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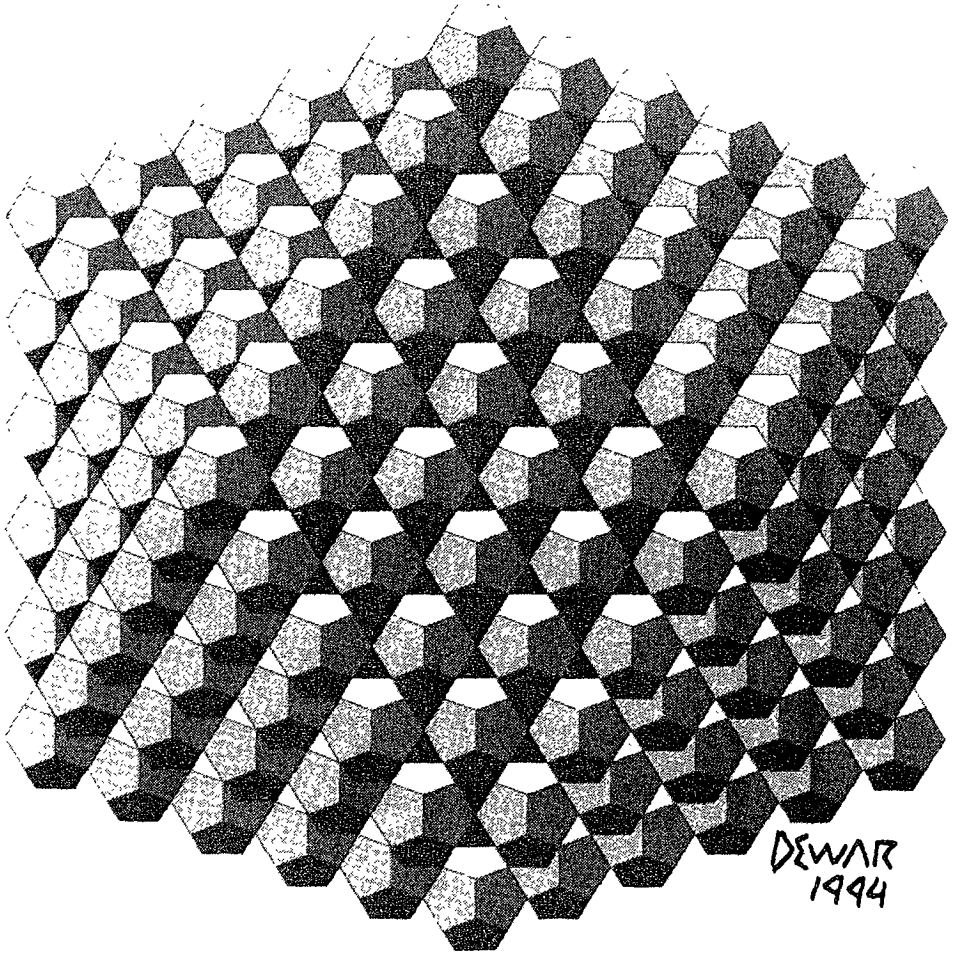


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# SYMMETRY RELATIONSHIPS IN MODULAR CRYSTAL STRUCTURES AND THEIR DISPLAY BY MEANS OF SYMBOLS

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Modular crystallography, in general, and modular mineralogy, in particular, belong to new developments of the modern science as acknowledged by the General Meeting of the International Mineralogical Association, Italy, 1994. The modular approach originates already from the earliest diffractional studies of crystal structures operating with atomic coordination polyhedra and their associations as some standard building building modules (Bragg, 1937, Belov, 1947). It seems though the very nature has choosen modules the energetic profitability and stability of which were approved for simple compounds and combines them at the formation of complex compounds. Therefore modularity is close to the concept of polysomatism (Thompson, 1978) which considers the diversity of "many substances" composed of some parts which are "elementary bricks" of some parent structures. However both notions are not identical. The modular approach aims construction, derivation and prediction of real and hypothetical crystal structures. Polysomatism combines formation conditions and properties of some end member structures in intermediate member structures of polysomatic series. Not always building modules can be found in some real structures composed solely of them and are present in combination only with modules of another kind. Modules of a given kind present in different structures need not be strictly identical but may be topologically similar or deviate in structure and composition from its classical state. Therefore they may be estimated by "degree of somacity" (correspondence to some definite structure). On the other hand, somatic parts may differ by degree of performance of a building function.

The existence of definite type modules being established according to the results of structural studies, the already found structures are described, understood and explained. In

addition hypothetical structures may be derived and predicted differing in relative amounts, sequence order, positions and orientations of the building modules. Thus, different kinds of modular structures are represented by mixed-module alternation sequences, ordered and random, periodic and aperiodic, by hybride structures, commensurate and incommensurate, stacking sequences of polytypes and OD (order-disorder) structures, both simple and complex, homogeneous and inhomogeneous.

The formation of particular module combinations, their occurencies and stability are, of course, defined by crystallochemical features influencing the "reactivity power" of modules, their tendency to associate with other modules of the same or other kinds. However, there is no necessity to know the exact pattern of interatomic bonds if symmetry considerations are taken into account. The symmetry approach, according to which symmetry equivalence comprises crystallochemical equivalence and the former (being more available) may be used instead of the latter (which may remain a hidden subject) has been proclaimed by Dornberger-Schiff (1964) for structures composed of layers related by some partial symmetry operations which may not be total operations converting the whole structure into itself. These structures displaying different degrees of order-disorder were called OD-structures, and a very consistent OD-theory has been developed for their description, analysis and derivation.

There are thus several main sources of the modular crystallography which combines principles of structural mineralogy, polysomatism, polytypism and OD-theory. Its formation and development were activized during the last decade which provided a number of new results and instructive examples of modular structures of many natural and synthetic compounds favourable for important deductions and generalizations (Zvyagin, 1993). It was also supported by effective applications in material sciences (study of semi- and superconductors).

The symmetry of modular structures is defined by the symmetry of separate modules and operations relating them. But most important is that symmetry bears a construction function in this case. It selects equivalent bonding and stacking variants for

adjacent modules and indicates possible positions and orientations of succeeding modules relative to the preceding ones. Modular structures may be subdivided into four categories which Dornberger-Schiff had introduced for OD-structures depending on the nonpolarity-polarity of modules and distribution of symmetry operations retaining or reversing the polarity sense of polar modules.

Crystal structures in general and modular ones in particular are complicated three-dimensional objects. Their understanding, description and subjecting to different operations require application of special means, e.g. modelling, imaging, use of coordination polyhedra and their associations as building modules simplifying the problem. However, the use of symbols which one could write and type, has proved to be most simple, available and at the same time effective for expressing, transfer and acception of structural information.

Capital letters designating somatic parts of definite substances (M-mica, P-pyroxene, S-spinel etc.) are convenient for description of alternation series of the type $X_mY_n\ldots$ The m,n-values characterize concentrations of somatic parts X and Y in polysomes which they form. The modules of stacking series are designated by letters or other symbols the form of which could express at some degree their symmetry and symmetry relationships. Thus, letters H, X, S and Z, A and V, N and $\mu$, n and u, m and w may be attributed to non-polar modules having mirror planes, two-fold rotation axes, inversion centers and related by reflexion, rotation and inversion operations. Letters b, d, p, q characterize polar modules related by the indicated operations. Combinations b/q, b/d, b/p specify modules composed of polar halves related by the indicated operations. If the modules are fixed and held in mind their positions and orientations, displacements and rotations, right- and left-hand states and symmetry operation symbols in general (e.g. $\bar{1}$, 2, $2_1$, m, c, n) may form notations of modular structures. The arrangement of symbols in the notations (e.g. from left to right) should correspond to the spatial arrangement of modules (e.g. to upward sequence of layer modules). The alternation of symbols will

reveal then translations, glide components, positions of symmetry elements inside and/or between the modules and define thus the lattice and space symmetry. It is easy to distinguish identical and independent modular structures described with such notations in different settings and coordinate systems and to subject them to different symmetry operations.

The distribution of operational symbols enables to identify simple and complex polytypes and to estimate the concentrations of the formers in the latters. Comparison of experimental data with modular features opens a possibility to establish crystallization conditions which provide materials having desired properties among members of polysomatic and modular series.

Principles of the modular crystallography may be useful in other areas operating with standard building units.

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