

MODULAR DESIGN OF NANOCOMPOSITE STRUCTURES BASED ON α - Al_2O_3 AND MECHANISMS OF STRUCTURAL TRANSFORMATIONS THEREIN

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ABSTRACT: A general approach to the study of the structure of all known forms of the solid state and of biological structures is possible on the basis of the concept “module” that is more general and unambiguous than “the lattice”. Potentialities of modular design for the estimation of the opportunities of their self-organization due to formation of perfect coherent boundaries between their regularly oriented crystallites in nanocomposites were shown by the examples of two-dimensional Penrose mosaics. There have been shown potentialities of combinatorial polymodular models for analyzing cooperative mechanisms of transformations $\alpha \rightarrow \gamma$ - Al_2O_3 , the reversible growth \rightleftharpoons dissolution of spinel inclusions in corundum, as well as dissolution of “tetrahedral anions” $[\text{SiO}_4]$, $[\text{MoO}_4]$ and $[\text{WO}_4]$ in amorphous corundum.

KEYWORDS: Module, Modular Design, Self-Organization, Nanocomposite, Amorphous State, Structural Cooperative Transformations.

A general approach to the structure of all solids, including crystals, is obviously possible only on the basis of the concept of “crystalline module”, more general than “lattice”. Modular generalization of crystallography which comprises all known states of solids was created on the basis of this concept [1-4].

One of the problems of the nanocomposite structure is the nature of nanolimitation of the size of particles and the structure of contacts between these particles. Self-organization of such nanocomposites and their stability and properties allow one to suggest a possibility of the formation of a regular structure of such contacts.

An important problem is the development of crystallochemical selection of structural components to form self-organizing nanocomposites, including biomimetic ones, and local rules of assembling the modules of structural components which could restrict the number of their possible combinations in a polymodular structure. Thus, there emerges an outlook of the development of modular design.

In parallel with the solution of these problems, the aim of this work is to design models of cooperative molecular mechanisms of structural transformations with local changes in composition.

Al_2O_3 , being a component of promising composites, appears to be an interesting object for solving the above problems. In addition, Al_2O_3 is amorphousized in thin layers because of external effects and transforms into its stable modification, corundum (α - Al_2O_3) [5], after being annealed. The existence of several polymorphous modifications of

Al_2O_3 allows one to apply a polymodular model of the nanocomposite consisting of crystallites of corundum and spinel-like modifications (γ , η , χ etc) of Al_2O_3 [6] to the analysis of reversible transformations of amorphous structure. Eventually, a reversible process - “formation \rightleftharpoons dissolution of spinel-like microinclusions (CoAl_2O_4 and NiAl_2O_4)” occurs upon annealing in oxidative medium and in vacuum [7,8]. No doubt that these processes are cooperative and can be analyzed by the modular design method.

1. Crystalline modules and their disclination and dispiration transformations into modules of regular non-Euclidian structures of constant curvature

The concept of the “crystalline module” is associated with N.V. Belov’s ideas on structural motifs that form the basis of his crystallochemical classification of the structures, derived from the closest packing [9]. In a crystal structure, the module is unambiguously chosen as a three-dimensional loop with no atoms inside and is translated along three directions. Modules in crystal contact on parallel faces (wholly or partly) comprising all the atoms of the crystalline structure; however, the entire space is not always filled [4,10]. If all ways of joining, the modules in crystal are taken into account, their three-dimensional loop corresponds to the crystal stoichiometry. The module symmetry is described by a point group corresponding to the point group of the crystal or to the subgroup of this group. Therefore, a crystalline module can be considered as a crystalline, quasimolecule, who somewhat differs from the chemical molecule and is a genuine building brick of the crystalline substance [10].

The rigid shell of the module is formed by two closed modules (cycles) which correspond to repeated loops of the atomic nets of the most important crystal faces. All needed information on the short (range) and long (range) order is contained in the module structure. Atomic chains, shared by two-dimensional loops in the crystalline module, correspond to the periods of atomic arrays of the face edges of the crystal [4]. The modular growth of a crystal resembles the knitting process whose elementary acts are completion of all two-dimensional cycles in three-dimensional modular loops. The structural motifs of crystal structures and relevant modules are shown in Fig.1,a-f.

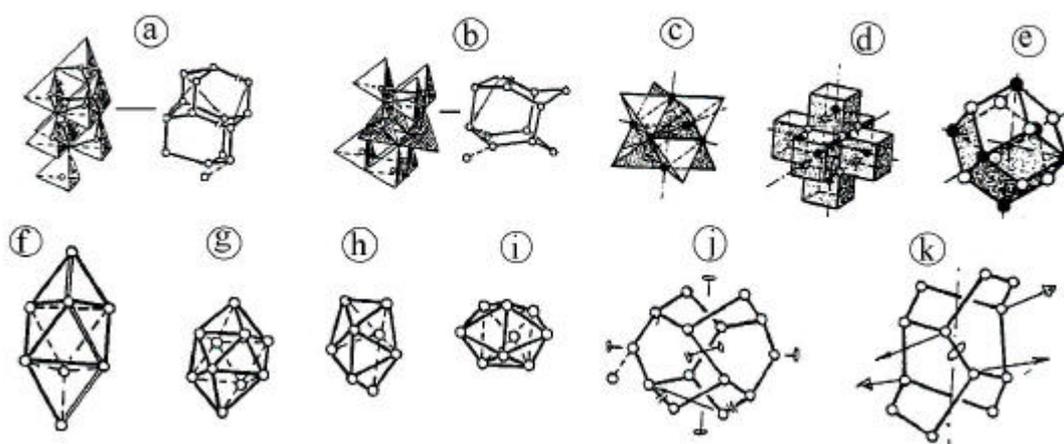


Fig.1. Structural motifs and modules of: **a** - diamond-sphalerite; **b** - wurtzite-ice IH; **c-e** - fluorite; **f** - FCC closest packing; **g-i** - Bernal polyhedra derived from FCC module; **j** - diamond-like K-module; **k** - H-module of parametric structures of “bound water”.

Rigid closed shells of the modules of some crystals (FCC, diamond, wurtzite) can be transformed into modules of regular non-Euclidian structures of constant curvature without appreciable changes in the bond lengths and bond angles caused by introduced disclinations or dispirations [4] (Fig.1,g-k). The transformed modules can only locally (inside a sphere of ~1,5 nm in diameter) coincide with the Euclidian space, characteristic of any atomic structure (all chemical bonds are central and have certain limitations in length changes, inherent in each bond). Regular extension of transformed modules in Euclidian space is possible only if they are one-dimensional rods or spirals, which can, in turn, form self-similar fractal structures [3,4].

Modular generalization of crystallography [4] encompasses the structures of all known forms of the solid state: crystals, as well as clusters, fullerenes, quasicrystals and their approximants [4,11], fractals [3], amorphous solids and nanocomposites, including biomimetic ones [6,12]. Structural models of cooperative configurational defects of the soliton-like type in perfect diamond-like crystals were designed on the basis of transformed modules [13,14]. In addition, the modular generalization of crystallography made it possible to deductively derive parametric system -forming fractal structures of “bound water” that serve as a basis for the formation of spatial structures of biopolymers and biosystems belonging to different hierarchical levels [2,3,15].

2. Binary parameters of modular self-organization of structures, including crystal structures

Unambiguous isolation of the modules and their extension in crystals (according to the face-to face type) does not allow as yet to understand the mechanism of their self-organization that is only determined by interatomic interactions. Hence, there should exist binary energy-geometric parameters characterizing these interactions and determining conditions of complete joining of all chemical bonds to form two- and three-dimensional modular loops. The role of completely closed cycles in the form of modules is important for the formation both of stable structures themselves and of back bonding needed for the control (correction of errors) over any self-organizing process [10].

In the general case, the bond length, d_{ij} , bond angle φ_{ijk} and the torsional angle of the bond Θ_{ij} , joined onto each other are such binary parametric of chemical bonds [16]. In symmetric crystal structures with all atoms in special positions, binary parameters become constant. A complete joining of tetrahedral Sp^3 bonds and the formation of two-dimensional hexacycles of different configurations in three-dimensional modules are possible only in the case of three definite values of torsional angles Θ_{ij} : 0° , $\sim 38^\circ$ and 60° [3,4,17], if other parameters are constant. Sufficiency of the only parameter for self-organization of the structures of diamond ($\Theta_{ij} = 60^\circ$) and “bound water” ($\Theta_{ij} \approx 38^\circ$) manifests itself in the fact that in these structures symmetry centers and two-fold axes bisect each bond. Furthermore, only the hexacycles in the chair-conformation in diamond are two-dimensional loops; in the structure of “bound water” these are the hexacycles with the twist-boat conformation.

Binary parameters determine joining of the bonds to form closed modular loops in all stable structures, including biological and aperiodic ones. Complete joining of all possible bonds between the turns of α -helix in the main chain is realized only at certain values of torsion angles of C_α -N and C_α -C bonds [18]. In all pentagonal Penrose mosaics the pentagons form closed modular loops by sharing edges (and symmetry planes). The structures of pentagons can easily be transformed into atomic ones by

connecting the central points of pentagons. To the bonds in “atomic” structures of different types modular loops will correspond the binary parameters $\varphi_{ijk}=72^\circ$ and 108° , $\Theta=0^\circ$ in mosaics. It is easier to define the type of a modular loop using three other types of “information” tiles in these mosaics (“rhomb”, “boat” and “star”) [4] (Fig.2).

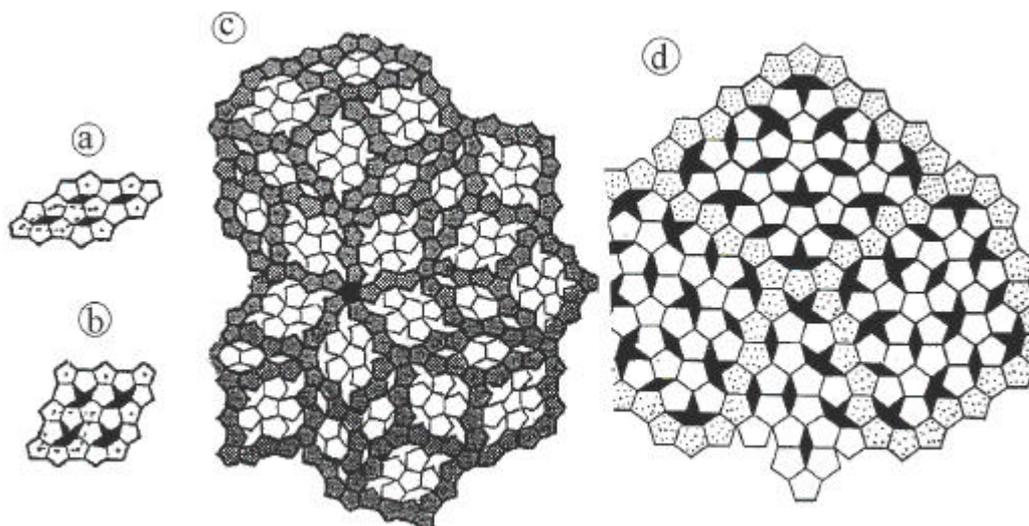


Fig.2. Polymodular combinatorial models of self-organizing two-dimensional “perfect” nanocomposites (with coherent boundaries): **a,b** - Modular loops of two types of nanocrystallites with four lattice cells; **c** – Nanocomposite of nanocrystals (**a, b**) in the Penrose mosaic; **d** – Nanocomposite from the crystallites of the same types.

3. Polymodular self-organizing combinatorial model of nanocomposite structure

The structure of quartz glass is usually considered either as a continuous random network model consisting of 5-, 6-, 7- and 8-membered cycles [19], or as a composite from nanocrystals of different SiO_2 modifications (microcrystallite model) [20]. In these models [SiO_4], tetrahedra are connected with each other sharing all vertices; however, the binary parameters Θ_{ij} and φ_{ijk} in three types hexacycles (two-dimensional modules of cristobalite, tridymite and quartz corresponding to the nets a prismatic-face) will be different. As a result, a two-dimensional model of the quartz glass structure, constructed only of hexacycles, will be aperiodic [20]. In such a combinatorial two-dimensional model the binary parameters of initial hexacycles are changed and the complicated problem of joining the tetrahedra vertices in the three-dimensional model of a- SiO_2 is retained. The use of initial three-dimensional crystalline modules and derived disclination-dispiration transformed modules completely removes the joining problem. It should only take into account the rules of combinatorial modular assemblage that do not roughly violate the local balance of valence efforts [21]. The modules may contact in such way that all atoms be the least involved and the positions occupied by the atoms of the same sorts be superposed.

Thus, the modular design was already used in designing the models of amorphous substances for tetrahedral structures of the SiO_2 type and for statistical close packing of equal sized spheres. In the first case the idea of using two-dimensional modular loops simply had no alternative and was realized in both approaches of designing the models of amorphous SiO_2 . In the second case, J. Bernal succeeded in empiric determination of the shape of the polyhedra of the “canonic holes”[22] that appeared to be the modules

disclinationally transformed from the initial crystalline R-module of FCC packing, equivalent to its rhombohedral unit cell (Fig.1,f-i). The extension of modular approach to designing models of amorphous solids for other substances, faced the absence of the concept “module” and the procedure of its unambiguous isolation in the crystal structure. Therefore, for such substances as Al_2O_3 , where the Al-octahedra in the structures of its different modifications are united by sharing edges and faces, there was no approach to designing models of the structures of amorphous state. In combinatorial models, modules of several types can be either modules of different modifications of the same substance (in the model of amorphous state), or modules of the structures of different substances (in the model of a composite).

In a two-dimensional mosaic, two types of modular loops, formed by pentagons around the information”tiles of the types “rhombus” and “boat”, can be simultaneously the modules and the unit cells of the lattice (outlined by dots in Fig.2,a,b). These modular loops join both in parallel and nonparallel positions (Fig.2,c,d) to form aperiodic structures. Self-organization of nanocomposites is possible due to the formation of a continuous network of low energy coherent boundaries between the crystallites of different structural components. In the mosaic model of the structure of a nanocomposite, (Fig.2,c) formed by crystallites of two different phases and containing four unit cells in each, the boundaries consisting of common fragments of contacting modular loops of different types are isolated. In the combinatorial model of a composite with minimal size of crystallites (one module) there is a much higher level of self-similar self-organization - the formation of domains which boundaries are rhombs with acute angles 36° and 72° (Fig.2,d); these rhombs are similar to those of the unit cells of lattices formed by the same modules (shown by dotted line in Fig.2,a,b).

Thus, it is seen, that with increasing the size of monodisperse crystallites of various structural composite components there appear new opportunities for their structural self-organization which can become a source of new structure - sensitive properties. The possibility of self-organization has been illustrated by the example of biomimetic nanocomposite (amorphous Al_2O_3 - hydroxylapatite - collagen - “bound water”) [6,12]. Crystallochemical criteria of the choice of structural components for producing such materials have also been formulated.

4. Modules of the crystal structures of α - and γ - Al_2O_3

Al_2O_3 (corundum), the most abundant naturally modification, as well as other modifications (γ , η , χ etc) having the structures of cubic and hexagonal spinel or derived structures are formed by layers of the octahedra populated by Al atoms according to the spinel and antispinel motifs (Fig.3,a-c respectively). In contrast to the monomodular corundum structure, built of octahedral layers of one type, the structures of other Al_2O_3 modifications are polymodular; these structures are determinate since they are formed by different types octahedral layers with more complex motifs. Alternation of the octahedral layers in the structures of corundum and spinel is shown in Fig.3,d,e, where the populated octahedra are hatched. In anti-spinel octahedral-layers the Al atoms populate octahedral hollows and also a part of tetrahedral hollows.

The crystalline module of corundum is shown in Fig.3,f as a large “flattened octahedron” with two pyramids which axes are directed along the C_3 axis (1/8 part of the octahedra from adjacent octahedral layers). The directions of joining the modules by sharing faces in the (0001) layer, along $\langle 1\bar{1}00 \rangle$ directions and between layers correspond to the vectors of periodic bond chain (PBC) (Fig.3,g) [23], who determine the directions of the

tangential growth of corundum. Two coplanar PBC vectors determine the formation of maximally smooth F-faces. Since the completion of modules is an elementary act of growth, it is evident that the smaller the crystallite, the greater is the probability of its morphology to be represented by F-faces of known structure. Thus, it is possible to have a rather adequate idea on the structure of the interface surface in the nanocomposite.

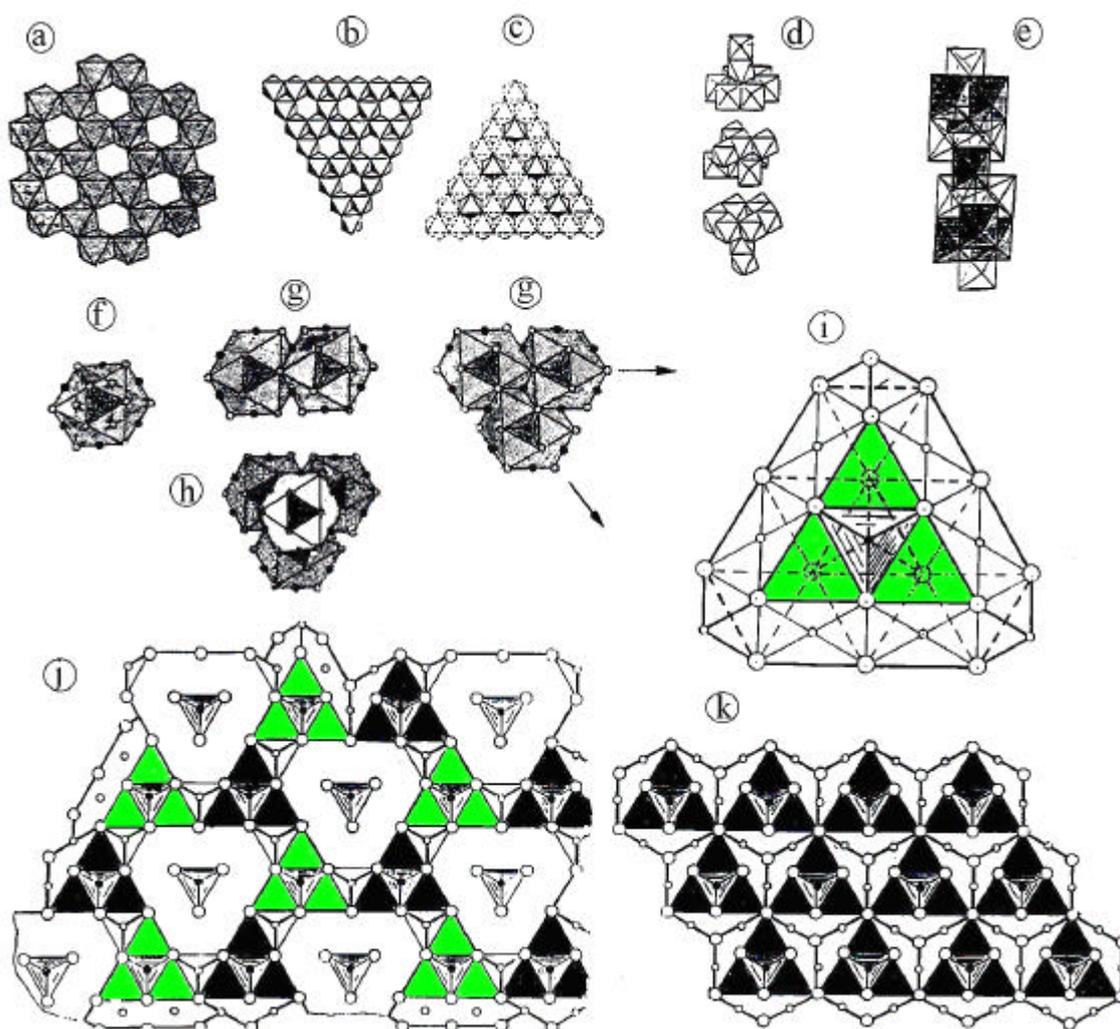


Fig.3: Motifs of octahedral layers in α - and γ - Al_2O_3 : **a**- corundum, **b**- spinel and **c**- antispinel; **d,e** - Algorithms of alternation of octahedral layers with relevant motifs in corundum structures (**d**) and cubic spinel (**e**); **f** - Corundum crystalline module (D_{3d} , 8 aluminum atoms and 12 oxygen atoms); **g** - Modular assemblage of the corundum layer; **h** - Modular layers in the corundum structure; **i** - Another type of module that together with the “corundum module” (**f**) fills the octahedral layer with the spinel motif; **j** - Modular assemblage (“face-on-face”) of the octahedral spinel layer from two types modules (“corundum” module (**f**) painted); **k** - Modular assemblage of the same layer (sharing edges) of the one type modules (**f**).

The octahedral layer of the spinel motif is formed by two types modules (Fig.3,g,h); one of the modules (Fig.3,h) is nearly the same as that in the corundum layer; however, the pyramids (with their axes along C_3) located on the same flattened “octahedron” are the 1/4 of the tetrahedron (but not the 1/8 of the octahedron). The other module of this layer is shown in Fig.3,i; the pyramids on its faces, parallel to the octahedral layers, are also 1/4 of the tetrahedron. As in the corundum layer, merely faces and all atoms of the layer, as

well as corresponding fractions of tetrahedral atoms in two antispinel layers adjacent to this layer participate in the assemblage. Deepenings at the joints of the spinel (Fig.3,j) and corundum layers (Fig.3,g) correspond to the 1/8 fraction of octahedra falling on the fraction of the modules of the spinel layer. They determine the unambiguous order in laying down the octahedral layers of two motifs assembled from modules. In both modules of the layer with spinel motif all pyramids situated along C_3 axes are replaced by 1/8 of octahedron. It is interesting that the two-dimensional spinel layers can be replaced by a monomodular one assembled from one type pseudocorundum modules (Fig.3,k). These modules, who contact each other along the edges instead of following the usual rule of assemblage “face-on-face”, will also encompass all atoms of the layer and atomic fractions of adjacent antispinel layers; however, deepenings between them (trigonal pyramids) will be large. Such a way of modular assemblage appeared to be very efficient for analyzing comparative mechanisms of the phase transition $\gamma \rightarrow \alpha\text{-Al}_2\text{O}_3$, solid state reversible transformation “formation \rightleftharpoons dissolution” of microinclusions of $(\text{CoAl}_2\text{O}_4)$ spinel upon annealing in various media and for the formation of Si, Ge, CdS nanocrystals upon ionic bombardment and successive annealing etc.

The octahedral layer of spinel motif (Fig.3,c) can also be tiled by modules of two sorts. Hence, five sorts of modules can be used in the three-dimensional combinatorial model of amorphous corundum: one module corresponding to the corundum structure and per two modules of the layers with spinel and antispinel motifs ($\gamma\text{-Al}_2\text{O}_3$).

5. Cooperative mechanisms of local structural transformations and solid phase reactions in composites based on $\alpha\text{-Al}_2\text{O}_3$

Combinatorial two-dimensional model of the octahedral layer in a nanocomposite consisting of α - and $\gamma\text{-Al}_2\text{O}_3$ crystallites can be assembled from the modules of one sort (Fig.3,k) only by changing the way of junction: in $\alpha\text{-Al}_2\text{O}_3$ by sharing faces, in $\gamma\text{-Al}_2\text{O}_3$ by sharing edges (Fig.4,a). This two-dimensional model is sufficient for analyzing cooperative mechanisms since it involves five atomic layers in the structures of α - and $\gamma\text{-Al}_2\text{O}_3$: three (O- Al -O) in the octahedral layer itself and one by one (Al) in two adjacent octahedral layers. Inclusions of $\gamma\text{-Al}_2\text{O}_3$ are coherent with $\alpha\text{-Al}_2\text{O}_3$ matrix: continuous arrays of one type modules are (formed) along three directions $\langle 11\bar{2}0 \rangle$ despite the changed way of its junction (Fig.4,a).

In the octahedral layer of Al_2O_3 two networks of oxygen atoms are common to adjacent layers. Hence only three atoms of twelve oxygen atoms in the $\alpha\text{-Al}_2\text{O}_3$ modular (Fig.3,f) belong to this module, since each oxygen atom in the octahedral layer is common to two modules ($12:(2 \times 2)=3$) (Fig.3,g). Six Al atoms of one octahedral layer in the corundum module are located on its lateral faces and are common to three modules in the layer ($6:3=2$) (Fig.3,g). Thus, composition of the octahedral layer of corundum and its module corresponds to the stoichiometry of Al_2O_3 .

In the octahedral layer with spinel motif, the same modules contact each other along edges (Fig.3,k); six Al atoms of the octahedral layer who are on the lateral edges of the module are shared with two modules ($6:2=3$). Of twelve oxygen atoms of the module one half ($12:2=6$) belongs to this layer, while the other half belongs to two adjacent layers. Of these six atoms, one half (3) is common to three modules in the layer ($3:3=1$) (Fig.3,k) while three oxygen atoms at the base of pyramids (the 1/4 of tetrahedron) entirely belongs to the module (3). On the whole, 3 aluminium and 4 oxygen atoms fall on one module of the spinel octahedral layer, isomorphous with corundum layer. This also

corresponds to the stoichiometry of spinel (AB_2X_4) in the layer and each module¹. The dissolution of spinel inclusions and $\gamma\text{-Al}_2\text{O}_3$ and the appearance of accumulated vacancies of oxygen atoms at the inclusion spot is possible after annealing. In the case of cooperative mechanism of dissolution of the inclusions coherent with spinel matrix the oxygen atoms do not change their positions in their network, common to the matrix spinel and $\gamma\text{-Al}_2\text{O}_3$ (Fig.4,b). Merely Al atoms are displaced in the directions indicated by arrows in Fig.4,a, which corresponds to a “displacement” of the modules in the same directions (these modules are not painted in Fig.4,a,b). After dissolution the modules in the inclusion structure are joined “face-on-face”(instead sharing edges) in the newly formed $\alpha\text{-Al}_2\text{O}_3$ layer on the internal surface of the cavity who appeared at the spot of inclusion. “Free” nodes of the oxygen network shown by thin: lines in the area of the cavity formed after dissolution of the inclusion is shown in Fig.4,b. It is those nodes where oxygen vacancies are formed since the oxygen atoms in $\alpha\text{-}$, $\gamma\text{-Al}_2\text{O}_3$ and spinel structures do not interact directly with each other. Reaction of dissolution of the spinel (CoAl_2O_4) inclusion in the $\alpha\text{-Al}_2\text{O}_3$ matrix upon annealing in vacuum² written as $3\text{CoAl}_2\text{O}_4 + 2\text{Al}_i \rightarrow 3\text{Co}_{(M)} + (8\text{Al}_{\text{Al}}^x + 12\text{O}_{\text{O}}^x)$ it is seen that $4/3$ moles of $\alpha\text{-Al}_2\text{O}_3$, one mole of metallic $\text{Co}_{(M)}$ (as a coating on the surface of the cavities) [7] are formed from one mole of spinel². In the case of repeated annealing in oxidizing atmosphere inclusions of CoAl_2O_4 spinel are again formed in these cavities.

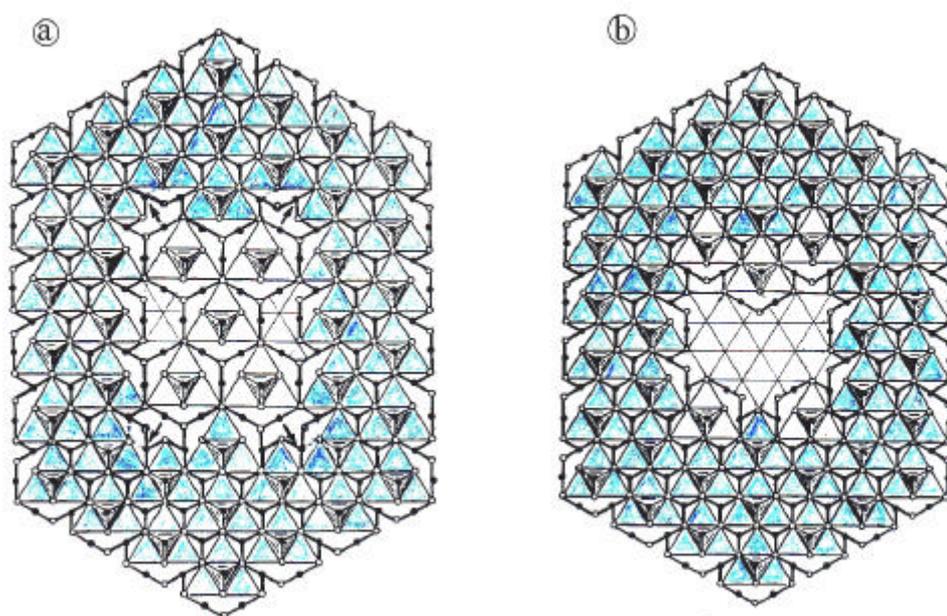


Fig.4: **a** - coherent inclusion of spinel or $\gamma\text{-Al}_2\text{O}_3$ in $\alpha\text{-Al}_2\text{O}_3$ matrix; **b** - cooperative mechanism of its dissolution upon annealing in vacuum; (modules (Fig.3,f) of the inclusion structure before and after dissolution not painted).

Dissolution of “tetrahedral” complex ions of Si, Mo and W that is possible only in amorphous Al_2O_3 consisting of nanocrystals of $\alpha\text{-}$, $\gamma\text{-}$ and $\eta\text{-Al}_2\text{O}_3$ modifications [25] is a peculiar “indicator” of such formation of vacancies. Dissolution of tetrahedral ions with large charge as $[\text{AO}_4]$ is impossible because of the local disbalance of valence. Furthermore, the repulsion forces of Al^{+3} and A^{+n} cations ($n \geq 4$) would be maximal since

¹ Stoichiometric vacancies statistically distributed over positions occupied by aluminium atoms in the layers of the spinel structure of $\gamma\text{-Al}_2\text{O}_3$ [9] are not taken into account in the AB_2X_4 composition.

² Notation of the reaction components referred only to corundum matrix are those by Kroger [24].

only “face-on-face” contacts with Al-octahedra and Si-tetrahedra are possible in the corundum structure, which would correspond to the shortest distance between contacting units. Tablet-shaped crystals of corundum appear only in a mineral-forming medium rich in silica. Si-cations who can not be dissolved in the corundum matrix prevent the tangential growth of its (0001) faces by forming streaks of minerals (pyrophilite or mica) with the same network of oxygen atoms as in corundum.

Formation of the nanocrystals of semiconductors (Si, Ge, CdS) in the surface layer of α - Al_2O_3 upon implantation of the ions of these semiconductors in (0001) substrates of α - Al_2O_3 can be explained by the formation of γ - Al_2O_3 inclusions in the surface layer. In this case amorphization of the surface layer of corundum substrate does occur. Being annealed, this layer is transformed into γ - Al_2O_3 and then into α - Al_2O_3 ; owing to accumulation of oxygen vacancies in the regions of the formation of γ - Al_2O_3 inclusions of semiconductor nanocrystals are formed. Structural correspondences of atomic nets (111) Si and (0001) α - Al_2O_3 , widely used in techniques of epitaxial structures, predetermine regular orientation of semiconductor nanocrystals in the annealed corundum substrate.

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