

Letter

Twins vs. modular crystal structures

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Abstract. The crystallographic nature of modular structures is analysed and discussed in terms of their symmetry and structure building operations. The modular crystal structures we discuss in this paper are homogeneous edifices, built by one or more types of modules related by a point-space operation, and the whole structure is described by an ordinary three-dimensional triperiodic space group. Because the term “twin” is often used, with or without modifiers, to describe symmetry operations that act as building mechanisms in modular structures, a comparison is made with twins, that are instead heterogeneous edifices, described not by a space group but by a (polychromatic) point group, where the individuals are related by operations in the vector space. A unifying scheme is proposed where the passage from heterogeneous to homogeneous structures, only apparently justified by a change of dimensions of the individuals, implies a change of space where the operations are defined.

Introduction

In the inorganic kingdom, many crystalline phases can be described as modular structures, i.e. structures built by periodically juxtaposing one or more types of modules. These modules are three-dimensional but less than triperiodic objects which can ideally be described as cuts from a (real or hypothetical) structurally and chemically homogeneous parent structure: the *archetype*. The symmetry of the modular structure is described by an ordinary space

group, whereas the building modules possess only a sub-periodic group.

The modules can be obtained from chemically different archetypes: the resulting structures are known as *polyarchetypal structures* (diarchetypal being the most frequent case) and are evidently also *heterochemical* (different composition) with respect to each of the archetypes. When instead the modules are obtained from the same *archetype*, they are known as *monoarchetypal structures* (Makovicky, 1997).

The generation of a series of structures from the periodic juxtaposition of modules is obtained by varying the relative orientation and/or position of adjacent modules. This juxtaposition in monoarchetypal structures may or may not promote a chemical change at the interface between two modules: the resulting structures are thus *heterochemical* or *isochemical* respectively.

Heterochemical monoarchetypal structures can also be described as polyarchetypal structures, if the interface region between a pair of identical modules, where the chemical change takes place, is considered as a different module. By this description, which corresponds to the formalism of polysomatic series (Thompson, 1978), all modular structures but the isochemical ones become polyarchetypal. As discussed below, the opposite is not always true. If not differently stated, hereafter we choose the definition of modules on the basis of their chemistry as taken from the archetype. The chemical changes – if any – occurring at the stage of the composition of modules in a new structure is thus considered part of the *structure building mechanism*, without the need to define an additional module (cf. Ferraris et al., 2004 for a comprehensive review of modular structures).

By a logical extension from subperiodic to triperiodic, a building module can be transformed into an individual. As a result, monoarchetypal and polyarchetypal structures are transformed respectively into twins and over/intergrowths. This passage is however only apparently justi-

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fied, the difference between twins and (heterochemical) over/intergrowths on one side, and modular structures on the other side being more fundamental, as we are going to show.

Twins vs. modular crystal structures

The existence of oriented crystal associations is known at least since Steno's dissertation (Steno, 1669), where we find the description of a "solid body" (a crystal) within another "solid body". Until relatively recent times, the term "twin" was unambiguously used in its original meaning, namely an oriented crystal association of *homogeneous* (same chemistry and same crystal structure) individuals, according to well-defined laws, forming a *heterogeneous* edifice. These laws are expressed through twin operations, relating the individuals of a twin, and are point-group operations [Friedel (1904; 1926); for a recent review see Hahn and Klapper (2003)].

Point-group operations describe the macroscopic symmetry of the ideal crystal and of its physical properties: they are defined in the vector space. Twin operations are thus mappings of the vector space, and a twin is described by a vector point group (rigorously speaking, by a *polychromatic* vector point group: Nespolo, 2004). Those operations that do not belong to the point group of the individuals are the twin operations (the chromatic operations).

In relatively recent times, the term "twin" has been also applied, with or without modifiers, to indicate building mechanisms of modular structures. This use may be misleading. The modular structures we are referring to are composed of planar modules whose mappings are operations defined in the point space, *i.e.* the ordinary physical space or crystal space (Wondratschek, 2002a, b). The operations relating pairs of modules in a modular structure are – in the most general case – space groupoid operations (Dornberger-Schiff, 1956; Sadanaga, 1978). When they are valid in the whole crystal space (global operations), they reduce to ordinary space-group operations. Furthermore, when they do not possess gliding components, they are site-symmetry group operations.

In the following we analyse different types of modular structures and their symmetry aspects with particular emphasis on the comparison with twins.

Origin on the "twin" ambiguity

Ito (1935, 1938, 1950), in his pioneer work on the X-ray investigation of polymorphic crystal structures, analysed the laws of composition of identical planar modules into modular structures. He introduced the concept of "twinned space groups": these are an extension of the ordinary three-dimensional space groups obtained by superimposing a group of operations (that Ito called *twinning group*) onto one of the ordinary three-dimensional triperiodic space groups. Among the operations of the twinning group, glide of a fraction of a cell parameter of the final structure is considered too, in addition to the symmetry operations of the ordinary space groups. A twinned space group may

coincide with an ordinary space group, or have symmetry elements in excess. These symmetry elements in excess are necessarily *local* symmetry elements, namely acting only on a subspace of the crystals space (Sadanaga et al, 1980): if they were global, the result would be again an ordinary space group. It follows that, as demonstrated by Sadanaga (1959), Ito's "twinned space groups" are actually crystallographic space groupoids; the complete derivation and analysis of their families was later performed by Dornberger-Schiff (1956,1964) and Fichtner (1977) in the framework of the theory of OD structures.

Ito extensively used the analogy between the operations relating individuals in twins and those relating layer modules in the polymorphic phases he was investigating – that nowadays we call polytypes (Guinier et al., 1984) – following the idea of a continuity between these two categories as a function of the dimension of the individuals. He also claimed that "gliding [...] has not yet been recognized as a twin element" (Ito, 1950, p. 2–4). Actually, the supposed continuity does not exist: individuals in twins are related by point-group operations (defined in the vector space), which cannot include gliding, whereas modules in modular structures are related by space-groupoid operations (defined in the point space), the analogy being only apparent. The vector-space operation relating individuals in twins is simply a mapping between different orientations of homogeneous individuals forming on the whole a *heterogeneous* edifice, whereas the point-space operations mapping modules in the modular structures here considered are *structure-building operations* giving rise to a *homogeneous* edifice, namely a monoarchetypal homogeneous modular structure.

Hahn and Klapper (2003, p. 397) try to define a boundary between twins and cell-twins in terms of the size range of the individual, suggesting the range of 100–1000 Å as a possible (rather broad) boundary, and state that "unit-cell twinning is a limiting case closely related to superstructures". Actually, there is no continuous transition from twins to cell-twins: the distinction in terms of point space vs. vector space that we have introduced is size independent and shows that the border between the two worlds of "twins" is not a matter of size but is conceptual.

Monoarchetypal structures as cell-twins: classification and features

The examples on which Ito developed his theory correspond to *isochemical* compounds whose structure is obtained by the juxtaposition of layers. These layers have different possible configurations at the interface deriving from the combination of reflection or rotation with three independent patterns of stacking: "gliding en echelon" (gliding in the same direction), "alternate gliding" (alternating regularly in two directions) and "complex gliding" (alternating irregularly in two directions, equivalent to the composition of "en echelon" and "alternate" gliding).

This description of the structure-building operation of layer structures anticipates by a few years the more complete and systematic derivation made by the OD school on the basis of the symmetry of layers and layer pairs (Dorn-

berger-Schiff, 1956, Dornberger-Schiff and Grell-Niemann, 1961). The stacking ambiguity of layers is explained in terms of two types of operations:

σ -operation: a coincidence operation transforming a layer into the adjacent one;

λ -operation: a symmetry operation transforming a layer into itself; the set of λ -operations constitutes a *layer-group* or di-periodic group (cf. Kopský and Litvin, 2002).

Ito's operations are σ -operations and the special case of polymorphism he dealt with corresponds to what nowadays is universally known as polytypism (Đurovič and Weiss, 1986)¹.

The phenomenon of polytypism was already known well before Ito's studies (Baumhauer, 1912, 1915; Ungemach, 1935). Nevertheless, Ito's adoption of the twinning analogy in describing the structure-building operations stimulated the investigation of a wider range of modular structures, which later have been named *cell-twins*. This term was introduced by Takéuchi et al. (1979), after a suggestion by Gabrielle Donnay. The polysynthetic structures analysed by Ito are isochemical and built by modules of the same size; nevertheless, his scheme does not exclude a change in the crystal chemistry, which is actually one of the characteristic features of what nowadays is known as *the cell-twinning mechanism*. The composition of modules to give a homogeneous structure may substantially alter the coordination polyhedra at the interface, resulting in what has been called a "chemical stress" (Hyde et al., 1979). This chemical stress may, at its turn, produce an alteration of the chemistry at the interface. Cell-twins may thus be classified in the following three types:

1. **polytypes:** cell-twins without chemical stress
2. **chemical twins:** cell-twins with chemical stress (Andersson and Hyde, 1974), subdivided in:
 - 2.1 **isochemical**, without chemical variation at the interface
 - 2.2 **heterochemical**, with chemical variation at the interface.

As an example of 2.1 we mention the case of CaTi_2O_4 (Bertaut and Blum, 1956). The module is the $\{311\}$ cut, $4 \times d\{311\}$ wide, of an anion lattice of the *ccp* type with Ti's at the octahedral sites, and the cell-twin operation is a reflection in a plane parallel to $\{311\}$. Ca is located in the mirror planes and its coordination is altered to di-capped trigonal prisms, but no chemical variation occurs to relieve this chemical stress (Fig. 1).

It should be emphasized that Ito and co-workers' results were until recently rarely known to large part of the researchers in the field, because published, partly in Japanese, in rare books and periodicals. For this reason, the concept of cell-twinning is frequently associated mainly with a heterochemical nature: the cell-twinning mechanism itself, however, is a structure-building mechanism independent from the possible occurrence of a change in chemistry. To indicate their specific use of the cell-twinning concepts as 'implying appreciable configurational and che-

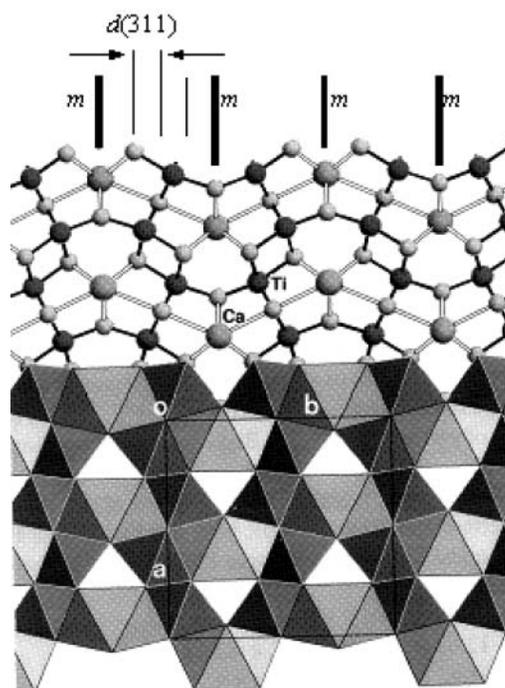


Fig. 1. Projection along $[001]$ of the structure of CaTi_2O_4 . Large spheres denote Ca, dark medium spheres Ti, and small spheres oxygen atoms. The Ti–O bonds are indicated by filled lines. The module is the $\{311\}$ cut, $4 \times d\{311\}$ wide, of an anion lattice of the *ccp* type with Ti's at the octahedral sites, and the cell-twin operation is a reflection in a plane parallel to $\{311\}$ (m in the figure) (modified after Takéuchi, 1997).

mical changes', Ferraris et al. (2004; page 9) adopted a different wording: '*unit-cell twinning*'. The same authors defined as *endopolytypy* the structure-building mechanism that does not change the configuration of the anion array, like in the example of CaTi_2O_4 given above.

It is important to emphasize that the term "cell-twin" was introduced because of an imperfect analogy between the twin operation (a vector-space operation) and the structure-building operation (a point-space operation) in mono-archetypal modular structures. These cell-twins are thus defined by the two following characteristics:

1. the **building modules** are *identical in chemistry* (monoarchetypal structures);
2. the **cell-twin operation** may *promote a chemical change*, but this change is not functional to the existence of the cell-twin operation. When a chemical change accompanies the cell-twin operation, the result is a structure-building mechanism that may give rise to a full *series* of structures with variable chemistry. The number of members of a series actually occurring depends on the thermodynamic and kinetic conditions.

Isochemical cell-twins: Ito twins

Ito's polysynthetic structures are isochemical and their building modules are identical. As we have seen above, they are either simply polytypes, when the configuration at the interface is not modified, or chemical twins without modifications of the chemistry at the interface. In the general scheme of cell-twins, they occupy a very special position, being the benchmark of what later came to be called "cell-twinning". Takéuchi (1997) called them "Ito twins".

¹ "Polymorphism of this kind, if it does exist, must evidently be distinguished from polymorphism, in which several entirely different structures are involved" (Ito, 1950, p. 1).

Heterochemical cell-twins

When the structure-building mechanism consisting of a polysynthetic repetition of the building module promotes a chemical variation, the category of heterochemical cell-twins arises. These are the modular structures that are often simply called “cell-twins” or “twins at unit-cell level”. In terms of the symmetry-hierarchical scheme developed here, they represent a subcategory, although undoubtedly the most important one, of cell-twins.

The building modules are (ideally) obtained from the same (real or hypothetical) archetype (monoarchetypal structures) and have thus the same chemistry. The chemical variation observed in the final structure derives from the creation or annihilation of coordination polyhedra at the boundary between two modules, following which extra atoms can take place or, on the contrary, part of the sites at the interface may be suppressed.

In the literature, these structures are often described as members of a homologous series. This alteration of the coordination at the interface of two modules recalls the similar mechanism observed in the so-called *shear structures* (Wadsley, 1963), the formation mechanism being called *crystallographic slip* (CS)².

When the chemical variation accompanying the cell-twinning operation is an integrant part of the cell-twinning mechanism, that gives rise to a *series* of structures, the chemistry of each member of the series depends on the width of the module, and on the frequency of repetition of the cell-twinning operation. This structure-building mechanism has been called *tropochemical cell-twinning* or TCT by Takéuchi (1997), and the resulting structures are members of a homologous series.

Chemical twinning merely assumes possible deviation in chemistry to relieve the chemical stress at the interface. TCT instead explains the change in chemistry in the different members as a necessary consequence of the series of cell-twinning: in particular, the variation of chemistry is expressible as a function of the frequency of cell-twinning. Such a significant feature of TCT series suggests that the frequency of relaxation in chemical stress due to non-stoichiometric substitution of cations is related to the degree of the substitution in a given chemical system.

The concept of TCT provides the crystallographic basis for the formation of certain classes of homologous series, as in the cases of $\text{Pb}_n\text{Bi}_2\text{S}_{(n+3)}$, with $n = 6, 3$ or $\text{V}_n\text{O}_{(2n-1)}$ with $2 < 2n - 1 < 7$ (Takéuchi et al., 1979).

As a special case of TCT, the concept of *contracted twins* has been introduced (Takéuchi, 1997); it corresponds to that of *extensive accretional homologous series* (Makovicky, 1997). Normally, members of a homologous/TCT series are built by the same module: this means that the module is (ideally) cut from the archetype with a given width, and this module is repeated polysynthetically via the homologous/TCT mechanism. In some cases, how-

ever, two modules may intervene, always cut from the same archetype but with different widths. Whereas the chemistry of the modules is identical, that of the resulting phase depends not only on the frequency of the building mechanism but also on the width of each module.

Polyarchetypal structures

The classification of cell-twins developed so far concerns structures built by modules with the same chemistry (monoarchetypal structures), the possible chemical changes produced by the structure building mechanism being not considered as forming a new module. Often, for the same heterochemical modular structure two different descriptions exist: monoarchetypal (the change in chemistry being promoted by the structure-building mechanism) or polyarchetypal (the change in chemistry being the result of the composition of modules with different chemistry). One example is that of biopyriboles (Thompson, 1978; see Ferraris et al., 2004, p. 41). These two descriptions correspond to the formalisms of the *accretional homologous series* and *polysomatic series* respectively: one or the other may be more advantageous depending on the purpose.

When however for a modular structure a monoarchetypal description is not possible (or not known), the concept of cell-twin is no longer justified. For example, the hexagonal ferrites can be described as built by two spinel-based units M and Y, M having a mirror plane at its middle and relating Y with its mirror image Y', so that the structure can be described as YMY'. Because M and Y have different chemistry, the structures resulting from the juxtaposition of the two modules have been called “non-conservative twins” (Van Landuyt et al., 1974). This further widened use of the term “twin” should be discouraged. In fact, replacing the point-space operation (cell-twin operation or structure-building operation) with the corresponding vector-space operation (the building modules become themselves triperiodic individuals), an oriented crystal association is obtained, which can be either an overgrowth (epitaxy: Royer, 1928, 1937, 1954) or an intergrowth (syntax: Ungemach, 1935; Donnay and Donnay, 1953). Therefore, whereas the passage from “twin” to “cell-twin” is partially justified by the parallel “individual” vs. “module”, the polyarchetypal nature of the so-called “non-conservative twins” prevents any logical parallel with “twins”. There is neither reason nor advantage in describing these structures as cell-twins, the latter being by definition monoarchetypal. The use of “non-conservative twinning” is thus discouraged. Several polyarchetypal structures for which a cell-twin building mechanism can be hardly proposed are described in chapter 4 of Ferraris et al. (2004).

OD twins and allotwins

The correspondence between the point-space symmetry of a crystal and its vector-space symmetry is not always straightforward. The point group and the site-symmetry

² As pointed out by Andersson and Hyde (1974) the term *crystallographic slip* is superior to *crystallographic shear* originally used by Wadsley (1963), because no lattice deformation occurs in the corresponding structures.

group of the lowest multiplicity Wyckoff position are not isomorphous in general, but only in the special case of symmorphic space groups. Analogously, when a modular structure forms a twin, the twin operations do not necessarily correspond to the site-symmetry component of the cell-twin operations building the individual in terms of its modules. This correspondence is however realized in the special case of OD twins.

Structures of polytypes in which geometrical equivalence of pairs of adjacent layers is preserved are **OD structures** (Dornberger-Schiff and Grell-Niemann, 1961). The OD interpretation presupposes that any polytype of a given polytypic substance may be considered as consisting of *disjunct* diperiodic parts, called *OD layers*, whose pairs remain geometrically equivalent in any polytype of the same family. The OD layers do not necessarily coincide with the layers commonly chosen on the basis of the chemical identity and/or cleavage properties. This means that the layers by which a polytypic substance is most commonly described from the *crystal-chemical* viewpoint are not always the most suitable layers to describe the *geometrical* equivalence of layer pairs. Furthermore, the choice of the OD layers in general is not absolute (Grell, 1984); their purpose is not to *explain* but to *describe* and/or *predict* polytypism of a substance based on symmetry. While all OD structures are polytypic, some polytypes may not exhibit OD character: the OD character of a polytype may be shown or hidden by a different choice of the layers and by a different degree of idealization in the description of the layers themselves (cf. Āurovič, 2004). In other words, the OD vs. non-OD character of a polytype is sometimes a matter of description, similarly to what happens for the monoarchetypal vs. polyarchetypal heterochemical structures described above.

When an OD structure forms a twin and the twin operation is isomorphous to one of the σ - or λ -operations relating layers in the OD structure, the result is an OD twin. OD twins were introduced long ago (Dornberger-Schiff, 1959; 1961), without giving however a unique definition, which we introduce here.

DEFINITION. OD twins are twins in which 1) the individuals have periodic OD structures of layers; 2) the twin operation is isomorphous to one of the possible σ - or λ -operations which follow from their OD symmetry described by the respective OD groupoid family.

The process leading to the formation of an OD twin is termed **OD twinning**.

OD twinning is a direct consequence of the stacking ambiguity of OD layers which is a substantial part of the definition of OD structures.

As a corollary, the individuals in an OD twin have an OD layer in common, and this common layer (Dornberger-Schiff, 1959, 1961) places OD twins in the frame of Holser's (1958) description. The classical theory of twinning (Friedel, 1904, 1926) shows that the *necessary conditions* for the existence of twins are imposed by the *lattice*. Such conditions may not be *sufficient* however, because the structure must be sufficiently coherent at the boundary for the twin to be able to form (Buerger, 1945). The statement of Friedel (1926, p. 482) that the occurrence of twins were due exclusively to lattice reasons ap-

pears overcome at present. Holser (1958) analysed the structural conditions in terms of a *slice of structure* shared by pairs of twinned crystals: any symmetry operation of the slice which is not present in the whole crystal structure is a possible twin operation. Note that this kind of shared slice is not always apparent in twins.

Closely related to twins and OD twins are the following categories:

Epitaxy: oriented overgrowth of individuals with different chemistry (Royer, 1928, 1937, 1954).

Syntax: oriented intergrowth of individuals with different chemistry (Ungemach, 1935).

Allotwinning: oriented association (over- or intergrowth) of isochemical OD structures. (Nespolo et al., 1999).

Allotwinning is somewhat intermediate between twinning and epitaxy/syntax, in that the *chemistry* of the individual is the same, but the individuals are not identical, differing in the stacking of layers.

Conclusions

In Fig. 2 we present a proposal for a unifying scheme where the different categories presented above are connected via a *triperiodic-to-subperiodic change in the nature of the individual* (building module), a *homogeneous to heterogeneous change in the nature of the edifice* and a *vector-space to point-space change in the nature of the mapping*.

The detailed classification presented in this article is not only a matter of terminology, but has a direct connection with the problem of establishing the boundaries between cell-twins (modular structures *at the unit-cell level*) and twins, which have been also described as modular structures *at the crystal level* (Ferraris et al., 2004). It has been shown that the boundary is not a matter of size but is conceptual: a modular structure is a homogeneous edifice that can be described by a space group, i.e. a crystal

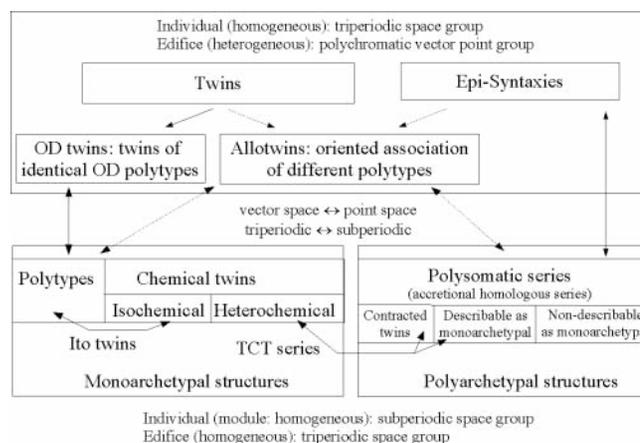


Fig. 2. Proposal for a unifying scheme including heterogeneous (individuals have triperiodic structure) and homogeneous (individuals = modules have diperiodic structure) associations. Allotwins are intermediate between twins and epi-syntaxies: despite the same chemistry, the individuals differ in their stacking sequence. Their homogeneous analogues are mixtures of different polytypic regions, and are thus intermediate between mono- and polyarchetypal structures.

structure in the common sense, where the structure-building operation is a point-space mapping. A twin, instead, is a heterogeneous edifice that cannot be described by a space group because it consists of at least two individuals which have the same crystal structure but with different orientation. The twin operation is a vector-space mapping.

From the viewpoint of the structural crystallographer, this distinction has important consequences on the structure solution strategy to be applied. When dealing with twins, with the exception of class I twins (*i.e.* where the twin operation is equivalent to an inversion centre: Catti and Ferraris, 1976), the twin law has to be known to solve, or to refine the structure, whereas the building principles of a modular structure (monoarchetypal or polyarchetypal) are often discovered once the structure has been solved. Its modular nature can be usefully exploited to obtain a model of related structures, but in principle the structure can be solved even without knowledge of its modular nature.

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