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The oriented attachment mechanism in the formation of twins – a survey
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Abstract

The direct and indirect evidences for the oriented attachment of pre-formed crystals as a
mechanism of twin formation are reviewed and discussed. Although rarer than the nucleation-stage
formation, this mechanism, often overlooked, has been demonstrated in laboratory experiments,
with the artificial production of twins. Moreover, the role of the oriented attachment in the
formation of natural twins, although more likely to occur in environments where crystals are free of
moving and interacting, is supported also by the occurrence of monoperiodic twins and of
plesiotwins, whose origin cannot be explained by a nucleation-stage formation. The so far observed
absence of diperiodic twins is discussed in terms of two-dimensional site-coincidence and twin
obliquity.

Key words: coincidence-site lattice; growth twins, oriented attachment, plesiotwinning, twinning,

Introduction

Twins may be classified according to several different criteria: their morphology, their lattice
(Nespolo and Ferraris, 2004; Ferraris et al., 2004), their structural, genetic and phase relations. From
the viewpoint of their genesis, twins are commonly classified (see Cahn, 1954; Hahn and Klapper, 2003)
into three categories: growth twins (twins formed during crystal growth); transformation twins (twins formed following a phase transition, in which symmetry elements lost in the transition act as twin elements); and mechanical or gliding twins (twins formed as a result of a structural shear in plastic deformation).

Growth twins are normally considered the result of accidental departure, during growth, from
condition of minimal energy that corresponds to the single (i.e. untwinned) individual. Under
conditions of supersaturation – and thus high nucleation rate – a crystallization unit (an atom or
group of atoms: Hartman and Perdok, 1955) may take a subminimum energy position, corresponding
to the birth of a second individual in twin relation with the original one. Before it
moves to the minimum energy position, corresponding to the unmodified growth of a single crystal,
it may be blocked by deposition of the next units and start growing in this alternative position, originating a second individual in twin orientation. This process is favoured by different factors, such as the incorporation of impurities on the surface, and fluctuation in thermodynamic conditions. It is precisely in these terms that Buerger (1945) gave structural conditions for the formation of twins, aimed at completing Friedel’s criteria (1904, 1926) of purely reticular nature.

Following Hartman’s (1956) definition of the twin composition plane, Curien and Kern (1957) and Kern (1961) introduced the notion of Initial Composition Plane (ICP). Depending on whether the ICP coincides with the twin plane or not, contact twins or penetration twins would develop respectively. Senechal (1980) criticized this hypothesis by showing that it cannot explain some forms of twins, and proposed instead a model in which a twin derives from a cluster, where a regular crystalline structure is not established yet.

The above theories try to explain the formation of growth twins at the nucleation stage, also called “single particle growth”: either simultaneously (Buerger, 1945), or by nucleation onto a surface that has already attained a certain size (Hartman, 1956). The literature documents however another origin of growth twins, which is less known and often overlooked: the oriented attachment (“agglutination”) of pre-formed crystals. Both mechanisms (“single-particle growth” and “agglutination”) have been confirmed in nanocrystals by observing the twin formation by High-Resolution Transmission Electron Microscopy (HRTEM) (Penn and Banfield, 1998, 1999). Unfortunately, in the case of nanocrystals the boundary between the two cases is somewhat speculative.

Actually, the oriented attachment as a mechanism of twin formation was already the object of several important investigations started at the end of the XIX century. Those old studies are nowadays mostly forgotten and the late-stage oriented attachment mechanism still meets difficulties in being accepted as one of the possible origins of twins, despite the numerous evidences of it. Without any ambition of compiling an exhaustive review, it seems worthwhile summarizing briefly some of the most convincing, direct or indirect, proofs of this origin, also considering that several of the original publications are not easily accessible, and to update them with further evidences coming from the studies of plesiotwins (Nespolo et al., 1999).

The classification of twins in terms of the periodicity of the common lattice

The geometrical theory of twinning as developed by the so-called “French school” (Friedel, 1904, 1926) explains the necessary conditions for the formation of twins in terms of the superposition of the lattices of the individuals. This superposition may be exact or approximate, may involve the entire lattice or a sublattice, and may concern or not all the three directions of periodicity.

In the largest number of cases, the twin lattice extends to the entire three-dimensional space: it either coincides with the lattice of the individuals (twinning by merohedry), or is a sublattice of it (twinning by reticular merohedry). These twins are known as triperiodic twins (“macles
tripériodique”: Friedel 1933). Because the largest majority of twins belong to this category, the “triperiodic” adjective is often omitted. The higher the twin index\(^1\) (which measures the degree of non-overlapping of the lattices) and the twin obliquity (which measures the deviation from exact overlap) are, the lower is the probability of occurrence of a triperiodic twin. Based on a large survey of known twins, Friedel (1923, 1926) gave empirical limits to these parameters: 5 for the twin index and 6° for the twin obliquity. A few exceptions to these empirical rules were found in restricted genetic environments, like the “Wheal Coast” twin \(2\overline{1}3\overline{1}\), index 6, and the “Cornish” twin \(2\overline{1}\overline{2}1\), index 7, in β-quartz (Drugman, 1928). Some twins reported in the older literature with unreasonable values of the twin index were re-interpreted as the result of a combination of twin laws (e.g. Drugman, 1927). This combination may become difficult to identify in the case of the so-called cumulative associations, i.e. oriented crystal associations of N individuals in which only the two outer ones are left because they have grown at the expenses of the other N-2 (Drugman, 1943).

When the degree of lattice coincidence in a plane is too low to justify the appearance of the crystal association on reticular bases, the category of plesiotwins (Nespolo et al., 1999) is applied. In this type of oriented crystal association the common lattice is still triperiodic, but the overlap is lower compared to triperiodic twins, and the corresponding index is too high to explain the formation of the association. For example, the “twin index” 13 in the klockmannite reported by Taylor and Underwood (1960) is much larger than the limit given by Friedel and does not justify its formation. As shown below, the oriented attachment of macrocrystals is a possible mechanism by which such a high-index association may have formed.

Friedel (1933) predicted the existence of twins having lattice coincidence rigorously only in one plane, and called them diperiodic twins (“macles dipériodique”). We are not aware of any examples of diperiodic twins.

All the above categories are oriented crystal associations. A further, rarer but important case exists, in which a common period can be found in only one direction, along a row in the composition plane. The common period is not enough to fix the relative orientation of the individuals, which is determined from the purely mechanical contact of pre-existing crystal faces. These rare twins are called monoperiodic twins (“macles monopériodique”: Friedel, 1933) and their discovery played an important role in demonstrating the twin formation by oriented attachment, as we discuss below.

The artificial production of spinel twins in lead nitrate

To our knowledge, the first experimental demonstration of the formation of triperiodic twins from pre-existing crystals was given by Gaubert (1896) in his studies on the artificial formation of spinel twins. Gaubert was interested in the formation of this type of twin in lead nitrate, in barite

\(^1\) The twin index corresponds to the ratio of number of lattice nodes in the unit cell of the twin to the number of nodes in the same cell restored by the twin operation.
and in a mixture of both salts. He observed that the crystallization of lead nitrate under slow evaporation from the solution gave single crystals of octahedral habit. On the other hand, stirring of the solution already containing crystals led to aggregation of crystals forming spinel twins (he reported 103 twins out of 172 crystals from the solution that had undergone stirring).

To add further evidence to the twin formation by oriented attachment of pre-existing crystals, Gaubert repeated the experiment after painting a certain number of lead nitrate crystals with methylene blue, putting them back in the saturated solution together with unpainted (colourless) crystals and stirring the solution. He observed the association of a painted crystal with a colourless one, either in a parallel orientation or corresponding to triperiodic twins according to the spinel law.

The production of monoperiodic twins in alum

In an experiment somehow similar to that of Gaubert (1896), Schaskolsky and Schubnikow (1933) demonstrated the formation of twins by oriented attachment of pre-formed crystals. They used alum as study material, and took a large octahedral face of a single crystal 2-3 cm in size, flat and kept horizontal, undergoing growth from a supersaturated solution. On this surface, they let fall several small crystals with cubic and octahedral shape, about 0.5 mm in size, obtained separately. The solution was stirred and most of the small crystals were thus removed from the surface of the large one. However, a few small crystals remained attached to the surface.

Crystals with octahedral habit, when falling on the surface of the larger crystal, took two orientations: either that corresponding to a parallel growth or that of the spinel twin law, showing thus the formation of triperiodic twins by oriented attachment, similarly to what happened in Gaubert’s experiment.

Instead, in the case of cubic habit of the small crystals, the orientation they took after falling on the larger octahedral surface corresponded to parallelism of one of the \(\langle 110\rangle\) diagonals of the cube with one of the edges of the octahedral face. The edges of an octahedron and the \(\langle 110\rangle\) directions are parallel to the same lattice row, thus the described oriented association corresponds to a monoperiodic twin. To confirm that this orientation does not correspond to a triperodic twin it is sufficient to note that there does not exist a rotation axis normal to the contact plane that is compatible with the symmetry of both individuals: a three-fold axis for the large crystal, but a fourfold axis for the small one (twofold if the structure, and not only the lattice, is taken into account).

The oriented attachment in \(\beta\)-quartz

The formation of twins by oriented attachment in natural crystals was demonstrated by Drugman (1927, 1928, 1930), during his systematic morphological study of twins in \(\beta\)-quartz. Two results of Drugman’s studies are of particular interest with respect to the twin formation: the occurrence of the Zinnwald monoperiodic twin, and the relative frequency of the Esterel vs.
Verespatak triperiodic twins.

**The Zinnwald monoperiodic twin and its formation by oriented attachment**

Among the twins from Four-la-Brouque (Auvergne), one of the localities that gave several twinned bipyramidal crystals of $\beta$-quartz (Drugman, 1930), one consisted of three crystals, two of which were twinned according to (1122), i.e. according to the Verespatak twin analogous of the Japan twin in $\alpha$-quartz. The third crystal was in the position corresponding to the so-called “Zinnwald group”. This group had already drawn the attention of several mineralogists, because of the apparent lack of any precise twin law. The repeated occurrence of this “group” excluded the possibility of an accidental contact without definite crystallographic orientation [i.e. a “bicrystal” according to Hahn et al. (1999)]. The crystallographic explanation of this unusual twin as a monoperiodic twin was later given by Friedel (1933): the two crystals are in contact via the (1010) face (hexagonal prism) on one crystal and the (1011) (hexagonal bipyramid) face of the other. The only common lattice row of these faces is [100], which is also the densest row. This orientation is resembles the contact between one octahedral and one cubic face in the alum artificial monoperiodic twins: in both cases, the densest row in the common plane is the only direction of common periodicity.

In the twin studied by Drugman, an accidental mechanical shock removed the third crystal, the one in Zinnwald position, showing the contact surface. There, no trace of spiral growth was found but the surface was plane and gleaming, parallel to (1010) of the small crystal and to (1011) of the large one. Drugman explained the formation of this monoperiodic twin by the oriented attachment of two pre-formed individuals. Once came into contact, the two individuals should have rearranged their mutual orientation to reach either parallelism, or the closest twin position. Taking into account the angle between the unique axes, in this case the twin plane would be (2021), a very rare twin (“Cornish law”) with high twin index (7) but low obliquity (1º25’) (Friedel, 1923), reported earlier again by Drugman (1927) in a complex four-individuals twin from Wheal Coates, Cornwall. The appearance, instead, of a monoperiodic twin must have come from a mechanical hindrance to the re-orientation, something that is likely only when the two interacting crystals have already reached a considerable size.

**Insights from the frequency of occurrence of twins**

In order for the oriented attachment to be active, the crystals must be in an environment favouring their motion and casual interaction. Furthermore, the composition plane of a twin formed by oriented attachment likely belongs to a well-developed form of the individuals. In this respect, twins in $\beta$-quartz found at the Esterel Mountains (Drugman, 1928) offer further insights. In the Esterel quartz-diorite formed by magmatic activity (Michel-Lévy, 1896), an unusually high frequency of (1011) Esterel twins - about twice that of the (1122) Verespatak twins - was found. The opposite relative frequency was instead reported in vein quartz where crystals are rooted in a matrix and cannot move around (Friedel, 1933).
The composition plane in the Verespatak twin does not correspond to a commonly well-developed form of $\beta$-quartz: the formation of such a twin by oriented attachment is thus a low probability event. Instead, the composition plane in the Esterel twin belongs to the hexagonal bipyramid, which, together with the hexagonal prism $\{1\overline{0}1\}$, is the most developed form of $\beta$-quartz. Furthermore, in the specific case of the twins studied by Drugman, the hexagonal prism was practically absent and the habitus of the $\beta$-quartz crystals consisted essentially in the hexagonal bipyramid $\{1\overline{0}1\}$. Both the occurrence frequency and the location of the composition plane suggest thus that the oriented attachment played an important role in the formation of the Esterel twins.

This evidence is further reinforced by the occurrence, in the same environment, of Zinnwald monoperiodic twins, whose origin, as discussed above, is most likely by oriented attachment of pre-formed crystals.

The “flying magic carpet” mechanism

Several years after Drugman’s systematic investigation of twins in $\beta$-quartz, direct confirmation of the oriented attachment as a mechanism of twin formation in macroscopic crystals came from Japanese researchers. Kitazawa et al. (1971) observed agglutination of CdI$_2$ crystals which adjusted their orientation just before agglutinating. Sunagawa et al. (1975) reported coalescence of several chlorite crystals in hydrothermal solutions, although rarely in crystallographic orientation. However, Sunagawa and Tomura (1976) showed that phlogopite crystals found in druses of lavas in several Japanese localities occur as multi-individual twins of widely different sizes, which cannot be formed during the nucleation stage. For this type of twins, they suggested the term “flying magic carpets”, to indicate thin lamellar crystals moving around in the crystallization medium while they are growing.

Diperiodic twins vs. plesiotwins

The discovery of monoperiodic twins led Friedel (1933) to recognize that his geometrical theory of twinning (Friedel 1904, 1926) applies specifically to triperiodic twins, and to foresee the possible existence of diperiodic twins also. In the latter case, the coincidence would be realized only in a two-dimensional lattice corresponding to the composition plane, in analogy to what happens in the case of diperiodic epitaxy (Royer, 1928, 1954). To our knowledge, no example of diperiodic twins has been reported so far. In a diperiodic twin the $\Sigma$ factor, which corresponds to the density of common nodes in the composition plane (the two-dimensional counterpart of the twin index: Baake and Pleasants, 1995), would be small (often 1), but the individuals would have no common period along the third direction.

Friedel (1926, pp. 247-249; see also Donnay and Donnay, 1959) derived the lattice conditions for twinning in each lattice system; they correspond to the conditions for a lattice row to be normal
to a twin plan, and require rational values of the parameters ratio. In a twin by (reticular) pseudo-merohedry, these conditions are only approximately obeyed. In a diperiodic twin the same conditions are not obeyed at all (otherwise a triperiodic twin would occur). Diperiodic twins can thus be described as the limiting case of twins by (reticular) pseudo-merohedry in which the obliquity outside the twin plane is very large and, as such, does not allow the formation of a triperiodic twin. Evidently, the boundary between the two categories cannot be exact.

On the other hand, plesiotwins have a large \( \Sigma \) factor but a low obliquity outside the (plesio)twin plane: despite the existence of a triperiodic common sublattice, they cannot be included in the category of triperiodic twins, because of their large index (plesiotwin index). Plesiotwins are known to occur especially in layered compounds, and in general do not obey the condition of structural continuation in the twin junction without violation of the immediate coordination of its atoms, a condition that, on structural basis, is considered a pre-requisite for the formation of triperiodic twins (Buerger, 1945). Their origin is likely in the oriented attachments of crystals that have already attained a relatively important size, as for the monoperiodic twins. In the case of nanocrystals, the oriented attachment is rapidly followed, when necessary, by a re-adjustment of the relative orientation until a minimum energy configuration is reached, which corresponds either to a parallel growth or to a triperiodic twin. However, when the oriented attachment involves macrocrystals, the individuals may be blocked in their original orientation, due to mechanical hindrance to the re-orientation. This “frozen” orientation may well correspond to a parallel growth or to a triperiodic twin, but statistically it may also produce a monoperiodic twin or a plesiotwin.

A direct confirmation of this mechanism was given by Sueno et al. (1971), who used the technique of dispersion in solution and drying applied to samples of layer compounds (talc, kaolinite, pyrophyllite, chlorite, gold). The result was a physical superposition of flakes of the same compound whose relative orientations were distributed inversely proportionally to the \( \Sigma \) factor. Identical result was obtained also on aggregates of SiC synthesized by sublimation. The same type of experiment, with similar results, was repeated by Takêuchi et al. (1972) on biotite flakes. These authors however found also single flakes of biotite showing plesiotwin orientation, whose formation must have been by oriented attachment. Finally, plesiotwins orientations were found also by Sunagawa and Tomura (1976) among the phlogopite twins formed by the “flying magic carpet” mechanism.

The occurrence of plesiotwins and the lack of diperiodic twins can be rationalized as follows. When two crystals approach with a random orientation and eventually come into contact, they tend to rearrange their orientation. If the mechanical hindrance is severe, they either remain without a definite crystallographic orientation, forming thus a “bicrystal”, or attain the configuration of a monoperiodic twin or of a plesiotwin. If that mechanical hindrance is less severe, the reorientation process goes further and a common two-dimensional (sub)lattice is obtained. In the latter case, the result is a triperiodic twin, unless the obliquity outside the composition plane (which in this case necessarily coincides with the twin plane) is so large that an approximate common period in the out-of-plane direction cannot be found; however, as mentioned above, this case so far has not been
Discussion

As documented above, the phenomenon of oriented attachment of macrorystals was known more than a century before and several direct and indirect evidences exist in the literature, from laboratory experiments as well as from the study of natural minerals. The formation of twins from the oriented attachment of pre-formed crystals was recently studied at nanoparticle level thanks to the direct structure imaging permitted by HRTEM observations (Penn and Banfield, 1998, 1999).

Pre-formed crystals coming into contact can take different orientations corresponding to parallel orientation, triperiodic twin, monoperiodic twin or plesiotwin. The first two cases are difficult to distinguish from the corresponding associations formed at an earlier stage: however, they were artificially obtained in laboratory experiments (lead nitrate; alum). Indirect but convincing evidence of their formation also in natural crystals comes from morphological studies and from the frequency of occurrence as a function of the formation environment.

Monoperiodic twins and plesiotwins instead do not find a reasonable explanation other than in the oriented attachment. It would in fact be difficult to explain the occurrence of these associations if they formed during the normal crystal growth process: the position that the crystallization unit should take would simply be too unstable with respect to the coordination of neighbour atoms at the interface. The origin of these oriented crystal associations is instead well explained in terms of two pre-formed individuals that first come into random contact and then tend to re-adjust their relative orientation to form a more stable oriented association. In this process, when a common two-dimensional lattice or sublattice of low $\Sigma$ factor (the two-dimensional equivalent of the twin index) is achieved, a twin is obtained, which is triperiodic unless the out-of-plane obliquity is so large that no common subperiod, even approximate, can be found in the third direction: in that case, a diperiodic twin would arise, of which no examples are known. Intermediate orientations, corresponding to a monoperiodic twin or to a plesiotwin, are a compromise between the original unstable contact and the mechanically hindered, although more stable, configuration of a triperiodic twin.

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