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Symmetry and Topology Codes of Cluster Self-Assembly for Icosahedral Structures of the $NaZn_{13}$-*cF*112 and TRB_{66}-*cF*1944 Family

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Abstract—Algorithms for combinatorial topology analysis have been developed that allow restoring symmetry and topology codes (program) of crystal structure cluster self-assembly for intermetallic systems. The analysis method is based on the determination of the chemical composition and structure of an intermetallic cluster-precursor and the construction of a basic 3D net of the structure in the form of a graph with the nodes corresponding to the positions of the centers of gravity of the cluster-precursors. The cluster self-assembly of icosahedral structures was modeled for the family of $NaZn_{13}$-*cF*112 and TRB_{66}-*cF*1944 structures, in which the unit cubic *cF*-cells contain 112 atoms ($8 \cdot NaZn_{13}$, $V = 1849$ Å^3) and 1608 atoms ($24 \cdot YB_{66}$, $V = 23440$ Å^3), respectively. The topological type of the basic 3D net in the $NaZn_{13}$ and TRB_{66} structures (with space group *Fm*-3*c*) corresponds to the primitive 3D net P_c (*Pm*–3*m*, *cP*1) with c.n. = 6. The cluster-precursor of the $NaZn_{13}$ structure is an icosahedral cluster Zn@Zn12. The cluster-precursor of the TRB_{66} structure containing 156 B atoms comprises 13 icosahedrons $(B_{12})_{13}$, with the icosahedron B_{12} in the center of the supracluster linked to the 12 icosahedrons forming an icosahedral shell. The Zn_{13} and $(B_{12})_{13}B$ cluster-precursors occupy positions 8*b* in the crystal structures with the highest crystallographically possible symmetry of $m\bar{3}$. The symmetry and topology code of the processes of self-assembly of 3D structures from the nanocluster-precursors—primary chain → microlayer → micronetwork—has been completely reconstructed. The large metal atoms A (with c.n. = 24) are spacers in the AZn_{13} structures, which occupy voids in the 3D nets from the Be_{13}, Co_{13}, Cu_{13}, Zn_{13}, and Cd_{13} icosahedrons. The atoms spacers in the TRB_{66} structures (3 TR and 39 B, TR = Y, Sm, Gd–Lu) statistically occupy the large voids in the 3D nets. The TRB_{66} crystal structure can be obtained from the $NaZn_{13}$ by the replacement (decoration) of all 13 Zn atoms with 13 icosahedral B_{12} clusters; and the system of bonds between the structural units is completely conserved in the process.

Keywords: cluster self-organization, crystal structure self-assembly, icosahedral nanoclusters-precursors, $NaZn_{13}$-*cF*112 structural type, TRB_{66}-*cF*1944 structural type

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INTRODUCTION

Modeling the *cluster self-assembly* of a crystal structure of an intermetallic compound consists in determining the composition and structure of a 3D nanocluster-precursor and recovery of the symmetry and topology codes (program) of the 3D self-assembly of the macrocrystal structure [1–12]. The structure of an intermetallic compound is presented in the form of a 3D net of connected nanocluster-precursors containing in some instances spacer clusters from few atoms in void spaces [1–12].

The symmetry and topology characteristics of the 3D nanocluster-precursors are the most important informative characteristics of all inorganic compounds [13, 14]. The high symmetry of inorganic crystal structures is due to retention of the high symmetry of the cluster-precursor during the formation of solid matter. The positions of each atom in the unit cell and the set of symmetry elements of the symmetry space group are predetermined by the unique structure and symmetry of the cluster-precursor S_3^0 and by the mechanism of their binding during the crystal structure self-assembly. The 3D macrostructure self-assembly occurs via the recognition of complementary sites on the surface of the 3D nanocluster, which ensures large-scale coherence in the location of nano-sized particles. The S_3^0 precursor clusters form a primary chain S_3^1 of the future macrostructure from which the microlayer S_3^2 and the micronetwork S_3^3 are formed. The space symmetry of the formed crystal structure is a result of the complex multistage evolution of the self-organizing system.

In this work the icosahedral structures $NaZn_{13}$ [15] and YB_{66} [16–18] were considered as objects of the study, in which unit cubic *cF*-cells with $V = 1849$ Å^3 and $V = 23440$ Å^3 contained 112 atoms ($8 \cdot NaZn_{13}$) and 1608 atoms ($24 \cdot YB_{66}$), respectively. The $NaZn_{13}$ and YB_{66} intermetallic compounds are characterized by the same space group $Fm\overline{3}c$ and, consequently, by the equivalent set of the symmetry elements. The point (noncrystallographic) symmetry of an icosahedral cluster corresponds to $m\ \overline{3}\,\overline{5}$ (point group order 120), but in the unit cells they can occupy positions corresponding to crystallographic point groups that are subgroups $m\overline{3}\,\overline{5}$, in particular T_h ($m\overline{3}$), group order 24, or D_{3d} ($\overline{3}m$), group order 12. In this case the information is preserved on the equivalent mechanism of the bonding of identical structural units in the icosahedral shell, which includes the equality of the bond lengths between the structural units forming 20 faces of the icosahedron. The space group $Fm\overline{3}c$ was established for intermetallic compounds $NaZn_{13}$ and YB_{66}, which contains elements with point symmetry $m\overline{3}$, and it can be suggested that these positions in the unit cells are occupied by the centers of the icosahedral crystal structure cluster precursors.

This work continues studies [1–12] in the area of the geometric and topological analysis of the structure of crystal phases and the modeling of the processes of the self-organization of chemical systems using modern computer techniques [2, 19, 20].

Techniques used for computer analysis. The geometric and topological analysis was performed using a complex of programs TOPOS [2, 19, 20] allowing conducting a multipurpose investigation of the crystal structure in the automated mode using the representation of structures in the form of contracted graphs (factor graphs). The data on the functional role of atoms during the formation of crystal structures were obtained by calculating the topological indices (coordination sequences, point and vertex symbols).

The algorithm for conducting the geometric and topological analysis using the TOPOS software included the following steps:

—calculation of the adjacency matrix using the AutoCN program;

—presentation of the crystal structure in the form of graph G1, which corresponds to the whole system of bonds of atoms, and graph G2, which characterized the type of basic net of cluster-precursors;

—calculation of the topological indices for graphs G1 and G2 carried out with the help of the ADS program.

To identify the nanocluster-precursor in the crystal structure the algorithm of the structure deconvolution into nanoclusters was used based on the following principles: the structure is formed as a result of the self-assembly from nanocluster-precursors; the centers of nanoclusters occupy the most symmetrical positions; nanocluster-precursors form the packing; i.e., they have no common atoms.

The sets of coordination sequences characterize the structural type unambiguously and are used to select the entire $NaZn_{13}$ and TRB_{66} family using the automated mode for processing the data presented in the ICSD [13, 14].

Symmetry and topology codes (program) of crystal structure self-assembly. The interactions between the particles in the crystal-forming system are characterized by a certain spatio-temporal sequence of elementary events [12]. This sequence can be presented as a *program of self-assembly* of the structure from nanoclusters S_3^0 (as a finite sequence of events).

The hierarchic sequence of the macrostructure self-assembly in the *crystallographic space XYZ* is determined during the modeling; hence, the symmetric and topological code of the structure formation is reconstructed as a sequence of significant elementary events characterizing the shortest (fastest) program of the cluster self-assembly.

The principle of the maximum space filling and, respectively, the requirement of the maximum extent of the complementary binding of S_3^0 nanoclusters is used during the structure self-assembly.

The minimal number of cluster precursors of the zero level S_3^0 that formed the nanocluster-precursor of the 3rd level of self-assembly (microframework S_3^3) is eight. This follows from the fact that each translation vector must be determined with the help of paired orientation ratios of the S_3^0 cluster precursors in the three dimensional *XYZ* space. The $Fm\overline{3}c$ space group identified for the $NaZn_{13}$-*cF*112 and YB_{66}-*cF*1944 contains elements with point symmetry $m\overline{3}$ corresponding to position 8*b* in the unit cell, which indicates that eight

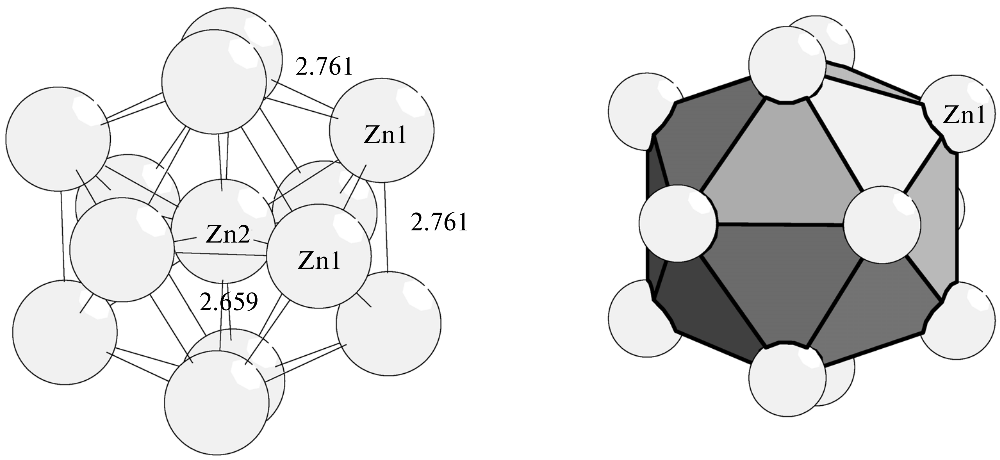

Fig. 1. $NaZn_{13}$. Cluster-precursor of crystal structure.
On the left is a structure model in the form of 13 bounded atoms; on the right, an icosahedral shell from 12 Zn atoms is highlighted. The numbers are the Zn–Zn bond lengths in Å.

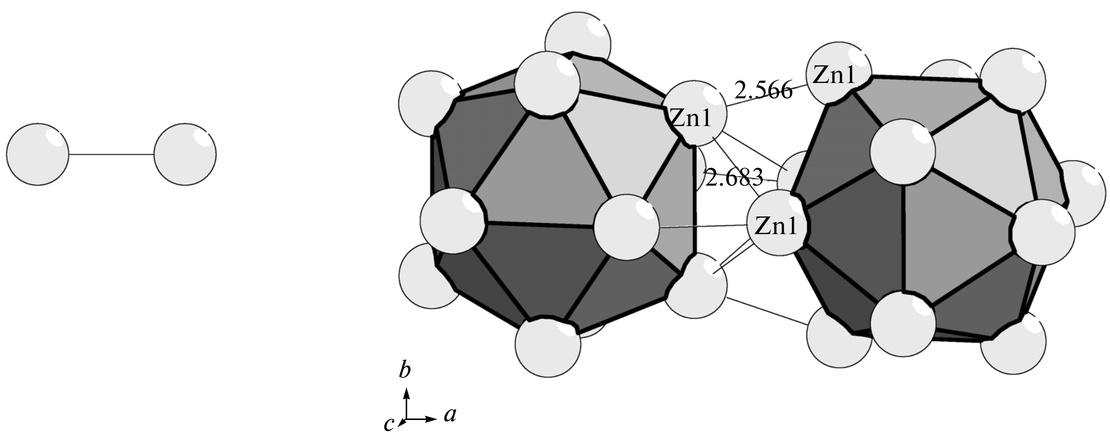

Fig. 2. $NaZn_{13}$. Primary chain from cluster-precursors.
On the left is an image in the form of G2 subgraph; on the right, it is in the form of a suprapolyhedral cluster.

cluster precursors are located in the unit cell forming the 3D microframework.

Structural type $NaZn_{13}$-*cF*112 [15]. *Crystallographic data.* Parameters of the cubic cell of $NaZn_{13}$: $a = 12.273$ Å, $V = 1848.64$ Å^3, and $Z = 8$. The Wyckoff sequence is *iba*. The Pearson symbol is *cF*112. The $NaZn_{13}$ structural type is established for 55 binary compounds AB_{13}, where A is a large metal atom with c.n. = 24, and $B_{13} = Be_{13}$, Co_{13}, Cu_{13}, Zn_{13}, and Cd_{13} [13, 14].

The set of elements with point symmetry for the space group $Fm\bar{3}c$: 432 (positions 8*a*), $m\bar{3}$ (positions 8*b*), $\bar{4}m.2$ (positions 24*c*), 4/*m* (position 24*d*), and others.

Cluster-precursor. The cluster-precursor of the crystal structure consists of 13 atoms and comprises an icosahedral cluster Zn@Zn12 (Fig. 1). The Zn1 atom in the icosahedral shell is linked to the five adjacent Zn1 atoms (distances Zn1–Zn1 = 2.761 Å) and to the central atom Zn2 (distances Zn2–Zn1 = 2.659 Å). The expected shortening of the bond length of the central Zn2 atom with the Zn1 atoms of the shell is 1.038.

In the Zn crystal structure (with the structural type Mg-*hP*2) the distances Zn–Zn = 2.659 and 2.878 Å and the change of the bond length is 1.082.

In the $NaZn_{13}$ crystal structure, the icosahedral center occupies position 8*b* with the highest possible crystallographic symmetry $m\bar{3}$.

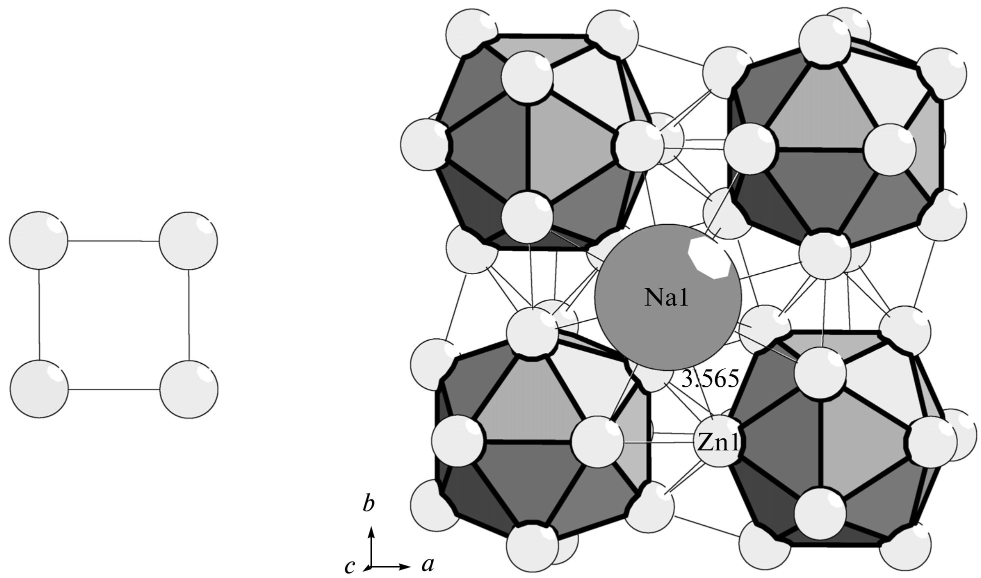

Fig. 3. $NaZn_{13}$. Microlayer from two primary chains.
On the left is an image in the form of a G2 subgraph; on the right, it is in the form of a suprapolyhedral cluster.

The topology type of the basic 3D net characterizing packing of the Zn_{13} cluster-precursors corresponds to the simple cubic 3D network P_c ($Pm\overline{3}m$, $cP1$) with c.n. = 6.

Primary chain. The self-assembly of the primary S_3^1 chains occurs in the direction of the X axis (Fig. 2). The symmetry of supracluster is $-4m.2$ (position 24c). The clusters-precursors in the primary chain are positioned at 90° angles and form the maximal possible number (eight) of bonds B–B. The lengths of the bonds between atoms Zn–Zn = 2.566 and 2.683 Å; hence, they are shorter in comparison to the Zn atoms in the shell (Zn–Zn = 2.761 Å).

Microlayer self-assembly. The S_3^2 microlayer is formed via the linking of the short S_3^1 chains positioned in parallel (Fig. 3). The adjacent icosahedrons from different primary chains in the microlayer are bound through the faces (according to the same mechanism considered above). The center of the supracluster occupies position 24d with $4/m$ symmetry. The Na spacer-atom is located above the center of the microlayer and forms three Na–Zn bonds with the length of 3.565 Å with each of the four icosahedrons.

Micronetwork self-assembly. The S_3^3 microframework is formed via the packing of microlayers (Fig. 4). The center of the supracluster occupies position 8a with symmetry 432. The Na atom is located in the center of the cavity and forms 24 Na–Zn bonds (three bonds with each of the eight icosahedrons).

Multiple condensation of the suprapolyhedral cluster from eight complementarily-bound icosahedrons results in the self-assembly of the 3D macrostructure. All the voids in the network are filled with the Na atom-spacers in the process.

The geometric characteristics of the polyhedrons in the intermetallic network structures (Zn–Zn bond lengths in the icosahedron shell) and the Zn–Zn bond lengths between the polyhedrons define the size of large A atoms of metals with c.n. = 24, which can fill these cavities. In the AZn_{13}-$cF112$ structural type with packing of smaller ~5–7 Å quasi-spherical structural units of icosahedral clusters Be_{13}, Co_{13}, Cu_{13}, Zn_{13}, and Cd_{13} with c.n. = 6, the small cavities in the 3D networks are completely occupied by the single A-atoms (Fig. 4). The family ABe_{13}, where A = Hf, Zr, Mg, Dy, Tb, Ce, Th, U, Np, Pu, Ca, Sr, and Ba, with parameter a changing in the range 10.005–10.485 Å, is the most numerous [13, 14].

Structural type YB_{66}-$cF1944$ [16–18]. *Crystallographic data*. The parameters of a cubic cell of YB_{66}: a = 23.440 Å, V = 23.440 Å^3, and Z = 24. The Wyckoff sequence is $j7i5gf$. The Pearson symbol is $cF1944$. The feature of the YB_{66} intermetallic compound is the sta-

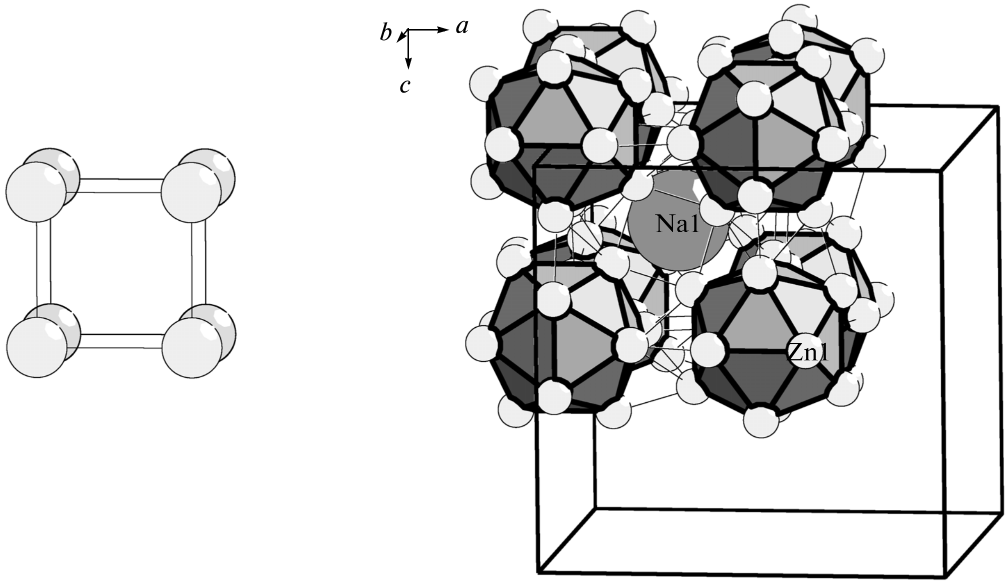

Fig. 4. $NaZn_{13}$. Microframework from two microlayers.
On the left, there is an image in the form of a G2 subgraph; on the right, it is in the form of a suprapolyhedral cluster.

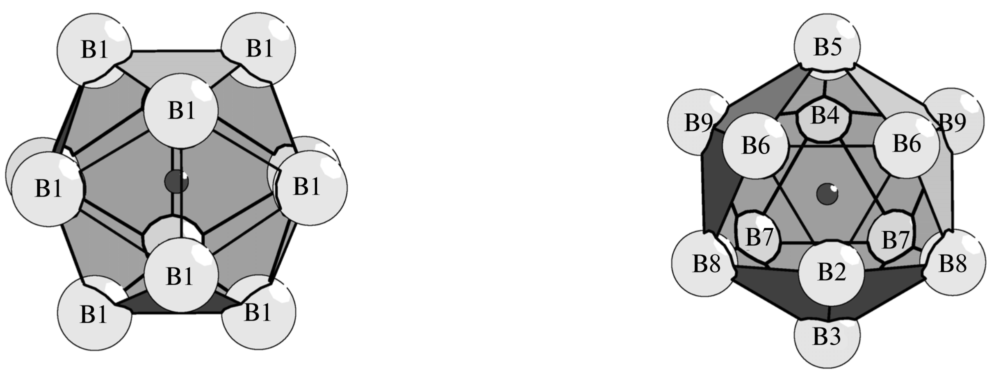

Fig. 5. YB_{66}. Crystallographically independent icosahedrons B_{12}.
On the left, there is an icosahedron with the center in position 8*b*, symmetry *m*–3. On the right, there is an icosahedron with the center in position 96*i*, symmetry *m*.

tistical occupation of large cavities of the network by Y atoms with a probability of 50% and by four atoms B10, B11, B12, and B13 with probabilities of 71, 65, 28, and 27.9% [16]. The YB_{66} structural type was established for compounds AB_{66}, where A-Y, Sm, and Gd–Lu [13, 14].

The TRB_{66} framework structure can be obtained from the $NaZn_{13}$ using the decoration procedure—the replacement of all the Zn node-atoms in the 3D graph G1 by icosahedral clusters B_{12}, while the system of bonds between the structural elements is completely conserved in the process.

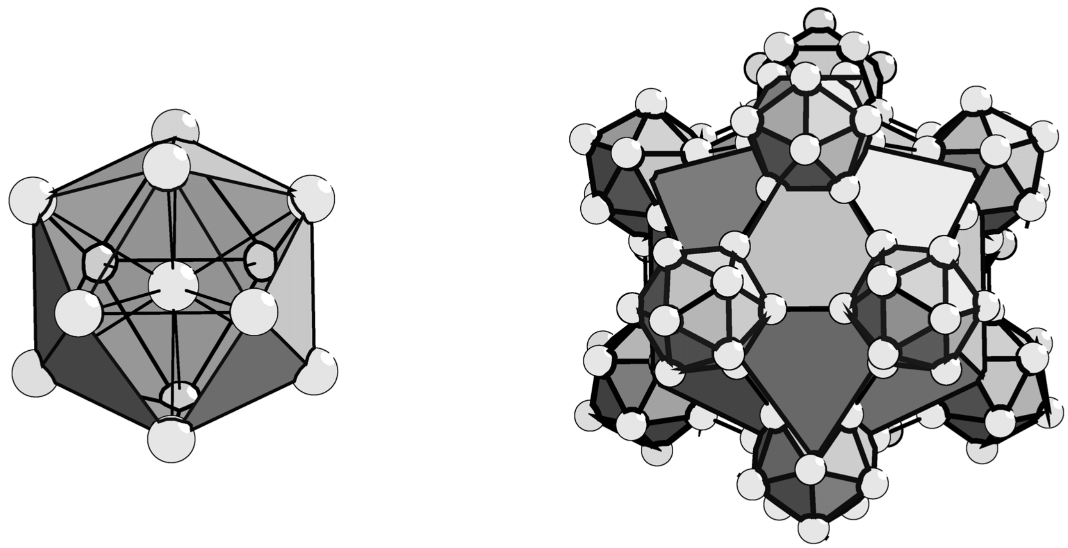

Fig. 6. YB_{66}. Cluster-precursor from 13 icosahedrons B_{12}. On the left, there is an image in the form of graph, on the right, it is in the form of a decorated suprapolyhedral cluster.

Cluster-precursor. The cluster precursor consists of 13 icosahedrons $(B_{12})_{13}$. The icosahedron B_{12} in the center of the cluster occupies positions 8*b* with *m*-3 symmetry similar to the position of the Zn2 atom. Each external icosahedron occupies positions 96*i* c with *m* symmetry similar to position of the Zn1 atoms and is bound to the five adjacent icosahedrons and the central icosahedron (Figs. 5 and 6). The shortest bond between the B1 atom (central icosahedron) and B2 atom (external icosahedron) is 1.623 Å.

The topology type of the basic 3D net characterizing the packing of the cluster-precursors $(B_{12})_{13}$ corresponds to the simple cubic 3D net P_c (*Pm*-3*m*, *cP*1) with c.n. = 6, similarly to the cluster-precursors B13 in $NaZn_{13}$.

Primary chain. The self-assembly of the S_3^1 primary chains occurs in the direction of the *X* axis (Fig. 7). The symmetry of supracluster is $\bar{4}m.2$ (position 24*c*). Atoms B in the eight adjacent icosahedrons and the atoms-spacers Y participate in the supracluster bonding that statistically (50%) occupy only four possible positions due to the short distances Y–Y = 2.554 Å, which makes their concurrent occupation impossible. The Y atom forms six Y–B bonds with two icosahedrons (Fig. 7).

Microlayer self-assembly. The S_3^2 microlayer is formed via the binding of the short S_3^1 chains aligned parallel to each other (Fig. 8). The adjacent icosahedrons from different primary chains in the microlayer are bound via the same mechanism considered above. The center of the supracluster occupies position 24*d* with symmetry 4/*m*. The atoms-spacers Y are located above or below the microlayer center and they form three bonds each with each of the four icosahedrons.

Micronetwork self-assembly. The S_3^3 microframework is formed during the microlayer's packing (Fig. 9). The center of the supracluster occupies position 8*a* with symmetry 432. Multiple condensation of the suprapolyhedron cluster from eight complementary-bound cluster-precursors results in the self-assembly of the 3D macrostructure.

In the YB_{66} intermetallic compound the packing of the large-sized quasi-spherical structural units of the cluster-precursors from 13 icosahedrons $(B_{12})_{13}$ with diameter of ~ 12 Å and c.n. = 6 is accompanied by the formation of large void spaces in the network (with the center in position 8*a*), which are statistically occupied by atom-spacers TR (Y, Sm, Gd–Lu) and B atoms. The locations of 72 positions that are statistically occupied by 38 atoms B (B10, B11, B12) in the large cavities of the 3D network are presented in Fig. 10. The atom B13 is located in the center of the cavity, which is shifted from the center by a distance of 0.647 Å. The adjacent positions of the B13 atom are located at a distance of 0.747 Å × 3 + 1.056 Å × 3 and 1.293 Å × 1 and cannot be occupied simultaneously. The occupancy of the position of the B13 atom cannot be more than 1/8. The shortest distance between the atom B13 and the adjacent atom B11 is 1.947 Å. In

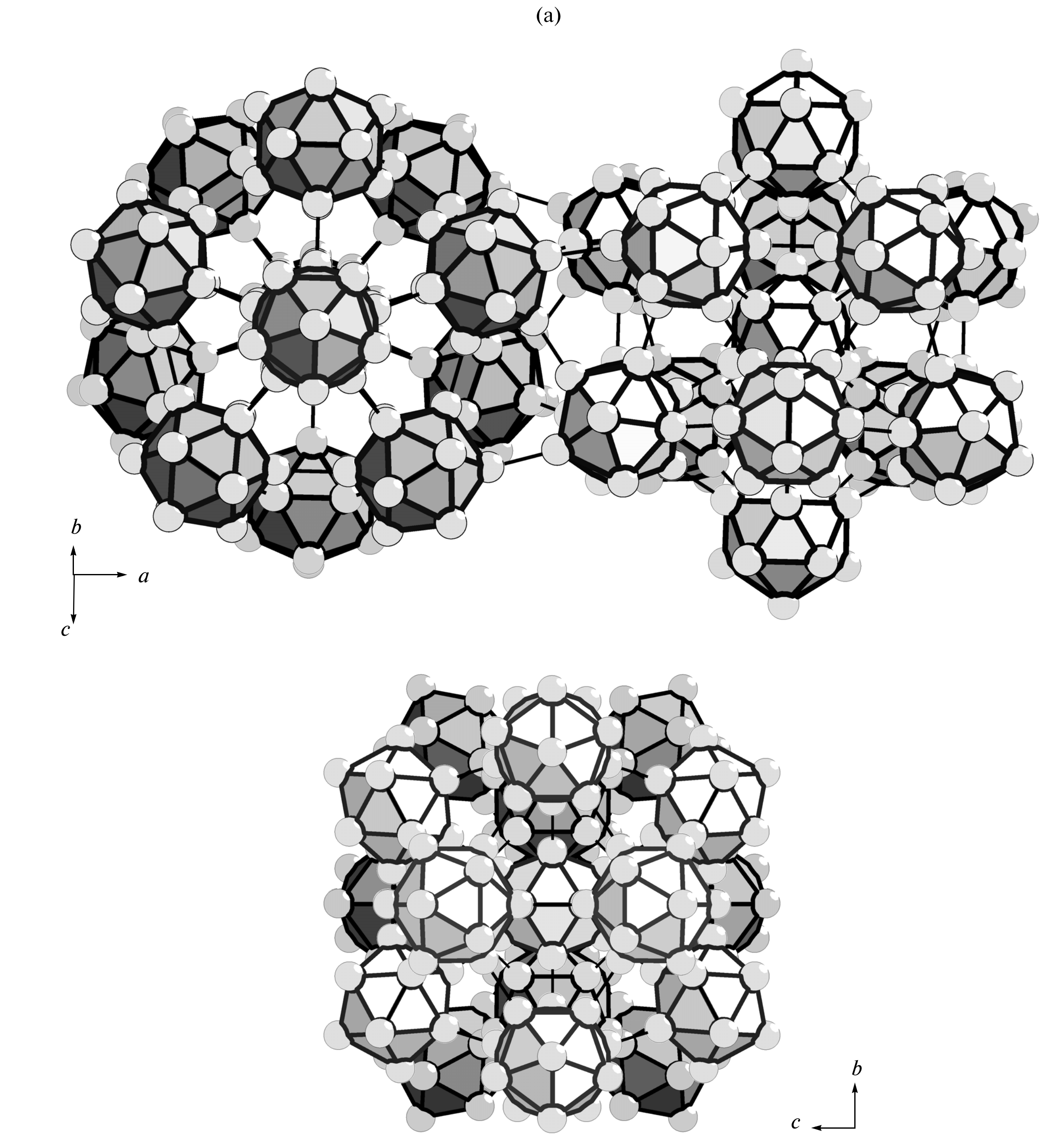

Fig. 7. YB_{66}. Primary chain from clusters-precursors $(B_{12})_{13}$.
(a) In the primary chain the complementary-bound clusters-precursors $(B_{12})_{13}$ are at a 90° angle and form the maximum possible number (eight) of B–B bonds (two projections); (b) atoms Y, statistically (50%) occupy positions between cluster-precursors $(B_{12})_{13}$ presented in the form of decorated suprapolyhedral clusters.

total 3 Y atoms and 38 + 1 B atoms are located in the large cavity (Fig. 10).

Y, Nd, Sm, and Gd–Lu represent atoms A, which can occupy voids in the icosahedral 3D network [14]. In systems with large-sized atoms A = La, Ce, Pr, and Eu, the first enriched phase is the compound of the CaB_6–*cP*7 type [21], and this family includes borides with A = Y, Er, Gd, Th, Pu, Nd, Sm, Ce, Yb, Ca, La, Eu, Sr, K, and Ba [13, 14]. The boron-enriched phase ScB_{15}-*oP*564 [14, 22] that does not have any analogs among the icosahedral structures of the intermetallic compounds is formed in the Sc–B system.

(b)

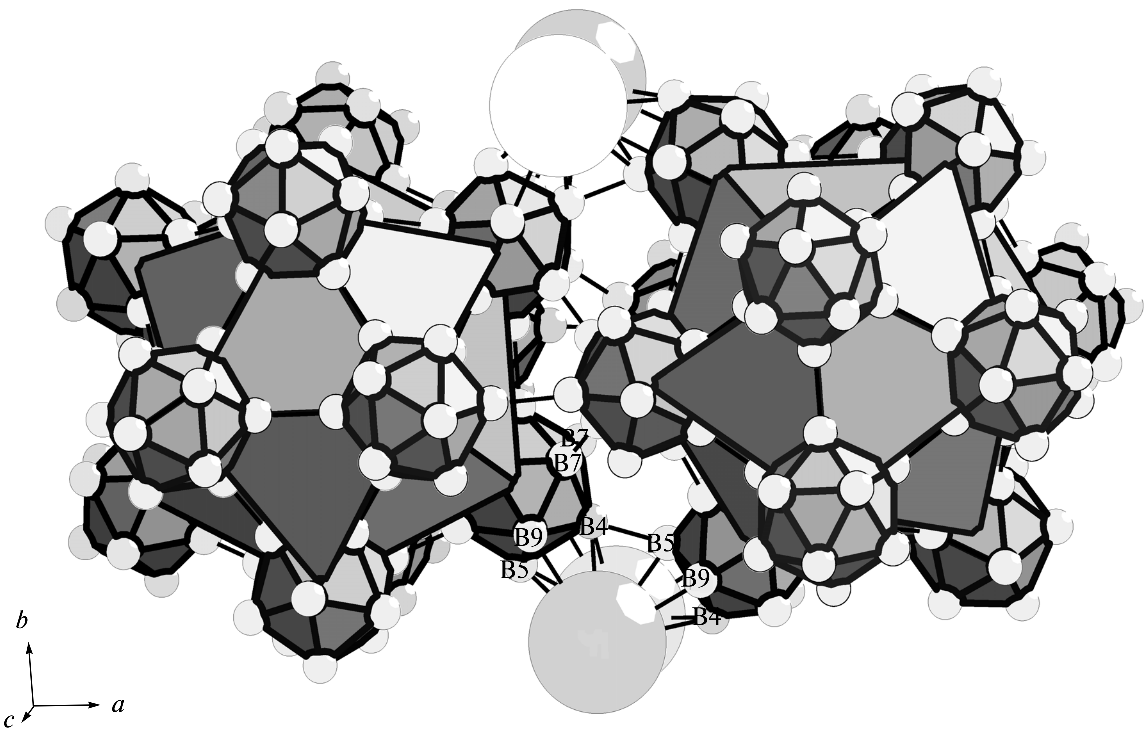

Fig. 7. (Contd.)

CONCLUSIONS

Algorithms are developed for the combinatorial-topological analysis that allow recovering the symmetry and topology code (program) of the cluster self-assembly of the intermetallic crystal structure. The method of analysis is based on the determination of the chemical composition and structure of the intermetallic cluster-precursor and construction of the basic 3D net of the structure in the form of a graph, with the nodes corresponding to the positions of the centers of gravity of the cluster-precursors.

The symmetry and topology code of the processes of self-assembly of the $NaZn_{13}$-*cF*112 and TRB_{66}-*cF*1944 3D structures with the space group *Fm*-3*c* from nanocluster-precursors was completely reconstructed in the form, primary chain → microlayer → microframework.

The cluster-precursor of the $NaZn_{13}$ crystal structure is an icosahedral cluster Zn@Zn12. The cluster-precursor in the TRB_{66} structure consists of 13 icosahedrons $(B_{12})_{13}$, and the icosahedron B_{12} in the center of the cluster is bound to all the 12 icosahedrons. The TRB_{66} network structure can be obtained from the $NaZn_{13}$ using the decoration procedure—the replacement of all Zn atoms in the nodes of the 3D graph G1 by the icosahedral clusters B_{12}; moreover, the system of bonds between the structural units is completely conserved in the process.

In the TRB_{66} structural type the packing of quasi-spherical structural units of the ~12 Å size (cluster-precursors from 13 icosahedrons $(B_{12})_{13}$) with c.n. = 6 is accompanied by the formation of large void spaces in the network, which are statistically occupied by the atoms-spacers 3 TR (Y, Sm, Gd–Lu) and 39 B atoms.

In the AZn_{13}-*cF*112 structural type with the packing of small structural units of size 5–7 Å and c.n. = 6 (icosahedral clusters Be_{13}, Co_{13}, Cu_{13}, Zn_{13}, and Cd_{13}) the voids in the 3D networks are occupied by the single atom-spacers of A-metals.

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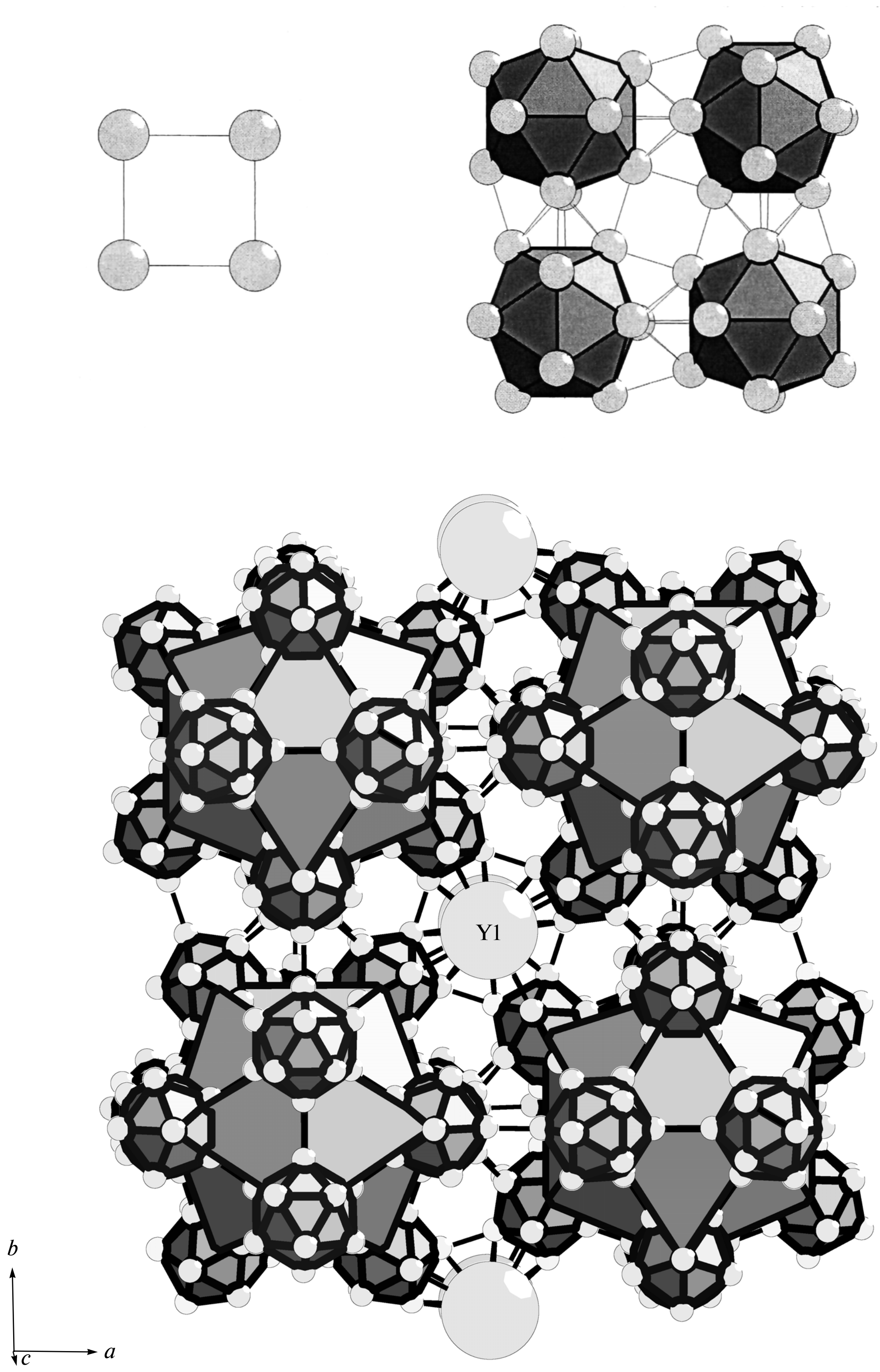

Fig. 8. YB_{66}. Microlayer from clusters-precursors. On the left, there is an image of supercluster in the form of a G2 subgraph; on the right, it is in the form of supercluster with Y atoms statistically (50%) occupying their positions.
The lower panel is microlayer from two bound primary chains.

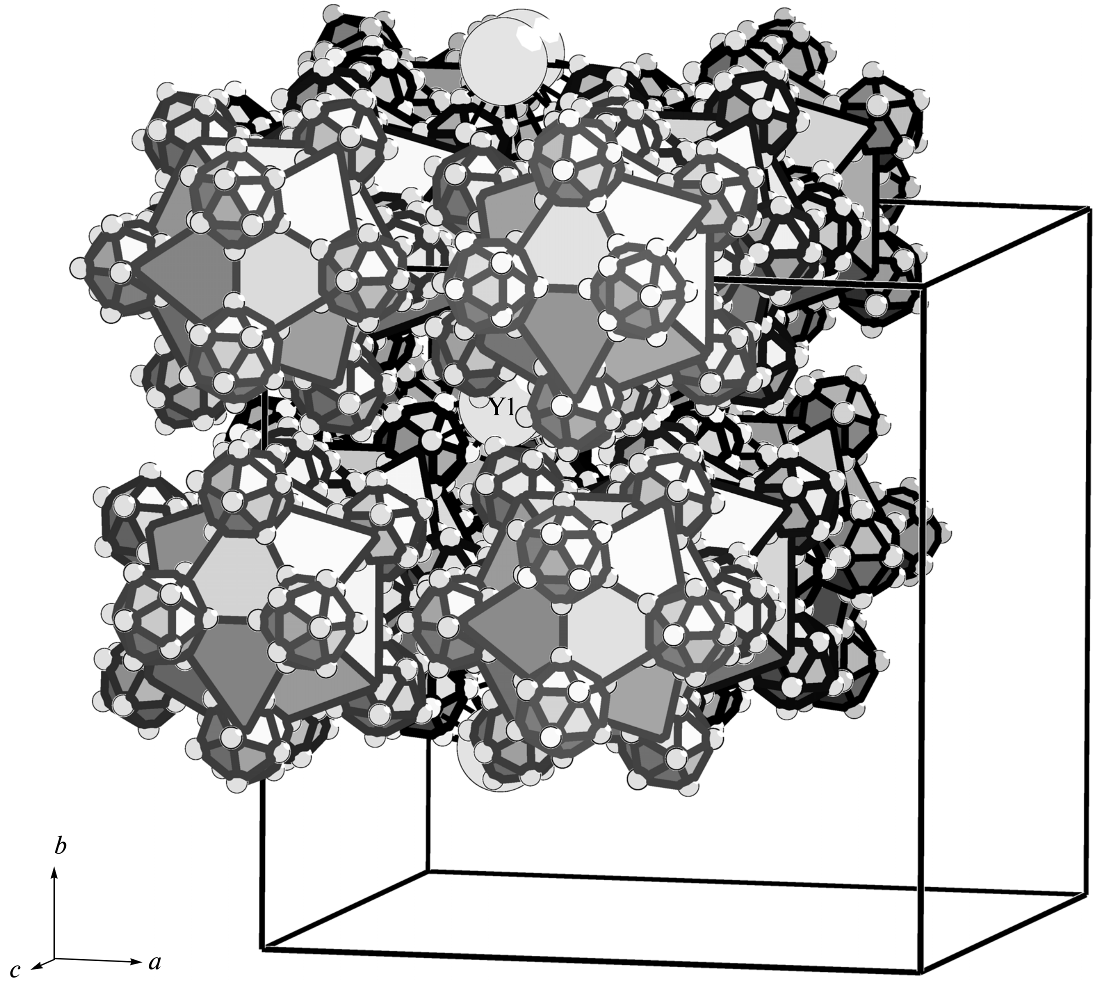

Fig. 9. YB_{66}. Microframework from two bound microlayers.

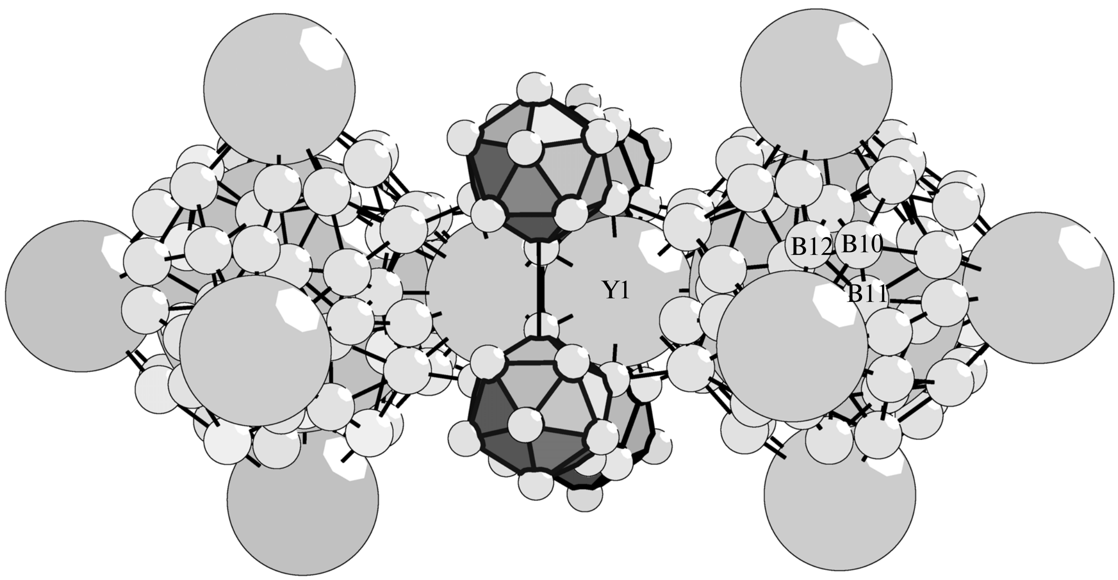

Fig. 10. YB_{66}. Positions of atoms-spacers B10, B11, B12, and Y statistically filling positions in the large cavities of a 3D network.

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