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ORIGINAL RESEARCH

A fascinating building unit: Mackay cluster in intermetallics

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Abstract We have performed topological analysis of the intermetallics containing two-shell nanoclusters. The crystal structures that include Mackay clusters are considered in more detail. Using the TTN collection of the ToposPro program package 22 topological types of intermetallics, in which Mackay cluster plays the role of primary nanocluster or local configuration, are found. The statistical data on the chemical composition of the nanoclusters are presented; the ways of local binding of the nanoclusters and the topology of the corresponding underlying nets are determined and classified.

Keywords Intermetallics · Nanocluster model · Mackay cluster · ToposPro program package · Topological analysis

Introduction

A 55-atom two-shell icosahedral-core Mackay cluster is known as one of possible structural units for complex alloys and quasicrystals and their approximants [1]; recently, it was isolated as a Pd_{55} unit in a coordination compound [2]. The cluster has the shell composition 1@12@42, where the first shell is icosahedral, and the second one contains 42 atoms that correspond to a dense packing of equal spheres, although the resulting density is a bit lower than for the crystallographic closest packings [3]. This fascinating cluster with maximal I_h point symmetry and quasispherical shape was predicted by Mackay [3] and then discovered in crystalline substances. A detailed geometrical description of hierarchic icosahedral clusters including Mackay and other related types was provided by Kuo [4]. However, no systematic study of Mackay clusters in intermetallic structures has been performed so far; in particular, their chemical composition, occurrence, mutual (local) connectivity as well as overall topological motifs were not listed and classified. We considered some intermetallic structures containing Mackay-type clusters [5], but did not analyze their connectivity. In [6], we applied a strict 'nanoclustering' algorithm for automated decomposition of intermetallic structures to clusters with icosahedral core and analyzed in more detail occurrence, composition, and binding of another two-shell 45-atom Bergman cluster, which also plays an important role in crystal chemistry of quasicrystalline phases. In this paper, we use the 'nanoclustering' algorithm to give a comprehensive review of all intermetallics, which contain Mackay cluster as a building block (*primary nanocluster*) or merely a local configuration of atoms. We collect the ways of connection of the Mackay-type structural units as well as the types of other primary nanoclusters that can be combined with Mackay clusters in the structure assembly. We believe that such information could be useful for elucidation, modeling, and prediction of new crystalline and quasicrystalline phases.

Dedicated to Professor Alan L. Mackay on the occasion of his 90th birthday.

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Objects and methods

We have used crystallographic data from the Inorganic Crystal Structure Database (ICSD, release 2015/2) [7] and Pearson's Crystal Data (version 2014/15) [8] for geometrical and topological analysis of intermetallics. Topological analysis of intermetallics was performed using the Topological Types of Nanoclusters (TTN) collection, which is included in the set of the ToposPro topological collections [9]. The TTN collection [6] contains information about 1006 polyhedral (single-shell) and 1011 multishell nanoclusters in intermetallic structures. The algorithm of searching for the intermetallic compound that can be constructed from a particular nanocluster includes the following steps:

(1) Extracting the desired type of nanocluster from the TTN collection;
(2) Performing the nanoclustering analysis of intermetallics containing this cluster as a primary nanocluster or as a local configuration.

To decompose the structure into cluster structural units, we have applied the 'nanoclustering' method [10], which is based on the following principles:

(1) The crystal structures of intermetallics are assembled of the primary polyhedral or multishell (onion-like) nanoclusters. In general, the primary nanocluster can be non-centered (i.e., it can have no atom in its center). The next level of the structure organization, *supracluster*, is formed by interconnections between the nanoclusters and characterizes their local binding. *Underlying net,* or the net of the centers of mass of the nanoclusters, describes the overall topology of the nanocluster assembling.
(2) The structure may contain single atoms that fill voids between the nanoclusters (Fig. 1). We call such atoms *spacers*. All atoms of the crystal structure should be included in the set of primary nanoclusters and spacers.
(3) The centers of primary nanoclusters occupy the highest-symmetry positions of the structure.
(4) The primary nanoclusters cannot have common internal atoms. The connectivity between the nanoclusters can be realized through common external atoms or through interclusters bonds (Fig. 2).
(5) According to *parsimony principle*, the crystal structure should be assembled from minimal number of primary nanoclusters.

Emphasize that the nanoclustering model provides an unambiguous algorithm to rationalize and classify intermetallic structures, but, strictly speaking, does not elucidate the process of their assembling. The stability of the nanoclusters should be explored separately. One more point is that beyond parsimony principle (5) the crystal structure can have many nanocluster models. Strictly speaking, all of them can have sense and be used to find correlations with other structures because any nanocluster model corresponds to some structure representation. For example, if we are interested in comparison of Mackay-based structures, we use those nanocluster models that contain Mackay clusters. Importantly, all the models are obtained with a strict algorithm and can be enumerated that allows us to avoid subjectivity when applying the method.

To describe the method of local binding of nanoclusters, we have proposed [6] the descriptor $Center@shell^{CN}_{v,e,f,b}$, where $Center = 1$ (centered nanocluster) or 0 (non-centered nanocluster), *shell* is the number of atoms in the nanocluster shell or the shell type name, for example, *ico* for icosahedral shell or *D*42 for deltahedral 42-atom shell, *CN* is the coordination number of the given nanocluster, and the subscript indices show the type of the nanocluster connection: by common vertices (v), edges (e), faces (f), or through metal–metal bonds (b) if the nanoclusters have no common atoms (Fig. 2). We use bold three-letter symbols of the Reticular Chemistry Structure Resource (RCSR) nomenclature [11] to designate the overall topology. The topological types (types of connectivity) of the underlying nets have been determined automatically with the ADS program of the ToposPro

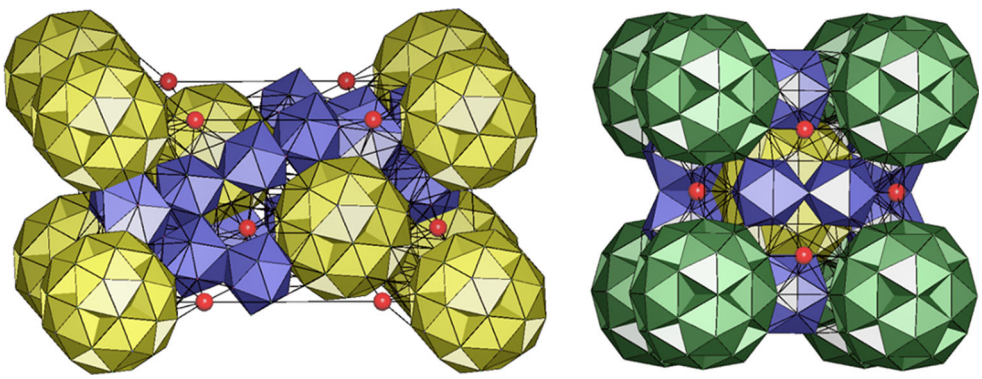

Fig. 1 (*left*) $Ga_{21.16}Mg_{40.84}Pd_{21}$ crystal structure: Pd4 atoms (in *red*) play a role of spacers in the nanocluster model; (*right*) Ag4 atoms (in *red*) fill the voids between Mackay (1@*ico*@*D*42) nanoclusters and icosahedra (1@*ico*) in the $Mg_{30}(Ag_{19}Al_{24})$ crystal structure (Color figure online)

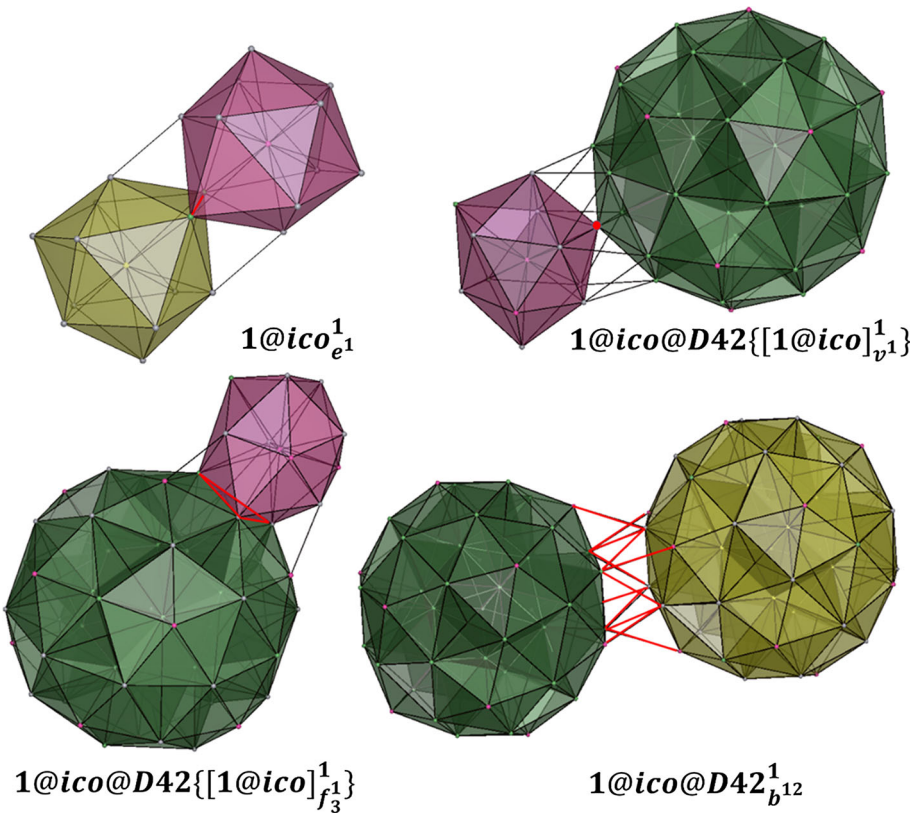

Fig. 2 Four connection types of nanoclusters in the $Mg_{30}(Ag_{19}Al_{24})$ crystal structure: by common edge (*top left*), vertex (*top right*), face (*bottom left*), or intercluster bonds (*bottom right*)

program package. Separately, we have described the *nanocluster skeleton*, i.e., the topology of the underlying net formed only by the major structural units, in this case, Mackay clusters. The classification of the compounds under consideration by all the topological descriptors mentioned above is given in the Supporting Information.

Results and discussion

With the TTN collection, we have revealed that in total 22 topological types of intermetallics, which include 181 crystal structures, contain Mackay cluster as a local configuration or as a primary nanocluster. Among them, we have found five topological types (60 structures), which can be completely constructed from two types of nanoclusters: Mackay cluster and icosahedron (see the first five types in Table S1 of the Supporting Information). Below we consider these types in more detail. In addition, we also describe two structures (ε-Al_4Cr and $Ru_{11.4}Cu_{31.4}Al_{57.2}$), which cannot be completely constructed from Mackay and icosahedral clusters but contain them in their nanocluster models.

$Ho_6Mo_4Al_{43}$ ($Yb_6Cr_{4+x}Al_{43-x}$) type—48 entries

The $Ho_6Mo_4Al_{43}$ topological type is the most abundant: more than 77 % of the found structures crystallize in this type. According to the results of the nanoclustering analysis, these intermetallics can be described in two ways: as a network of three non-equivalent icosahedra or as an assembly of Mackay cluster and icosahedron. The parsimony principle implies that the size and number of the primary nanoclusters should be minimal; therefore, the second model is more preferable. Each icosahedron is connected to other five by vertices and faces and to three Mackay clusters through two triangular faces. The Mackay cluster is surrounded by 12 icosahedra and eight Mackay clusters. The symbols for local topology are $1@ico\{[1@ico]^{3+2}_{v^1+f_3^1}+[1@ico@D42]^{3}_{f_3^2}\}$ and $1@ico@D42\{[1@ico]^{12}_{f_3^2}+[1@ico@D42]^{2+6}_{f_3^3+e^1}\}$, respectively (Fig. 3). The topology of the underlying net for all nanoclusters is described by the point symbol $\{3^{12}.4^{15}.5\}_4\{3^{48}.4^{78}.5^{57}.6^7\}$. Note that the authors of [12] mentioned the polyhedra with icosahedral shape, but did not find the Mackay clusters. This fact once again confirms that many important structural units are overlooked during the traditional analysis of intermetallic crystal structures in terms of coordination polyhedra. The scheme of formation of the structure is shown in Fig. 4.

$Al_{56.14}Cr_{14.29}$ (ε-Al_4Cr) type—one entry

The $Al_{56.14}Cr_{14.29}$ crystal structure [13] is an example of an extremely complex intermetallic compound: there are 682

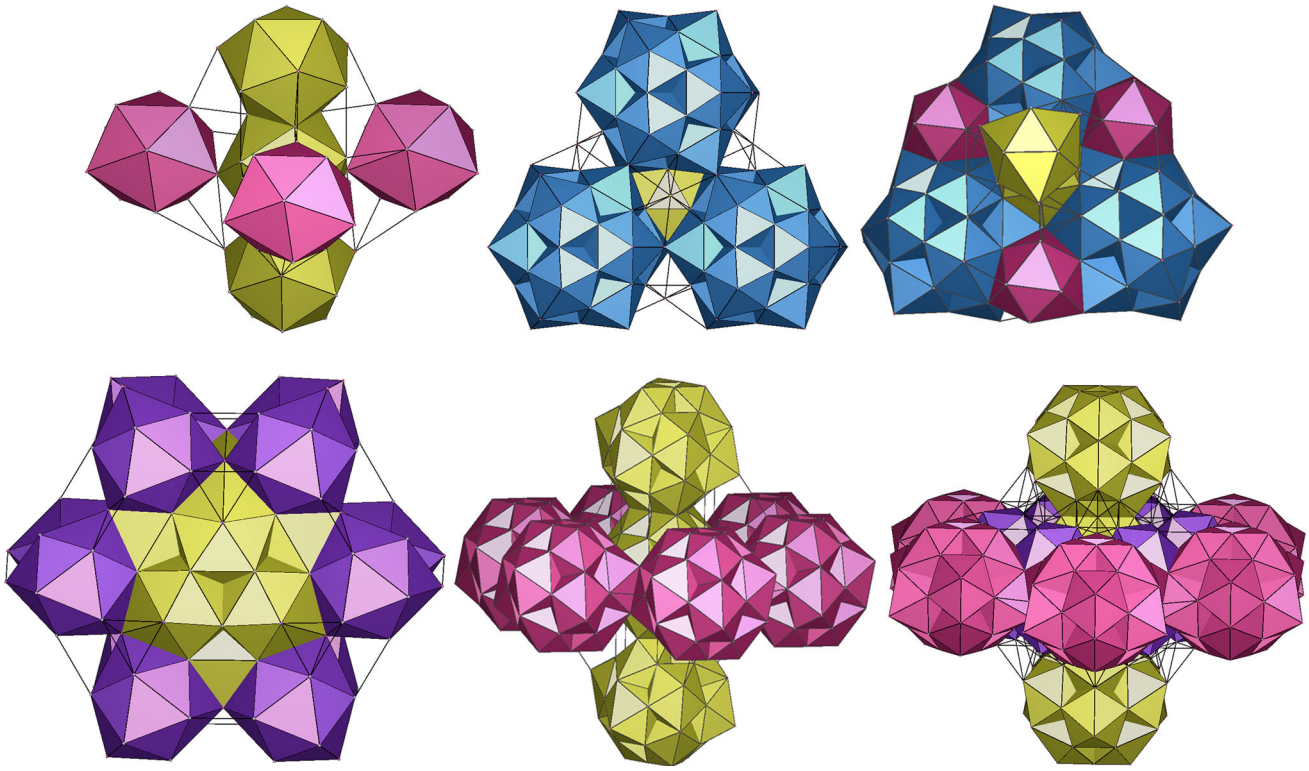

Fig. 3 Crystal structure of $Ho_6W_4Al_{43}$: (*top*) local binding of the nanoclusters, where the central icosahedron is connected to five other icosahedra through vertices and faces and to three Mackay clusters through two triangular faces; the *supracluster symbol* is $1@ico\{[1@ico]^{3+2}_{v^1+f^1_3}+[1@ico@D42]^{3}_{f^2_3}\}$; (*bottom*) a typical environment for Mackay cluster with 12 icosahedra; the supracluster symbol is $1@ico@D42\{[1@ico]^{12}_{f^2_3}+[1@ico@D42]^{2+6}_{f^3_3+e^1}\}$

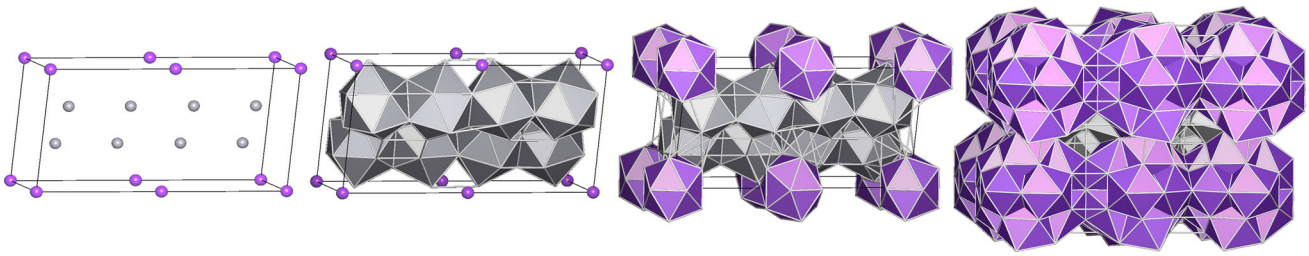

Fig. 4 Formation of the $Ho_6W_4Al_{43}$ structure with nanoclusters: The *gray balls* (Al6) are the centers of icosahedra, and the *purple balls* (W2) are the centers of Mackay clusters (Color figure online)

atoms in the unit cell. The nanoclustering procedure gives enormous number (19935) of possible models for this structure. However, only six of them are composed of minimal (six) different primary nanoclusters, while the most complicated models contain up to 13 primary nanoclusters. Although the models, where the building units are only Mackay clusters and icosahedra, have not been found, we have revealed regular Mackay clusters centered by Cr10 atoms in four of the six minimal structure representations. As an example, we show one of the nanocluster models with icosahedra, Mackay and other two-shell nanoclusters centered by Al13 atoms (Fig. 5). We do not give the local binding symbols here because of their high complexity. Interestingly, the authors of the structure investigation [13] especially pointed out absence of Mackay polyhedra and talked about first icosahedral shells only.

$Ga_{21.16}Mg_{40.84}Pd_{21}$ type—one entry

The authors of the structure determination [14] provided a very detailed description of the Mackay cluster: Its chemical composition, disordering and packing, but they did not proposed any descriptors for its local binding, and did not determined the overall topology of the nanocluster skeleton. We have described the structure as a combination of two types of clusters: an icosahedron and a Mackay cluster

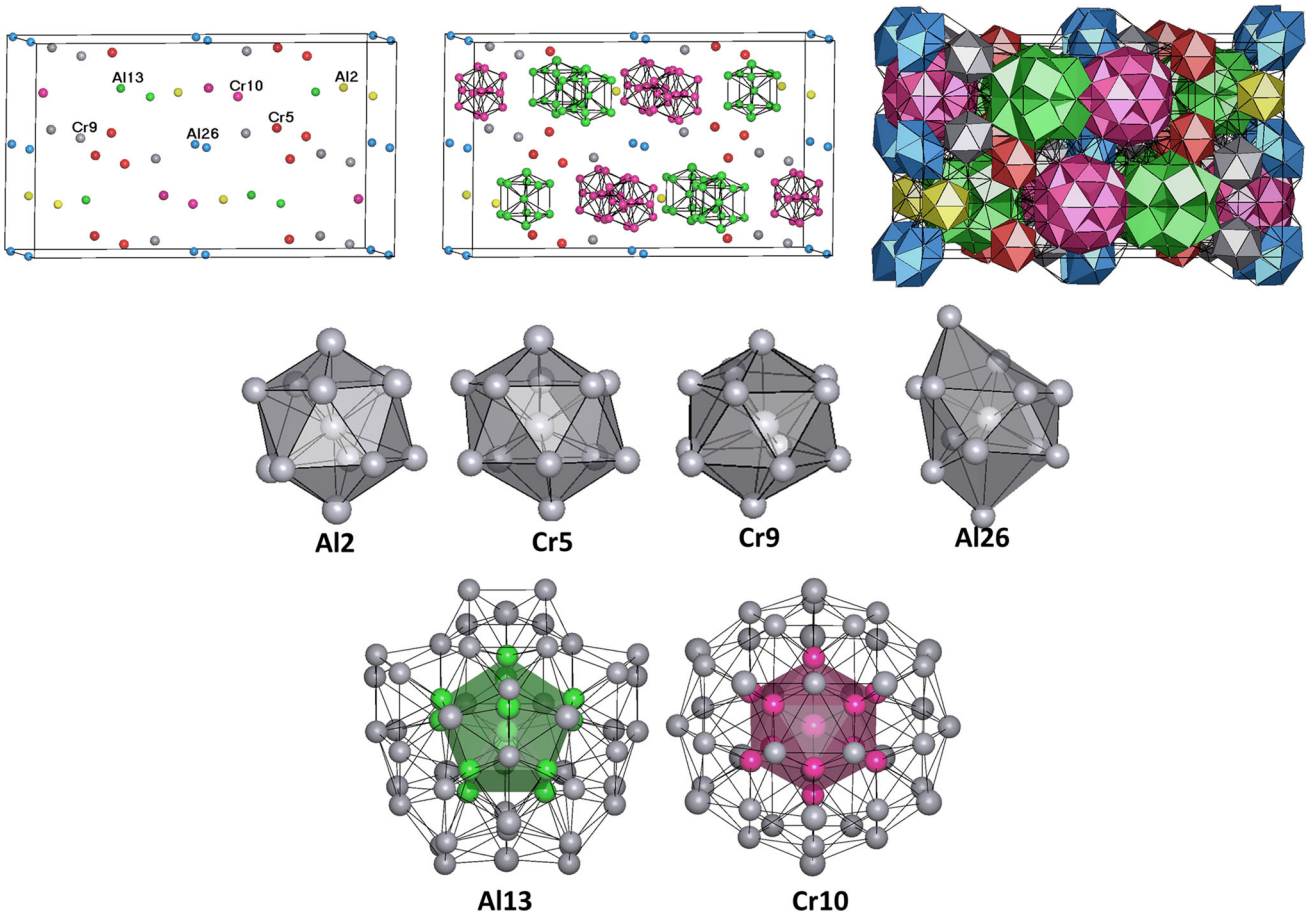

Fig. 5 Nanocluster model of the ε-Al_4Cr crystal structure: (*top left*) centers of different nanoclusters selected in *gray*, *blue*, *yellow*, *pink*, *green* and *red*; (*top middle*) first shell of the Mackay nanocluster (*pink*) and 1@12@46 nanocluster (*green*) are shown; (*top right*) the full nanocluster representation. (*Bottom*) Building units in the ε-Al_4Cr crystal structure: four different icosahedra, nanocluster 1@12@46 and Mackay nanocluster. The names of the atoms centering the building units are specified below (Color figure online)

as well as a Pd atom as a spacer. The Mackay clusters are packed according to a face-centered cubic (**fcu**) motif (Fig. 6), each of them is surrounded by 12 icosahedra over the triangular faces; the symbol of local binding is $1@ico@D42\{[1@ico]^{12}_{f^1_3}\}$. Local coordination for the icosahedron is described by the $1@ico\{[1@ico]^{3+2}_{e^1+v^1}+[1@ico@D42]^{2}_{f^1_3}\}$ symbol.

$Mg_{30}(Ag_{19}Al_{24})$ type—one entry

The authors [15] described the $Mg_{30}(Ag_{19}Al_{24})$ approximant using rhombic triacontahedra (RT). They discussed in detail the chemical composition of the Mackay cluster centered by Ag2 atom and mentioned that RTs around (0,0,0) and (½, ½, ½) have different composition and distances, but they are topologically equivalent. The

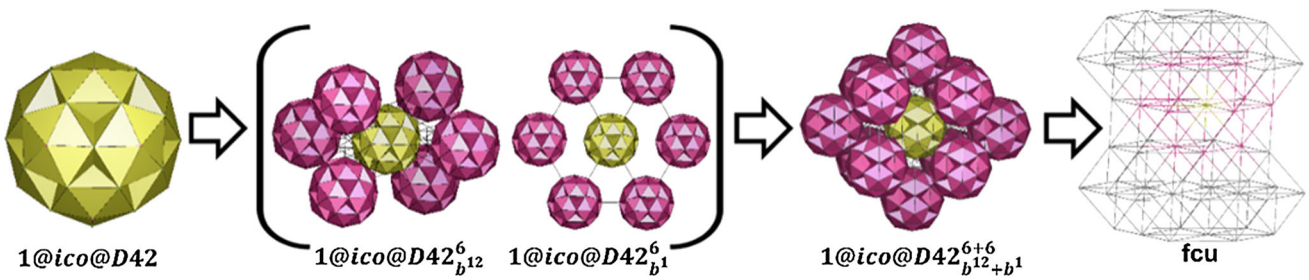

Fig. 6 $Ga_{21.16}Mg_{40.84}Pd_{21}$ crystal structure: condensation of Mackay clusters into a supracluster $1@ico@D42^{6+6}_{b^{12}+b^1}$ and the underlying net of a 12-coordinated **fcu** underlying topology

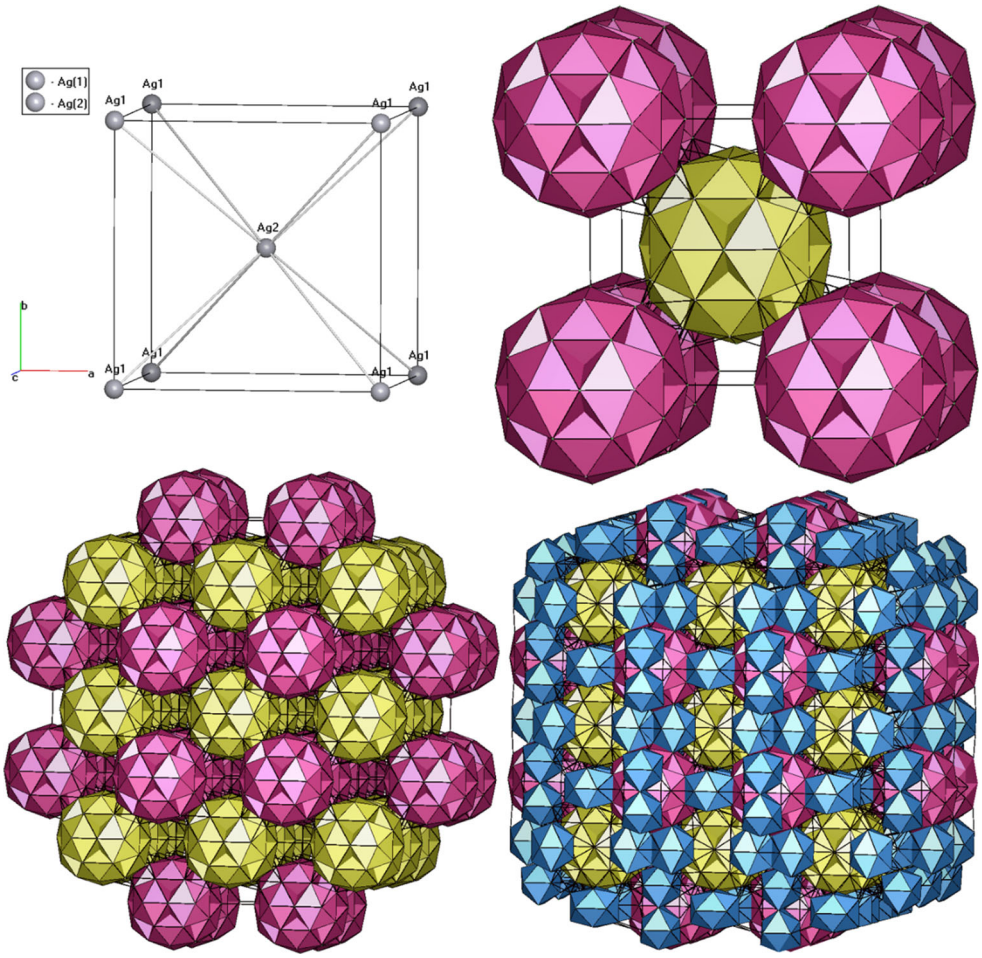

Fig. 7 (*Top*): 8-coordination of the centers of the Mackay clusters Ag1 and Ag2 (*left*); binding of Mackay clusters by means of 12 interatomic contacts between clusters (*right*); (*bottom*): condensation of Mackay clusters into an underlying net with the **bcu** topology (*left*); complete nanocluster representation of the structure; the centers of *blue* icosahedra are Ag4 atoms (*right*) (Color figure online)

nanocluster approach gives the following description: Two non-equivalent Mackay clusters are assembled in accordance with an 8-coordinated **bcu** motif (Fig. 7); additionally, they are connected to 12 Ag-centered icosahedra (Table S1).

$Ru_{11.4}Cu_{31.4}Al_{57.2}$ type—one entry

The structure of $Ru_{11.4}Cu_{31.4}Al_{57.2}$ is strongly disordered and referred to a 1/1-rational approximant [16]. The authors of the structural investigation noted that Mackay and Mackay-like clusters with the centers at 1*a* and 1*b* positions (Fig. 8) should be classified as fundamental structural units for this icosahedral phase. In Fig. 4 of their paper, the authors [16] showed the packing of the found clusters. We just note that $Ru_{11.4}Cu_{31.4}Al_{57.2}$ has two different models with Mackay and Mackay-like clusters. One of them consists of Mackay, Mackay-like nanoclusters and an icosahedron, while the second one contains a Mackay nanocluster, icosahedra and another 12-vertex polyhedron. Notwithstanding that these models do not completely fit our criteria of searching due absence of models only with Mackay and icosahedral clusters, they are both interesting. In Table S1, we show the second nanocluster model of the $Ru_{11.4}Cu_{31.4}Al_{57.2}$ crystal structure.

$Sc_{57}Rh_{13}$ type—five entries

In [5], we considered one of the nanocluster models of the $Sc_{57}Rh_{13}$ type as an assembly of two Mackay clusters and one icosahedron. The Mackay clusters form an underlying net with the **bcu-x** topology; the voids in the corresponding nanocluster skeleton are filled by icosahedra. As shown in Fig. 9, the Mackay clusters have a typical environment of 12 icosahedra, the symbols for local binding are $1@ico@D42\{[1@ico]^{12}_{v^1}\}$ and $1@ico@D42\{[1@ico]^{12}_{f^1_3}\}$, which means that one of Mackay clusters is connected to each icosahedron by one vertex, and another one is connected to all 12 icosahedra by means of triangular faces. Complex descriptor for local binding of icosahedral nanoclusters shows the ways of connectivity with each kind of nanoclusters and

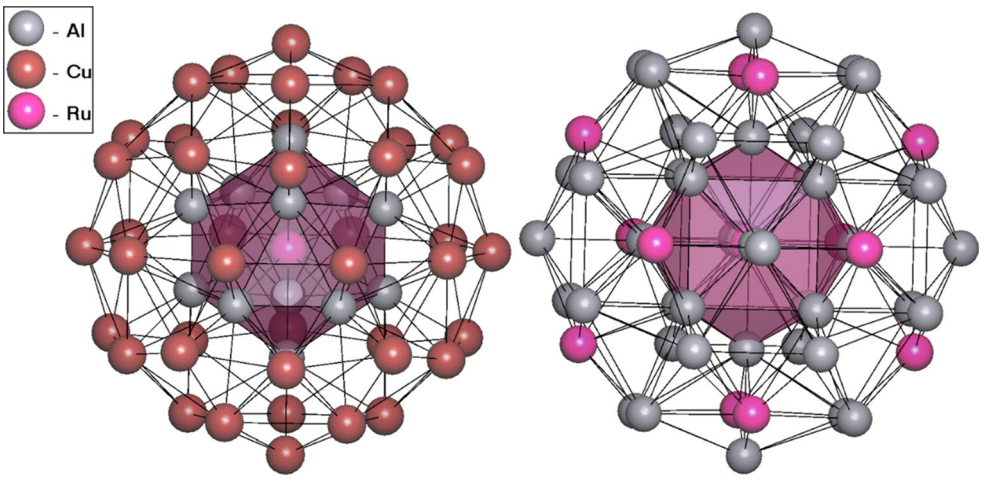

Fig. 8 Mackay (1@*ico*@*D*42) and Mackay-like (1@14@*D*42) clusters in the $Ru_{11.4}Cu_{31.4}Al_{57.2}$ crystal structure

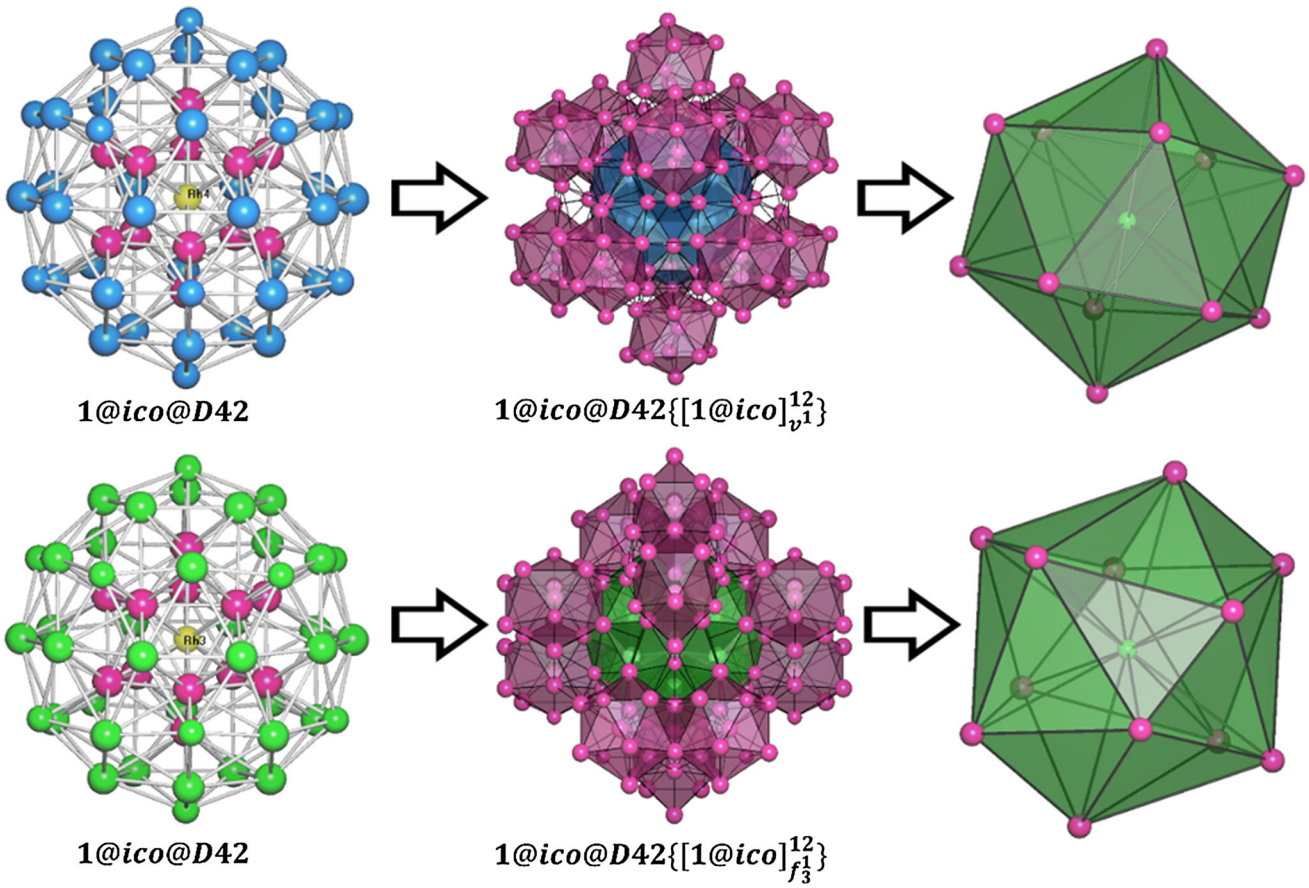

Fig. 9 $Sc_{57}Rh_{13}$ crystal structure: Mackay clusters centered by Rh3 and Rh4 atoms (*top left);* the $1@ico@D42\{[1@ico]_{v^1}^{12}\}$ (*top middle*) and the $1@ico@D42\{[1@ico]_{f_3^1}^{12}\}$ (*bottom middle*) supraclusters, and 12 icosahedra are connected to Mackay cluster through vertices or through triangular faces; (*right*): 12-coordinated nodes in the underlying net: *green balls* are the centers of mass of the Mackay clusters, *red balls* are the centers of mass of icosahedra, respectively (Color figure online)

consists of three parts: $1@ico\{[1@ico]_{e^1}^{1}+[1@ico@D42]_{f_3^1}^{2}+[1@ico@D42]_{v^1}^{2}\}$. As in many other cases, the authors [17] missed two-shell Mackay clusters, but considered the assembling of icosahedra.

$Ag_{17}Mg_{54}$ type—five entries

In this topological type, Mackay clusters form an underlying net with the **bcu-x** topology. The simplest nanocluster model consists of one Mackay cluster and two

non-equivalent icosahedra. The Mackay clusters have an unusual environment in the model: Each of them is surrounded by 16 icosahedra in the $1@ico@D42\{[1@ico]^{8+8}_{f_3^1+v^1}\}$ fashion (Table S1). Each non-equivalent icosahedron is bound to three other icosahedra (by one edge to an icosahedron of the same type and by two vertices to other two icosahedra) as well as to four Mackay clusters (by two faces and two vertices): $1@ico\{[1@ico]^{1+2}_{e^1+v^1} + [1@ico@D42]^{2+2}_{f_3^1+v^1}\}$. In spite of the unusual local binding, a typical nanocluster skeleton (**bcu-x**) is realized. Four of the five structures are slightly disordered, only $Ag_{17}Mg_{54}$ has no disordering [18]. The disordering can concern the central atom of icosahedron (in $Sc_{8.5}Mn_{1.2}Ga$ [19] and $Sc_{3.5}Au$ [20]), the icosahedron shell (in $Mg_{51}Zn_{20}$ [21] and $Sc_{8.5}Mn_{1.2}Ga$), the first shell (in $Mg_{51}Zn_{20}$ and $Sc_{8.5}Mn_{1.2}Ga$) or the second shell of the Mackay cluster (in $Sc_{8.5}Fe_{1.2}Ga$).

Correlations between chemical composition and topological descriptors

One of the remarkable features of local binding is that Mackay cluster is surrounded by 12 icosahedra in five of the seven topological types considered above. At the same time, there are no clear regularities in the environment of icosahedra. The most common overall topologies are **hex** (hexagonal primitive) and **bcu-x** (body-centered cubic). To look for the correlations of topological descriptors and chemical composition of the nanoclusters, we have considered only ordered crystal structures. A peculiarity is that the homogeneous (consisting of just one sort of atoms) first shell of Mackay cluster is realized in all cases. The Mackay clusters have chemical composition with general formulae $A@M12@M^1{12} + M^2{30}$ or $A@M12@M^1{6} + M^2{24} + M^3{12}$ (Table S2). Moreover, the first chemical composition leads to a body-centered cubic (**bcu** or **bcu-x**, i.e., 8-coordinated or (8 + 6)-coordinated) overall topology, while the second one gives rise to a hexagonal (**hex**) underlying net. The most typical compositions of the icosahedra are $A@M^1{2} + M^2{10}$ and $A@M^1{3} + M^2{9}$, while $A@M^1{2} + M^2{2} + M^3{8}$ occurs only in the $Mg_{30}(Ag_{19}Al_{24})$ crystal structure.

Concluding remarks

We have analyzed all intermetallics that contain Mackay cluster as a building unit. With the nanocluster approach, we have found these crystal structures in an automatic mode, classified, and considered topological descriptors and chemical composition of the Mackay clusters. The correlations found between the chemical composition and topological descriptors will be included into the knowledge database of the ToposPro program package. The obtained information about preferred ways of binding of building units could be useful for modeling and prediction of new intermetallic compounds.

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