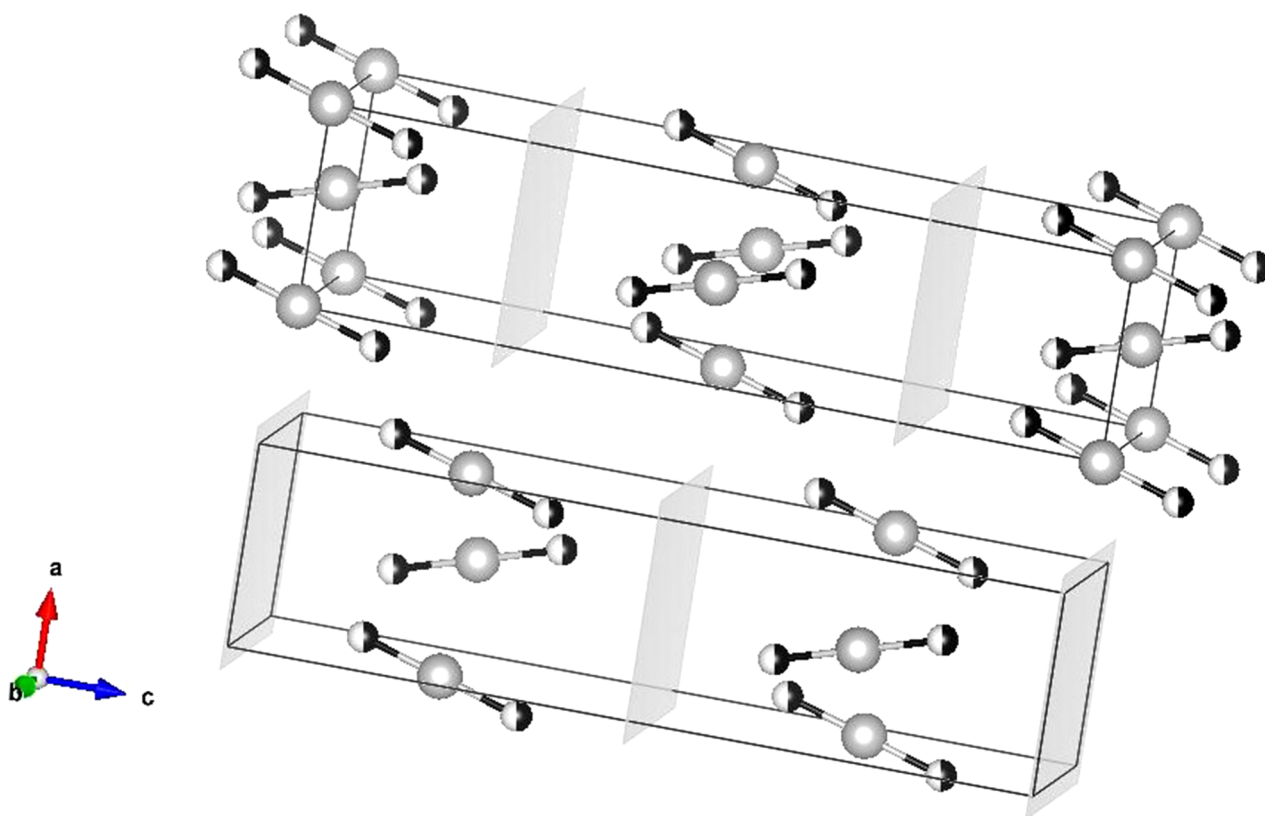
Cryst. Res. Technol. **50**, No. 6, 442–450 (2015)

CRYSTAL
Research&Technology

Original Paper

Fig. 6 Common substructure in the marcasite (101) twin for the different positions of the composition surface, shown as shaded rectangle, when the restoration operation is taken as a (xy0) glide in the setting of L_T. Same conventions as in figure 5. Although the degree of restoration is exactly the same as in figure 5, in this case the substructure common to the twinned individuals would be far away from the composition surface, which is physically meaningless.

only the atoms (quasi)-restored by a and n glides, *i.e.* half of the atoms in the structure of marcasite. The a (xy0) and n (xy¼) operations restore black atoms but not white ones; the opposite is true for n (xy0) and a (xy¼). We call two glide planes *neighbouring planes* if their z-coordinates differ by $\pm$ ¼. When the plane at (xy0) acts as a glide, it restores the black atoms on or close to its neighbouring planes and does not restore the white atoms on or close to itself. When the plane at (xy¼) acts as n glide, it restores the atoms on or close to it without restoring the white atoms on or close to its neighbouring planes. The opposite is true when the roles of the planes are interchanged: n (xy0) restores the white atoms on or close to its plane without restoring the black atoms on or close to its neighbouring planes; at the same time, a (xy¼) restores the white atoms on or close to its neighbouring planes without restoring the black atoms on or close to its own plane. The conclusion is that each of the restoration operations maps one fourth of the marcasite structure onto the corresponding atoms in the twinned orientation. However, the n glides restore atoms close

to the plane, while the a glides restore atoms far from it (figures 5 and 6). When the (xy0) plane in the setting of $\mathcal{H}$ acts as a twin plane during crystal growth, it is clearly the n glide operation that is responsible for the structural continuity.

5 Discussion

The structure of marcasite is composed of one iron orbit and one sulphur orbit under $\mathcal{G} = Pnnm$. When expressed in the setting of the twin lattice, which corresponds to $\mathcal{H} = A\bar{1}$, each of these splits into sub-orbits some of which possess an eigensymmetry $\mathcal{E}$ containing a restoration operation, *i.e.* an operation whose linear part coincides with the twin operation. This restoration operation is an n glide which restores one fourth of the orbits every $c/4$ in the setting of $\mathcal{H}$ – *i.e.* every fourth of the period along the direction [305] quasi-perpendicular to the twin plane. This means that every $c/4$ (in the setting of $\mathcal{H}$) a mistake during the growth of marcasite may occur

which would result in a change of orientation preserving an almost perfect structural continuity across the composition surface for one fourth of the atoms. Although the substructure restored is only one-fourth of the whole crystal structure of marcasite, it actually represents half of the structure around the composition surface, *i.e.* where the structural continuity plays a fundamental role for the formation of the twin. This important continuity justifies and explains the formation of the twin.

Actually, the errors in the mapping of atoms from the two individuals across the composition surface produced by the restoration operation are slightly underestimated because in the above analysis the twin lattice has been treated as exactly *oA*; however, the deviation from this metric symmetry is only 0.92º on α, whose influence on the computed value of d_{min} is negligible. Furthermore, the values of d_{min} are so small (0 and 0.0028 Å) that the restoration can be regarded as practically perfect.

Key words. crystallographic orbits, eigensymmetry, pseudosymmetry, marcasite, twinning.

References

[1]   M. J. Buerger, Am. Mineral. **30**, 469–482 (1945).
[2]   M. Nespolo and G. Ferraris, Eur. J. Mineral. **16**, 401–406 (2004).
[3]   M. Bravais, J. Ecole Polytechn. **XX**(XXXIV), 248–276 (1851).
[4]   E. Mallard, Bull. Soc. fr. minéral. **8**, 452–469 (1885).
[5]   G. Friedel, Étude sur les groupements cristallins. Extrait du Bulletin de la Société de l'Industrie minérale, Quatrième série, Tomes III e IV. (Société de l'Imprimerie Théolier J. Thomas et C., Saint-Étienne, 1904), pp. 485.
[6]   G. Friedel, Leçons de Cristallographie. (Berger-Levrault, Nancy, Paris, Strasbourg, 1926), pp. XIX+602.
[7]   M. Nespolo and G. Ferraris, Acta Crystallogr. **A63**, 278–286 (2007).
[8]   M. Nespolo and G. Ferraris, Z. Kristallogr. **220**, 317–323 (2005).
[9]   M. Nespolo and G. Ferraris, Acta Crystallogr. **A62**, 336–349 (2006).
[10] M. A. Marzouki, B. Souvignier, and M. Nespolo, IUCrJ. **1**, 39–48 (2014).
[11] M. A. Marzouki, B. Souvignier, and M. Nespolo, Acta Crystallogr. **A70**, 348–353 (2014).
[12] M. A. Marzouki, B. Souvignier, and M. Nespolo, Acta Crystallogr. **A71**, (in press, 2015).
[13] M. Nespolo and B. Souvignier, J. Min. Petr. Sci. (submitted, 2015).
[14] M. Nespolo, Cryst. Res. Techn. **51**, (in press, 2015).
[15] H. Wondratschek, Mineral. Petr. **48**, 87–96 (1993).
[16] H. Takeda, J. D. H. Donnay, and D. Appleman, Z. Kristallogr. **125**, 414–422 (1967).
[17] D. E. Canfield, Encyclopedia of Astrobiology (Springer, Berlin, Heidelberg, 2011), pp. 1616–1617.
[18] T. Zoltai and J. H. Stout, Mineralogy: Concepts and Principles (Burgess, Minneapolis, 1984).
[19] G. Brostingen and A. Kjekshus, Acta Chem. Scand. **24**, 1925–1940 (1970).
[20] G. Brostingen, A. Kjekshus, and C. Rømming Acta Chem. Scand. **27**, 2791–2796 (1973).
[21] M. Rieder, J. C. Crelling, O. Sustai, M. Drabek, Z. Weiss, and M. Klementova, Inter. J. Coal Geol. **71**, 115–121 (2007).
[22] C. Palache, H. Berman, and C. Frondel, The system of mineralogy of James Dana and Edward Salisbury Dana, Vol. I, seventh ed., third printing, (Wiley, New York and Chapman, London, 1952).
[23] V. Goldschmidt. Atlas der Kristallformen. (Carl Winters Universitätsbuchhandlung, Heidelberg, 1913).
[24] M. Nespolo and G. Ferraris, Eur. J. Mineral. **21**, 673–690 (2009).
[25] E. Kroumova, J. M. Perez-Mato and M. I. Aroyo, J. Appl. Crystallogr. **31**, 646 (1998).
[26] M. I. Aroyo, J. M. Perez-Mato, C. Capillas, E. Kroumova, S. Ivantchev, G. Madariaga, A. Kirov and H. Wondratschek, Z. Kristallogr. **221**, 15–27 (2006).
[27] W. Fischer and E. Koch, in: International Tables for Crystallography Volume A: Space-group Symmetry, edited by Th. Hahn (Wiley, 2005), Chap. 14.
[28] C. Capillas, E. S. Tasci, G. dela Flor, D. Orobengoa, J. M. Perez-Mato, and M. I. Aroyo, Z. Kristallogr. **226**, 186–196 (2011).
[29] K. Momma and F. Izumi, J. Appl. Cryst. **44**, 1272–1276 (2011).