research papers

Structures of the ZrZn$_{22}$ family: suprapolyhedral nanoclusters, methods of self-assembly and superstructural ordering

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A combinatorial topological analysis is carried out by means of the program package *TOPOS*4.0 [Blatov (2006), *IUCr Comput. Commun. Newsl.* **7**, 4–38] and the matrix self-assembly is modeled for crystal structures of the ZrZn$_{22}$ family (space group $Fd\bar{3}m$, Pearson code cF184), including the compounds with superstructural ordering. A number of strict rules are proposed to model the crystal structures of intermetallics as a network of cluster precursors. According to these rules the self-assembly of the ZrZn$_{22}$-like structures was considered within the hierarchical scheme: primary polyhedral cluster → zero-dimensional nanocluster precursor → one-dimensional primary chain → two-dimensional microlayer → three-dimensional microframework (three-dimensional supraprecursor). The suprapolyhedral cluster precursor AB_2X_{37} of diameter ~ 12 Å and volume ~ 350 Å^3 consists of three polyhedra (one AX_{16} of the $\bar{4}3m$ point symmetry and two regular icosahedra BX_{12} of the $\bar{3}m$ point symmetry); the packing of the clusters determines the translations in the resulting crystal structure. A novel topological type of the two-dimensional crystal-forming 4,4-coordinated binodal net AB_2, with the Schläfli symbols 3636 and 3366 for nodes A and B, is discovered. It is shown that the ZrZn$_{22}$ superstructures are formed by substituting some atoms in the cluster precursors. Computer analysis of the CRYSTMET and ICSD databases shows that the cluster AB_2X_{37} occurs in 111 intermetallics belonging to 28 structure types.

1. Introduction

For a long time the analysis of complex metal alloys basically consisted of determining the nearest atomic environment, *i.e.* coordination numbers (CN) and coordination polyhedra for all atoms (Villars, 1994; Daams & Villars, 2000). In the last few years crystal chemistry has turned from traditional analysis of primary structural units (coordination polyhedra, complex groups) to the analysis of building units (Ferey, 2000) or suprapolyhedral invariants (Ilyushin & Blatov, 2002) constructed of primary units.

The main feature of such an analysis is the consideration of regularities in the packing and connectivity of ensembles of the primary structural units that can help in understanding the ways in which the structure is assembled. In the case of intermetallics (including quasicrystals), this leads to various cluster approaches when the structural units are represented by nested polyhedra (Chabot *et al.*, 1981; Yang *et al.*, 1987; Berger *et al.*, 2007; Fredrickson *et al.*, 2007; Steurer & Deloudi, 2008); these approaches are purely geometrical and do not examine all the interatomic bonds: distances between atoms

within the same polyhedron can be larger than distances between atoms of different polyhedra (Chabot *et al.*, 1981). The overall structure is considered ***homo***- or ***hetero-polyhedral***,[1] hence, the problem of arranging atoms into two groups, ***framework-forming*** ($A, B, C, \ldots$) and ***peripheral*** (X), emerges. This problem is difficult to solve since the two groups can include chemically equivalent atoms or some polyhedra can be empty, not containing central atoms. The polyhedral approaches are very effective to analyze the intermetallic 'monsters' with extremely complicated structures that were treated long ago (Samson, 1961), but remain debatable even now. Here the main problem is an ambiguous choice of the structural units, so different models exist for the same intermetallic compound depending on the specific view of the author.

Below we consider a possible way to solve the problems mentioned above using the example of intermetallic 'monsters' from the $ZrZn_{22}$ family. The structure of the archetype of this family, $ZrZn_{22}$, was determined by Samson (1961). Chemical and structural analogues of $ZrZn_{22}$ are $MeBe_{22}$ (Me = Mo, W, Re; Sands *et al.*, 1962; Kripyakevich & Zarechnyuk, 1968). The $ZrZn_{22}$ family includes the intermetallics with superstructural ordering, belonging to the $Mg_3Ti_2Al_{18}$ (Samson, 1958) and $CeCr_2Al_{20}$ (Kripyakevich & Zarechnyuk, 1968) structure types. The structure type $CeCr_2Al_{20}$ consists of more than 100 ternary compounds, including the series AB_2Zn_{20} with A = Zr, Hf, Nb and B = Mn, Fe, Ru, Co, Rh, Ni (Gross *et al.*, 2001); the closest to $ZrZn_{22}$ by composition is $ZrMn_2Zn_{20}$. Recently, Benbow & Latturner (2006) synthesized 18 new intermetallic compounds $RMn_2Tr_xZn_{20-x}$ $2 < x < 7$; R = rare-earth metal; Tr = Al, In) and showed that all of them refer to the $CeCr_2Al_{20}$ structure type.

Different descriptions of the crystal structures of this family ($ZrZn_{22}$, $CeCr_2Al_{20}$, $Mg_3Ti_2Al_{18}$) were given by Pearson (1972) and Kripyakevich (1977). Pearson (1972) separated these compounds into a special group of structures with giant unit cells and described them with the coordination polyhedra to be the 16-vertex Friauf polyhedra (a combination of a regular tetrahedron and a truncated tetrahedron) of Zn or Al atoms. Kripyakevich (1977) complicated the geometrical model by adding an 'empty' octahedron consisting of six X atoms. However, it remains unclear why such complicated structures as well as their superstructures emerge.

Below for the first time a method of matrix self-assembly is applied to the $ZrZn_{22}$-like structures using the computer technique of combinatorial topological analysis implemented in the program package *TOPOS*4.0 (Blatov, 2006). The self-assembly method follows the general hierarchical scheme (Ilyushin, 2003, 2004): primary polyhedral cluster → zero-dimensional suprapolyhedral cluster-precursor → one-dimensional primary chain → two-dimensional microlayer → three-dimensional microframework (three-dimensional

supraprecursor). This work follows on from our investigations (Ilyushin & Blatov, 2002; Ilyushin *et al.*, 2002, 2004; Shevchenko *et al.*, 2009) of the geometrical and topological properties and matrix self-assembly of crystal structures on the suprapolyhedral level.

2. Methods and objects

We have modeled the crystal structures in two stages. In the first stage the framework-forming atoms ($A, B, C \ldots$) were properly selected as the centers of the primary polyhedral clusters according to the following rules:

(i) The clusters are built according to an adjacency matrix of the structure that includes all bonds between atoms. One atom is considered as being central ($A, B, C \ldots$), *i.e.* all its bonds are contained within the cluster. All other (peripheral) atoms of the cluster are obtained by successive growth of n coordination shells around the central atom. Thus, the topology of the cluster was determined by the so-called *shell graph* SG_n (Blatov & Proserpio, 2009). We emphasize the fact that, in general, this model differs from the above-mentioned model of nested polyhedra, where more focus is on the geometrical forms of polyhedra irrespective of the chemical connectivity within the polyhedron. The model can be easily extended to the case of 'empty' polyhedra where the central atom is absent; this extension will be considered in future work.

(ii) The clusters have the highest symmetry (the framework-forming atoms occupy the most symmetrical positions).

(iii) Any cluster is centered with a highly coordinated atom.

(iv) The clusters have no common internal atoms (do not interpenetrate), but can have shared external atoms.

(v) Ordinarily the clusters include all atoms of the structure. In some cases there can be a few atoms that are spacers between clusters.

(vi) If several models obey the rules (i)–(v) (for instance, in the case of low-symmetry crystals) they should all be enumerated and tested to see if they provide different methods of self-assembly (*i.e.* give rise to different zero- to three-dimensional supraprecursors).

When the first primary polyhedral cluster AX_n is found the next framework-forming atom (B) should be chosen according to the same rules among the atoms not belonging to the AX_n cluster. The procedure is then repeated until all inequivalent atoms are included in the primary polyhedral clusters. Then the simplified representation of the structure as a three-dimensional net, whose nodes are the framework-forming atoms, is found.

At the second stage the hierarchic sequence of the self-assembly in the crystallographic space was determined and the zero-, one-, two- and three-dimensional supraprecursors were revealed. We also ascertained how the translation vectors relate to the dimensions and cluster coordination number (CCN) of the zero-dimensional cluster precursor at the template stage of the system's evolution. While modeling nD supraprecursors, we used the principle of maximum connection for the clusters, *i.e.* the supraprecursors of a higher level

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[1] Some basic definitions crucial to the subsequent analysis are in bold italic font and collected in Appendix *A* (*cf.* Ilyushin & Blatov, 2002; Ilyushin *et al.*, 2002, 2004; Ilyushin, 2003, 2004).

Table 1
Characteristics of atoms in the $ZrZn_{22}$ three-dimensional net.

Atom	Environment	Wyckoff position	Site symmetry	Coordination sequence $\{N_k\}$		
				$k = 1$	$k = 2$	$k = 3$
Zn1	Icosahedron	16c	$\bar{3}m$	12	42	96
Zn2	Combination of hexagonal prism and bipyramid	16d	$\bar{3}m$	14	54	114
Zn3	Combination of pentagonal prism and bipyramid	48f	2mm	12	42	98
Zn4	Combination of pentagonal prism and bipyramid	96g	m	12	48	108
Zr	Friauf polyhedron	8b	$\bar{4}3m$	16	58	108

are formed as a maximally connected group of clusters of the preceding level. This principle also rules the formation of zero-dimensional supraprecursors from primary polyhedral clusters.
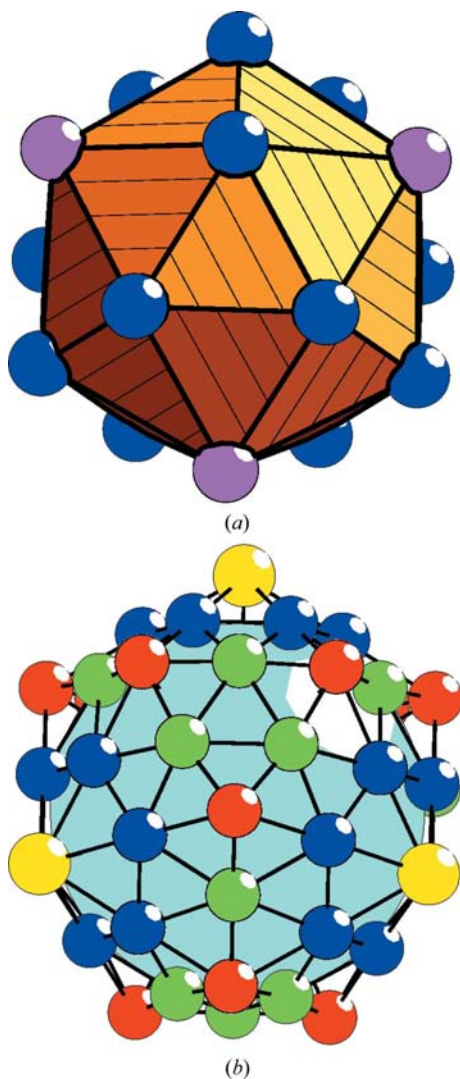

(a)

(b)

Figure 1
First *(a)* and second *(b)* coordination shells of a Zr atom in the $ZrZn_{22}$ crystal structure. Zr atoms are yellow balls. Atoms Zn1–4 are selected in red, purple, green and blue.

The zero-dimensional supraprecursor plays a key role in the structure self-assembly, is composed from primary polyhedral clusters and has clear physical meaning: it is the base for constructing a primary chain (one-dimensional supraprecursor). The primary chains then unite in a microlayer (two-dimensional supraprecursor) and the microlayers form a microframework (three-dimensional supraprecursor); as a result, the zero-dimensional supraprecursor determines the structure periodicity. All atoms are involved in the self-assembly with specified functional roles.

The steps of the analysis were as follows:

(i) All 43 chemically different completely determined crystal structures of the $ZrZn_{22}$ family belonging to three structure types ($ZrZn_{22}$, $CeCr_2Al_{20}$ and $Mg_3Ti_2Al_{18}$) were taken from the Inorganic Crystal Structure Database (ICSD, release 2008/1) and the CRYSTMET database (release 2004).

(ii) For all the crystal structures the adjacency matrices were computed using the *AutoCN* program of the *TOPOS* program package. Only those interatomic interactions that corresponded to the major faces of atomic Voronoi–Dirichlet polyhedra with solid angles $\Omega \leq 1.5\%$ of 4π steradian were taken into account. As a result, three-dimensional periodic structures were represented as three-dimensional nets.

(iii) Owing to the high crystallographic complexity of the considered structures the method of ***coordination sequences*** has been used to analyze topological properties of the three-dimensional nets. This method allows one to establish either functional difference of the atoms in the nets by differences in their coordination sequences $\{N_k\}$, or their equivalence if they are characterized by identical sets $\{N_k\}$. Coordination sequences $\{N_k\}$ for all inequivalent atoms were computed with the *IsoTest* program of the *TOPOS* program package.

(iv) The framework-forming and peripheral atoms as well as primary polyhedral clusters were determined with a specially designed *TOPOS* procedure according to the above-mentioned rules.

3. Functional roles of atoms in the self-assembly and primary polyhedral clusters

The crystal structure of $ZrZn_{22}$ was determined in the cubic space group $Fd\bar{3}m$ (No. 227) with $a = 14.103$ Å, $V = 2805.0$ Å^3 (Samson, 1961). The Wyckoff sequence for the five inequivalent atoms (1 Zr and 4 Zn) is *gfdcb*; Zr atoms are allocated in the most symmetrical ($\bar{4}3m$) position 8b and have the largest CN = 16. Zn(1–4) atoms occupy the positions corresponding to the subgroups of the point group $\bar{4}3m$: 16c ($\bar{3}m$; CN = 12), 16d ($\bar{3}m$; CN = 14), 48f (2mm; CN = 12), 96g (2; CN = 12), respectively. Thus, the total number of atoms in the *F* cubic cell is 184, *i.e.* the Pearson code for this structure type is *cF*184. Only one (Zn1) of 12-coordinated Zn atoms has the icosa-

Table 2
Functional roles of atoms in the self-assembly.

Atom	CN	Environment	Functional role
Zr (A)	16	X_{16}	Central atom of the AX_{16} polyhedron
Zn1 (B)	12	X_{12}	Central atom of the BX_{12} polyhedron
Zn2 (X)	14	A_2X_{12}	Links two AX_{16} polyhedra
Zn3 (X)	12	B_2X_{10}	Links two BX_{12} polyhedra
Zn4 (X)	12	ABX_{10}	Links AX_{16} and BX_{12} polyhedra

hedral environment, the coordination polyhedra of Zn3 and Zn4 atoms are combinations of pentagonal prisms and bipyramids (Table 1, *cf.* Samson, 1961).

Coordination sequences for all the analyzed phases are equivalent and are given in Table 1 for the archetype atoms. They are all different, starting from the third coordination shell, which indicates that all Zn atoms are functionally
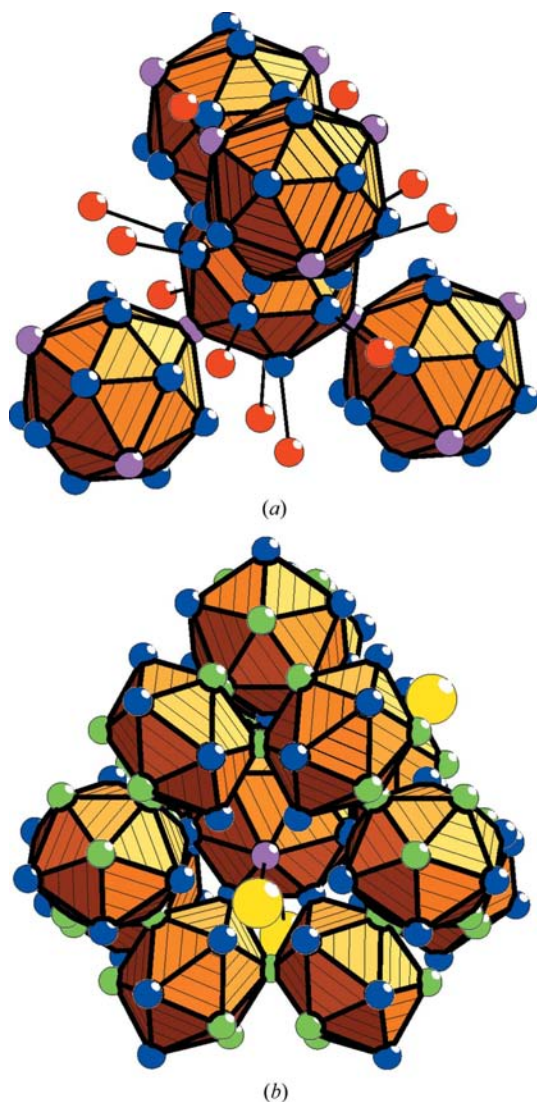
distinct. The role of each atom in the self-assembly is determined as follows:

(i) Zr atoms are considered as central atoms A of framework-forming polyhedra as they occupy the most symmetrical positions and have the largest CN = 16 = 4 Zn2 + 12 Zn4 (Fig. 1a). Accordingly, the Zn2 and Zn4 atoms are assigned to the group of the peripheral X atoms forming the coordination shells of the framework-forming Zr atoms.
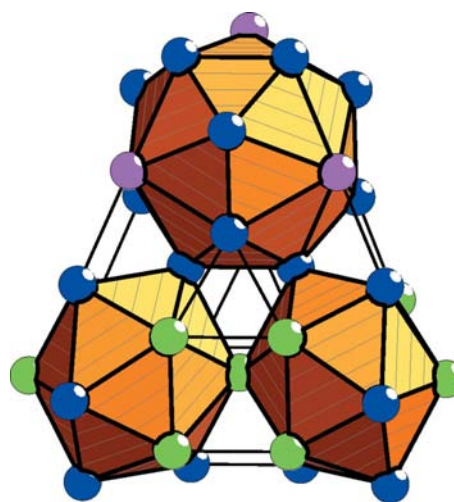
(ii) In the second coordination shell of the Zr atom there are 58 atoms that in fact lie on the surface of the $ZrZn_{16}$ polyhedron (Fig. 1b, Table 1). Among them there are both X atoms and 4 Zr as well as 12 other framework-forming atoms (Zn1) with CN = 12 = 6 Zn3 + 6 Zn4, each of which is connected with the $ZrZn_{16}$ polyhedron only by one X node. The positions of the framework-forming atoms Zr and Zn1 are shown in Fig. 1(b); they are allocated above the peripheral Zn2 atoms of the $ZrZn_{16}$ polyhedron. Other peripheral 18 Zn3 and 24 Zn4 atoms are projected to the centers of 42 edges of the $ZrZn_{16}$ polyhedron. As a result, all the framework-forming atoms are isolated from each other and vertex-connected through the peripheral Zn2, Zn3 and Zn4 atoms only (Figs. 2a and b).

Thus, for all crystallographically independent atoms the following functional roles in the self-assembly were established: A = Zr, B = Zn1 and X = Zn2, Zn3, Zn4 (Table 2), *i.e.* the $ZrZn_{22}$ structure is heteropolyhedral. We emphasize that the zinc atoms with icosahedral coordination are recognized as framework-forming according to the proposed algorithm.

4. Zero-dimensional suprapolyhedral cluster precursor and the methods of superstructural ordering

4.1. Suprapolyhedral composition

According to the stoichiometric relation between the framework-forming atoms $A:B$ = 1:2 the zero-dimensional

Figure 2
The method of connecting (a) $ZrZn_{16}$ polyhedra, (b) a $ZrZn_{16}$ polyhedron and $ZnZn_{12}$ polyhedra. The colors of atoms coincide with Fig. 1.

Figure 3
Zero-dimensional cluster precursor AB_2X_{37}. The colors of atoms coincide with Fig. 1.

cluster precursor AB_2X_{37} consists of one AX_{16} Friauf polyhedron and two BX_{12} icosahedra connected by vertices (X atoms), and has a nanosize diameter of ~ 12 Å and volume ~ 350 Å^3 (Fig. 3). The center of the cluster is allocated to the $96g$ (m) position. Note that the framework-forming polyhedra are vertex-shared at all stages of the structure formation (Table 2)
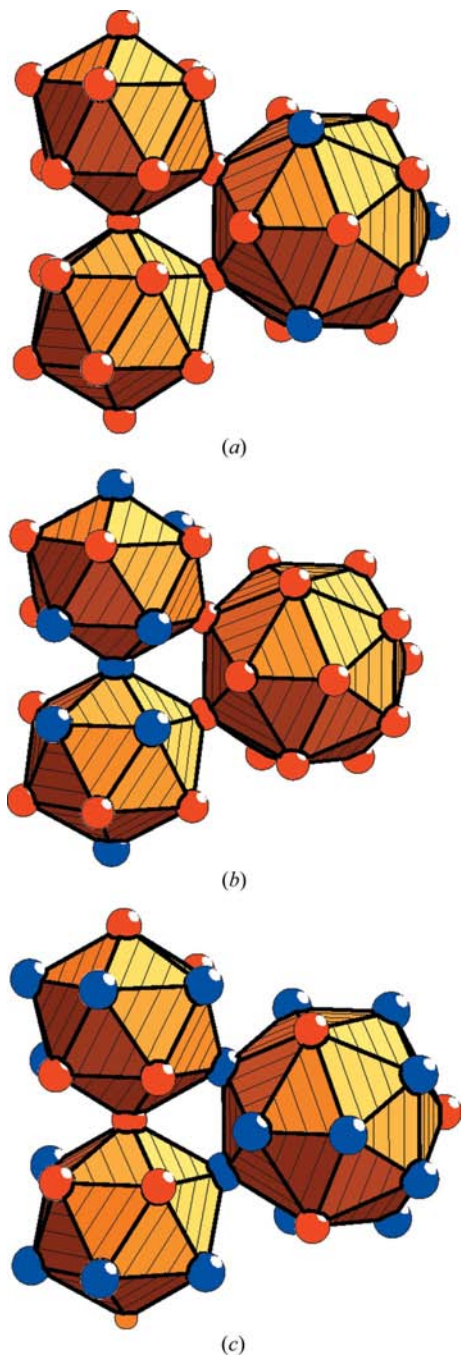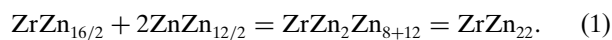
$$ZrZn_{16/2} + 2ZnZn_{12/2} = ZrZn_2Zn_{8+12} = ZrZn_{22}. \quad (1)$$

(a)

(b)

(c)

Figure 4
Three methods of substituting peripheral X atoms in AB_2X_{20} with X' atoms: (a) $AB_2X_2'X_{18}$, (b) $AB_2X_6'X_{14}$ and (c) $AB_2X_{12}'X_8$. X' atoms are blue.

Thus, the complicated composition $ZrZn_{22}$ is, to some extent, determined by the bifunctional behavior of Zn atoms at crystallization; they can play the role of both central and peripheral atoms of framework-forming polyhedra. Various methods of substitution of these atoms lead to the $ZrZn_{22}$ superstructures.

4.2. Chemical composition and superstructures

The following basic methods of superstructural substitution of atoms in the zero-dimensional cluster precursor keep the space symmetry $Fd\bar{3}m$:

(i) The only method of substituting the framework-forming B atoms of icosahedra gives the composition AB_2X_{20} that corresponds to the structure type $CeCr_2Al_{20}$.

(ii) Three methods of substituting peripheral X atoms in AB_2X_{20} with X' atoms:

(iia) substituting four $16d$ positions in the coordination shell of the A atom leads to the composition $AB_2X_{4/2}'X_{18} = AB_2X_2'X_{18}$. This method is realised in the structure type $Mg_3Ti_2Al_{18}$ owing to the bifunctional behaviour of Mg atoms: they play the role of both framework-forming A atoms and X' atoms, while all Al atoms are peripheral (Fig. 4a).

(iib) substituting six $48f$ positions in the coordination shell of both B atoms results in the composition $AX_{16/2} + 2BX_{6/2}'X_{6/2} = AB_2X_6'X_{14}$ (Fig. 4b).

(iic) substituting $96g$ positions (12 and 6 X atoms in the clusters AX_{16} and BX_{12}, respectively) gives the composition $AX_{12/2}'X_{4/2} + 2BX_{6/2}'X_{6/2} = AB_2X_{12}'X_8$ (Fig. 4c).

(iii) Any combination of two methods (ii) results in an inverted composition corresponding to the remaining method, where the atoms X and X' are swapped. For instance, the
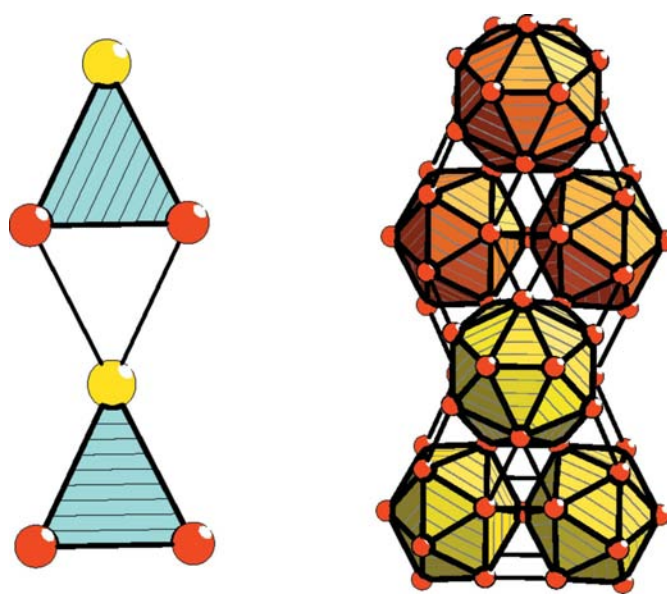

Figure 5
One-dimensional primary chain shown as a net (left) and as a union of two zero-dimensional cluster-precursors (right). The filled rings of the net correspond to the zero-dimensional cluster precursors, and the other circuits characterize the links between them.

combination (ii$b$) + (ii$c$) gives the composition $AB_2X'_{18}X_2$ to be equivalent to $AB_2X'_2X_{18}$ [method (ii$a$)] if $X \leftrightarrow X'$.

We are not aware of the intermetallics strictly corresponding to (ii$b$), (ii$c$) or (iii) superstructures. However, a number of compounds obtained by Benbow & Latturner (2006) have the composition very close to the idealized formulae mentioned above.

4.3. Bond-length restrictions

Since the positions of A and B atoms have no degrees of freedom, the distances between the centers of primary polyhedra depend on the unit-cell dimension a only: $R(A-A) = 0.433a$, $R(B-B) = 0.354a$ and $R(A-B) = 0.414a$ that restricts the bond lengths $A-X-A$, $B-X-B$ and $A-X-B$, respectively. Therefore, the bonds are strongly differentiated within the primary polyhedra (e.g. for ZrZn$_{22}$: 2.50–2.80 Å in

BX_{12}). This was mentioned by Samson (1961), but was explained by different metallic valences of zinc atoms.

5. Structural method of the self-assembly

A one-dimensional primary chain is directed along the diagonal of the unit cell. Two BX_{12} icosahedra of an AB_2 cluster link with the AX_{16} polyhedron of another AB_2 cluster, according to the key-lock mode (Fig. 5). As a result, the one-dimensional primary chain is generated by two complementary connected cluster precursors sharing two vertices. The distance $d^2 = 2a^2$ between centers of the zero-dimensional cluster precursors determines one of the independent translations.

A two-dimensional microlayer is formed by sharing two vertices of parallel one-dimensional primary chains stacked along another diagonal within the same plane (Fig. 6). The
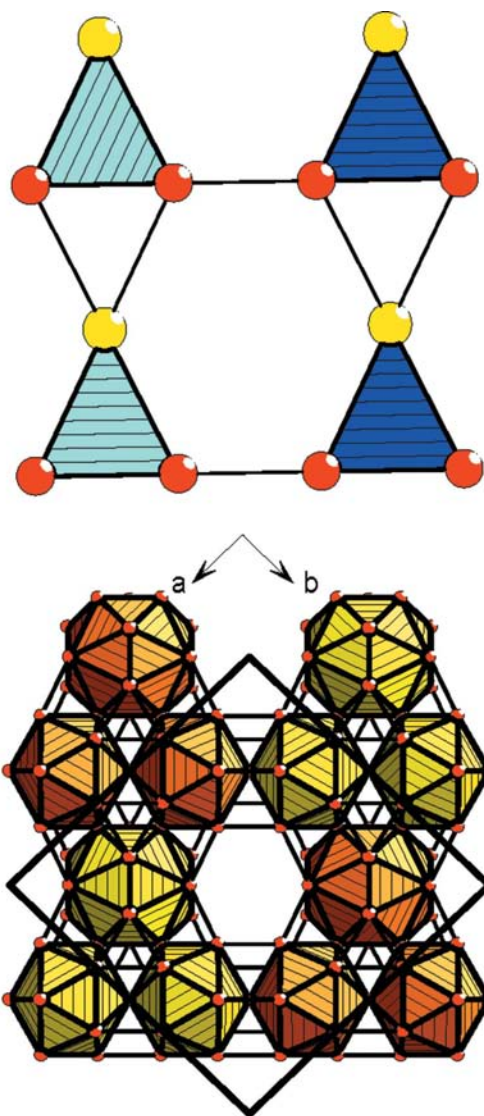

Figure 6
Two-dimensional microlayer shown as a net (left) and as a union of two primary chains (right). The zero-dimensional cluster precursors belonging to different chains are differently colored in the net.
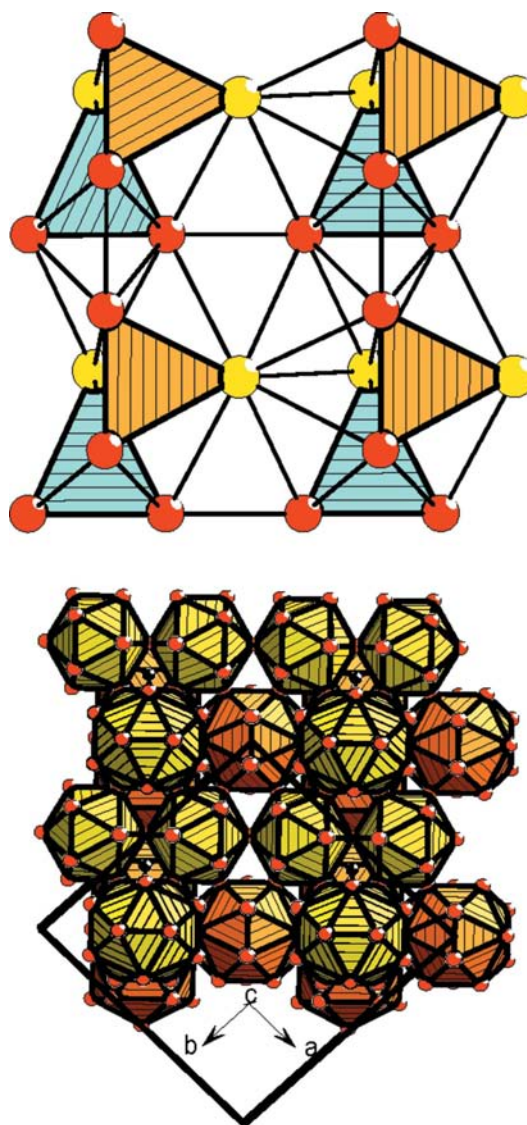

Figure 7
Three-dimensional microframework shown as a net (left) and as a union of two microlayers (right). The zero-dimensional cluster precursors belonging to different microlayers are differently colored in the net.

Table 3
Structure types containing AB_2X_{37} clusters.

Pearson symbol	No. of representatives[†]	Example	CRYSTMET/ICSD Code
$cF184$	43	$ZrZn_{22}$	457705 (CRYSTMET)
$cI160$	20	$Li_{13}Cu_6Ga_{21}$	58814 (CRYSTMET)
$cI162$	9	$Na_{26}Au_{40}Ge_{15}$	AL7317 (CRYSTMET)
$cF464$	5	$Li_{18}Cu_5In_4Ga_{31}$	101106 (CRYSTMET)
$tP34$	5	Ti_8Bi_9	182380T (CRYSTMET)
$hR159$	2	$Mg_{23}Al_{30}$	137636 (CRYSTMET)
$mC50$	2	$Mg_{2.3}Ir_{2.7}$	414044 (ICSD)
$oC344$	2	$Na_{15}In_{27}$	3038 (CRYSTMET)
$oP52$	2	$Nb_6Ni_{5.25}Al_{1.75}$	130444 (CRYSTMET)
$oP74$	2	$Nb_{28}Ni_{33.5}Sb_{12.5}$	450263 (CRYSTMET)
$tP906$	2	$Al_{12.33}Li_{5.79}$	107778 (CRYSTMET)
$cF488$	1	$Li_{13}Na_{29}Ba_{19}$	416631 (ICSD)
$cP157$	1	$K_{49}Tl_{108}$	370032 (ICSD)
$cF1192$	1	$Cd_{1.89}Na_{1.11}$	102030 (ICSD)
$hP57$	1	$Gd_3Pt_4In_{12}$	450852 (CRYSTMET)
$hP238$	1	$K_{39}In_{80}$	471066 (CRYSTMET)
$hR441$	1	$Cd_{58.34}Na_{49}Sn_{37.69}$	240010 (ICSD)
$hR53$	1	$Mn_{44.1}Si_{8.9}$	AL6803 (CRYSTMET)
$mC90$	1	K_6CdPb_8	410552 (ICSD)
$mC110$	1	Mg_4Zn_7	457103 (CRYSTMET)
$mP86$	1	$Ta_{1.108}Al$	245112 (ICSD)
$oC1088$	1	$Mg_{402.29}Zn_{685.71}$	412350 (ICSD)
$oP26$	1	Th_6Cd_7	131011 (CRYSTMET)
$oP56$	1	$MoNi$	AL1173 (CRYSTMET)
$oP100$	1	$Au_{11}In_6Na_8$	107435 (ICSD)
$oP248$	1	$K_{18}Na_5In_{39}$	3083 (CRYSTMET)
$oP758$	1	$Na_{172}Ni_2In_{197}$	457733 (CRYSTMET)
$tP226$	1	$In_{11.76}Na_7$	106858 (ICSD)

† The number of completely X-ray investigated structures.

cluster precursor completely integrated into the layer has CCN = 4. The simplified net of the framework-forming atoms is 4,4-coordinated binodal AB_2 and has a novel (not described in the literature) topology with the Schläfli symbols 3636 and 3366 for A and B nodes, respectively.

A three-dimensional supraprecursor (microframework) is assembled by superposing microlayers along [001] and consists of eight zero-dimensional cluster precursors (Fig. 7). Successive condensation of the three-dimensional supraprecursors results in self-assembly of the whole crystal structure.

6. Clusters AB_2X_{37} in other intermetallics

In order to find the regularities of self-assembling at the nanolevel it is important to determine how often the AB_2X_{37} nanoclusters participate in the crystal formation of other intermetallics. For this purpose, we have implemented into *TOPOS* the procedure of searching for any distinct finite fragment in the quotient graph of the atomic net. The computer analysis of the CRYSTMET and ICSD databases shows that this kind of nanocluster occurs in 111 intermetallics belonging to 28 structure types (Table 3, see supplementary material[2]). Thus, the clusters AB_2X_{37} are rather widespread in the methods of crystal self-assembly. However, differences in chemical composition of the intermetallic system can give rise

[2] Supplementary data for this paper are available from the IUCr electronic archives (Reference: SO5023). Services for accessing these data are described at the back of the journal.

to other supraprecursors, where the clusters AB_2X_{37} can be a constituent part. For instance, the crystal structure of Mg_4Zn_7 (Table 3) is described by four primary clusters: two Friauf polyhedra and two icosahedra combining into large nine-center 109-atom zero-dimensional supraprecursors that include AB_2X_{37} clusters $MgZn_2(Mg_{17}Zn_{20})$ (Fig. 8a). The microlayer formed with the supraprecursors is shown in Fig. 8(b).

One can suppose that the cluster AB_2X_{37} can in turn be a template for more complicated cluster precursors containing additional polyhedra. It would be important to find these more complicated types of nanoclusters to classify their self-assembly methods and to determine their frequency in inter-metallics. We emphasize that the proposed approach allows one to consider the structures of intermetallics at a new level,
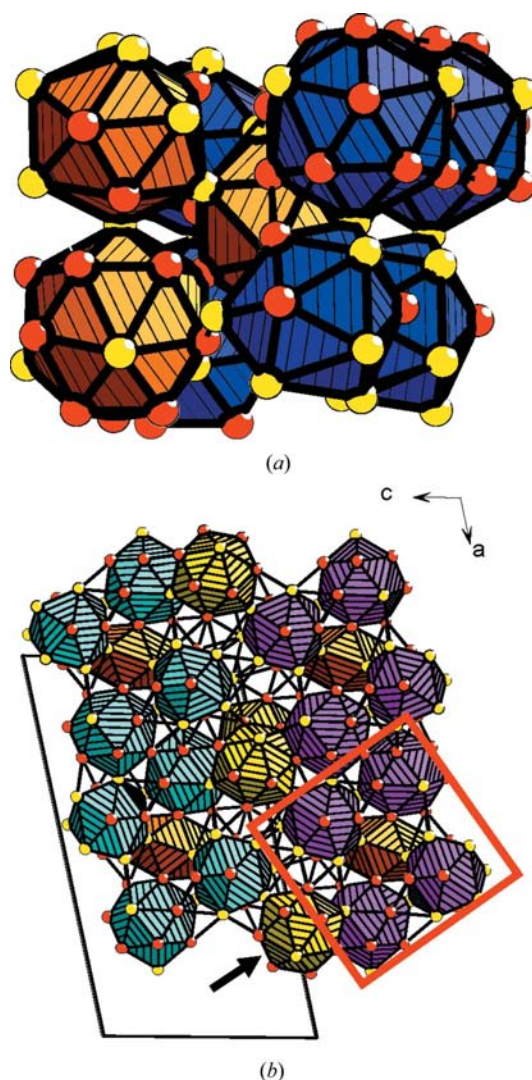

(a)

(b)

Figure 8
Mg_4Zn_7 crystal structure: (a) 109-atom zero-dimensional supraprecursor with AB_2X_{37} cluster (brown); (b) two-dimensional microlayer shown as a union of two primary chains (left and right), each of which consists of two zero-dimensional supraprecursors (one of them is selected with a red square). Mg and Zn atoms are shown by yellow and red balls. Four yellow Friauf polyhedra $Mg(Mg_4Zn_{12})$ (one of them is indicated by arrow) serve as spacers between the chains.

suprapolyhedral, while the program package *TOPOS* automatically determines whether a given supraprecursor is unique or it is a typical template for another cluster precursor.

7. Conclusions

Depending on the matter in hand, researchers have selected different clusters in the atomic net of structures of this kind and as a consequence they have often described the same crystal structure in quite different ways. Moreover, they do not propose a common representation for a series of compounds; every crystal structure is uniquely described according to the motto 'I see it in that way'. As a result, the possibility to search for general regularities of the structure self-assembly is lost. In this paper we have used a number of universal principles that allow one to avoid subjective conclusions when constructing the structure model. These principles were realised as a computer procedure that makes routine the treatment of extremely complicated structures and provides the consideration of the whole set of structural data from electronic databases to test the proposed models. As a result, we have obtained a uniform description of the entire $ZrZn_{22}$ family as well as structural relations between 28 structure types of intermetallics.

The results obtained show that one can extract the information on the nano-level of crystal structure self-assembly and draw definite conclusions about the composition and properties of crystal-forming cluster precursors resting upon the X-ray crystallographic data. The principles of search for the cluster precursors mentioned above can be used to analyze other intermetallics as well as substances with other non-directional atomic interactions (ionic and molecular crystals). The limits of the proposed self-assembly scheme will be determined in future work.

APPENDIX *A*
Some basic definitions

Framework-forming polyhedron: an elementary (primary) polyhedral structural unit (cluster) AX_n consisting of the central (framework-forming) atom A and n peripheral X atoms directly connected to A. The crystal structure is referred to as homopolyhedral or heteropolyhedral if it contains only one kind or several kinds of framework-forming polyhedron. In the heteropolyhedral structures, different letters (A, B, C . . .) are used for the central atoms of different framework-forming polyhedra.

nD suprapolyhedral cluster-precursor or *nD supraprecursor* ($n = 0$–3): an n-dimensional cluster consisting of two or more framework-forming polyhedra and corresponding to the nth level of the system self-organization. The condensation of the cluster-precursors at all consecutive structure assembly stages follows some complementary binding method. nD supraprecursor always consists of 2^n zero-dimensional supraprecursors.

Three-dimensional net: the topological representation of a three-dimensional crystal structure as an infinite three-periodic simple graph, whose nodes and edges correspond to atoms and interatomic bonds.

Coordination sequence for node A in a three-dimensional net: the set $\{N_k\}$, where N_k is the number of nodes in the kth coordination sphere of A.

Cluster coordination number (CCN): the number of neighboring cluster precursors connected with the cluster in a two-dimensional layer or a three-dimensional framework.

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