

[p18] Modular aspects in mineral and inorganic structures.

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Warning: *modular structure* is not a synonym of *modulated structure* even if some confusion occurs in literature. In common language, the polytypes and polysomes here discussed are 'modulated' by the repetition of modules but, in principle, they do not imply incommensurate periodicity.

The emphasis on both simple (coordination polyhedra) and complex (aggregates of polyhedra) structural modules to describe inorganic structures (where the 'natural' module molecule is usually absent) can be traced back to the infancy of structural mineral chemistry. However, only the introduction of the *polysomatic series* for a unified modular interpretation of the structures of micas, pyroxenes and amphiboles¹ opened the field of *modular crystallography*². Structural modularity is present in the following cases.

- *Polysomatic series*: a group of compounds is based on different ratios and stackings of at least two structural modules *A* and *B* and form an A_nB_m series which shows additive chemical and structural properties. *Homologous series* have been introduced³ which not necessarily require additive properties and have been subdivided as:
 - a) *accretional homologous series* = polysomatic series;
 - b) *merotypic series*: both common and peculiar modules are present in the crystal structures of the members;
 - c) *plesiotypic series*: the structures of the members are based on modules which have common features but may contain additional peculiar parts.
- *Polytypism*: a special case of polymorphism where different structures of the same compound are based on the different stacking of the same layer and only the lattice parameter along the stacking direction changes.
- *Twinning*: oriented association of single domains of the same compound from nano- to macro-scale. If the oriented domains differ in chemistry or in polytypism, the terms epitaxy/syntaxy (for over- and inter-growth) and allotwinning⁴ are used, in the order.

The concept of modularity is useful for classification purposes, but its capability of inspiring structural modeling and interpretation of structural and compositional anomalies at nano-scale is by far more important. Several examples of structural modeling are reported in literature with particular reference to the application of the OD theory⁵ in polytypes and additive properties in polysomatic (or accretional homologous) series². More sophisticated, even if less general methods, have been proposed for long-period polytypes as the PID (Periodic Intensity Distribution)^{6,7}.

In the lecture examples of structure modeling, interpreting nanometric polysomatic defects in HRTEM images and unravelling twins will be shown.

The structure of the new titanosilicate nafertisite, $(\text{Na,K},\bullet)_4(\text{Fe}^{2+},\text{Fe}^{3+},\bullet)_{10}[\text{Ti}_2\text{O}_3\text{Si}_{12}\text{O}_{34}](\text{O,OH})_6$, has been modeled⁸ after realising that its composition and cell parameters can be obtained by addition of one (010) *M* mica module to the structure of astrophyllite,

$(\text{K,Na})_3(\text{Fe,Mn})_7[\text{Ti}_2\text{O}_3\text{Si}_8\text{O}_{24}](\text{O,OH})_4$, and the structure of the latter mineral is obtained in the same way from that of bafertisite, $\text{Ba}_2(\text{Fe,Mn})_4[\text{Ti}_2\text{O}_4\text{Si}_4\text{O}_{14}](\text{O,OH})_2$. The three minerals are members of the *heterophyllosilicate polysomatic series* B_mM_n (*B* is a module of bafertisite) which intersects other series. The heterophyllosilicates have been recently described by a different choice of modules⁹. Other multiple modular approaches to the same compounds are known^{2,10}; this flexibility can be usefully exploited.

As application of the OD theory to obtain polytypes from an average structure, the case of brochantite, $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$, will be shown¹¹. The application of the PID to identify a long period polytype will be illustrated by the oxibiotite-8A₂ case¹². Nanometric polysomes in HRTEM images and consequences on microprobe analyses will be discussed for the serpentine-like silicate carlosturanite¹³.

Structural crystallography is giving a revival to twins¹⁴ and new aspects have been recently explored^{4, 15, 16, 17}. Subtle aspects of the metric twinning¹⁷ will be discussed in connection with the structure of a new mineral (not yet approved by IMA).

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