Topology of intermetallic structures: from statistics to rational design

Tatiana G. Akhmetshina,[a] Vladislav A. Blatov,[a,b] Davide M. Proserpio,[a,c] Alexander P. Shevchenko[a]*

[a]Samara Center for Theoretical Materials Science (SCTMS), Samara University, Ac. Pavlov St. 1, Samara 443011, Russia

[b]School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, People's Republic of China

[c]Dipartimento di Chimica, Università degli Studi di Milano, Via C. Golgi 19, 20133, Milano, Italy

CONSPECTUS: More than 38,000 substances made only of metal atoms are collected in modern structural databases; we may call them intermetallic compounds. They have important industrial application and yet they are *terra incognita* for most of our undergraduate students. Their structural complexity and synthesis not easily adaptable to first years laboratory keep them away from the standard curricula. They have been described over the years following alternative and complementary views such as coordination polyhedra, atomic layers, polyatomic clusters. All these descriptions, albeit relied on grounded principles, have been applied on a subjective basis and never implemented as a strict computational algorithm. Sometimes, the authors generated multiple views of the same structure reported with beautifully drawn figures and/or photos of hand crafted models in seminal works of the pre-computer age. With the use of our multi-purpose crystallochemical program package ToposPro we explored the structural chemistry of intermetallics with objective and reproducible topological methods that allow us to reconcile different structure descriptions. After computing the connectivity pattern between the metal atoms on the basis of Voronoi partition of the crystal space we were able to group the 38,000 intermetallic compounds into 3,700 sets of crystal structures with the same topology of atomic net. We have described the different views used in the literature and showed that 12-vertex polyhedra are the most frequent (33%) and that almost half of them are icosahedron-like (46%), followed by cuboctahedron (25%) and unexpectedly by bicapped pentagonal prism (13%). Looking for layers we have found that the hexagonal lattice, which corresponds to the closest packing of spheres on a plane, exists in more than 11,000 crystal structures confirming the close packed nature of intermetallics. We have also applied the nanocluster approach, which goes beyond the first coordination sphere looking for structural units as multi-shell clusters that assemble the whole structure. This approach shows that 41% of intermetallics can be assembled with a single nanocluster and that 22.4% of these are packed according to the face-centered cubic motif of the closest packing of spheres in a three-dimensional space. We have shown that our approach can easily adopt any other building model and hence could become a platform for a universal predictive scheme. Within this scheme, all the structural descriptors can be related to experimental data and theoretical modeling results, and then can be used to synthesize new intermetallic compounds and to foresee novel materials.

Introduction

In the crystal chemistry of inorganic structures, intermetallic compounds are rightfully considered to be the most complex: at present there are known intermetallics with more than 23,000 atoms per unit cell.[2] Intermetallics can be defined as compounds of at least two metals with an ordered, not statistical as in alloys, arrangement of atoms. Keeping in mind the prevalence of metals in the Periodic Table the diversity of intermetallic structures is quite expected. Besides purely scientific interest, intermetallics are important for industry as construction, magnetic and shape memory materials, conductors and superconductors, etc. For a better understanding of correlations between physical properties and structure we need, first of all, to understand the structure itself. But what does 'understand' mean? In accordance with the epigraph to this paper, we should find a way to simplify the structure. Therefore, chemists have always been trying to decompose crystal structures of intermetallics and describe them in a simpler way as ensembles of structural units, which can occur in different extended architectures. There are three types structural units, which are traditionally selected in intermetallic structures: coordination polyhedra,[3,4] atomic layers[5] and polyatomic clusters;[6,7] sometimes they can be combined in the same architecture. However, all these methods of description are essentially subjective, because the choice of structural units often depends on the preferences of the researcher. As a result, extremely complicated intermetallics like β-Mg_2Al_3[8,9] gained many quite different descriptions.[5,10–12] Recently[13] we have proposed polyshell onion-like nanoclusters as a special kind of cluster structural units. The nanocluster approach implemented as a computer algorithm into our program package ToposPro[14] makes the description of even extremely complex intermetallic structures fully automated and unbiased. These advantages allowed us to develop a database of intermetallic nanocluster structural units, the Topological Types of Nanoclusters (TTN) collection.[15] We believe that creation of such comprehensive datasets of building blocks is one of important steps from spontaneous synthesis to rational design and prediction of new intermetallics. In this respect, it would be very fruitful if other structural models

mentioned above would be formalized and used for a high-throughput screening of the structural databases. This paper outlines a possible way to uniting all these models within a universal approach.

Topological models of intermetallics

For geometrical and topological analysis of intermetallics, we have used the crystallographic data from the Inorganic Crystal Structure Database (ICSD, release 2016/2)[16] and Pearson's Crystal Data (version 2014/15).[17] In total, these databases include more than 38,000 structures composed only by metal atoms. We have arranged them over 3,708 topological types, *i.e.* groups of crystal structures with the same topology of atomic net.[18] The connectivity between metal atoms was determined from the Voronoi partition of the crystal space by accounting for all interatomic contacts with solid angles of the faces of the Voronoi polyhedra no less than 1.5% of the total solid angle 4π steradian.[19] Atomic partial occupation may also be taken in account.

The actual version of ToposPro[14] has tools for separation of all mentioned kinds of structural units in an automated mode. These tools are integrated into a user-friendly system, which provides combined application of all the models to whole classes of intermetallic compounds.

Coordination polyhedra. To determine types of coordination polyhedra (CP) we have applied two methods:[20] the Voronoi approach, which uses the topological property of duality of coordination and Voronoi polyhedra, and the fingerprint approach, which compares geometrical shapes of polyhedral solids by their angular parameters (fingerprints). The latter method allows one to determine the degree of distortion (DRank) of the given polyhedron compared to the regular one; the higher Drank the more distorted the polyhedron (Fig. 1).
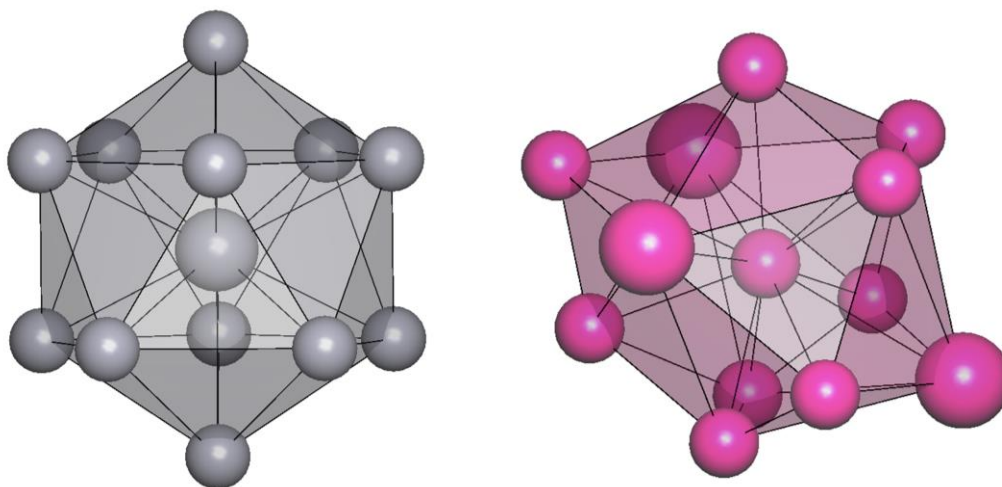
Figure 1. A regular icosahedron Ag@Ag12 (DRank=0.001) in the $Mg_{32}(Ag_{13}Al_{36})$ crystal structure[21] (left) and one of the most distorted icosahedra Co@Pr3Co9 (DRank=6.626) in the Pr_2Co_7 crystal structure[22] (right).

Icosahedral polyhedra often play a role of structural units (polyhedral nanoclusters) in intermetallics.[6] For instance, in the Ca_3Ag_8 crystal structure[23] the Ag(1) atoms have a quite regular icosahedral environment (DRank=0.361) and these icosahedra assemble the whole structure by packing into a **pcu** motif (Fig. 2). Hereafter we denote the *underlying nets*, i.e. the nets of centers of structural units,[18] with bold three-letter symbols of the Reticular Chemistry Structure Resource (RCSR) nomenclature[24] or ToposPro *N*D*k-n* symbols.[18]
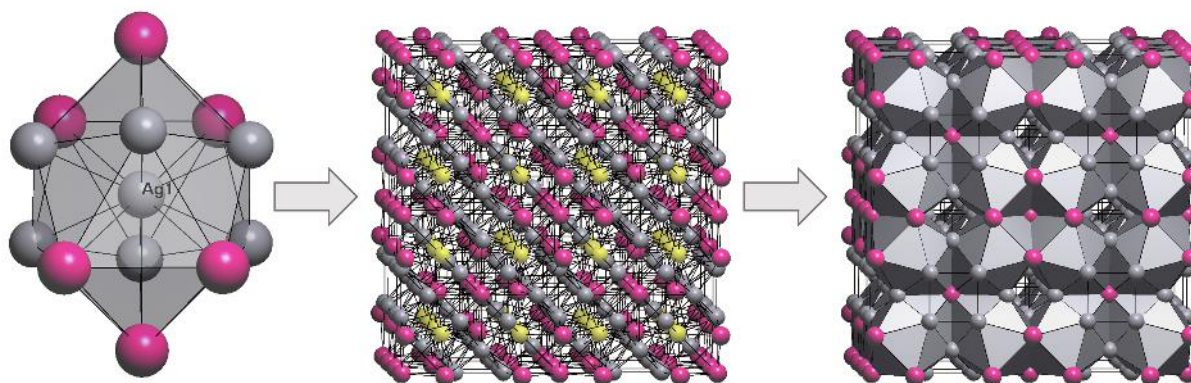

Figure 2. Crystal structure of Ca_3Ag_8: a regular icosahedron around an Ag(1) atom (left), the Ag(1) atoms selected in yellow (middle) and the CPs of the Ag1 atoms (right).

Atomic layers. To recognize planar atomic layers of a particular topology we have used the unique ability of ToposPro to search for any structural motif, either geometrically planar or corrugated, in the infinite net.[14] For instance, the $CoGa_3$ crystal structure[25] can be considered as a combination of two plane nets with the **tts** and 2,3L1 topologies (Fig. 3). For the study we have selected 17 topologically dense nets, which are not subnets of each other, among the set of two-periodic eleven uninodal Kepler-Shubnikov nets[26] and 454 theoretically generated binodal plane nets. These 17 nets (Fig. 4) can be treated as ancestors for other nets, which are their subnets, i.e. can be obtained from them by removing some nodes (atoms) or edges (bonds) (Fig. 3). We have considered the net dense if its nodes had coordination numbers 4, 5, 6 or 7, i.e. close to six, the coordination number of the hexagonal (**hxl**) net, which describes the densest packing of equal balls on a plane.
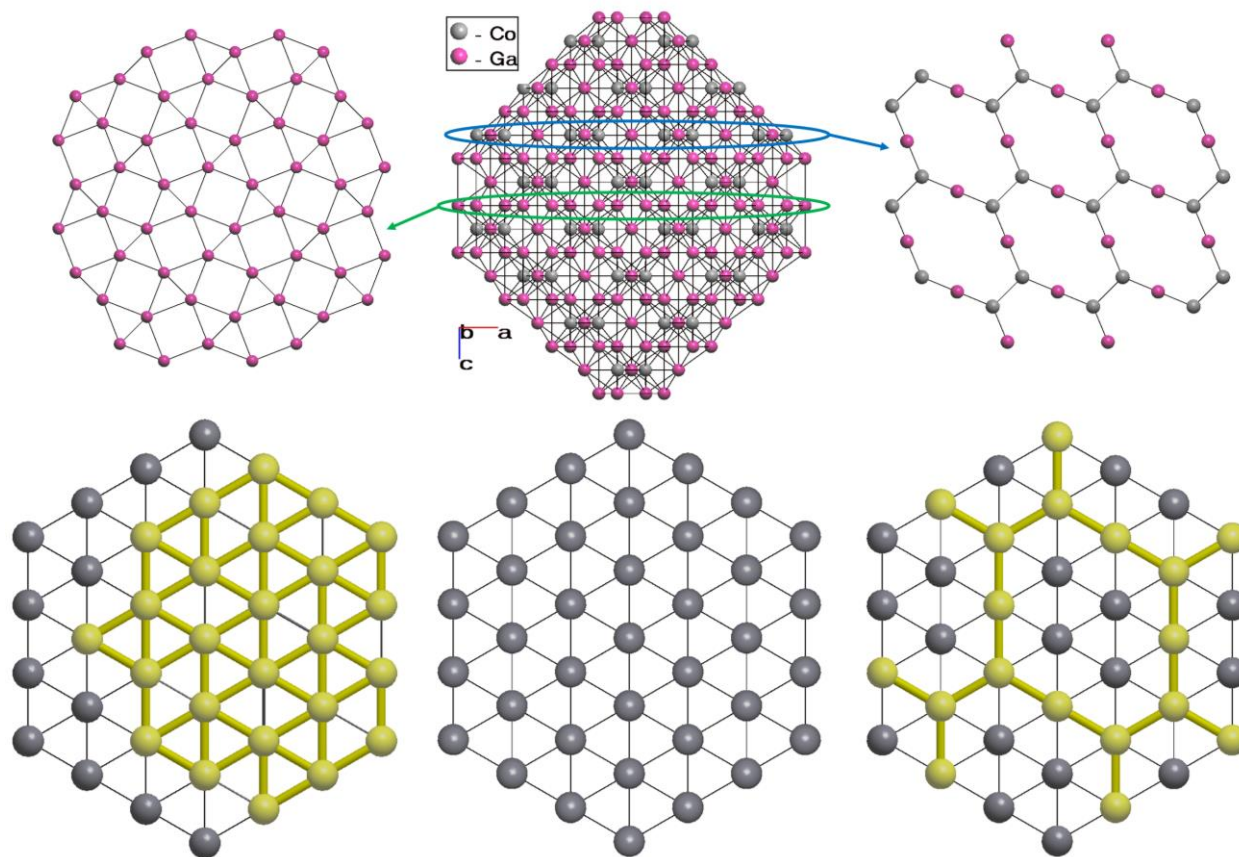

Figure 3. (Top) Decomposition of the $CoGa_3$ crystal structure on the atomic layers with the **tts** (left) and 2,3L1 (right) topologies; (bottom) the **tts** (left) and 2,3L1 (right) nets are highlighted in yellow as subnets of the **hxl** net (middle).
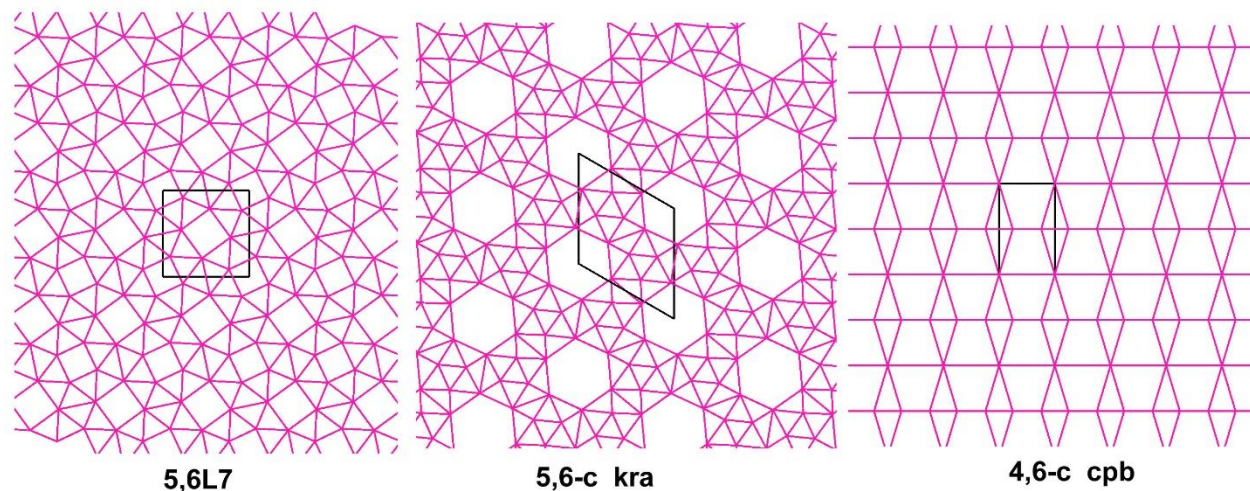
6

5,6L7   **5,6-c kra**   **4,6-c cpb**

Figure 4. Some examples of the generated binodal nets selected for the analysis. For each net the coordination numbers of nodes are specified.

Nanoclusters. To decompose crystal structure to nanoclusters we have used the ToposPro Nanoclustering procedure,[13] which is based on a strict algorithm and the following principles:

(i)   The crystal structures of intermetallics are assembled of the primary structural units that are multishell (onion-like) nanoclusters. The next level of the structure organization, *supracluster*, is formed by several connected primary nanoclusters and characterizes their local binding. The underlying net, which is composed by the centers of mass of the nanoclusters, describes the overall topology of the nanocluster assembly.

(ii)   The structure may contain single atoms or small polyhedral groups of atoms that fill the voids between the nanoclusters and are called *spacers*. All atoms of the crystal structure should be included in the set of the primary nanoclusters and spacers.

(iii) The centers of the primary nanoclusters occupy the highest-symmetry positions of the structure; structural units should be as much regular as possible.

(iv)   The primary nanoclusters cannot have common internal atoms. The connectivity between the nanoclusters can be realized through common external atoms or through intercluster bonds. This rule restricts the size and the number of the primary nanoclusters.

7

(v)   According to the *parsimony principle*, the crystal structure should be assembled with minimal number of primary nanoclusters.

The nanocluster analysis extends the coordination polyhedron concept: it goes beyond the first coordination sphere and analyses polyshell structural units. For instance, the CoMnSb crystal structure[27] can be described as an assembly of two-shell 1@14@26 nanoclusters centered by Mn atoms (Fig. 5).

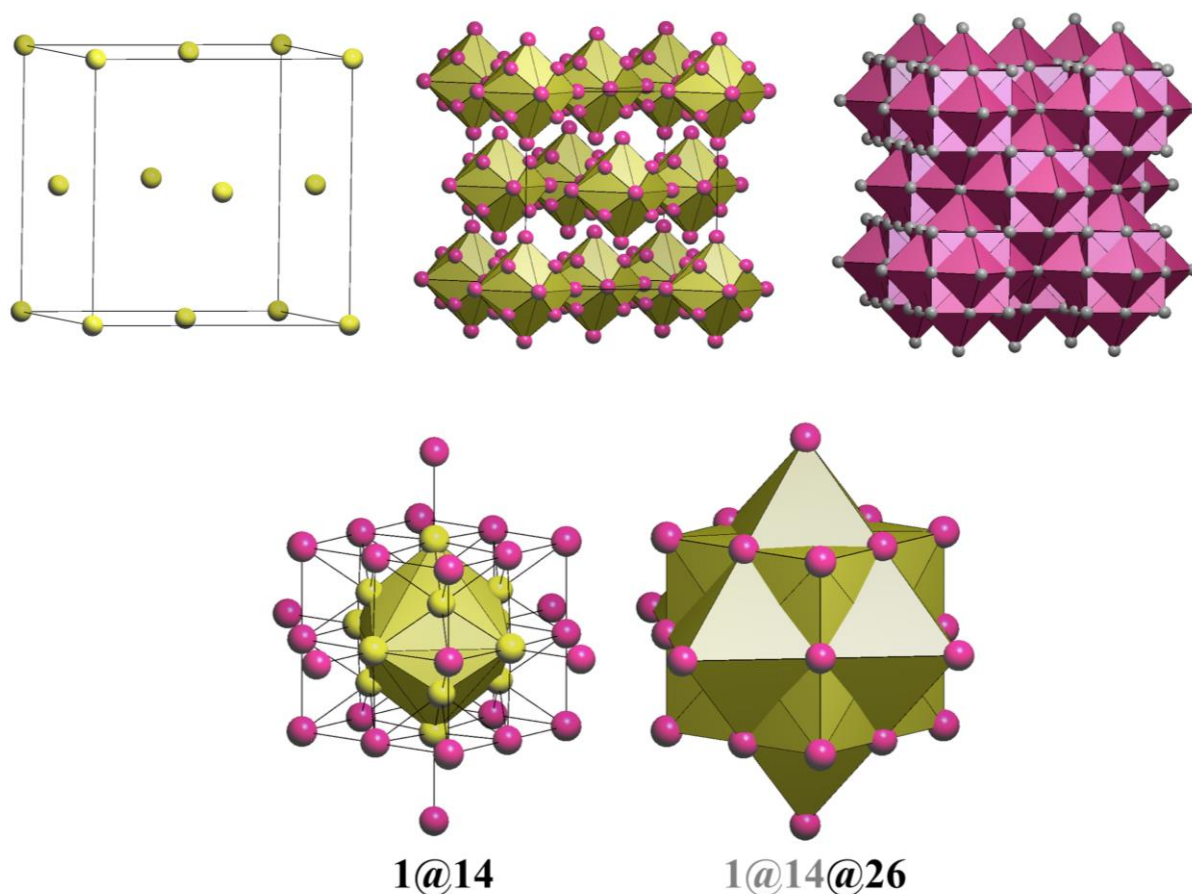1@14   1@14@26

Figure 5. Assembly of the CoMnSb structure with two-shell 1@14@26 nanoclusters: (top left) centers of the nanoclusters (Mn atoms), (top middle) first shells and (top right) the complete assembly; (bottom) the architecture of the nanocluster: the first (left) and second (right) polyhedral shells.

From statistical analysis to prediction

Why do we need different models to describe intermetallics? What is the best model for a particular structure? What useful information can we extract from the model? To answer these key questions we should first consider the results of the analysis of all intermetallics with the three models.

Coordination polyhedra. The concept of the structure description in terms of coordination polyhedra is the oldest in crystal chemistry. It is one of the most natural chemical treatments: to consider atoms together with their nearest environment. The books by Kripyakevich[28] and Gladyshevskii[29] are probably the first attempts to classify all intermetallic structures in accordance with the shape of atomic coordination polyhedra. However, these classifications were performed manually and by this reason could not encompass all known intermetallics and obtain comprehensive statistical data on the local atomic environment of metal atoms and overall architecture of the whole structure. Later on, there appeared other comprehensive reviews of structure, taxonomy geometrical and physical properties of intermetallics including rich statistical data,[30–32] but they did not concern topological properties. With the ToposPro tools, we are able to obtain both geometrical and topological information on crystal structures, which will be discussed below. The most frequently encountered are the coordination numbers 12, 14, 10 and 9 (Fig. 6). Extremely large coordination numbers (20-28) are usually realized in clathrates, for example in the structure of $Rb_8Na_{16}Ge_{36}$,[33] where Rb and Na atoms are located in cages of 28 and 20 Ge atoms, respectively.
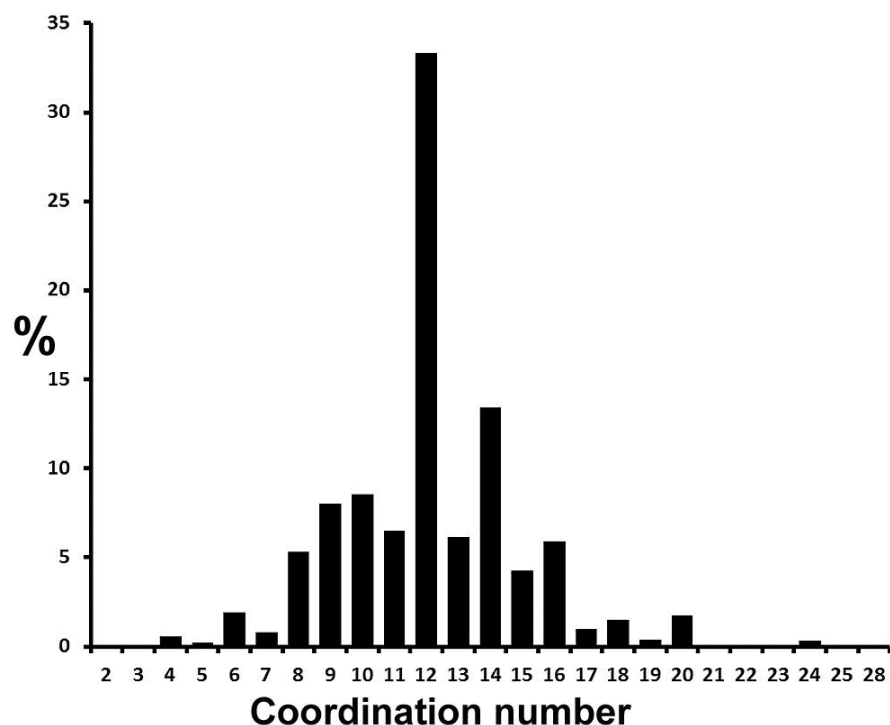
Figure 6. Distribution of coordination numbers in intermetallics.

The most typical coordination number 12 (one third of all structures) is not surprising because it is the largest number of equal spheres that can be in contact with the central one;[34] this number was widely discussed in crystal chemistry with respect to close packings of metal atoms. However, the question is not trivial of what kind of CP is the most abundant for this coordination number because the TTN collection contains 207 topologically different 12-vertex polyhedra. Nonetheless, the answer that we have obtained was quite expected: the most frequent is icosahedron, which corresponds to the uniform surrounding of an atom by 12 other similar atoms (Fig. 7). Frank and Kasper noted long ago[35] that the icosahedral coordination is more common than others in the complex intermetallic structures, and our results confirm it: almost a half of 12-coordinated atoms have icosahedral polyhedra. The second place is occupied by cuboctahedron, which is realized in a quarter of cases. This could also be expected: cuboctahedron is one of coordination polyhedra in the periodic close packings, which are well-known models in crystal chemistry of metals. However, the third position belongs not to another coordination polyhedron of the periodic close packings, hexagonal cuboctahedron, which occupies just the fifth place, but to bicapped pentagonal prism.
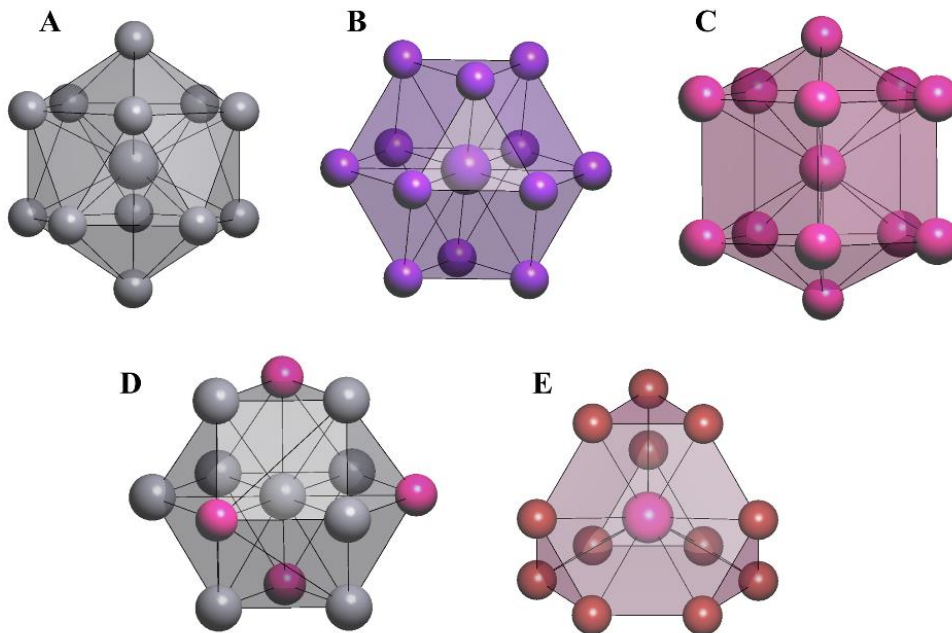
Figure 7. Occurrence (in parentheses) of 12-vertex coordination polyhedra in intermetallics: A – icosahedron (46%), B – cuboctahedron (25%), C - bicapped pentagonal prism (13%), D - hexagonal cuboctahedron (12%), E - truncated tetrahedron (3.5%).

However, the topological types of CPs not always exist in geometrically ideal forms as shown in Fig. 7. While the icosahedral and cuboctahedral CPs indeed tend to be more or less regular, the bicapped pentagonal-prismatic ones are often distorted (Fig. 8). The types of distortion can be quite different (Fig. 9) that shows how difficult is to classify the CP shape manually.

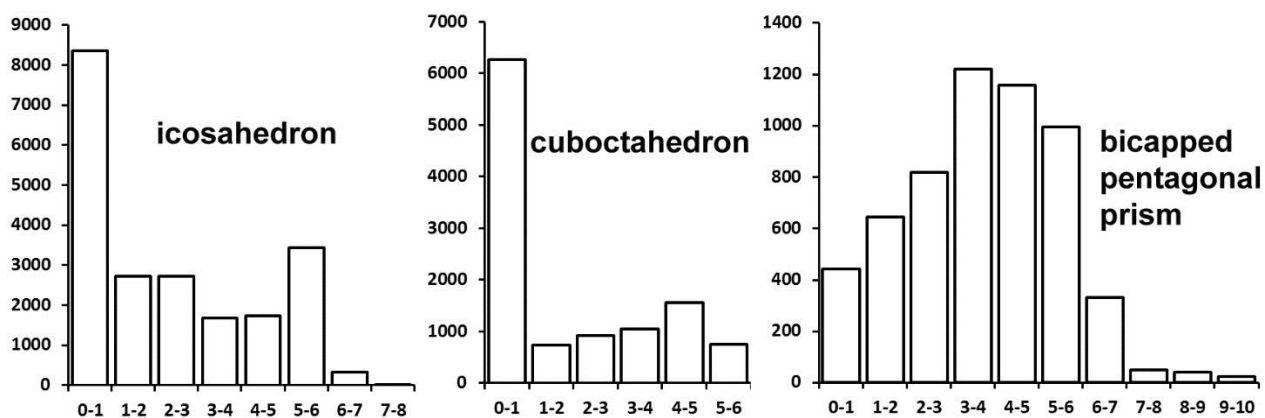## Distribution of the DRanks over coordination polyhedra

Figure 8. The distributions of the most typical 12-coordinated polyhedra on the degree of distortion (DRank) ranged from 0 to 10.
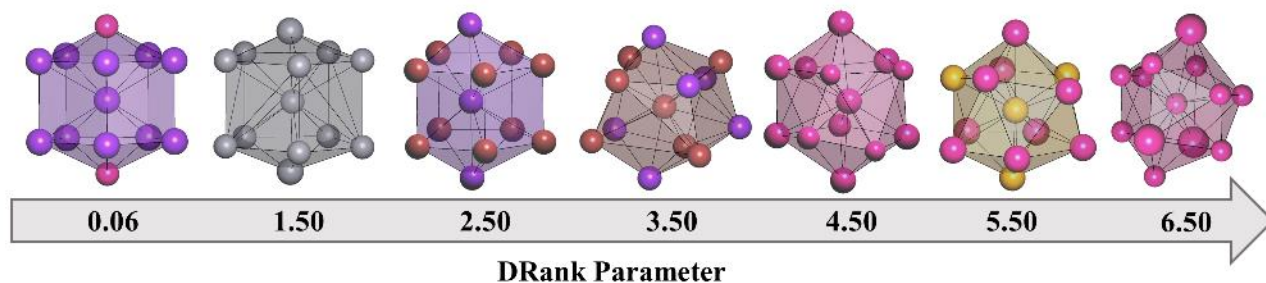
Figure 9. Different shapes of bicapped pentagonal prisms depending on the degree of the distortion.

Atomic layers. Pearson in his famous book[5] proposed topology of atomic layer as a more universal and informative taxon than coordination polyhedron. He did an enormous manual work to find all plane nets in crystal structures and performed a new classification for 590 out of 650 known structural types of intermetallics as stackings of atomic layers (see fig.7.1, part 1 in his book). It was an attempt to spread the model of closely packed hexagonal layers, which was quite successful for metals, to any intermetallics by consideration of other topological types of planar layers. That was also a way to go beyond the coordination polyhedron and to create a collection of infinite (periodic) structural units. It seemed impossible to apply this manual classification to sharply increasing amount of crystal data; that is why the Pearson's book remains the only comprehensive review in this field. Nonetheless, the crystal chemists still use the atomic layers concept for description of separate structures or short series of intermetallics especially to find correlations between different structure types. With the ToposPro program package, we are able to check the occurrence of any plane net. In particular, out of the 17 ancestor nets mentioned above we have found only the **hxl** net in 188 topological types, which include 11,740 intermetallic structures. Crystal structures can be solely assembled with the **hxl** layers as, for instance, the close-packed metals; they can also combine with other nets. Pearson described some cases of such combination, for instance, the $MgCu_2$ (Laves phase) structure type[36] can be represented as a packing of hexagonal **hxl** nets and kagome (**kgm**, which is a subnet of **hxl**) nets. We should keep in mind that structure description in terms of atomic layers depends on the chosen direction: there is an alternative representation of the $MgCu_2$ (see p.308, part 2 in the Pearson's book).

Note that there is no strict criterion of what role a layer plays in the crystal structure: whether this is a fundamental building block or simply a fragment in the crystal. At least, high occurrence could indicate the role. We see that the **hxl** topological motif is the most common and it agrees with the exceptional role, which it has been playing in crystal chemistry for a century.

Nanoclusters. Letters are arranged into words, words into phrases and sentences. It is natural and logical and is reasonable to assume a similar hierarchy in crystals, where atoms play a role of letters, and nanoclusters are words. In 2006, Mackay with co-authors[6] formulated the idea of the grammar for crystals. One of the advantages of such concept is that we can use these structural units (nanoclusters) for modelling not only periodic crystals, but quasicrystals as well. For instance, Mackay[37] and Bergman[38] clusters play an important role in the models of the icosahedral quasicrystals and quasicrystal approximants. Nanoclusters allow us to go beyond the coordination polyhedra and atomic nets and to find deeper correlations between quite different intermetallics.

Below we consider the simplest nanocluster models, which are built with just one type of nanocluster. The TTN collection contains information on 1,234 nanoclusters that can form such 'mono-nanocluster' models. Among them, there are 1,148 single-shell (polyhedral), 75 two-shell and 11 three-shell nanoclusters. In total, 993 topological types and 15,919 (41%) intermetallic structures can be assembled with these structural units and that 22.4% of these are packed according to the face-centered cubic motif (**fcu**) of the closest packing of spheres in a three-dimensional space. For instance, the $Li_{17}Ge_4$ crystal structure[39] can be assembled from three-shell nanoclusters with a 1@14@50@96 configuration, which form an **fcu** architecture (Fig. 10). Interesting is that nine of the 11 structures that can be described by three-shell nanoclusters model have the **fcu** topology of the underlying net, while the remaining two structures are organized in a body-centered cubic **bcu-x** motif.
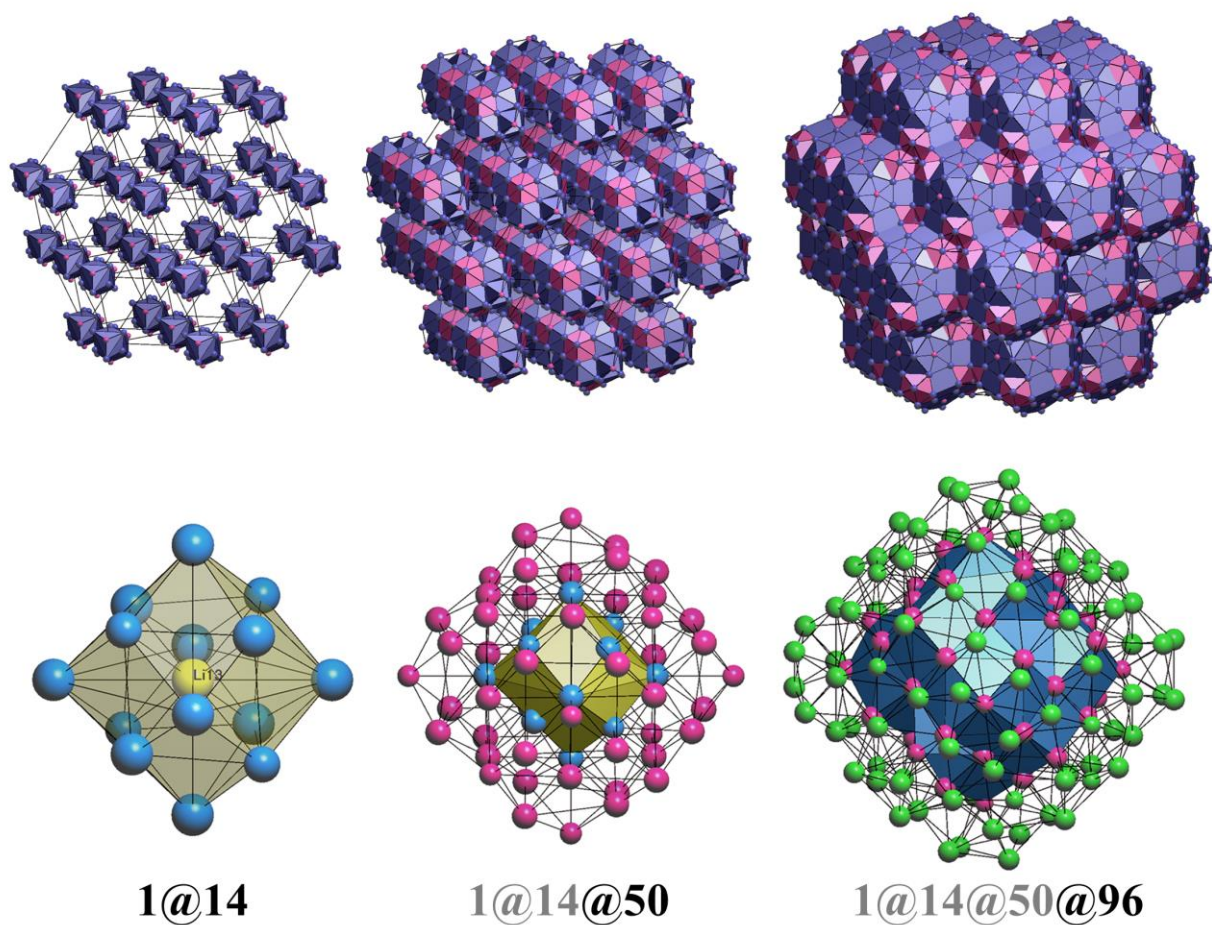
Figure 10. Shell-by-shell growing of the nanoclusters in the $Li_{17}Ge_4$ crystal structure: (left) first 14-atom shell; (center) second 50-atom shell; (right) third 96-atom shell.

Combination of models. What structural unit or model is the best to describe the structural motif? In general, this question is incorrect, because different models give us different views of the same structure and allow us to understand it better. Moreover, different topological motifs can maintain each other. For instance, the crystal structure of $PtSn_4$[40] can be represented as a stacking of layers of two types, consisting of Pt and Sn atoms. The Sn atoms form a **tts** net, while Pt atoms are placed between the Sn layers just in the middle of the squares of the **tts** net (Fig. 11).
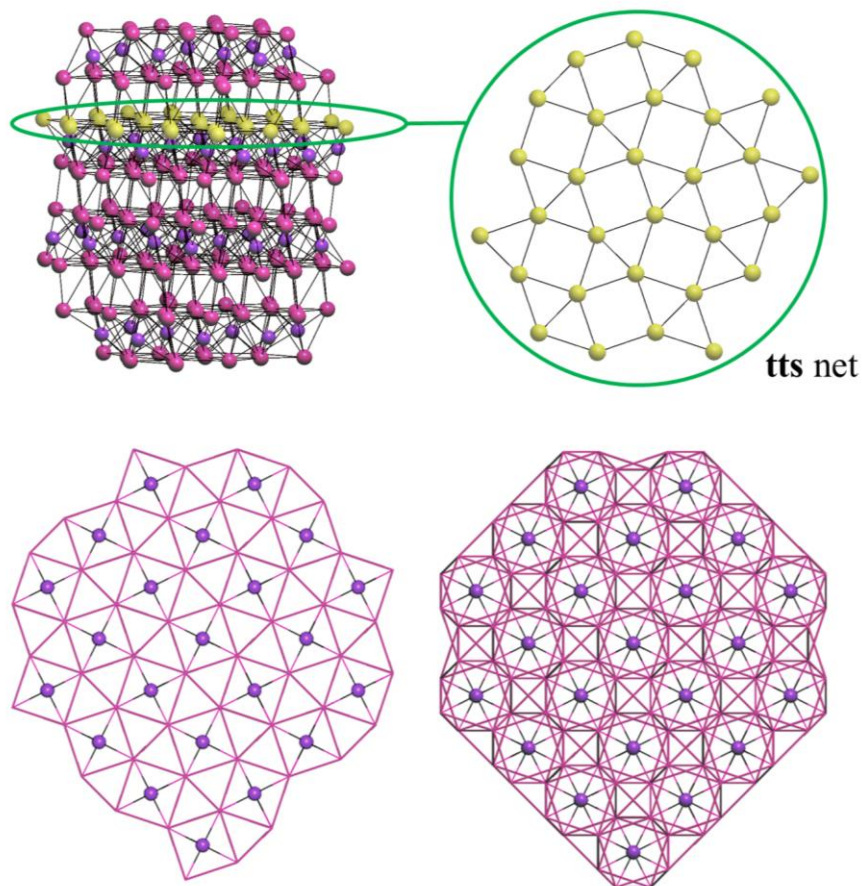
Figure 11. (Top) The crystal structure of PtSn$_4$: the Sn atoms (red balls) form layers with the **tts** topology (one of the **tts** layers is highlighted in yellow); (bottom) an arrangement of Pt atoms (violet balls) between the **tts** layers of Sn atoms.

On the other hand, the structure can be represented as a packing of Pt@Sn8 tetragonal-antiprismatic coordination polyhedra in accordance with the 12T24 motif; each polyhedron is connected to 12 others (Fig. 12). Obviously, the polyhedral packing model correlates with the **tts** layered topology: the Pt@Sn8 tetragonal antiprisms stabilize the Sn$_4$ squares, while the 12T24-type assembling arranges these squares in a **tts** motif. According to the TTN collection, the cluster 1@8 is widespread: there are 117 topological types of intermetallics, which include 1385 crystal structures; all these structures can be described as packings of 1@8 or 1@8-based nanoclusters. Using the information one can find relations between these structures and PtSn$_4$.
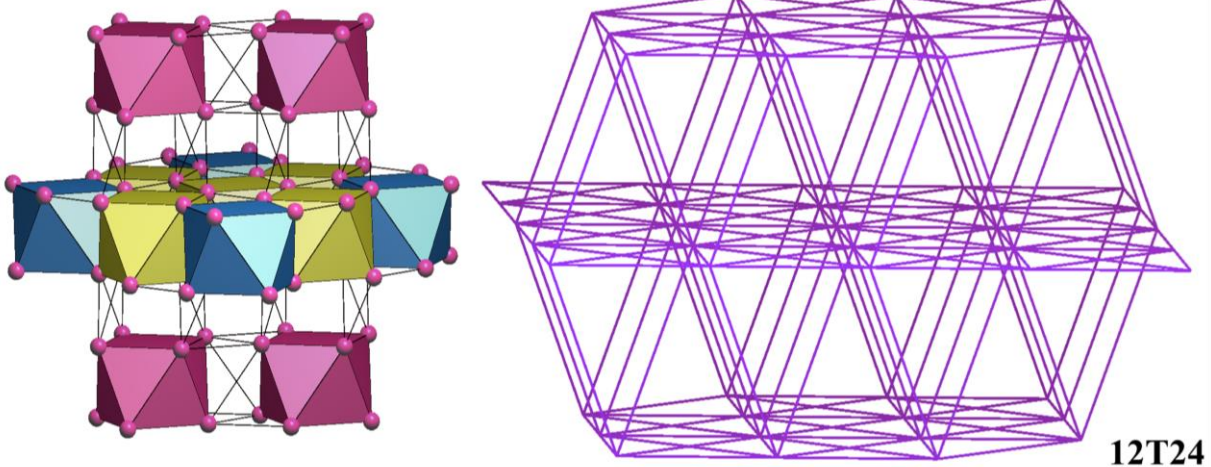
15

Figure 12. Supracluster of the 12-coordinated nanoclusters Pt@Sn8 (left) and the resulting underlying net with the 12T24 topology (right).

Other models. As there is no conventional way or 'the best' model to describe intermetallics, the structure representation can be quite arbitrary. A criterion of robustness of the structure description could be a high occurrence of the proposed structural units and/or the corresponding underlying net in other intermetallics. For example, the authors[41] described the $Al_{2.9}Ta_{2.7}V_{1.4}$ crystal structure as composed of a pentagonal-antiprismatic columns (Fig. 3 in the original work). We have proposed an alternative nanocluster description of this structure.[15] Is the pentagonal-antiprismatic columnar model reasonable since it does not fit the main models considered above? Using the ToposPro tools, we have found the columnar units of this topology in 1,011 structures, which spread over 41 topological types. For instance, in the Ga_3Nb_5 crystal structure[42] these columns, which were not mentioned by the authors, are formed by intersection of the CPs of Nb atoms (Fig. 13).
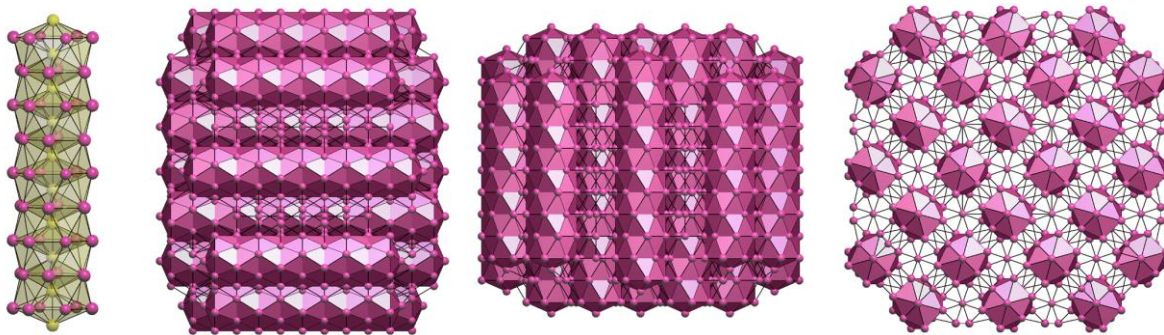
Figure 13. From the left to the right: a columnar fragment and a packing of the fragments in the Ga$_3$Nb$_5$ crystal structure in the [100], [010] and [001] projections.

As we see, such columns are quite widespread in intermetallics and indeed can be treated as structural units. It is not surprising: this structural unit consists of interpenetrating icosahedra, which are very common. This means that the number of structural models can be essentially extended; we should consider different reasonable structure descriptions, check if they encompass many intermetallics and collect the abundant models in the databases like the TTN collection. This information can then be used in searching for structural correlations and in prediction of new intermetallics. Importantly, when choosing the set of reference structural units we do not use any predetermined archetypes; the set is being formed during the analysis of crystal structures and the most important units are selected in accordance with their occurrence.

Structure prediction. Prediction of the crystal structure of intermetallics is a great challenge because of many non-ignorable influencing factors. Compared to other classes of chemical compounds, like covalent, coordination or ionic compounds, for which simple geometrical and topological models show a good predictive power, intermetallics require a more complicated approach. From crystallochemical point of view, the main reason is that the local and overall structure features are strongly interrelated in intermetallics; in most cases, it is not enough to know the nearest environment of atoms to make an assumption about the whole structure. On the quantum-mechanics level, this means that the electronic structure of separate atoms and atomic ensembles and the band structure essentially interdepend and can

17

vary in a wide range. Thus, a way to a robust predictive scheme could include search for as many as possible correlations between local and overall geometrical/topological structure properties and then establishing their reflections to the electronic properties. Good examples of such correlations (close packing model, Hume-Rothery rules, Zintl-Klemm concept)[30,32] were found in the 20th century but they are still rather exceptions than parts of a universal scheme.

The approach described in this paper could become a platform for such a universal predictive scheme. The geometrical/topological models have essential advantages as they are simple enough to be applied to long lists of crystal structures, rest upon reliable and abundant experimental data, and are easy to be interpreted. We can now outline their expected development and transformation in the near future and determine their place in the structure prediction scheme (Fig. 14).
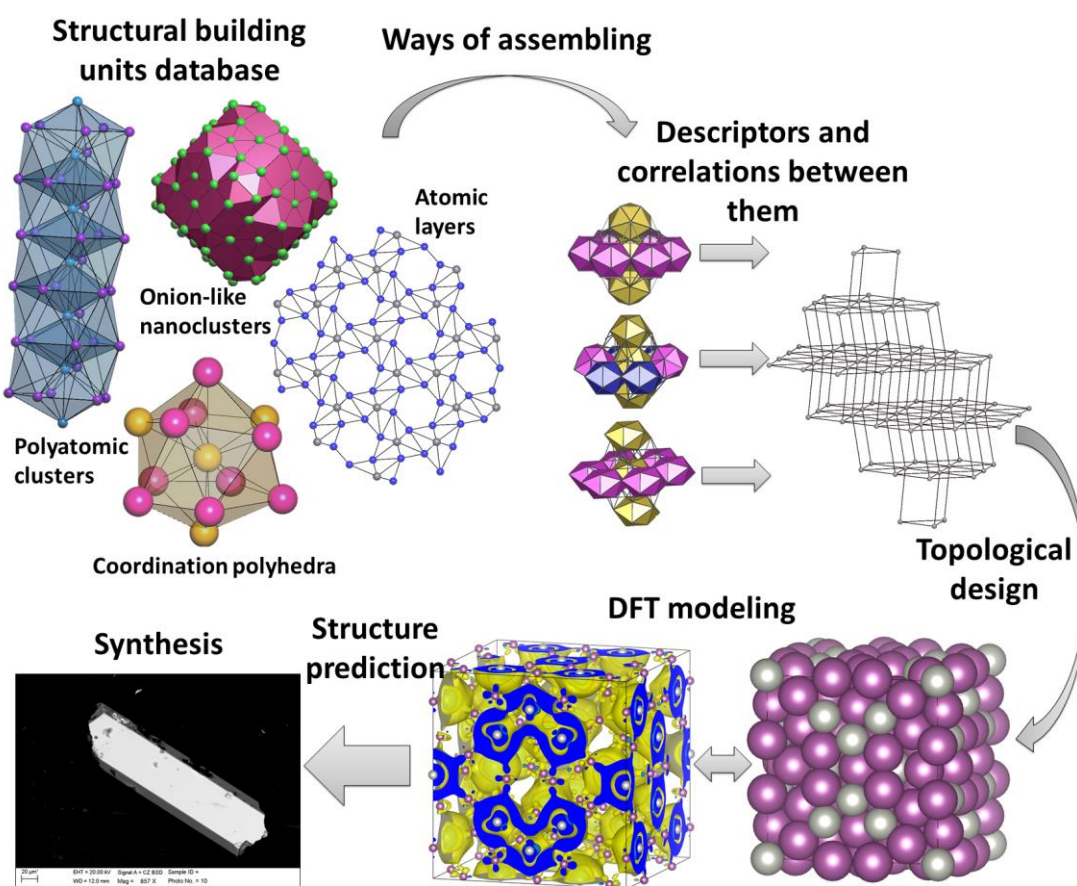

Figure 14. General scheme of prediction of intermetallic structures.

First, the set of models should be extended to include atomic ensembles of any shape, size and topology if they were often found in the experimental structures. The criterion of a high abundance could be considered primary for a structural unit to be included into a crystal model. As we see, quite different atomic configurations (polyhedra, nanoclusters, layers, columns, etc.) can fit this criterion, moreover, they can coexist in the same structure that points to correlations between them. A knowledge database should be created, which accumulates all abundant structural groups and their correlations.

Second, the methods of assembling of the structural units should be determined in the form of underlying nets. This will extend correlations also between quite different structural units as they can be assembled in a similar way as was already shown for different intermetallic clusters assembled in accordance with the Laves phase motif.[11]

Third, a number of new descriptors of local geometry and topology should be invented to make denser the network of structural correlations. For example, the descriptor of the local connection of nanoclusters[15] allows one to link the supracluster motifs with the entire crystal architecture.

Last, the information on the electronic and band structure from already existing[43] and specially developed databases should be inserted into the knowledge database and the structural-electronic correlations should be revealed and stored.

The resulting knowledge database can then be used in future expert systems for machine learning and predicting intermetallic structures with a much higher reliability than of any experienced human expert.

Conclusion remarks

The predictive power of any crystal-chemical approach depends on the number and robustness of structural correlations behind it; any rational model, which is based on physically reasonable principles and described by a strict algorithm, is a tool to collect such correlations. We are still far from being able to state that structural chemistry of intermetallics has a strong predictive power, far by the distance that we should cover but very likely not by the time. Fast development of high-throughput data mining methods, machine learning algorithms, software and databases for storage and analysis of experimental information should drastically speed up extracting knowledge and applying it in computer expert

systems. In this paper, we have outlined a crystallochemical approach, which we believe could serve a universal tool for formalization of this process. The key point is to rationalize the architecture of intermetallic structures, and the topological methods can naturally solve this task. Having an idea about building blocks and methods of their assembling we will be able to reveal deeper regularities, which will include the electronic component of the intermetallic crystal. The topological information could also serve as a basis for simulating crystal growth of intermetallics[44] like it was recently done for other classes of chemical compounds.[45] In general, the topological methods let us simplify diverse and complicated intermetallic structures in a proper way and, hence, understand the knowledge behind them.

Notes

The authors declare no competing financial interest.

AUTHOR INFORMATION

*Vladislav A. Blatov, Samara University, Ac. Pavlov St. 1, Samara 443011, Russia. Phone: +7-8463356798, Fax: +7-8463345417, blatov@samsu.ru.

BIOGRAPHICAL INFORMATION

Tatiana G. Akhmetshina was born in 1995 in Novokuibyshevsk, Samara region. She is a student of Samara University, Chemistry Department, since 2013. Her diploma work is devoted to topological analysis of intermetallics and application of the topological methods to the design of new structures.

Vladislav A. Blatov was born in 1965 in Samara (former Kuibyshev), Russia. He is Full Professor at the Chemistry Department of Samara University since 1998 and Head of Samara Center for Theoretical Materials Science (SCTMS) since 2013. His research interests concern geometrical and topological methods in crystal chemistry and their computer implementation in the program package ToposPro being developed since 1989.

Davide M. Proserpio (1962, Italy) is associate Professor at the University of Milano (Italy) since 2003. He has special interest in Topological Crystal Chemistry from coordination networks to intermetallics looking for nets, knots and entanglements.

Alexander P. Shevchenko was born in 1967 in Samara (former Kuibyshev), Russia. He was assistant professor at the Chemistry Department of Samara University since 2002 and Senior Research Scientist of Samara Center for Theoretical Materials Science (SCTMS) since 2013. His research interests lie in the field of geometrical crystal chemistry, extracting information from structural databases and development of software for these purposes.

REFERENCES

(1) Strugatsky, A.; Strugatsky, B. *The waves blow out the wind*; Znanie: Moskow, 1988 (in Russian).

(2) Weber, T.; Dshemuchadse, J.; Kobas, M.; Conrad, M.; Harbrecht, B.; Steurer, W. Large, Larger, Largest - A Family of Cluster-Based Tantalum Copper Aluminides with Giant Unit Cells. I. Structure Solution and Refinement. *Acta Crystallogr. B* **2009**, *65*, 308–317.

(3) Damasceno, P. F.; Engel, M.; Glotzer, S. C. Crystalline Assemblies and Densest Packings of a Family of Truncated Tetrahedra and the Role of Directional Entropic Forces. *ACS Nano* **2012**, *6*, 609–614.

(4) Damasceno, P. F.; Engel, M.; Glotzer, S. C. Predictive Self-Assembly of Polyhedra into Complex Structures. *Science* **2012**, *337*, 453–457.

(5) Pearson, W. B. *The Crystal Chemistry and Physics of Metals and Alloys*; Wiley-Interscience: New York, 1972.

(6) Lord, E. A.; Mackay, A. L.; Ranganathan, S. *New Geometries for New Materials*; Cambridge University Press: Cambridge, 2006.

(7) Bonneau, C.; O'Keeffe, M. Intermetallic Crystal Structures as Foams. Beyond Frank-Kasper. *Inorg. Chem.* **2015**, *54*, 808–814.

(8) Samson, S. The Crystal Structure of the Phase β-Mg_2Al_3. *Acta Crystallogr.* **1965**, *19*, 401–413.

(9) Feuerbacher, M.; Thomas, C.; Makongo, J. P. A.; Hoffmann, S.; Carrillo-Cabrera, W.; Cardoso, R.; Grin, Y.; Kreiner, G.; Joubert, J. M.; Schenk, T.; Gastaldi, J.; Nguyen-Thi, H.; Mangelinck-Noel, N.; Billia, B.; Donnadieu, P.; Czyrska-Filemonowicz, A.; Zielinska-Lipiec, A., Dubiel, B.; Weber, T.; Schaub, P.; Krauss, G.; Gramlich, V.; Christensen, J.; Lidin, S.; Fredrickson, D.; Mihalkovic, M.;

Sikora, W.; Malinowski, J.; Bruhne, S.; Proffen, T.; Assmus, W.; de Boissieu, M.; Bley, F.; Chemin, J-L.; Schreuer, J.; Steurer, W. The Samson Phase, β-Mg_2Al_3, Revisited. *Z. Kristallogr.* **2007**, *222*, 259–288.

(10) Yang, Q.-B.; Andersson, S.; Stenberg, L. An alternative description of the structure of $NaCd_2$. *Acta Crystallogr. B* **1987**, *43*, 14-16.

(11) Blatov, V. A.; Ilyushin, G. D.; Proserpio, D. M. Nanocluster Model of Intermetallic Compounds with Giant Unit Cells: β, β′-Mg_2Al_3 Polymorphs. *Inorg. Chem.* **2010**, *49*, 1811–1818.

(12) Wolny, J.; Duda, M.; Kozakowski, B. Simple Model of Mg_2Al_3 : β and β′ Phases. *J. Phys. Conf. Ser.* **2010**, *226*, 12035.

(13) Blatov, V. A. Nanocluster Analysis of Intermetallic Structures with the Program Package TOPOS. *Struct. Chem.* **2012**, *23*, 955–963.

(14) Blatov, V. A.; Shevchenko, A. P.; Proserpio, D. M. Applied Topological Analysis of Crystal Structures with the Program Package ToposPro. *Cryst. Growth Des.* **2014**, *14*, 3576–3586.

(15) Pankova, A. A.; Akhmetshina, T. G.; Blatov, V. A.; Proserpio, D. M. A Collection of Topological Types of Nanoclusters and Its Application to Icosahedron-Based Intermetallics. *Inorg. Chem.* **2015**, *54*, 6616–6630.

(16) Belsky, A.; Hellenbrandt, M.; Karen, V. L.; Luksch, P. New Developments in the Inorganic Crystal Structure Database (ICSD): Accessibility in Support of Materials Research and Design. *Acta Crystallogr. B* **2002**, *58*, 364–369.

(17) Villars, P.; Cenzual, K. Pearson's Crystal Data Crystal Structure Database for Inorganic Compounds (on CD-ROM). ASM International (Materials Park, Ohio, USA) 2009.

(18) Alexandrov, E. V.; Blatov, V. A.; Kochetkov, A. V.; Proserpio, D. M. Underlying Nets in Three-Periodic Coordination Polymers: Topology, Taxonomy and Prediction from a Computer-Aided Analysis of the Cambridge Structural Database. *CrystEngComm* **2011**, *13*, 3947.

(19) Blatov, V. A. Voronoi–Dirichlet Polyhedra in Crystal Chemistry: Theory and Applications. *Crystallogr. Rev.* **2004**, *10*, 249–318.

(20) Shevchenko, A. P.; Blatov, I. A.; Kitaeva, E. V; Blatov, V. A. Local Coordination versus Overall Topology in Crystal Structures : Deriving Knowledge from Crystallographic Databases. *Cryst. Growth Des*. **2017**, *17*, 774−785.

(21) Spiekermann, S.; Kreiner, G. Investigations in the Ag-Mg and Ag-Al-Mg Systems I. Models for Cubic Approximants of Icosahedral Quasicrystals in the Ag-Al-Mg System. *J. Alloys Compd.* **1997**, *261*, 62–82.

(22) Fersi, R.; Mliki, N.; Bessais, L.; Guetari, R.; Russier, V.; Cabié, M. Effect of Annealing on Structural and Magnetic Properties of Pr_2Co_7 Compounds. *J. Alloys Compd.* **2012**, *522*, 14–18.

(23) Calvert, L. D.; Rand, C. The Crystal Structure of Ag_8Ca_3. *Acta Crystallogr.* **1964**, *17*, 1175–1176.

(24) O'Keeffe, M.; Peskov, M. A.; Ramsden, S. J.; Yaghi, O. M. The Reticular Chemistry Structure Resource (RCSR) Database of, and Symbols for, Crystal Nets. *Acc. Chem. Res.* **2008**, *41*, 1782–1789.

(25) Schubert, K.; Lukas, H.L.; Meissner, H.G.; Bhan, S. Zum Aufbau Der Systeme Co-Ga, Pd-Ga, Pd-Zn und Verwandter Legierungen. *Z. Met.* **1959**, *50*, 534–540.

(26) Smirnova, N. L. On Kepler-Shubnikov Nets. *Crystallogr. Rep*. **2009**, *54*, 743–748.

(27) Ksenofontov, V.; Melnyk, G.; Wojcik, M.; Wurmehl, S.; Kroth, K.; Reiman, S.; Blaha, P.; Felser, C. Structure and Properties of CoMnSb in the Context of Half-Metallic Ferromagnetism. *Phys. Rev. B* **2006**, *74*, 134426.

(28) Kripyakevich, P. I. *Structural Types of Intermetallic Compounds*; Nauka: Moscow, 1977 (in Russian).

(29) Gladyshevskii, E. I.; Bodak, O.I. *Crystal Chemistry of Intermetallic Compounds of Rare-Earth Metals*; Vischa Shkola: Lviv, 1982 (in Russian).

(30) *Intermetallic Chemistry*; Vol. 13, Ferro, R.; Saccone, A. (Eds.) Pergamon, 2008.

(31) Pöttgen, R.; Johrendt, D. *Intermetallics : Synthesis, Structure, Function*; De Gruyter, 2014.

(32) Steurer, W.; Dshemuchadse, J. *Intermetallics : Structures, Properties, and Statistics*; Oxford University Press: Oxford, 2016.

(33) Bobev, S.; Sevov, S. C. Clathrates of Group 14 with Alkali Metals: An Exploration. *J. Solid State Chem.* **2000**, *153*, 92–105.

(34) Boerdijk A.H. Some Remarks Concerning Close Packing of Equal Spheres. *Philips Res. Rep*. **1952**, *7*, 303–313.

(35) Frank, F. C.; Kasper, J. S.; IUCr. Complex Alloy Structures Regarded as Sphere Packings. I. Definitions and Basic Principles. *Acta Crystallogr.* **1958**, *11*, 184–190.

(36) Friauf, J. B. The Crystal Structures of Two Intermetallic Compounds. *J. Am. Chem. Soc.* **1927**, *49*, 3107–3114.

(37) Mackay, A. L. A Dense Non-Crystallographic Packing of Equal Spheres. *Acta Cryst.* **1962**, *15*, 916-918.

(38) Bergman, G.; Waugh, J. L. T.; Pauling, L. The Crystal Structure of the Metallic Phase $Mg_{32}(Al,Zn)_{49}$. *Acta Crystallogr.* **1957**, *10*, 254–259.

(39) Zeilinger, M.; Fässler, T. F. Structural and Thermodynamic Similarities of Phases in the Li–Tt (Tt = Si, Ge) Systems: Redetermination of the Lithium-Rich Side of the Li–Ge Phase Diagram and Crystal Structures of $Li_{17}Si_{4.0-x}Ge_x$ for X = 2.3, 3.1, 3.5, and 4 as well as $Li_{4.1}Ge$. *Dalt. Trans.* **2014**, *43*, 14959–14970.

(40) Kubiak, R.; Wołcyrz, M. X-Ray Investigations of Crystallization and Thermal Expansion of $AuSn_4$, $PdSn_4$ and $PtSn_4$. *J. Less Common Met.* **1985**, *109*, 339–344.

(41) Harbrecht, B.; Rheindorf, N.; Wagner, V. τ-$Al_{2.9}Ta_{2.7}V_{1.4}$, a New Type of Pentagonal Antiprismatic Columnar Structure. *J. Alloys Compd.* **1996**, *234*, 6–11.

(42) Kubiak, R.; Drys, M.; Lukaszewicz, K. The Crystal Structure Refinement of Nb_5Ga_3. *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **1973**, *21*, 907–910.

(43) Isayev, O.; Oses, C.; Toher, C.; Gossett, E.; Curtarolo, S.; Tropsha, A. Universal Fragment Descriptors for Predicting Properties of Inorganic Crystals. *Nat. Commun.* **2017**, *8*, 15679.

(44) Taylor, J.; Teich, E.; Damasceno, P.; Kallus, Y.; Senechal, M. On the Form and Growth of Complex Crystals: The Case of Tsai-Type Clusters. *Symmetry (Basel).* **2017**, *9*, 188.

(45) Anderson, M. W.; Gebbie-Rayet, J. T.; Hill, A. R.; Farida, N.; Attfield, M. P.; Cubillas, P.; Blatov, V. A.; Proserpio, D. M.; Akporiaye, D.; Arstad, B.; Gale, J. D. Predicting Crystal Growth via a Unified Kinetic Three-Dimensional Partition Model. *Nature* **2017**, *544*, 456–459.