Topical Review

Metallic alloys at the edge of complexity: structural aspects, chemical bonding and physical properties

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Abstract
Complex metallic alloys belong to the vast family of intermetallic compounds and are hallmarked by extremely large unit cells and, in many cases, extensive crystallographic disorder. Early studies of complex intermetallics were focusing on the elucidation of their crystal structures and classification of the underlying building principles. More recently, ab initio computational analysis and detailed examination of the physical properties have become feasible and opened new perspectives for these materials. The present review paper provides a summary of the literature data on the reported compositions with exceptional structural complexity and their properties, and highlights the factors leading to the emergence of their crystal structures and the methods of characterization and systematization of these compounds.

Keywords: quasicrystals, quasicrystalline approximants, intermetallics, structural complexity, chemical bonding, structure-property relationships

(Some figures may appear in colour only in the online journal)

1. Introduction

Intermetallic compounds represent an important class of solid materials with numerous applications. Unlike simple alloys, whose crystal structures can be derived from the structures of elemental metals by statistical mixing in the atomic sites, intermetallic compounds crystallize with atomic arrangements different from those of the constituting elements. The formation of such structures is governed by a combination of geometric factors, such as the ratio of the atomic sizes, and electronic requirements, i.e. optimization of the chemical bonding. Since metallic systems typically demonstrate significant electron delocalization around atomic centers, chemical bonding in simple alloys lack directionality similarly to ionic bonding in salt-like compounds. Consequently, such alloys usually adopt crystal structures derived from 3D close packings. Different combinations of metallic and covalent bonds can though be present in intermetallic compounds, leading to increasing structural complexity which is reflected in the materials’ properties. The latter range from metallic, originating from delocalized bonding, to narrow-gap semiconductors as the result of prevailing strongly localized chemical interactions.

The great diversity of the bonding patterns as well as spatial arrangement, frequently including atomic disorder, result in a
rich and complex structural chemistry for intermetallic compounds. A particular acknowledgement of this complexity is the widely used classification of certain intermetallic structures as complex metallic alloys (CMAs) [1]. This class encompasses materials composed of metallic elements and crystallizing with large unit cells. The spatial scales of translational symmetry in such compounds greatly exceed the typical interatomic distances, leading sometimes to glass-like properties, e.g. abnormally low thermal conductivity [2]. Historically, the first metallic structures recognized as exceptionally complex were the binary intermetallic phases in the systems Na–Cd, Mg–Al, and Cu–Cd [3–5]. Although the compounds in these systems displayed relatively simple approximate compositions—NaCd3, MgAl2, Cu2Cd—the crystal structures were hallmarked by huge unit cells with hundreds of atoms and extensive disorder. Since then, many more structures boasting extraordinary complexity have been discovered and characterized in different multicomponent systems [6] including the extreme case Al55.4Cu5.4Ta39.1 with over 20,000 atoms per unit cell. The application of the term ‘intermetallic compound’ has expanded to a wide range of substances showing peculiar metal–metal interactions and is not limited anymore to systems containing exclusively metallic elements, but is extended to representatives with some lighter main group elements. In the light of these developments, representatives of different families of compounds have been described as CMAs. Examples include metal-rich borides [8, 9], carbides [10, 11], and nitrides [12–14]. A special place in this family is reserved for Si and Ge. These two rather semi-metals have been frequently observed in formation of compounds isostructural to those of pure intermetallics [15, 16].

Initial studies of CMAs were limited to elucidation of their crystal structures. The extreme structural complexity precluded theoretical investigations, owing to the lack of computational resources and suitable theoretical methods, whereas the frequently encountered disorder and hence varying compositions made directed synthesis and further physical property measurements exceedingly challenging. With the advance of theoretical calculations nowadays, first-principle investigations of CMAs have become possible [17–19]. The analysis of electronic structure and chemical bonding aided in rationalization of the sophisticated atomic arrangements, extending thereby the simple historical valence electron counting rules developed for various classes of intermetallics [20]. Developments in the field of mathematical topology and its applications to crystal structures enabled new ways of classifying complex intermetallic structures and put them in a broader context of 3D nets [21]. With optimization of the synthetic conditions, phase-pure samples of CMAs have become feasible. Examination of their physical and chemical properties have revealed that many of these compounds have potential applications as thermoelectric [22], catalytic [23], or construction materials [24]. The importance of complex intermetallic systems and the need for their systematic studies led to the creation of the European Network of Excellence complex metallic alloys (NoE CMA) in 2005 (now the European Integrated Center for the Development of New Metallic Alloys and Compounds [25]).

In this review paper, we will focus on the reported data on CMA with particular focus on their crystal structures and physical properties. As has been shown in the recent work [6] the number of reported compound decreases exponentially with the size of the unit cell. There is just a single representative with the unit cell volume over 100,000 Å³, around 100 over 10,000 Å³ and more than 4500 over 1000 Å³. Having no doubts about the complexity of the extreme representatives, the lower limit for CMA or the border between ‘simple’ and ‘complex’ is still uncertain. Several approaches exist in the literature regarding how the structural complexity should be defined, in particular with respect to the size of the unit cell. One of such approaches suggests that an intermetallic compound can be regarded a CMA if there are more than 100 atoms in its primitive unit cell [26]. Although this definition suffers from arbitrariness, it allows easy analysis and screening of crystal structure databases. Herein, we will adhere to this interpretation of a CMA. However, compounds, which do not strictly satisfy the proposed definition but display interesting physical phenomena stemming from complex atomic arrangements in their crystal structures will also be highlighted.

2. Experimental and theoretical characterization of CMA

Intermetallic phases, including CMA, are usually obtained by high-temperature treatment of the constituting elements in inert reaction vessels, although some other approaches are widely used as well, such as spark plasma sintering [27], flux growth [28], and soft chemistry methods [29]. Production of new compounds in a multicomponent system usually requires exhaustive or selective exploration of the phase space. Although structural complexity per se does not necessarily impede preparation of single-phase samples, extensive disorder and possible homogeneity ranges in many complex intermetallic compounds complicate synthesis of pure materials with targeted compositions.

Preliminary examination of crystalline samples prepared using any of the methods mentioned above typically involves powder x-ray diffraction analysis (PXRD), whereas thorough crystallographic characterization is usually accomplished by means of single-crystal x-ray diffraction (SCXRD). For crystals of CMA, the reciprocal space is populated by a large number of Bragg reflections, which often hinders structure determination with laboratory x-ray diffraction instruments. High-resolution SCXRD measurements employing synchrotron facilities are frequently indispensable in these cases [7].

When suitable single crystals are not available, ab initio structure determination from PXRD data [30] or electron diffraction on microcrystals [31] can be utilized to generate and refine a model of the crystal structure.

Since x-ray diffraction provides distribution of electron density averaged over all unit cells in a measured sample, additional techniques may be necessary for unambiguous assignment of atomic chemical types or for resolving local structural features, especially in crystallographically disordered materials. Such techniques include, among others,
After the crystal structure of an intermetallic compound has been established, further insights can be obtained through first-principle based methods, e.g. the factors responsible for the stabilization of a particular atomic arrangement or particular physical properties. Since ab initio treatment of highly complex and/or disordered materials is usually computationally demanding, idealized models or crystal structure fragments are commonly used for calculations [35–37]. Electronic instabilities inferred from such calculations often point toward perturbations of the translational order in the approximate model and enable explanation of the experimentally observed complexity. Depending on the employed computational approach, such instabilities can be described in terms of, e.g. excessive ‘chemical pressure’ [38, 39] or under-optimization of chemical bonding [40–42].

Whereas electronic structure calculations provide information on energy landscapes in the ground state, entropy may be an important factor causing complex atomic arrangements in metallic materials at finite temperatures. Development of crystallographic disorder and hence distortion of translational symmetry normally takes place upon heating [43]. In the extreme case, crystallinity can be completely destroyed by rapid quenching of metallic melts with the formation of metallic glasses [44]. Glass-like properties are also observed for many crystalline CMAs with large unit cells. Besides affecting electronic and heat transport [2, 45], perturbation of translational symmetry has a strong impact on cooperative electronic phenomena, such asagnetism. Spin-glass magnetic behavior has been reported in complex intermetallics with extensive disorder [46, 47]. Nevertheless, disorder-free CMA phases can exhibit long-range magnetic order or superconductivity in the ground state, even when the unit cell sizes greatly exceed the length scales of the interatomic distances [48–50]. However, thorough characterization of physical properties for such materials remain challenging due to extreme complexity of their crystal structures and large number of bands in the electronic spectra.

3. Frank–Kasper phases

Frank–Kasper (FK) phases, polytetrahedral or topologically close packed (TCP) structures, represent one of the most populated groups [6] of intermetallics. In contrast to close packed structures of pure metals Mg (hcp) or Cu (ccp), FK phases are formed by two or more metals with distinct atomic sizes leading to different coordination numbers and certain variety of structural motifs. Ideal FK polyhedra have coordination numbers (CN) 12, 14, 15 and 16 (figure 1) possessing local symmetries $I_3$, $D_{5h}$, $D_{3h}$ and $T_d$, respectively. However, the real solid-state compounds frequently exhibit a significant degree of distortion. Classic FK phases include in line with quite simple and wide spread, e.g. Laves or A15 phases, a good number of really complex formations. A broad overview of existing and potentially existing, but not yet experimentally confirmed FK patterns can be found in the work of Sikirić [51]. Here we focus on the most complex representatives and their occurrence in the periodic table. This family includes also a large number of quasicrystals and their approximants, which will be considered in a separate section.

Among the classic FK only so-called M, P and R phases—represented by Nb$_{30}$Ni$_{12}$Al$_{13}$ (52 atoms/cell) [52], Cr$_{10}$Mo$_{25}$Ni$_{21}$ (56 atoms/cell) [53], and Co$_5$Cr$_2$Mo$_3$ (159 atoms/cell) [54] respectively, can be assigned to moderately complex. All these alloys can be presented as direct structural derivatives of the $\sigma$ phase (such as CrFe, 30 atoms/cell) [55] and are closely related to each other with nearly identical numbers of atoms per corresponding primitive unit cells. They exhibit a full set of FK type polyhedra with the smallest atoms havingicosahedral coordination (CN = 12). The larger ones have CN = 14, 15 and 16, with 14 being the most frequent. The R phase is more common, though 90% of the known representatives contain Si/Ge or, alternatively, small atoms like ferrous metals, and, on the other hand, forms almost exclusively with W, Mo, Mn, or V. Participation of different transition metals has been observed solely in the form of impurities (up to 5 at.%) [56]. The single exception in this d metal rich family is an s-p system (s, p and d refer to the valence shell electrons of the constituting atoms) representative $\varepsilon$-Mg$_2$Al$_3$ [57].

Although $s$-$p$ systems are well-represented in the simple FK structures, e.g. Laves phases [58], they are rarely observed in the complex formations. Besides the $\varepsilon$-Mg$_2$Al$_3$, only the $\mu$-type related phases K$_5$Cs$_6$ [59] and Mg$_2$Zn$_7$ [60] can be assigned to that group. It shall also be noted that Mg plays a special role in these systems being able to form compounds with both $p$ and $d$ elements extending the FK family. K$_5$Cs$_6$ is a unique representative being formed solely by $s$ elements. Its structure is closely related to the $\mu$ phase with identical coordination polyhedra and even their ratio. Due to participation of the large alkali metals its unit cell is about five times larger (~2300 Å$^3$) than that one of the $\mu$ phase (~500 Å$^3$). This type also offers another unique combination for the FK phases an
The spd system Li₈(Al,Cu)₁₈ [61], Mg₂Zn₁₂ is significantly more complex compared to the classic Laves phase MgZn₂ [62]. This compound keeps nearly the same 2:1 ratio of the icosahedral/Friauf units, however, with the minor presence of the two remaining FK polyhedra.

The remaining complex FK alloys include Mn₇₇Fe₄Si₁ [63], Mn₄₅Co₄₀Si₁₅ [64, 65], V₄₁Ni₃₆Si₂₃ [66] and V₂(Co,Si)₃ [67] types and show major Si contents. Three formers are exclusive representatives of their own structure types while the last one contains six alloys. Mn₇₇Fe₄Si₁₉ (K phase), Mn₄₅Co₄₀Si₁₅ (X phase), and the above-mentioned R type alloys are closely related, all representing plane-layered TCP structures. Both V₂(Co,Si)₃ and V₄₁Ni₃₆Si₂₃ represent monoclinic derivatives with the latter being the most complex within the related compounds. Both structures can also be described in terms of rumpled layers stacked together resembling those of the K or R phase. The V₂(Co,Si)₃ type is the most represented and interestingly does not contain any other silicides but solely Al and Mg compounds [67, 68]. As in two previous groups, Mg forms a binary solid solution Mg₂Ir₃−ₓ [68] introducing a new transition metal to the family of complex FK phases.

4. Beyond Frank–Kasper—an extended nestle of complexity

In contrast to classic FK phases a good number of complex intermetallics in general follows FK building principles but contain a minor amount of structural peculiarities, e.g. defects, disorders or moderate changes in atomic coordination, e.g. octahedral fragments, moving them slightly away from close packed structures. Though their classification in this group is somewhat arbitrary, the majority of polyhedra in the crystal structure (but not all) are of FK type. Each of the subgroups here contain some characteristic features, though any clear separation is hardly possible, and a reasonable overlap can be observed.

4.1. Giant unit cells

The classical examples include a few so-called Samson phases, until recently the most complex representatives of intermetallics. Three of them, ~β-Mg₂Al₁₃ [4, 37], ~NaCd₂ [3], and ~Cu₃Cd₃ [5] (all compositions are non-stoichiometric), contain over 1000 atoms per crystallographic unit cell, the majority of coordination numbers are in the range 12–16 and represented by icosahedra or Friauf polyhedra as the main coordination units. Although, the structures contain polyhedra with unusual coordination numbers 13 and 11 and exhibit both positional and occupational disorders leading to a less dense packing. Similarly, ~Cu₃Cd₃ is complemented with pentagonal prisms leading to octahedral voids. This compound shows key features of a Mackay type approximant crystal (see below). A few other examples—Mg₂Zn₂₅ [69], Al₆₉Ta₃₉ [70], and Mg₂Cr₄Al₁₅ type [71, 72] are the cases with all coordination numbers being 12, 14, 15 or 16 but not all coordination polyhedra satisfying FK criteria, though they include features of bcc type packing, e.g. capped pentagonal or hexagonal prisms introducing octahedral voids. A group of closely related compounds with the (approximate) composition AB₆ also belongs to this family. The prominent examples are ~Na₄₄Tl₇ [73], ~Mg₆Pd [74] and the fully ordered Mg₂Ir₇ [75] type phases. This series partially belongs to a larger family of γ-brass derivatives and will be discussed from a different viewpoint below. ~Na₄₄Ir₇ and ~Mg₂Pd remind of ~Cu₃Cd₃ due to the presence of a large number of pentagonal prisms, but contain at least one position with lower coordination numbers, nine and ten, respectively. The ordered variant of the ~Mg₆Pd type has later been observed in the Mg–Ir system with the stoichiometry closer to 7:1—Mg₂₉Ir₄ [76].

4.2. γ-brass superstructures

γ-brass is a class of intermetallics that formally belongs to the Hume–Rothery phases (alloys) whose stability is defined by valence electron concentration and geometric requirements. Historically the name comes from the Cu–Zn alloys having ~33–39 w.% Cu contrary to α, β and other mixed types long before the era of the x-ray structural analysis. Due to its mechanical properties and gold-like appearance, brasses are used in multiple daily applications. The crystal structure of Cu₃Zn₈ was first solved in 1931 [77] and followed by several
isostructural findings whose compositional analysis revealed an empirical 21 valence electrons/13 atoms rule as the electronic stability criterion. Further intensive explorations in the field of intermetallics [16, 78, 79] revealed that γ-brass motifs are not so rare and the stability ranges are not so strict or well-defined. The classical γ-brasses are moderately complex, but the identical structural motifs are base or major building units in a number of CMAs. The classical γ-brass cluster itself can be described with two approaches based on the central tetrahedral core. According to the first one the cluster consists of a central tetrahedron surrounded by a bigger tetrahedron followed by an octahedron and finally a cuboctahedron (figure 2 left). The second one appears more native for homoatomic specimens and consists of four interpenetrating icosahedra around one common tetrahedron (figure 2 right). A detailed overview of the γ-brass cluster distribution in intermetallics has been published recently [80], so we will mainly focus on the main tendencies and peculiarities within the most complex cases.

The majority of these cases contain γ-brass clusters combined with other cluster types, so strict electronic requirements are not applicable in general. The most closely related is γ′-brass—a 2 × 2 × 2 F superstructure with the NaTi type of cluster packing, i.e. polyhedral Zintl phase (see chapter 7). Some of them, in fact, fulfill electronically an extended Zintl phase formalism, e.g. Li32Si15 can be represented as [Li32Si15]+[Li32−xSi15+x]+ [16]. γ′-brass structures may include slightly modified building units including additional, distorted or missing shells including the centered 27 atom bcc type cluster, 29 atom α-Mn type cluster, 22(30) atom clusters with missing(extra) inner tetrahedron etc. The most numerous representatives of this family belong to the Dy4CoCd [81] and the Sm11Cd45 type [82] being on the other hand also the most electron rich. The former almost exclusively consist of γ-brass clusters with single transition metal atoms filling the voids. A truly pure F type γ-brass is observed only in Cu40.5Sn11 type [83] with four compositionally different 26 atoms clusters filling the space. The 26 atom cluster in combination with different clusters (not limited to γ-brass ones) has been observed in a plenty of other F type representatives including the above mentioned Samson phases—Mg8Pd [74], ~Na44Ti7 [73], or Al60Ta39 [70]. The most complex in this group is perhaps Ba16Na29Sn308 type with up to 542 atoms per cell [84]. Competing derivatives with classical 26 atom cluster include a quite represented ThaMn23 [85] and Sc11Ir4 [86] types. It is worth noting that the γ-brass cluster has never been observed for pure metals and is also quite rare in compounds and even more rarely observed as a formally isolated structural fragment. In this light, homoatomic Li26 clusters in Li13Na29Ba19 (~20 000 Å3) and double fused Li icosahedral clusters. The same units are observed in the ternaries Li33:Ba13:Ca3 and Li18:Na8:Ba15.3 (up to 900 atoms per unit cell and over 30000 Å3) [96]. Surprisingly, the role of Ca or Na in these phases can be played by the more electronegative In resulting in the isostructural compound BaLi10.6In1.6 [97]. This example shows how diffuse sometimes the border between formally polar and unpolared formations is. Li feels equally comfortable with both the active metals and the main group elements, but in both cases tends to form homoatomic motifs separated from the rest of the structure where it may also play some roles. The last case in this subgroup, Li13Na29Ba19 (~20000 Å3) [14] shows complete segregation of Li polyicosahedral units forming the γ-brass clusters. All these compounds exhibit coordination numbers from 12 to (rarely) 17 and display the majority of FK type polyhedra. However, due to significant difference in the atomic sizes, larger empty Ba6 octahedra can also be observed.

5. Quasicrystals, approximants and approximant-like structures

After their discovery four decades ago [98], quasicrystals (QCs) received broad recognition and started penetrating various areas of fundamental research and daily applications [99]. Though aperiodic ordering has been observed in a variety of unexpected areas and scales (e.g. in the so called soft QC systems [100–102]), all classical solid state QCs belong almost exclusively to intermetallics, while a few metalloids (Si, Ge and recently Te) can also be involved [103]. Due to practically unlimited unit cells (due to the absence of the translational symmetry) all QCs are by default considered complex. They can be systematized based on the rotational symmetry and thereafter on local structural motifs. Two main classes can be outlined—formations with 3- and 2-dimensional quasiperiodic ordering, each of them containing a number of subgroups. QCs are in turn followed by slightly less complex structurally related but fully crystalline approximant crystals (ACs). The latter serve as useful hints for understanding of the atomic ordering in aperiodic formations and are related to the corresponding quasicrystals according to \( a_{qp} = a_{qp}(p + qτ)/(2 + τ)^3 \) [104], where \( q/p \) (two neighboring Fibonacci numbers) denotes the order of the approximant, and \( τ \) is the golden ratio.
mean \( \tau = (\sqrt{5} + 1)/2 \). So higher are the \( q \) and \( p \), so closer is the atomic ordering to the approaching QC phase, while those of the order 2/1 (and higher) already contain all necessary building units present in QCs.

5.1 3D quasiperiodic formations

3D aperiodic formations or icosahedral quasicrystals can be divided into three main groups based on Bergman (B) [105], Tsai (T) [106] and Mackay (M) [107] type clusters as their core building units. All of them can be represented in terms of multiple endohedral clusters starting from an icosahedron (B and M types, figure 3) or positionally/orientationally disordered tetrahedron (T type, figure 3). Initial studies showed that these three types are quite well separated electronically based on valence electron count, showing just a minor overlap for the B and T types (1.9–2.1 e/a). However, recent discoveries proved the almost complete overlap of their areas of existence [103, 108]. On the other hand, the valence electron count for the transition metals has always been in part controversial leading to somewhat arbitrary numbers. According to this classification QCs fall in the area between the Hume-Rothery alloys and the electron precise Zintl phases sharing the space with a few other groups that will be discussed below. They possess features of all these classes and therefore cannot be strictly assigned to any of them. Chemically, these three types are separated based on the representative elements and their combination and not less important the ‘forbidden’ elements. For example, B and T types are strictly separated by the active metals involved, with Na belonging to the B type and Ca to the T type. On the other hand, the M type always contains either Al or Zn but no electropositive (group I–III) metals. Rare earth metals are, as a rule, representatives of the T type, though can be found in the B type but solely in the simultaneous presence of both Mg and Zn [109, 110]. Li and Mg can (sometimes simultaneously) participate in both the cationic and the anionic substructures and therefore may also be observed in the both B and T types but in different roles [111, 112].

The B type is frequently ascribed to the FK type since its approximants belong to tetrahedrally close packed structures and exhibit identical polyhedra with the coordination numbers 12, 14, 15 and 16, as discussed above, and interestingly all of them in the same structure simultaneously. The vast majority of stable QC phases of this type contain Mg, and a few unique cases were observed with Li [113], Na [103] and in the Zr–Ti–Ni system [114]. The T type has many common features with the B type e.g. identical second and third shells and similar fifth shell but atoms types participating in each of...
them are different (figure 3). The central position is different quantitatively (12 versus 4 atoms) but due to significant orientational disorder the inner tetrahedron in the $T$ type emulates a cuboctahedron moving at least little closer to the $B$ type. The fourth shells are completely different, while the fifth one in the $T$ type can be considered as a complex derivative of the $B$ type. Cluster types in each of these types are identical at the body center and at the origin. The $M$ type in this view is definitely more complex as a clear difference of the origin and the body cluster shells become evident above the third level. Icosidodecahedra at the origin are surrounded by rhombicosidodecahedra sharing triangles with the central icosidodecahedron and preventing its further expansion.

All types’ approximants of the order $1/0$, $1/1$ and $2/1$ are known [115–118], with all of them of the order $1/1$ and higher being complex enough to be considered in this work. A unique $3/2$–$2/1$–$2/1$ approximant has been detected and most important refined solely for the Bergman type [119]. A rhombohedral distortion variant of the $2/1$ approximant of the $T$ type [120] and a tetragonal superstructural variant of the $i$-Li–Cu–Al [121] are also known in Ca$_3$Cd$_{17}$Al and 7–Al$_{56}(\mathrm{Cu,\ Zn})_11\mathrm{Li}_{33}$, respectively. It shall be noted that some of the discovered isostructural phases have never been formally considered as approximants due to missing (not detected) QCs, e.g. Na–Au–Tl phases [122]. On the other hand some systems contain multiple candidates for the approximant position [103]. Limited cases are known where the cluster packing does not allow a clear identification of the approximant type being a combination or a derivative of the known types. For example, Al$_{67}$Pd$_{11}$Mn$_{14}$Si$_7$ [123] and Al$_{67–0.125}$Pd$_{11–0.375}$Mn$_{14–1.25}$Re$_{5}$Si$_8$ solid solution [124] are considered as $1/1$ approximants of the Mackay type QCs; however, a detailed analysis of their cluster shells revealed one cluster sequence being with little exclusions close to the Bergman type while the other one is of a new type starting from an icosahedron followed by cuboctahedral motifs pointing towards a new $M$ subtype. Similar deviations from the classic $M$ type have also been observed in Mo$_7$Sn$_{21}$Zn$_40$/V$_7$Sn$_{12}$Zn$_{40}$ [125, 126] An even more complex case has been observed in Al$_{23.8}$Cu$_{17.7}$Ge$_{50.2}$Pd$_{16}$ containing three different pseudo-Mackay clusters only partially following the shell sequence in the classical Mackay type approximants.

5.2. 2D quasiperiodic structures

2D quasiperiodic structures exhibit in-layer quasiperiodic ordering combined with a periodic stacking of those layers. Multiple symmetry-based subgroups of 2D QCs are known with heptagonal ($h$, 7-), octagonal ($o$, 8-), decagonal ($d$, 10-) and dodecagonal ($dd$, 12-fold) being the most frequently observed. Heptagonal quasicrystals have not been yet experimentally confirmed and the potential approximants include relatively simple borides and carbides [115]. A few octagonal QCs have been detected as metastable phases during rapid solidification [128–131]. One possibly stable dodecagonal QC has been observed for a tantalum telluride [132] and some metastable $dd$ phases were observed in transition metals bulk alloys or thin films [133–135]. A few $dd$-QC approximants have been observed in the same Ta–Te system exhibiting pretty large unit cells with some analogy to the 3D approximants of the different orders [136, 137]. The structural motifs in $dd$-QCs and approximants are represented by squares and equilateral triangles (less frequent empty hexagons due to disorders) with local five- and six-fold centers (figure 4).

The vast majority of the 2D formations belong to the decagonal systems including the historical discovery [98]. Most of them are preferably Al based while Zn- and rarely Ga-based formations could also be observed [115]. Since $d$-QCs are mostly represented by transition and post transition elements, their area of existence partially overlaps with the above-discussed 3D QCs of the $M$ type. $d$-QCs with the broad stability ranges have been observed in two particular systems with the late 3d metals—Al–Ni–Co and Al–Cu–Co, while most others are restricted to nearly point compositions [138]. A completely chemically isolated case is a so-called FK $d$-QC phase in the RE–Mg–Zn systems [139, 140] with Mg$_5$Zn$_7$ [60] serving as the closest crystalline approximant. It is worth noting that RE–Mg–Zn systems are known for the $B$ type $i$-QC phases and particularly in Y–Mg–Zn both $d$ and $i$ phases have been found to coexist [141]. TEM investigation revealed that this $d$-QC form a standard 2-layer model and is best described with the help of additional interstitial layers leading to the observed ~25% increase in the layer thickness [140].

$d$-QC approximant structures (figure 5), in analogy with the corresponding quasicrystals, are also characterized by the layer periodicity (roughly 4A per each pair along the ten-fold axis) and, in analogy with the icosahedral approximants, by the order. With a unique exception, all the structures are orthorhombic or monoclinic with the $\beta$ angle approaching pentagonal $\approx108^\circ$. Most of the structures with 4 and higher layer periodicity satisfy all requirements for complex alloys including various approximants of the orders $1/1$ $1/1$, $2/1$ $1/1$ and $3/2$ $2/1$ [142–145], while certain representatives contain over 500 [146] or even 1000 (Al$_{47}$Cr$_{108}$, Al$_{47}$Cr$_{108}$Cr$_{63}$Fe$_{51}$Al$_{42}$ [31, 145, 147]) atoms per unit cell moving towards the level of complexity of a quasicrystal. A number of Mg$_5$Zn$_7$-related structures, potential $d$-QC approximants has been detected in the systems where actual $d$-QCs has never been found. If Li$_{12.5}$Mg$_{13.5}$Zn$_{39.5}$Al$_{15.1}$ [148] is still in likely expected area
blocks along the c axis (10, 11, 13, 15, 17 and even 27) naturally leading to extremely elongated unit cells with $c/a = 8$ and up to 21. Most of the compounds are well ordered, not at least due to electronic restrictions—14 valence electrons per transition metal [162]. Whereas some solid solubility in both d and p parts can be tolerated it is still strictly controlled by the electronic criteria [158, 163]. Interestingly, these substitutions have been found to follow Fibonacci sequence [163] that is rare besides quasicrystals however was observed in a series with similar building principles—preferentially homoatomic honeycomb Au networks [164]. A detailed investigation of a selected solid solution RuGa$_5$Sn$_8$ $(8 + 3x + 4y = 14)$ revealed by means of electron microscopy that at certain Ga/Sn ratios the unit cell c parameter becomes incredibly large (up to 270 Å) [163] pointing towards either very fine long-range ordering of the third component or to incommensurate modulation.

7. Polyanionic structures in polar intermetallic compounds

Intermetallic compounds with sizeable transfer of the electron density between the constituting elements are usually referred to as polar. Typical examples include binary and multinary phases containing highly electronegative elements, such as alkali, alkaline-earth, or rare-earth metals (the so called ‘active metals’) and metallic or metalloid elements with high electronegativity.

Crystal structures of polar intermetallic compounds can often be formally broken down into cationic and anionic fragments. Whereas the cationic substructure typically comprises isolated cations of the corresponding active metals, the anionic part may display extensive covalent bonding between the chemical species, resulting in polyanions of different dimensionalities. The presence of such structural units frequently yields complex atomic arrangements due to the inherent combination of different bonding patterns within a given crystal structure.

Chemical compositions and structural peculiarities of many polar intermetallic compounds can be rationalized within the Zintl concept, widely used in solid state chemistry [165]. In the frame of this approach, a complete electron transfer is assumed from the atoms of the electropositive metals to the polyanionic part of the structure. In an ideal Zintl phase, such redistribution of electron density leads to a state where all atoms adopt a stable closed shell (octet) electronic configuration. The formation of covalent bonds, i.e. ‘extra’ electron pairs, within the polyanionic substructure serves as a way of saturating the electron count of the bonded atoms. With all the atoms adopting an octet state, the chemical bonding in Zintl phases gets optimized, i.e. there appears an energy gap between the occupied bonding and empty antibonding electronic states. From the physics perspective, this should yield a semiconducting ground state, which is indeed observed for many Zintl phases. The Zintl method offers a simple electron counting scheme, which can be especially efficiently applied to compounds of main group elements and, to some extent, to transition metal-bearing phases [166].
Although polarity of chemical bonding is especially pronounced when highly electropositive and electronegative elements are combined in one compound, polyanions can be formally identified in crystal structures of various intermetallic phases, including the classical CMAs described in the previous chapters. Polyanionic building blocks can adopt atomic arrangements similar to those encountered in common intermetallic types, e.g., gamma brasses [82, 167–169] and FK phases or quasicrystalline phases and approximants [170, 171], even in crystal structures that do not formally belong to these types. The large diversity of possible anionic units gives rise to numerous compositions with unusual crystal structures or even unique structure types. The most complex crystal structures demonstrating polyanions are found with the elements of group 12–15. Giving an overview of all reported polyanionic structures in CMAs is hardly possible and would go beyond the scope of this contribution. Therefore, in the following chapters, we will focus on the main bonding principles leading to structural complexity in intermetallic phases and highlight some of the physical property studies performed for the discussed representatives.

### 7.1. Polyanions of group 12 elements

We start our discussion with polyanions of group 12 elements—Zn, Cd, and Hg. These metals show relatively high electronegativities and often act as electron acceptors when combined with active metals. In addition, they demonstrate a notable tendency to form homoatomic clusters, typically linked together yielding extended 3D polyanions. The complex atomic arrangement in the Samson phase NaCd2, described in chapter 4.1, is an example of this structural chemistry. Another CMA from the same binary system is Na25Cd41 [172]. Although this compound does not demonstrate structural disorder and is apparently a line phase, its primitive hexagonal unit cell accommodates 167 atoms. The Cd species in the structure are strongly interlinked with 6, 8, 9, or 10 nearest neighbors.

Two moderately big families of binary CMAs with group 12 polyanions belong to the Gd18Cd58 [173–182] and Sm11Cd45 structure types [82, 176, 183, 184]. The former can be described as a hexagonal quasicrystalline approximant [182]. This type is adopted by a number of zincides, cadmides, and mercurides. The Sm11Cd45 structure bears similarities with γ-brasses and is observed for some cadmides and mercurides, but has not been reported for Zn compounds. In contrast to the structure of γ-brass, which is made up of 26-atom clusters (figure 2), there are two types of clusters in the structure of Sm11Cd45, composed of 27 and 29 atoms, which makes it an intermediate variant between the structures of Li2Pb5Sb and α-Mn, built up of exclusively 27- and 29-atom clusters, respectively [82]. Similarly to most other polar intermetallic compounds with Zn and its congeners, the anionic substructure in the Sm11Cd45 type can be viewed as a 3D framework.

Other complex binary compounds with extended 3D polyanions of Cd include quasicrystalline approximants Ca13Cd76 [185], Ce3Cd37 [186], and Eu3Cd35 [187].

Among the binary mercurides (amalgams), the two compounds Na8Hg52 [188] and Ba20Hg103 [189] demonstrate especially complex crystal structures. The Na structure can be described as consisting of infinite chains of face-sharing polyhedral clusters encapsulating Na atoms and arranged in a pseudo-hexagonal rod packing [188]. The structure of Ba20Hg103 adopts cubic symmetry and boasts four kinds of fused clusters resembling sodalite cages (truncated octahedra) [189]. Interestingly, both structures display no significant crystallographic disorder and owe their complexity solely to peculiarities of the chemical bonding. Introduction of Cd in the structure of Ba20Hg103 results in an isotypic compound, Ba20Cd5Hg99, whereas inclusion of Zn slightly changes the filling and local arrangement in one of the clusters and yields a different composition, Ba20Zn1Hg99 [189].

Mixing of different group 12 elements can sometimes lead to complex structures not observed for compositions with a single element of this group. Examples of CMAs resulting from partial ordering of the atoms constituting their polyanions are CaZn1.31Hg3.69 [190], crystallizing in the derivative of the B20Hg103 type, and BaZn0.6Hg3.4 [191], adopting a new structure type with a mixed occupied Zn/Hg polyanionic framework related to the Hg substructure in the moderately complex amalgam RbB2Hg25 [191, 192].

In a similar way, addition of an element that does not tend to mix with $M$ ($M = \text{Zn, Cd, Hg}$) or changes the electronic count and thereby affects the chemical bonding can be employed to create multinary CMAs. In this case, partial or complete ordering of $M$ and the extra element in the polyanionic substructure may lead to new topologies. Thus, several binary compounds with relatively simple crystal structures have been reported in the Ca–Zn system. However, a complex ternary intermetallic phase with the composition Ca23Ni12Zn36 can be grown by adding a small amount of Ni to the Ca–Zn melt [28]. In this compound, Zn forms icosahedra around the Ni atoms, decorated by additional Zn atoms and interconnected by Zn–Zn bridges (figure 7).

By introducing Li to the Ca–Zn binary system, two complex structures with the compositions Ca12Li3Zn59,3 and Ca12Li3Zn75,3 can be produced [193]. In the cluster representation, both structures denote different stacking variants of dimers of face-sharing hypho-icosahedra (i.e. icosahedra with three missing vertices each) and trimers consisting of two hypho-icosahedra sandwiching a regular icosahedron.
Even for the binary combinations that are known to form complex structures, transition to ternary and multinary systems upon addition of extra elements proved to be a viable way to produce new CMAs. Introduction of Cu or Al to the Ca–Cd system results in two structures with large unit cells: Ca$_{10}$Cu$_2$Cd$_{27}$ [194] and the already mentioned in chapter 5.1 Ca$_3$AlCd$_{17}$ [120]. Whereas the former composition, crystallizing in a monoclinic superstructure of the 1/1 Bergman approximant, displays atomic sites with mixed and partial occupation, the latter one is well-ordered and represents a rhombohedrally distorted variant of the 2/1 Tsai-type approximant. Other examples of complex ternary structures with group 12 polyanions are occupationally-disordered Na$_{49}$Sn$_{37.5}$Cd$_{58.5}$ [195], displaying empty icosahedral clusters in the structure along with other polyhedral units, and perfectly ordered Ce$_{20}$Mg$_{19}$Zn$_{81}$, related to the structure of Ba$_{20}$Hg$_{103}$ [196].

Geometrical restraints of the polyanionic frameworks may also be used to vary the structural complexity. An illustration of this approach is the structure of K$_{29}$NaHg$_{48}$, which crystallizes differently from the binary Na or K mercurides [50]. Apparently, the significantly mismatching sizes of the K$^+$ and Na$^+$ ions constituting the cationic substructure yield a new atomic arrangement which can efficiently accommodate both types of cations. The structure contains two sorts of Hg$_{12}$ clusters surrounded by isolated K species: icosahedral clusters centered by Na and hexagonal antiprismatic clusters centered by K (figure 8). Magnetization measurements indicate a superconducting transition in this compound at about 2.5 K.

We conclude this chapter with a short mention that the chemistry of Zn and its congeners in the realm of intermetallics is sometimes replicated by Mg. Examples include the isostructural GdMg$_{5+y}$ [197] and (Ce, Y)Mg$_{5+y}$ [198, 199], crystallizing in a defect Sm$_{11}$Cd$_{45}$ variant.

### 7.2. Trielides (Group 13)

Similarly to Zn and its congeners, elements of group 13 (triel, Tr) readily form homoatomic polyanionic moieties. Such anionic structures frequently possess subunits with icosahedral symmetry, which explains another name of triels—‘icosagens’ [200]. The largest number of complex polyanionic structures is found in the intermetallic compounds with triels (such compounds are referred to as trielides). This can be in part explained by the aptness of homoatomic bond formation, high chemical affinity of triels to most elements, including noble metals, ease of substitutional disorder, and low toxicity of all of triels, except...
the heaviest member, thallium Tl, which encouraged their studies. In addition, small spatial requirements for the atoms of the lightest group 13 element, boron B, make it easy to realize different patterns of atomic packings in crystal structures. All this leads to great structural complexity, which is observed even for binary compounds. Furthermore, the crystal structure of the tetragonal and rhombohedral modifications of elemental boron can be classified as complex [201–203]. Both modifications can accommodate some metal atoms, which is sometimes accompanied by formation of defects in the boron framework [204–206]. Some boron-rich binary systems do not adopt intercalated variants of boron modifications, but can be structurally related to them [207–209]. Although, in most of these systems, a high boron to metal ratio makes their description as polyanions impossible, their crystal structures [242]. In contrast to the above-given examples with extended polyanions, another complex gold-containing trielide, Na12K38Tl48Au2, demonstrates isolated all capped trigonal prisms $Tr_{11}$ (figure 9). The formal charge of the latter structural unit implies that the $A_{5}Tr_{11}$ compounds are not electron-balanced, according to the notation (A $^{+}\cdot$)[Tr$_{11}$]$^{3-}$ ($\gamma$), and should show metallic properties, which is observed experimentally [224]. By removing excessive electrons, semiconducting properties can be achieved, e.g. in Cs$_8$Ga$_{11}$Cl, in which Cl adopts a cubic environment of the Cs atoms and is not bonded to any of the Ga species [224]. In contrast, in the ternary derivative Cs$_8$Tl$_{11}$Pd$_x$ ($x \approx 0.8$), the Pd atoms are accommodated inside the Tl$_{11}$ cluster [225].

Mixing of two different triels in the anionic substructure typically results in substitution variants of the binary structure types, as in Na$_{17}$Ga$_{29}$In$_{12}$–20, adopting the K$_7$In$_{41}$ structure [219]. Introduction of an electronegative element from groups 11–12 or 14 either leads to a ternary derivative of a known binary structure (e.g. Na$_{33}$Cd$_3$Ga$_{56}$, Na$_{36}$Ag$_2$Ga$_{73}$, Li$_{18}$Cu$_{3}$_Ga$_{31}$In$_{4}$, and Mg$_{11}$Cu$_6$Al$_{13}$, crystallizing in the K$_{17}$In$_{41}$ type [170, 226–228]) or yields new polyanionic arrangements. The latter option is exemplified by such compositions as Na$_{34}$M$_x$Ga$_{105-x}$ $(M = Cu, Au, Zn)$ [149, 229, 230] and K$_{15}$M$_x$In$_{105-x}$ $(M = Mg, Au, Zn)$ [231, 232], crystallizing isotypically in a rhombohedral distorted variant of the Bergman phase (see chapter 5.1), which can be alternatively described as a stuffed derivative of the $\beta$ modification of boron. Note that Mg behaves here as an analog of the group 12 elements.

It is worth noting that Au appears to serve as an efficient trigger of structural complexity in trielides. Although gold compounds are known to display different sorts of polyanionic units with varying degrees of complexity, most of such phases are not classified as CMAs following the definition used in the present work [164, 233–240]. Yet, many gold-bearing trielides demonstrate exceedingly large unit cells with a high number of atoms. Besides the above-mentioned examples, such compounds are represented by, e.g. Na$_{29}$Au$_{12}$In$_{6}$, containing pentagonal bipyramids Au$_4$Au$_3$In linked by extra Au and In species into a 3D polyanionic framework [150]; Na$_{123}$Au$_{33}$Ga$_{275}$, possessing icosahedral and fused double-icosahedral clusters building a framework by different interconnection modes [241]; and structurally related CsAu$_{14}$Ga$_{33}$ and CsAu$_{12}$Ga$_{6}$, hallmarking by the presence of Au/Ga tetrahedral stars in their crystal structures [242]. In contrast to the above-given examples with extended polyanions, another complex gold-containing trielide, Na$_{12}$K$_{38}$Tl$_{48}$Au$_2$, demonstrates isolated [Tl$_7$]$^{7-}$ and [Tl$_6$]$^{8-}$ clusters, along with isolated monatomic Au$^{+}$ ions [243] (figure 10). Formal charge partitioning results in the electron-balanced formula (Na$^{+}$)$_2$(K$^{+}$)$_{38}$([Tl$_7$]$^{7-}$)$_3$([Tl$_9$]$^{9-}$)$_3$(Au$^{+}$)$_2$. Transport measurements indicate that this compound is a metallic Zintl phase [243].

The latter compound provides an example of another common approach to highly complex structures, which involves combining elements of significantly different atomic sizes in the cationic sublattice. Other relevant examples are the structures of A$_5$Na$_{28}$In$_{48}$ $(A = K, Rb, Cs)$ [244], adopting a defect K$_{29}$Na$_{2}$Hg$_{48}$ type, with interlinked empty In$_{12}$ icosahedra and Na-centered NaIn$_{12}$ hexagonal antiprisms, Li$_8$Na$_{3}$Ga$_{19.56}$ [245] and Rb$_{10}$Na$_{6}$Ga$_{25}$Sn$_{20}$ [246], exhibiting fused double Ga icosahedra, and Na$_{15}$K$_7$Ga$_{80}$, displaying trimeric units of condensed Ga icosahedra [247, 248].

Figure 9. Crystal structure of K$_3$In$_{11}$ viewed along [110] (a) and [001] (b). A close-up view of the [In$_{11}$]$^{11-}$ ion (c). K and In atoms are shown in green and blue, respectively.
Introduction of a transition element in triel-based polyanions may also result in structures satisfying the CMA definition. Thus, the group-10-containing trielides $A_{10}MTR_{10}$ ($A = Na, K; M = Ni, Pd, Pt; Tr = Ga, In$) [249, 250], $Na_{86}M_{2}In_{97}$ ($M = Ni, Pd, Pt$) [251], and $Na_{172}M_{2}In_{197}$ ($M = Ni, Pd, Pt$) [252] all bear transition-metal-centered $MTR_{10}$ clusters. However, whereas these clusters are isolated in the former structure, in the latter two, they are encapsulated within large fullerene-like cages of different composition, based on $Tr$ and $A$ atoms.

A vast family of transition-metal-bearing aluminides $RE_{6}M_{4}Al_{13}$, where $RE$ can be a rare-earth metal, calcium, or uranium and $M$ is an element of groups 4–6 [253–259] represents another example of structural complexity. The crystal structure of the prototypic $Ho_{6}Mo_{4}Al_{13}$ can be described as consisting of fused Ho-centered $Ho_{16}$, and Mo-centered $MoAl_{10}$ and $MoAl_{13}$ polyhedra (figure 11). The polyanionic framework exhibits extensive Al–Al bonding. The rare-earth atoms are located in the vertices of stacked Kagomé nets. Magnetic measurements on some of the representatives indicate competing magnetic interactions, possibly due to the structure-imposed geometric frustration [257, 258].

In the above-given examples of transition-metal-containing trielides, the high triel to transition metal ratio results in large spatial separation between the transition metal atoms. By increasing the transition metal content, metal–metal bonding mediated by overlap of the partially filled d-states can be realized. Complex transition-metal-rich phases with triel-based polyanions include, among others, SrNi$_{2}$In$_{5.1}$, crystallizing in an orthorhombic superstructure of the $NaZn_{13}$ type [260], and the related compounds Ce$_{2}$Rh$_{10}$Ga$_{11}$ and Ce$_{2}$Rh$_{22}$Ga$_{11}$, described as complex intergrowths of $Mg_{2}Cu_{2}$- and CeCo$_{3}$B$_{2}$-type slabs [261].

73. Tetrilides (group 14)

The structural chemistry of polar intermetallic compounds with the group 14 elements (tetrils, $Tt$) resembles that observed in the systems within groups 12 and 13, e.g. formation of extended 3D homoatomic frameworks, as well as shares common structural features with pnictides (compounds with the group 15 elements), e.g. occurrence of polyanionic units of lower dimensionalities. The lightest group 14 element, carbon, is unique in many respects, and the structural chemistry of carbides will not be discussed in this chapter. Homoatomic $Tt–Tt$ interactions in tetrilide polyanions typically occurs via two-center two-electron bonding, which makes it possible to apply the Zintl approach for crystal structure rationalization.

3D polyanions based on homoatomic tetrel networks are represented by numerous cage-like units in binary and multinary systems. Most of such systems belong to the large family of tetril-based clathrates. Several different clathrate types have been identified, with some of them fulfilling the definition of CMAs. Thus, the tetrilides with the composition $A_{x}Tt_{25}$ ($A = K, Ba; Tt = Si, Ge, Sn$) and their ternary and defective variants crystallize in a chiral clathrate structure, displaying fused pentagonododecahedral tetrel cages $Tt_{20}$ [262–271]. Compounds with the general formula $A_{x}Tt_{6x−y}$, ($A = Rb, Cs; Ba; Tt = Ge, Sn$) crystallize in the so-called clathrate I structure with ordered vacancies in the tetrel framework [272–277]. The anionic framework in clathrate I is based on fused 20- and 24-atom $Tt$ polyhedra (figure 12(a)). Ternary derivatives of this superstructure are also known, for instance, $K_{2}LiGe_{44} □_{28}$ [284]. The anionic framework in these compounds comprises tin tetrahedra [34]. In the latter structure, Li occupies atomic positions within the framework. Whereas representatives of the clathrate I and II types (figure 12(b)), having idealized compositions $A_{x}X_{6}$ and $A_{2}X_{136}$, respectively, have been extensively studied, in part due to their possible thermoelectric and electrochemical applicability [278–283], examples of another clathrate structure, type III, with the ideal formula $A_{10}X_{72}$, are scarce. Complex members of this type include $Cs_{80}Na_{13.4}Sn_{172.4}$ and $Cs_{133}Rb_{106}Na_{31.2}Sn_{172.4}$ [284]. The anionic framework in these compounds comprises tin cages of 20, 24, and 26 atoms (figure 12(c)). A related family of compounds, $A_{2}Na_{10}Sn_{23}$ ($A = K, Rb, Cs$), exhibits a clathrate-like structure, with layers of fused $Sn_{20}$ pentagonododecahedra separated by isolated $Sn_{24}$ tetrahedra [265].

A number of binary tetrilides display complex structures without 3D polyanions. Illustrative examples are structurally related $Ca_{31}Sn_{20}$ and $A_{3}Sn_{23}$ ($A = Ca, Yb$), exhibiting isolated $[Sn_{5}]^{6−}$ dumbbells along with $[Sn_{12}]^{13−}$ or $[Sn_{9}]^{14−}$ linear oligomers [285–288]; $Ca_{14}Si_{19}$, with complex quasi-2D Si-based slabs; $A_{4}Ge_{9}$ ($A = Rb, Cs$), with isolated $[Ge_{9}]^{3+}$ clusters [289], and $A_{12}Si_{17}$ ($A = K, Rb$), with isolated $[Si_{5}]^{4+}$ clusters alongside $[Si_{4}]^{5+}$ tetrahedra [290, 291].

Isolated $[Sn_{16}]^{6−}$ clusters are observed in the crystal structure of the complex ternary phases $A_{x}Li_{3}Sn$ ($A = K, Rb$) [292]. The germanide $Li_{3}Na_{2}Ge_{13}$ demonstrates isolated Li-centered $[LiGe_{13}]^{11−}$ units of truncated-tetrahedral shape along with $[Ge_{4}]^{14−}$ tetrahedra [293]. Even more complex isolated units are found in the structure of $Ba_{8}Pb_{2}Sn_{20}$ [294], bearing 56-atom tetramers of fused $Sn_{20}$ pentagonododecahedra [84].

Among ternary tetrilides, one of the most structurally complex family encompasses phases with the general composition $RE_{17}M_{25+2},Tt_{12+2y}$, where $RE$ is a rare-earth metal, $M$ is Cr, Fe, Co, or Ni, and $Tt$ is Ge or Sn [46, 47, 294–306]. All these compounds, despite small structural differences,
crystallize in giant face-centered cubic unit cells with more than 1000 atoms. Due to the structural complexity and disorder, the thermal conductivity of these materials is notably low [2]. Magnetic measurements revealed competing magnetic interactions, resulting in multiple transitions and glassy magnetism [46, 47, 301–306].

A number of rather complex layered structures are known in the quaternary systems $RE$–$TM$–$Tr$–$Tt$ ($RE$ = rare-earth metal, and $TM$ = 3d element) [307] that, however, do not completely satisfy the complexity criteria of this review. Though, upon crystallization from liquid Al, a pseudoternary CMA Er$_{44}$Mn$_{55}$(Al/Si)$_{237}$ can be prepared [48]. In the crystal structure of this material, five symmetrically independent Mn atoms are surrounded by the statistically mixed Al/Si species, with coordination numbers of 6, 8 ($\times 2$), 9, and 11. The corresponding polyhedra
link by corner- and edge-sharing, and by homoatomic (Al/Si) bonds.

7.4. Pnictides (Group 15)

Elements of group 15 (pnictogens, \(Pn\)) frequently form poly-anionic units in their compounds with metals (metal pnictides). Homoatomic clusters or cages are not as common for pnictides as for the elements of groups 12–14, and the occurrence of such building units becomes less typical upon going from the lightest (P) to the heaviest pnictogens (Bi) (note that nitrogen is deliberately excluded from the discussion due to the very different chemistry it exhibits). Examples of pnictide CMAs with isolated cage-like polyanionic blocks include the binary Zintl phases \(A_3As_7\) (\(A = \text{Li, K, Rb}\)) [308–310] and \(A_3Sb_7\) (\(A = \text{Rb, Cs}\)), as well as the solid solution \(K_3As_7-\delta\) [311]. Although they adopt several different structure types, all of these structures accommodate \([Pn_7]^{3-}\) clusters, typically arranged in a close-packed manner. These clusters are isoelectronic and isostructural to the \(P_4S_3\) molecule and can be viewed as consisting of fused pentagonal and trigonal rings. Similar \([As_7]^{3-}\) clusters are observed in the crystal structure of the complex ternary Zintl phase \(Cs_4Zn(As_7)_2\) (figure 13) [312]. In this compound, the Zn atoms are sandwiched between the \(As_7\) units forming isolated \([Zn(As_7)_2]^{4-}\) anions with Zn in distorted tetrahedral environment of the As atoms.

Isolated polyanionic clusters are also observed in the notably complex structure of the isotypic Zintl compounds \(Sr_2Sb_2Pn_4\) (\(Pn = P, As\)) [313, 314]. In this case, though, no \(Pn–Pn\) bonding is taking place, but single bonds between the Sn atoms emerge instead. Ethane-like \(Sn_2Pn_6\) units in staggered conformation link by sharing the \(Pn\) vertices to form isolated six-membered rings \([Sn_{12}Pn_{24}]^{16-}\), comprising the anionic substructure.

This example demonstrates that the aptness of some \(p\) elements to form homoatomic bonds can be successfully employed to provide an extra degree of complexity to polyanions in pnictides. Other examples of CMAs resulting from the application of this strategy include \(Eu_7Ga_5Sb_8\) (Ga–Sb + Ga–Ga bonds) [315] and \(K_8In_5Ge_5As_{17}\) (Ge–As + In–As + Ge–Ge + As–As bonds) [316], both showing quasi-2D polyanionic slabs in their crystal structures. Cage-like 3D anionic frameworks hallmarked by extensive disorder were found in the crystal structure of \(Ba_{23}(M_{1-x}Ge_x)_{20}Sb_{25-\delta}\) (\(M = \text{Ga, In}\), which can be regarded as a derivative of the clathrate-I type [45]. Structural complexity and defect-driven disturbance of periodicity result in glass-like thermal conductance in these compounds, with the lattice thermal conductivity as low as 0.2–0.4 \(W m^{-1} K^{-1}\) in the temperature range between 323 and 823 K.

The clathrate-I type atomic arrangement can also be realized in the form of a complex orthorhombic superstructure adopted by coinage-metal-bearing pnictide clathrates \(Ba_8M_{16}P_{30}\) (\(M = \text{Cu, Au}\)) [317, 318]. Similarly to other clathrates and related cage compounds, these materials exhibit inherently low thermal conductivity. By proper chemical doping, the thermoelectric figure of merit \(ZT\) in these phases can be increased up to about 0.6 at \(T \approx 800\) K [319].

While homoatomic polyanionic cages are rare in pnictides, extended linear or 2D homoatomic moieties are frequently observed [320–322]. In some cases, packing effects or electronic instabilities, e.g. Peierls distortion, result in structural breakdown of the propagating chains or sheets with the decrease of dimensionality and the formation of isolated building blocks, such as linear or bent oligomers or polyatomic rings. First-principle calculations indicate that the tendency of the homoatomic extended pnictides structures to

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**Figure 13.** Crystal structure of \(Cs_4Zn(As_7)_2\) (a) and an isolated \([Zn(As_7)_2]^{4-}\) unit (b). Cs, Zn, and As atoms are shown in green, blue, and brown, respectively.
undergo spontaneous bond length alternation is correlated with the extent of the s-p orbital mixing and diminishes upon going down the group [321, 323].

A good illustration of this trend is the large and actively studied family of pnictides with the general composition $A_{14}MnPn_{11}$ ($A = Ca, Sr, Ba, Yb, Eu; M = Al, Ga, In, Mg, Mn, Zn, Cd; Pn = P, As, Sb, Bi$) [324–348]. They all crystallize in the Ca$_{14}$AlSb$_{11}$ type and possess three types of anions in their crystal structure—isolated tetrahedral $[MPn_4]^{10-}$, linear $[Pn_3]^{7-}$, and monatomic $Pn^{3-}$ units (figure 14). In the case of trivalent $M$ atoms, such as Al, Ga and In, the composition is formally electron-balanced, $(A^{2+})_4[MPn_4]^{10-}[Pn_3]^{7-}[Pn^{3-}]_4$, and hence shows semiconducting behavior, in line with the predictions of the Zintl approach. In contrast, for divalent $M$ species, an electron–hole $(h^+)$ appears, causing metallic behavior: $(A^{2+})_4[MPn_4]^{10-}[Pn_3]^{7-}[h^{+}]_4$. A noteworthy structural moiety in $A_{14}MnPn_{11}$ is the linear anion $[Pn_3]^{7-}$. Theoretical calculations indicate that the chemical bonding in this anion is of hypervalent (i.e. electron-rich) type, and $[Pn_3]^{7-}$ can be classified as four-electron three-center species. Whereas this species is undistorted in the crystal structure of antimonides and bismuthides and displays ideal point group symmetry $D_{x,y}$, it tends to split into a monatomic $Pn^{3-}$ ion and a single-bonded $[Pn_2]^{14-}$ dumbbell in the structures of phosphides and arsenides. Note that the transformation $[Pn_3]^{7-} \leftrightarrow Pn^{3-} + [Pn_2]^{14-}$ does not involve any changes of the electron count, and a single structure can accommodate a certain ratio of both forms, with them being statistically disordered.

The complex crystal structure of the $A_{14}MnPn_{11}$ leads to a low thermal conductivity in these phases, similarly to other CMAs. By optimization of the charge carrier concentration, high values of electrical resistivity and Seebeck coefficient can be achieved, resulting in good thermoelectric performance at high temperatures [349, 350]. Thus, Yb$_{14}$MnSb$_{11}$ is considered one of best thermoelectric materials for $T > 1000\,K$ with a dimensionless figure of merit, $ZT$, of about 1.0 in this temperature region [22]. In addition, magnetic properties of the Mn-containing representatives of this family have been actively studied. Most of the antimonide and bismuthide members were found to order ferromagnetically at temperatures $T \approx 35–65\,K$ and display colossal magnetoresistance, with the latter being related to nearly half-metallic band structures in these phases [329, 339, 341–343, 351–354]. Introduction of additional magnetic species, e.g. rare-earth ions, lead to emergence of new magnetic interactions and give rise to various low-temperature phenomena, such as glassy magnetic transitions and magnetic clustering [49, 355, 356].

Recognition of Zintl pnictides as potential materials for high-temperature power generation has resulted in discovery of many new complex structures with polyanionic units. The two isotypic phases Ba$_2$Cd$_3$Sb$_8$ [357] and Eu$_2$Zn$_3$Sb$_8$ [358] belong to this group of materials and display exceedingly sophisticated mode of the polyanion construction (figure 15). Besides the isolated (i.e. not bonded to the transition metal atoms) Sb$^{3-}$ and [Sb$_2$]$^{3-}$ units, the structure contains oligomeric polyanions $[M_xSb_{12}]^{26-} (M = Cd, Zn)$ consisting of four edge- and corner-sharing $MSb_4$ tetrahedra and terminated by a ‘dangling’ Sb–Sb dumbbell.

Many metal pnictides display various combinations of anionic subunits within one crystal structure, which naturally leads to high complexity of the atomic arrangements. In addition, compounds of pnictogens with transition metals (TM) can be stabilized by direct TM–TM interactions of two-center or multicenter character, realized via the $d$-electrons from the TM penultimate shells. In the realm of Zintl phases, this principle is exemplified by the ternary arsenides $K_{3x}Nb_7As_{3x}$ and $Cs_{6x}Nb_3As_6$ [359]. The anionic substructure of the former compound accommodates isolated $[NbAs_4]^{10-}$ tetrahedra and $[Nb_2As_6]^{30-}$ dimers of edge-sharing tetrahedra. Similar dimers serve as the unique polyanionic type in the structure

![Figure 14](https://example.com/figure14.png)

*Figure 14.* Crystal structure of the Ca$_{14}$AlSb$_{11}$ type (left). Ca, Al, and Sb atoms are shown in green, blue, and brown, respectively. A close-up view of the hypervalent $[Pn_3]^{7-}$ anion (top right) and its distortion to $[Pn_2]^{14-}$ and $Pn^{3-}$ anions upon going to lighter pnictogens (bottom right).
of Cs₆Nb₂As₆. The Nb atoms in these dimeric units have an average oxidation state of +4.5. One unpaired electron which provides unusual chemical bonding between the Nb atoms in the dimer reveals itself in the magnetization measurements, which show expected paramagnetic behavior.

Within the group of pnictides displaying metallic properties, a number of polar transition-metal-rich phosphides and arsenides adopting complex crystal structures are known. Typical representatives include $\text{RE}_6\text{Rh}_{32}\text{P}_{17}$ ($\text{RE} = \text{La, Ce}$) [360], $\text{RE}_{25}\text{Ni}_{49}\text{P}_{33}$ ($\text{RE} = \text{Ce–Nd, Sm, Gd–Er}$) [361], $\text{RE}_12\text{Fe}_{57.5}\text{As}_{41}$ ($\text{RE} = \text{La, Ce}$) [362], and others. All of them show extensive metal–metal bonding.

A notable case of pnictide CMAs with extended poly-anions are the structurally similar compounds $\text{Ba}_2\text{Mn}_{1-x}\text{Bi}_2$ ($x \approx 0.15$) and $\text{Ba}_2\text{Zn}_{1-x}\text{Sb}_2$ ($x \approx 0.3$) [363]. Both structures demonstrate transition-metal centered $\text{Pn}$ coordination polyhedra linked in various modes to form star-like subunits propagating in one direction. In addition, homoatomic two-center and hypervalent $\text{Pn–Pn}$ bonding is observed. However, whereas $\text{Ba}_2\text{Mn}_{1-x}\text{Bi}_2$ ($x \approx 0.15$) represents a highly-reduced compound with an average Mn oxidation state of about +1.5 and is expected to be metallic, $\text{Ba}_2\text{Zn}_{1-x}\text{Sb}_2$ ($x \approx 0.3$) nearly conforms to the perfect Zintl electron count and exhibits a (pseudo)gap in its electronic spectrum.

8. Summary

The present contribution summarizes basic underlying mechanisms causing the emergence of CMAs. Structural complexity in intermetallic systems is a frequently observed phenomenon originating from compositional or chemical bonding inhomogeneities. The driving forces for the formation of CMAs is the optimization of atomic packing, e.g. by release of geometrical strains and fulfilling dense occupation of space, or enhancement of chemical bonding interactions by electronic optimization. The former usually involves alleviation of crystallographic defects by, e.g. complete or partial ordering of distinct chemical species or realization of certain stacking sequences of akin building blocks. In chemistry, the concept of ‘chemical pressure’ has been widely used to rationalize such phenomena [38, 39]. Optimization of chemical bonding commonly results in separation of a crystal structure into regions with different patterns of interactions, such as two-center and multi-center bonds, or chemical bonding with different degrees of polarity [40–42]. The latter allows description of certain crystal structures in terms of polyanions. Elements of group 12–15 are the most common constituents of anionic building fragments in intermetallics, as they easily form chemical bonds with many elements and may show homooatomic bonding as well. Upon going from group 12 to group 15, the tendency to form extended 3D polyanionic units becomes less pronounced, leading to structural moieties of lower dimensionalities. In such cases, particular chemical bonding patterns may propagate along specific crystallographic directions, creating ‘chemical bonding anisotropy’ [364]. Recognition of repeating structural units or templates in CMAs allow reduction of their complex atomic arrangements to simpler known structures, which sometimes requires employment of methods inherited from mathematical topology, graph-theoretical approaches or number theory [21, 188, 200, 365]. At the same time, developments in computational methods make first-principle calculations on complex intermetallics more and more feasible. Yet, satisfactory theoretical description of exceptionally complex representatives remain problematic, as such compounds challenge the approaches of classic crystallography implemented in computational algorithms. Even determination of their structures often calls for the use of large-scale facilities, such as synchrotron sources, as laboratory equipment is often not capable of providing complete data [7]. As the scales of periodicity start exceeding interatomic distances significantly, the properties of such compounds become similar to those of glass-like materials. This trend is reflected in low thermal conductivity and glassy
magnetic behavior in some of the reported measurements [2, 45, 47]. CMAs offer therefore a platform for design of new thermoelectric and magnetically frustrated systems. Although at present, detailed physical properties are not available for many CMAs, with the advancement of experimental and theoretical methods, investigations in this hard-to-tackle yet prolific family of materials may bring new fascinating results.

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References
[1] Dubois J-M and Belin-Ferré E 2011 Complex Metallic Alloys: Fundamentals and Applications (Weinheim: Wiley)
[2] Schmitt D C, Haldolaarachchige N, Xiong Y, Young D P, Jin R and Chan J Y 2012 Probing the lower limit of lattice thermal conductivity in an ordered extended solid: Gd14.5Co34.5Sn12, a phonon glass–electron crystal system J. Am. Chem. Soc. 134 5965–73
[3] Samson S 1962 Crystal structure of NaCd2 Nature 195 259–62
[4] Samson S 1965 The crystal structure of the phase β-Mg2Al3 Acta Crystallogr. 19 401–13
[5] Samson S 1967 The crystal structure of the intermetallic compound Cu3Cd, Acta Crystallogr. 23 586–600
[6] Dshemuchadse J and Steurer W 2015 Some statistics on intermetallic compounds Inorg. Chem. 54 1120–8
[7] Weber T, Dshemuchadse J, Kobas M, Conrad M, Harbrecht B and Steurer W 2009 Large, largest—a family of cluster-based tantalum copper aluminides with giant unit cells. I. Structure solution and refinement Acta Crystallogr. B 65 308–17
[8] Brgoch J, Yeninas S, Prozorov R and Miller G J 2010 Structure, bonding, and magnetic response in two complex borides: Zr2Fe1+1Ru5+1B2 and Zr2Fe1+1Ru1+1Rh1+1B2 J. Solid State Chem. 183 2917–24
[9] Deringer V L, Goerens C, Esters M, Dronskowski R and Fokwa B P T 2012 Chemical modeling of mixed occupations and site preferences in anisotropic crystal structures: case of complex intermetallic borides Inorg. Chem. 51 5677–85
[10] Zaikina J V, Schellenberg I, Benbow E M, Pöttgen R and Latturner S E 2011 Influence of the La/M network on magnetic properties of Mn4 tetrahedra in intermetallic compounds La23–xMn8MxC12 (M = Ge, Sn, Sb, Te, Bi) Chem. Mater. 23 1768–78
[11] Guo Y and Fredrickson D C 2016 On the functionality of complex intermetallics: frustration, chemical pressure relief, and potential rattling atoms in Y11Ni6Co4 Inorg. Chem. 55 10397–405
[12] Smetana V, Babizhetskyy V, Vajenine G V and Simon A 2008 Darstellung und Kristallstruktur der Phasen Li112Na52B30E12 (E = N, H, x = 0–1) Z. Anorg. Allg. Chem. 634 489–52
[13] Ovchinnikov A, Bobnar M, Prots Y, Bornmann H, Sichelschmidt J, Grin Y and Höhn P 2018 Ca12[Mn20N51] and Ca113[Mn20N60]: structural complexity by 2D intergrowth Angew. Chem., Int. Ed. 57 11579–83
[14] Smetana V, Babizhetskyy V, Vajenine G V and Simon A 2006 Li14B9N6: the first Li/Ba subnitride Inorg. Chem. 45 10786–9
[15] Goward G R, Taylor N J, Souza D C S and Nazar L F 2001 The true crystal structure of Li12M4 (M = Ge, Sn, Pb)–revised from Li25M5 J. Alloys Compd. 329 82–91
[16] Nesper R and von Schniering H G 1987 Li25Si13, a Zintl phase as well as a Hume–Rothery phase J. Solid State Chem. 70 48–57
[17] Mizutani U, Asahi R, Sato H, Noritake T and Takeuchi T 2008 Failure of the Hume–Rothery stabilization mechanism in the Ag3Li gamma-brass studied by first-principles FLAPW electronic structure calculations J. Phys.: Condens. Matter 20 275228
[18] Vrtnik S, Jazbec S, Jagodič M, Korelec A, Hoslar N, Jagličiž Z, Jeliči J, Feuerbacher M, Mizutani U and Dolinšek J 2013 Stabilization mechanism of γ-Mg21Al12 and β-Mg2Al complex metallic alloys J. Phys.: Condens. Matter 25 425703
[19] Zhuang H L, Chen M and Carter E A 2018 Orbital-free density functional theory characterization of the β-Mg2Al3 Samson phase Phys. Rev. Mater. 2 073603
[20] Mizutani U and Sato H 2017 The Physics of the Hume–Rothery electron concentration rule Crystals 7 9
[21] Akhmetshina T G, Blatov V A, Proserpio D M and Shevchenko A P 2018 Topology of intermetallic structures: from statistics to rational design Acc. Chem. Res. 51 21–30
[22] Brown S R, Kauzlarich S M, Gascoin F and Snyder G J 2006 Three-dimensional reconstruction of the electron crystal system Z. Anorg. Allg. Chem. 634 55–103
[23] Goward G R, Taylor N J, Souza D C S and Nazar L F 2001 Interaction of lanthanum or cerium with nickel and arsenic: phase diagrams and structural chemistry Three-dimensional reconstruction of the electron crystal system J. Alloys Compd. 329 82–91
[24] Veremchuk I, Beekman M, Antonyshin I, Schnelle W, Baitinger M, Nolas S G and Grin Y 2016 Binary alkali–metal silicon clathrates by spark plasma sintering: Preparation and characterization Materials 9 593
[25] Stoianovic M and Latturner S E 2007 Growth of new ternary intermetallic phases from Ca/Zn eutectic flux J. Solid State Chem. 180 907–14
[26] Roslova M et al 2017 Synthesis of a Cu-filled Rh2Si3 framework: microwave poloyl process versus high-temperature route Inorg. Chem. 56 11513–23
[27] Babizhetskyy V, Le Sénéchal C, Bauer J, Depeyrier S and Guérin R 1999 Interaction of lanthanum or cerium with nickel and arsenic: phase diagrams and structural chemistry J. Alloys Compd. 287 174–80
[28] Zou X D, Mo Z M, Hovmöller S, Li X Z and Kuo K H 2003 Three-dimensional reconstruction of the n-AlCrFe phase by electron crystallography Acta Crystallogr. A 59 526–39
[29] Sieve B, Chen X Z, Henning R, Brazis P, Kannewurf C R, Cowen J A, Schultz A J and Kanatzidis M G 2001 Cubic aluminum silicides Rh2Ru12Al2Sb6(Al,Si)12–x (RE = Pr, Sm) from liquid aluminum. Empty (Si, Al)12 cuboctahedral
clusters and assignment of the AI/Si distribution with neutron diffraction J. Am. Chem. Soc. 123 7040–7
[33] Tucker P C, Nyeifer J, Chen B, Orazowski A, Stilwell R and Luttner S E 2012 A tale of two metals: new cerium iron borocarbide intermetallics grown from rare-earth/transition metal eutectic fluxes J. Am. Chem. Soc. 134 12138–48
[34] Liang Y, Carrillo-Cabrera W, Ormeci A, Böhme B, Baitinger M and Grin Y 2015 The 200 × 200 × 200 superstructure in the clathrate-I. KLi4Ge41–xAlx41–3x Z. Anorg. Allg. Chem. 641 339–47 K 1900
[35] Mizutani U, Matsuda T, Itoh Y, Tanaka K, Domae H, Mizuno T, Murasaki S, Miyoshi Y, Hashimoto K and Yamada Y 1993 Electronic structure and electron transport properties of quasicrystals and approximant crystals in Al−TM and Mg−Ga−Al−Zn alloy systems J. Non-Cryst. Solids 156–8 882–8
[36] Takeuchi T and Mizutani U 1995 Electronic structure, electron transport properties, and relative stability oficosahedral quasicrystals and their 1/1 and 2/1 approximants in the Al−TM and Mg−Ga−Al−Zn alloy systems J. Non-Cryst. Solids 156–8 882–8
[37] Feuerbacher M et al 2007 The Samson phase, β-Mg2Al3, revisited Z. Kristallogr. 222 259–88
[38] Osman H H, Salvadó M A, Perttierra P, Engelkemier J, Fredrickson D C and Recio J M 2018 Chemical pressure maps of molecules and materials: merging the visual and physical in bonding analysis J. Chem. Theory Comput. 15 104–14
[39] Fredrickson D C 2018 Parallels in structural chemistry between the molecular and metallic realms revealed by complex intermetallic phases Acc. Chem. Res. 51 248–57
[40] Steinberg S and Drönskowski R 2018 The crystal orbital Hamilton population (COHP) method as a tool to visualize and analyze chemical bonding in intermetallic compounds Crystal 8 225
[41] Savin A, Nesper R, Wengert S and Fassler T F 1997 ELF: the electron localization function Angew. Chem., Int. Ed. 36 1808–32
[42] Wagner F R, Kohout M and Grin Y 2008 Direct space decomposition of ELI-D: interplay of charge density and pair-volume function for different bonding situations J. Phys. Chem. A 112 9814–28
[43] Mehrer H 1996 Diffusion in intermetallics Mater. Trans., JIM 37 1259–80
[44] Wang W H, Dong C and Shek C H 2004 Bulk metallic glasses Mater. Sci. Eng. R 44 45–89
[45] Pan M-Y, Qi H-J, Liu X-C, Bai M-C and Xia S-Q 2018 Ultralow lattice thermal conductivity in Ba23M10Ge90Sb156 (M = Ga, In): quaternary compounds containing Ba-centered dodecahedral Chem. Mater. 30 4713–20
[46] Liu J, Mudryk Y, Zou J D, Pecharsky V K and Gschneider K A 2014 Antiferromagnetic cluster spin-glass behavior in Pr1.16Ca0.85Sn1.55, a compound with a giant unit cell J. Alloys Compd. 600 101–6
[47] Liu J, Xie W, Gschneider K A, Miller G J and Pecharsky V K 2014 Spin-glass behavior in a giant unit cell compound Tb1.1Fe625Ge315K1 J. Phys.: Condens. Matter 26 416003
[48] Caha P and Kanatzidis M G 2013 Quaternary aluminum silicones grown in Al flux: RE2M10Al12M6S4 (RE = Ho, Er, Tb) and Eu2Mn6S6(AlSi)24 Inorg. Chem. 52 9931–40
[49] Ovchinnikov A, Prakash J and Bobev S 2017 Crystal chemistry and magnetic properties of the solid solutions Ca14-xRE2MnBi11 (RE = La–Nd, Sm, and Gd–Ho; x ≈ 0.6–0.8) Dalton Trans. 46 16041–9
[50] Deiseroth H-J and Biebl E 1999 Na30K5H9Ga15: a contradiction to or an extension of theoretical concepts to rationalize the structures of complex intermetallics? J. Solid State Chem. 147 177–84
[51] Dutour Sikirić M, Delgado-Friedrichs O and Deza M 2010 Space fullerenes: a computer search for new Frank–Kasper structures Acta Crystallogr. A 66 602–15
[52] Shoemaker C B and Shoemaker D P 1967 The crystal structure of the M phase, Nb–Ni–Al Acta Crystallogr. 23 231–8
[53] Brink C and Shoemaker D P 1955 A variation on the σ-phase structure: the crystal structure of the P phase, Mo–Ni–Cr Acta Crystallogr. 8 734–5
[54] Komura Y, Sfy W G and Shoemaker D P 1960 The crystal structure of the R phase, Mo–Co–Cr Acta Crystallogr. 13 575–85
[55] Yafel H 1983 Atom distributions in sigma phases. I. Fe and Cr atom distributions in a binary sigma phase equilibrated at 1063, 1013 and 293 K Acta Crystallogr. B 39 20–8
[56] Bardos D I, Gupta K P and Beck P A 1961 New ternary R-phases with silicon Nature 192 744–5
[57] Samson S and Gordon E K 1968 The crystal structure of ε-Mg23Al16 Acta Crystallogr. B 24 1004–13
[58] Ormeci A, Simon A and Grin Y 2010 Structural topology and chemical bonding in Laves phases Angew. Chem., Int. Ed. 49 8997–9001
[59] Simon A, Brämer W, Hillenkötter B and Kullmann H-J 1976 Neue Verbindungen zwischen Kalium und Cäsium Z. Anorg. Allg. Chem. 419 253–74
[60] Yarmolyuk Y P, Kripayevich P and Mešnik E 1975 Crystal structure of the compound Mg2Zn Acta Crystallogr. 50 538–42
[61] Pavlyuk V, Dmytriv G, Tarasiuk I, Pauly H and Ehrenberg H 2008 Li8Cu121-xAl1x (x = 1.16): a new structure type related to Laves phases Acta Crystallogr. C 64 115–17
[62] Friauf J B 1927 The crystal structure of magnesium di-zincide Phys. Rev. 29 34–40
[63] Shoemaker C B and Shoemaker D P 1977 The crystal structure and superstructure of the K phase, Mn17Fe9Si9 Acta Crystallogr. B 33 743–54
[64] Manor P C, Shoemaker C D and Shoemaker D P 1972 The crystal structure of the X phase (Mn, Co, Si) Acta Crystallogr. B 28 1211–8
[65] Yarmolyuk Y P, Kripayevich P and Gladyshevsky E 1970 Crystal structure of the X-phase in the Mn–Co–Si system Sov. Phys. Crystallogr. 15 226–30
[66] Shoemaker C B and Shoemaker D P 1981 The structure of the I phase, V4Al2Ni2Si23, a pseudo superstructure Acta Crystallogr. B 37 1–8
[67] Khan A U, Gytis A, Yan X, Rogl P, Saccone A, Pomjakushin V and Giester G 2011 Phase relations and crystal structure of τ6-Ti6(Al0.43Si0.57) Inorg. Chem. 50 4537–47
[68] Hlukhy V and Pöttgen R 2004 Mg21–xIr3x (x = 0.30)–a binary variant of the monoclinic α2(2Co0.63Si0.37) type Solid State Sci. 6 1175–80
[69] Černý R and Renaudin G 2002 The intermetallic compound Mg21Zn24 Acta Crystallogr. C 58 1154–58
[70] Mahne S and Harbrecht B 1994 Al0.6Ta0.4–a new variant of a face-centred cubic giant cell structure J. Alloys Compd. 203 271–9
[71] Samson S 1958 The crystal structure of the intermetallic compound Mg3Cr2Al18 Acta Crystallogr. 11 851–7
[72] Samson S 1961 The crystal structure of the intermetallic (Y) compound Zr2X2 Acta Crystallogr. 14 1229–36
[73] Samson S and Hansen D A 1972 Complex cubic A15 compounds. I. The crystal structure of Na5Ti Acta Crystallogr. B 28 930–5
[74] Samson S 1972 Complex cubic A15 compounds. II. The crystal structure of Mg5Pd Acta Crystallogr. B 28 936–45
[75] Westin L and Edshammer L-E 1972 Crystal structure of IrMg44 Acta Chem. Scand. 26 3619–26
[76] Bonhomme F and Yvon K 1995 Cubic Mg73Ir43A11 crystallizing with an ordered variant of the Mg74Pd-type structure J. Alloys Compd. 227 L1–3
J. Phys.: Condens. Matter 32 (2020) 243002

[77] Bradley A J and Gregory C H 1931 IX. A comparison of the crystal structures of CuZn60 and CuCd60. Phil. Mag. 12 143–62

[78] Noritake T, Aoki M, Towata S-i, Takeuchi T and Mizutani U 2007 Structure determination of structurally complex A15Li64 gamma-brass Acta Crystallogr. B 63 726–34

[79] Brandon J K, Pearson W B, Riley P W, Chieh C and Stokhuyzen R 1977 γ-brasses with R cells Acta Crystallogr. B 33 1088–95

[80] Pankova A A, Blatov V A, Ilyushin G D and Proserpio D M 2006 γ-brass polyhedral core in intermetallics: the nanocluster model Inorg. Chem. 52 13094–107

[81] Dogan A, Rayaprol S and Pöttgen R 2007 Structure and magnetic properties of RE2CoCd and RE2RhCd (RE = Tb, Dy, Ho) J. Phys.: Condens. Matter 19 0976213

[82] Fornasini M L, Chabot B and Parthé E 1978 The crystal structure of Sm12Ca45 with γ-brass and α-Mn clusters Acta Crystallogr. B 34 2093–9

[83] Booth M H, Brandon J K, Brizard Y R, Chieh C and Pearson W B 1977 γ-brasses with F cells Acta Crystallogr. B 33 30–6

[84] Bobev S and Sevov S C 2002 Naked clusters of 56 tin atoms in the solid state J. Am. Chem. Soc. 124 3359–65

[85] Nyman H and Andersson S 1979 On the structure of Mn5Si3, Th4Mn23 and γ-brass Acta Crystallogr. A 35 380–3

[86] Chabot B, Cenzual K and Parthé E 1980 Sc11Ir3, Sc11Os3, Sc11Ru3, and Zr11Os3 with a new cubic structure type described by means of a cluster concept Acta Crystallogr. B 36 7–11

[87] Smetana V, Babizhetskyy V, Vajenine G V and Simon A 2006 Li22 clusters in the compound Li11Na29Ba19 Acta Crystallogr. C 62 611–7

[88] Rollier M A and Arreghini E 1994 (Fe, Ni)Zn6.5, a Colloidal quasicrystals with 12-fold and 18-fold diffraction symmetry Proc. Natl Acad. Sci. 100 1810–4

[89] Smetana V, Lin Q, Pratt D K, Kreyssig A, Ramazanoglu M, Corbett J D, Goldman A I and Miller G J 2012 A sodium-containing quasicrystal: using gold to enhance sodium’s covalency in intermetallic compounds Angew. Chem., Int. Ed. 51 12699–702

[90] Brandon J K and Kelton K F 1993 Rev. Mod. Phys. 65 213–30

[91] Bergman G, Waugh J L T and Pauling L 1957 The crystal structure of the metallic phase Mg17Al12 Acta Crystallogr. 10 254–9

[92] Obrowski W 1963 Alloys of ruthenium with boron, beryllium and aluminium Metall (Berlin) 17 108–12

[93] Brandon J K, Kim H S and Pearson W B 1979 The crystallographic analysis of InMn3, a new form of γ-brass structure with a P cell Acta Crystallogr. B 35 1937–44

[94] Lidin S, Jacob M and Larson A-K 1994 (Fe, Ni)Zn6.5, a superstructure of γ-brass Acta Crystallogr. C 50 340–2

[95] Smetana V, Babizhetskyy V, Hoch C and Simon A 2006 Refinement of the crystal structure of barium tetralithium, superstructure of γ–brass Polyhedron 25 533–40

[96] Pham J, Meng F, Lynn M J, Ma T, Kreyssig A, Kramer M J, Goldman A I and Miller G J 2018 From quasicrystals to crystals with interpenetrating icoshedra in Ca–Al–Mg in situ variable-temperature transformation J. Am. Chem. Soc. 140 1337–47

[97] Brühne S, Uhlrich G, Kreiner G and Assmus W 2006 Local atomic three-dimensional real-space structural analysis of icosahedral Mg–Zn–Re (RE = Y or Ho) alloys: strategy, method and models Phil. Mag. 86 463–8

[98] Nikiura B A, Tsai A P, Inoue A and Masumoto T 1994 Stable Zn–Mg–rare-earth face-centred icosahedral alloys with pentagonal dodecahedral solidification morphology Phil. Mag. Lett. 69 351–5

[99] Ishimasa T, Kaneko Y and Kaneko H 2002 A Zn-based icosahedral quasicrystal classified into the same structure type as Cd-based icosahedral quasicrystals? J. Alloys Compd. 342 123–7

[100] Guo J, Abe E and Tsai A 2000 Stable icosahedral quasicrystals in the Cd-based alloys MRS Online Proc. Library Archive 643

[101] Shen Y, Poon S J, Dmowski W, Egami T and Shiflet G J 1987 Structure of Al–Li–Cu icosahedral crystals and Penrose tiling Phys. Rev. Lett. 58 1440–3

[102] Yi S and Kim D 2000 Stability and phase transformations of icosahedral phase in a 41.5Zr41.5Ti17Ni alloy J. Mater. Res. 15 892–7

[103] Steurer W and Deloudi S 2009 Crystallography of Quasicrystals: Concepts, Methods and Structures vol 126 (Berlin: Springer)

[104] Pham J, Kreyssig A, Goldman A I and Miller G J 2016 An icosahedral quasicrystal and its 1/0 crystalline approximant in the Ca–Au–Al system Inorg. Chem. 55 10425–37

[105] Dubois J-M 2012 Properties and applications of quasicrystals and complex metallic alloys Chem. Soc. Rev. 41 6760–77

[106] Iwahara M, Kihara K and Horiuchi T 1991 Superconductivity of the element Ga and its alloys with Zn, In, and Sn J. Solid State Chem. 87 138–43
comparison with the Al–Ni–Co system Phil. Mag. Lett. 77 205–11

[140] Sato T J, Abe E and Tsai A P 1998 Composition and stability of decagonal quasicrystals in the Zn–Mg–rare-earth systems Phil. Mag. Lett. 77 213–9

[141] Yi S, Park E S, Ok J B, Kim W T and Kim D H 2002 Quasicrystals and related approximate phases in Mg–Zn–Y Micron 33 565–70

[142] Grin Y, Burkhart U, Ellner M and Peters K 1994 Crystal structure of orthorhombic CoAl13 J. Alloys Compd. 206 243–7

[143] Matsuo Y, Kaneko M and Yamanou T 1997 The structure of an Al3Mn-type Al3(Mn, Pd) crystal studied by single-crystal x-ray diffraction analysis Phil. Mag. Lett. 76 357–62

[144] Matsuo Y and Hiraga K 1994 The structure of Al3Pd: close relationship to decagonal quasicrystals Phil. Mag. Lett. 70 155–61

[145] Zhang B, Li X Z, Steurer W, Schneider J and Frey F 1995 New crystalline approximant of the decagonal quasicrystal in Al–Pd–Ru alloy Phil. Mag. Lett. 72 239–44

[146] Sugiyama K, Nishimura S and Hiraga K 2002 Structure of a W–(AlCoNi) crystalline phase related to Al–Co–Ni decagonal quasicrystals, studied by single crystal x-ray diffraction J. Alloys Compd. 342 65–71

[147] Mo Z M, Zhou H Y and Kuo K H 2000 Structure of a1-Al50.8Co16.8Fe7.8Ga6.6, a giant hexagonal approximant of a quasicrystal determined by a combination of electron microscopy and x-ray diffraction Acta Crystallogr. B 56 392–401

[148] Lee C S and Miller G J 2001 Li26Mgs(Zn13B13)Al1: a new intermetallic phase containing building blocks for decagonal quasicrystals Angew. Chem., Int. Ed. 40 4740–2

[149] Smetsa V, Corbett J D and Miller G J 2013 Na2Al4Cu7Fe60Ga6: the diversity of pseudo-5-fold symmetries in the Na–Au–Ga system J. Solid State Chem. 207 21–8

[150] Zachwieja U 1996 Na4Au3In6: ein gold—indium-Polyedergerüst mit pentagonal-bipyramidalen Au4In,In8-Nullkörpern in Al4CoNi,In5-Verbindungen Z. Anorg. Allg. Chem. 622 1581–6

[151] Fredrickson D C, Lee S and Hoffmann R 2004 The Nowotny chimney ladder phases: whence the 14 electron rule? Inorg. Chem. 43 6159–67

[152] Jeitschko W, Holleck H, Nowotny H and Benesovsky F 1963 Die Verbindungen RuGa und RuGa2, Monatsh. Chem. 94 838–40

[153] Poutcharovsky D J, Yvon K and Parthé E 1975 Diffusionless phase transformations of Ru3Si3, Ru3Ge3 and Ru3Sn3: I. Crystal structure investigations J. Less Common Met. 139 134–9

[154] Völlenkle H, Wittmann A and Nowotny H 1967 Die Kristallstruktur von Rh13Ga17 und Ir5Ga3, Monatsh. Chem. 98 176–83

[155] Fiecher G, Völlenkle H and Nowotny H 1968 Die Kristallstruktur von Ir5Ge3 Monatsh. Chem. 99 877–83

[156] Völlenkle H, Preisinger A, Nowotny H and Wittmann A 1967 Die Kristallstrukturen von Cr11Ge19, Mo13Ge23 und V12Ge23: Z. Kristallogr. 124 9–25

[157] Zwilling G and Nowotny H 1973 Zur Struktur der Defekt-Mangansilicide Kristallstruktur von Mn22Si17 Monatsh. Chem. 104 668–75

[158] Villars P, Cenzual K and Gladyszhevskii R 2014 Handbook of Inorganic Substances (Berlin: Walter de Gruyter GmbH & Co KG)

[159] Schwommen O, Preisinger A, Nowotny H and Wittmann A 1964 Die Kristallstruktur von Mn10Si19 und deren Zusammenhang mit Disilicid-Typen Monatsh. Chem. 95 1527–37
Smetana V, Rhodhouse M, Meyer G and Mudring A-V 2017 Gold intermetallics: structural versatility through exclusive bonding motifs Acc. Chem. Res. 50 2633–41

Tillard-Chaibonnel M, Belin C and Chouaini N 1993 Crystal structure of sodium gold gallium, Na42Ga41Au275 Z. Kristallgeom. Cryst. Mater. 206 310–2

Smetana V, Steinberg S and Mudring A-V 2017 Layered structures and disorders polyanionic nets in the cation-poor polyintermetallics Cs2Au2Ga26 and Cs2Au2Ga26 Crystal Growth Des. 17 693–700

Huang D, Dong Z-C and Corbett J D 1998 Na12K38Tl48Au2: a metallic Zintl phase with naked icosahedral fragments Ti63+ and Zn63+ and Au Inorg. Chem. 37 5881–6

Sevov S C and Corbett J D 1993 Synthesis, characterization, and bonding of indium clusters: A1Na28In58 (A = K, Rb, Cs) with a novel cubic network of arachno- and closo-In12 clusters Inorg. Chem. 32 1612–5

Charbonnel M and Belin C 1984 Synthesis and crystal structure of the new non stoichiometric phase Li2Na5Ga19.56 J. Chem. 8 595

Charbonnel M and Belin C 1987 Synthesis and x-ray crystal structure of the new nonstoichiometric phase Rb0.60Na0.25Ga0.25J. Solid State Chem. 67 210–8

Belin C and Charbonnel M 1986 A new intermetallic phase K4Na2Ga45.57: synthesis and x-ray crystal structure J. Solid State Chem. 64 57–66

Flot D, Vincent L, Tillard-Chaibonnel M and Belin C 1998 Na2K8Ga24.57: a new sodium potassium gallide phase containing trimeric icosahedral gallium clusters Acta Crystallogr. C 54 174–5

Henning R W and Corbett J D 1999 Formation of isolated nickel-centered gallium clusters in Na10Ga10Ni and a 2D network of gallium octahedra in K6Ga3 Inorg. Chem. 38 3883–8

Sevov S C and Corbett J D 1993 K10In10Z (Z = Ni, Pd, Pt): Zintl phases containing decacaindium clusters centered by transition elements J. Am. Chem. Soc. 115 9089–94

Sevov S C and Corbett J D 1993 Carbon-free fullerene: condensed and stuffed anionic examples in indium systems Science 262 880–3

Sevov S C and Corbett J D 1996 A new indium phase with three stuffed and condensed fullerene-like cages: Na13.67Zn1.28(Z = Ni, Pd, Pt) J. Solid State Chem. 123 344–70

Niemann S and Jeitschko W 1994 Ternary aluminides A6TaAl3 with A = Y, Nd, Sm, Gd–Lu, Th and U and T = Cr, Mo, W, Z. Metallkd. 85 345–9

Niemann S and Jeitschko W 1995 Ternary aluminides A6TaAl3 (A = Y, Nd, Sm, Gd–Lu, and T = Ti, V, Nb, and Ta) with H0.6Mo0.4Al3 type structure J. Solid State Chem. 116 131–5

Condron C L, Strand J D, Canfield P C and Miller G J 2003 The intermetallic compound Gd6TaAl13 Acta Crystallogr. E 59 i417–8

Verbovyt'sky V, Ląkta K and Tomala K 2008 The crystal structure and magnetic properties of the Gd4CrAl13 compound J. Alloys Compd. 450 114–7

Kangas M J, Treadwell I J, Haldolaarachchige N, McAlpin J D, Young D P and Chan J Y 2013 Magnetic and electrical properties of flux grown single crystals of Lu0.75Mg0.25 (Ln = Gd, Yb; M = Cr, Mo, W) J. Solid State Chem. 197 523–31

Treadwell I J, Watkins-Curry P, McAlpin J D, Prestigiacomo J, Stadler S and Chan J Y 2014 Substitution studies of Mn and Fe in Lu0.75W0.25 (Ln = Gd, Yb) and the structure of Yb0.75Ti0.25 J. Solid State Chem. 210 267–74

Moussa C, Berche A, Pasturel M, Barbosa J, Stepnik B, Dubois S and Tougait O 2017 The U–Nb–Al ternary system: experimental and simulated investigations of the phase equilibria and study of the crystal structure and electronic properties of the intermediate phases J. Alloys Compd. 691 893–905

Hoffmann R-D, Muts I, Zaremba V and Pöttgen R 2009 SrNi1.7Fe1.3 (8–9) new superstructure in the NaZn13 family Z. Kristallogr. 224 446–53

Avzuragova V A, Nesterenko S N and Tursina A I 2017 Ternary gallides of the CEX2Rb13+xGa26 (x = 0–5) structure family Russ. Chem. Bull. 66 2015–20

Schniering H G v, Kröner R, Carrillo-Cabrera W, Peters K and Nesper R 1998 Crystal structure of the novel chiral clathrate, BadIn4Ge2 Z. Kristallogr.—New Crystal. Struct. 213 705–6

Fässler T F and Kronseder C 1998 K8Sn12Bi12 and K8Sn25—two Phases with Chiral Clathrat-structure und ihr Verhalten gegenüber Ethyldiamin Z. Anorg. Allg. Chem. 624 561–8

Kim S-J, Hu S, Uher C, Hogan T, Huang B, Corbett J D and Kanatzidis M G 2000 Structure and thermoelectric properties of Ba3Ga25−xSnx (x = 0, 1) J. Solid State Chem. 153 321–9

Bösev S and Sevov S C 2000 Synthesis and characterization of A1Na10Sn23 (A = Cs, Rb, K) with a new clathrate-like structure and of the clathrate Rb2Na10Sn25 Inorg. Chem. 39 8930–7

Carrillo-Cabrera W, Curda J, von Schnering H G, Paschen G and Grin Y 2000 Crystal structure of hexabarium pentacosagermanide, Ba6Ge25 Z. Kristallogr.—New Crystal. Struct. 215 207–8

Fukuoka H, Ueno K and Yamanaka S 2000 High-pressure synthesis and structure of a new silicon clathrate Ba24Si100 J. Organomet. Chem. 611 543–6

Carrillo-Cabrera W, Curda J, Peters K, Paschen S, Grin Y and Schnering H v 2001 Crystal structure of the chiral clathrate NaB4Ge24Z Z. Kristallogr.—New Crystal. Struct. 216 183–4

Carrillo-Cabrera W, Cardoso Gil R, Paschen S and Grin Y 2003 Crystal structure of barium europium germanide, Ba6EuGe25 (x = 0.6), a chiral clathrate Z. Kristallogr.—New Crystal. Struct. 218 397–8

Carrillo-Cabrera W, Bornmann H, Paschen S, Baenitz M, Steglich F and Grin Y 2005 Ba4Ge23: low-temperature Ge–Ge bond breaking during temperature-induced structure transformation J. Solid State Chem. 178 715–28

Kim J-H, Okamoto N L, Kishida K, Tanaka K and Inui H 2007 Crystal structure and thermoelectric properties of type-III clathrate compounds in the Ba–In–Ge system J. Appl. Phys. 102 094506

Carrillo-Cabrera W, Budnyk S, Prots Y and Grin Y 2004 Ba4Ge43 revisited: a 2d × 2d × 2d superstructure of the clathrate-I type with full vacancy ordering Z. Anorg. Allg. Chem. 630 2267–76

Okamoto N L, Tanaka K and Inui H 2006 Crystal structure and thermoelectric properties of type-III clathrate compounds in the Ba–In–Ge system J. Mater. 54 173–8

Kaltzoglou A, Hoffmann S D and Fässler T F 2007 Order–disorder phase transition in type-I clathrate Cs6Sn44+3 Eur. J. Inorg. Chem. 2007 4162–7

Kaltzoglou A, Fässler T, Christensen M, Johnsen S, Iversen B, Presniakov I, Sobolev A and Shevelkov A 2008 Effects of the order–disorder phase transition on the physical properties of AlSn44+3 J. Mater. Chem. 18 3630–7

Kaltzoglou A, Fässler T F, Gold C, Scheid E-W, Scherer W, Kume T and Shimizu H 2009 Investigation of substitution...
effects and the phase transition in type-I clathrates RhB6,Css−Sn₄₈−Sn₄₈⁺⁺(1.3 < x < 2.1) using single-crystal x-ray diffraction, Raman spectroscopy, heat capacity and electrical resistivity measurements J. Solid State Chem. 182 2924–9

[277] Aydemir U et al 2010 Crystal structure and transport properties of BaGe₄Cu₄₂ Dalton Trans. 39 1078–88

[278] Okamoto N L, Kishida K, Tanaka K and Imai H 2006 Crystal structure and thermoelectric properties of type-I clathrate compounds in the Ba–Ga–Ge system J. Appl. Phys. 100 073054

[279] Christensen M, Johnsen S and Iversen B B 2010 Crystallography and transport properties in type-I clathrate structure and thermoelectric properties of the new ternary thallium stannides with a giant unit cell J. Alloys Compd. 314 177–80

[280] J. Alloys Compd. 2015 Type I clathrates as novel silicon anodes: an electrochemical and structural investigation Adv. Sci. 2 1500057

[281] Ganguli A K, Guloy A M, Leon-Escamilla E A and Aydemir U 2010 Interaction of the lithium of Ba₈Al₁₆Si₃₀ and Pr₁₁₇Co₅₂Sn₁₁₂ Cell structure and magnetic properties of the new ternary compound Pr₁₁₇Co₅₂Sn₁₁₂ J. Alloys Compd. 491 49–52

[282] Kovnir K and Shatruk M 2011 Magnetism in giant unit cells—crystal structure and magnetic properties of R₁₁₇Co₅₂Sn₁₁₂ (R = Sm, Tb, Dy) Eur. J. Inorg. Chem. 2011 3955–62

[283] M. D. future of intermetallic compounds from metal flux reactions J. Alloys Compd. 577 838–43

[284] Quènèvede V and Sevov S 2001 Clathrate III of group 14 exists after all J. Am. Chem. Soc. 123 3389–90

[285] Fornasini M L and Franceschi E 1977 The crystal structure of Ca₃Sn₂₀ Acta Crystallogr. B 33 3476–9

[286] Bovey S and Sevov S C 1997 The crystal structure of Ca₃Sn₂₀ Acta Crystallogr. B 33 3476–9

[287] Ganguli A K, Guloy A M, Leon-Escamilla E A and Corbett J D 1993 Calcium–tin (Ca₃₁Sn₂₀) and related compounds: novel Zintl phases containing dimers and pentamers of tin or lead Inorg. Chem. 32 4349–53

[288] Leon-Escamilla E A and Corbett J D 1999 Solid state compounds with tin–tin bonding, Yb₃Sn₃², a novel compound containing oligomeric tin anions Inorg. Chem. 38 738–43

[289] Palenzona A, Manfrinetti P and Fornasini M L 2000 Phase diagram of the Ca–Sn system J. Alloys Compd. 312 165–71

[290] Quènèvede V and Sevov S C 1997 Ge₄₆⁺⁺: a deltahedral Zintl ion now made in the solid-state Angew. Chem., Int. Ed. 36 1754–6

[291] Leon-Escamilla E A and Corbett J D 1999 Solid state compounds with tin–tin bonding, Yb₃Sn₃², a novel compound containing oligomeric tin anions Inorg. Chem. 38 738–43

[292] Quènèvede V, Todorov E and Sevov S 1998 Synthesis and structure of isolated silicon clusters of nine atoms J. Am. Chem. Soc. 120 3263–4

[293] Bovey S and Sevov S C 2000 Arachno-[Sn₄₈−]⁺⁺ or close-[Li₄S₄]₋? synthesis and characterization of A₃Li₄S₄₈ (A = Rb, K) Angew. Chem., Int. Ed. 39 4108–10

[294] Scherf L M, Zeilinger M and Fässler T F 2014 Li₃₂Na₂Ge₁₉—a compound demonstrating cation effects on cluster shapes and crystal packing in ternary Zintl phases Inorg. Chem. 53 2196–101

[295] Pecharskij V K, Bobod O I, Bel’skii V K, Starodub P K, Mokra I R and Gladyshevskiy E I 1987 Tb₁₁₁Fe₁₂₂Ge₁₁₂ crystal structure Kristallografiya 32 334–8

[296] Bodak O I, Mrz O Y and Pecharskij V K 1990 Sm–Fe–Ge system Neorg. Mater. 26 773–5

[297] Fedyna M F, Bodak O I and Pecharskij V K 1991 Interaction in Pr–Co–Ge system Neorg. Mater. 27 1092–4

[298] Bodak O I, Oleksin O Y and Pecharskij V K 1992 Er(Tm)–Fe–Ge systems Neorg. Mater. 28 493–7

[299] Salamakha P S, Prots Y M, Sologub O L and Bodak O I 1994 The neodymium—(vanadium, chromium, manganese)—germanium systems J. Alloys Compd. 215 51–4

[300] Salamakha P, Sologub O, Bocelli G, Otani S and Takabatake T 2001 Dy₁₂₅Co₅Sn₁₁₂, a new structure type of ternary intermetallic stannides with a giant unit cell J. Alloys Compd. 314 177–80

[301] He W, Zhang J and Zeng L 2007 Rietveld refinement of ternary compound Gd₁₃Fe₅Ge₁₅ Powder Diff. 22 312–5

[302] He W, Zhang J, Yan J, Fu Y and Zeng L 2010 Crystal-structure and magnetic properties of the new ternary compound Pr₇₁Co₅Sn₁₁₂ J. Alloys Compd. 1491 49–52

[303] Madryk Y, Manfrinetti P, Smetana V, Liu J, Fornasini M L, Provino A, Pecharsky V K, Miller G J and Gschneider K A 2013 Structural disorder and magnetism in rare-earth (R) R₁₁₇Co₅₁Sn₁₁₂ J. Alloys Compd. 557 252–60

[304] Liu J, Smetana V, Gschneider K A G Jr, Miller G J and Pecharsky V K 2013 The crystal structure and magnetic properties of Pr₁₁₇Co₅₁Sn₁₁₂ J. Alloys Compd. 11 17E120

[305] Reyes L E, McDougald R N, McCandless G T, Khan M, Young D P and Chan J Y 2015 Eutectoid flow growth and physical properties of single crystal Ln₁₇₁Sn₁₁₂₋ₓSn₁₁₂₋ₓ (Ln = Gd–Dy) Cryst. Growth Des. 15 295–304

[306] Chai P, Abramchuk M and Shatruk M 2016 Synthesis, crystal structure, and magnetic properties of giant unit cell intermetallics R₁₁₇Co₅₁Sn₁₁₂₋ₓ (R = Y, La, Pr, Nd, Ho) Crystals 6 6

[307] Latturner S E 2018 Clusters, assemble: growth of intermetallic compounds from metal flux reactions Acc. Chem. Res. 51 40–8

[308] Hönle W, Buresch J, Peters K, Chang J-H and von Schnering H G 2002 Crystal structure of the low-temperature modification of trilithium heptaneasride, LT-L₃[As₈] Z. Kristallogr.—New Cryst. Struct. 217 485–6

[309] Emmerling F and Röhr C 2002 Alkalimetall-Arsenide A₃A₅, and A₃A₅ (A = K, Rb, Cs), Synthesen, Kristallstrukturen, Schwingungsspektren Z. Naturforsch. B 57 963–75

[310] Hönle W, Buresch J, Peters K, Chang J-H and von Schnering H G 2002 Crystal structure of the low-temperature modification of trilithium heptaneasride, LT-L₃[As₈] Z. Kristallogr.—New Cryst. Struct. 217 489–90

[311] Hönle W, Buresch J, Peters K, Chang J-H and von Schnering H G v 2002 Crystal structure of the low-temperature modification of trilithium heptaneasride, LT-L₃[As₈] Z. Kristallogr.—New Cryst. Struct. 217 491–3

[312] He H, Tyson C and Bovey S 2011 New compounds with [As₇]³⁺ clusters: synthesis and crystal structures of the Zintl phases Cs₂SnNaAS, Cs₂ZnAS₄, and CsCdAS₄ Crystals 1 87–98

[313] Eisenmann B and Rößler U 1998 Cyclische Phosphido(thio)stanat(111)-Anionen [Sn₃P₃]²⁻ in Sr₂[Sn₃P₃] Z. Anorg. Allg. Chem. 624 406–10

[314] Liu X-C, Pan M-Y, Li X, Xia S-Q and Tao X-T 2014 Synthesis, polymerisation, and electronic structures of Sr₂Sn₃As₄ Inorg. Chem. Front. 1 689–94

[315] Park S-M, Kim S-J and Kanatzidis M G 2004 Eu₇Ga₆Sb₈: a Zintl phase with Ga–Ga bonds and polymeric gallium antimonide chains J. Solid State Chem. 177 2867–74

[316] Shreeve-Keyer J L, Haushalter R C, Lee Y-S, Li S, O’Connor C J, Seo D-K and Wangbo M-H 1997 New layered materials in the K–In–Ge–As System:
K(In,Ga)As$_2$ and K(In,Ga)As$_3$. J. Solid State Chem. 130 234–49

Dünner J and Mewis A 1995 Ba$_x$Cu$_{1-x}$P$_2$—eine neue ternäre Variante des Clathrat Strukturtyps Z. Anorg. Allg. Chem. 621 191–6

Falmer J, Lebedev I O, Riddatt V, Kaseeman D C, Sen S, Dolyiniuk J-A, Lee K, Olenev A V and Kovnir K 2013 Clathrate Ba$_4$As$_{13}P_9$: the ‘golden standard’ for lattice thermal conductivity J. Am. Chem. Soc. 135 12313–23

Wang J, Dolyiniuk J-A and Kovnir K 2018 Unconventional clathrates with transition metal–phosphorus frameworks Acc. Chem. Res. 51 31–9

Mills A M, Lam R, Ferguson M J, Deakin L and Mar A 2002 Chains, planes, and antimonides Coord. Chem. Rev. 233 207–22

Papoin G A and Hoffmann R 2000 Hypervalent bonding and consequences J. Solid State Chem. 152 123–44

Ovchinnikov A, Makongo J P A and Bobev S 2018 Yet again, new compounds found in systems with known binary phase diagrams. Synthesis, crystal and electronic structure of Nd$_3$Bi$_3$ and Sm$_3$Bi$_3$. Chem. Commun. 54 7089–92

Ovchinnikov A and Bobev S 2018 Undistorted linear Bi chains with hypervalent bonding in La$_3$(TiBi)$_5$ from single-crystal x-ray diffraction Acta Crystallogr. C 74 618–22

Cordier G, Schäfer H and Stelter M 1984 Darstellung und Struktur der Verbindung Ca$_4$AlSb$_{11}$ Z. Anorg. Allg. Chem. 519 183–8

Brook S L, Weston L J, Olmstead M M and Kauzlarich S M 1993 Synthesis, structure, and properties of A$_4$AlSb$_{11}$ (A = Ca, Sr, Ba) J. Solid State Chem. 107 513–23

Sommer M, Carrillo-Cabrera W, Peters K and Schiering H G V 2019 Synthesis of three new hypervalent compounds and crystal structure of tetradecapotassium As$_3$ polyatomic unit, As$_4$(P$_3$AlP)$_3$ and two new hypervalent bonding in La$_3$(TiBi)$_5$. Croat. Chem. Acta 52 (https://hrcak.srce.hr/137306) = (A$_4$Sb$_{11}$; 47 C).

Rataf E, Bruns P, Hernandez C J, Kauzlarich S M and Augustin M P 2002 Magnetic resonance study of a series of phosphorus-containing Zintl compounds: Ca$_{14}$AlP$_{11}$, Ca$_{14}$AlSb$_{11}$ and Eu$_4$MnP$_{11}$ J. Solid State Chem. 152 252–67

Young D M, Caroten C C, Olmstead M M and Kauzlarich S M 1995 Exploring the limits of the Zintl concept for the Al$_{14}$MnP$_{11}$ structure type with M = Zn, Cd Chem. Mater. 7 93–101

Helm A O, Ozawa T C, Wahlstrom S M, Morton S A, Dan Waddill G and Tobin J G 2003 X-ray photoelectron spectroscopy studies of Yb$_{14}$MnSb$_{11}$ and Yb$_{14}$SnSb$_{11}$ J. Solid State Chem. 176 262–75

Baranets S and Bobev S 2018 Inhomogeneous and V K Pecharsky (New York: Elsevier) pp 177–213.

Kuznetsov S M, Thomas M M, Odink D A and Olmstead M M 1991 Calcium gallium arsenide, Ca$_2$GaAs$_{11}$: a new compound containing discrete GaAs$_6$ tetrahedra and a hypervalent As$_3$ polyatomic unit J. Am. Chem. Soc. 113 7205–8

Kuznetsov S M and Kuromoto T 1991 Exploring the structure and bonding of the Zintl compounds: A$_4$GaAs$_{11}$ (A = Ca, Sr, Ba) J. Solid State Chem. 64 343–52 (https://broca.srce.hr/137306).

Carrillo-Cabrera W, Sommer M, Peters K and von Schiering H G 1996 Synthesis, structure and vibrational spectra of Ba$_4$InP$_{11}$ Chem. Ber. 129 1015–23

Chan J Y, Wang M E, Rehr A, Kauzlarich S M and Webb D J 1997 Synthesis, structure, and magnetic properties of the rare-earth Zintl compounds Eu$_4$MnP$_{11}$ and Eu$_4$InP$_{11}$ (Pn = Sb, Bi) Chem. Mater. 9 2131–8

Hu Y, Wang J, Kawamura A, Kovnir K and Kauzlarich S M 2015 Yb$_4$MgSb$_{11}$ and Ca$_4$MgSb$_{11}$—new Mg-containing Zintl compounds and their structures, bonding, and thermoelectric properties Chem. Mater. 27 343–51

Tan W J, Liu Y T, Zhu M, Zhu T J, Zhao X B, Tao X T and Xia S Q 2017 Structure, magnetism, and thermoelectric properties of magnesium-containing antimonide Zintl phases Sr$_4$AlSb$_{11}$ and Eu$_4$MgSb$_{11}$ Inorg. Chem. 56 1646–54

Tan W, Wu Z, Zhu M, Shen J, Zhu T, Zhao X, Huang B, Tao X T and Xia S Q 2017 A$_4$MgBi$_{11}$ (A = Ca, Sr, Eu): magnesium bismuth based Zintl phases as potential thermoelectric materials Inorg. Chem. 56 10576–83

Hu Y and Kauzlarich S M 2017 Yb$_4$MgBi$_{11}$ structure, thermoelectric properties and the effect of the structure of the low lattice thermal conductivity Dalton Trans. 46 3996–4003.

Kim H and Kauzlarich S M 2005 Structure and magnetic properties of Ca$_4$MnP$_{11}$, Z. Kristallogr. 220 1–7

Payne A C, Olmstead M M, Kauzlarich S M and Webb D J 2001 Structure, magnetism, and magnetoresistance of the compounds Eu$_4$MnP$_{11}$ and Eu$_4$MnSb$_{11}$ Chem. Mater. 13 398–406

Rehr A, Kuromoto T Y, Kauzlarich S M, Del Castillo J and Webb D J 1994 Structure and properties of the transition-metal Zintl compounds A$_4$MnP$_{11}$ (A = Ca, Sr, Ba, Pn = As, Sb) Chem. Mater. 6 93–9

Kuromoto T Y, Kauzlarich S M and Webb D J 1992 Structure and properties of the transition-metal Zintl compounds: A$_4$MnBi$_{11}$ (A = Ca, Sr, Ba) Chem. Mater. 4 435–40

Chan J Y, Olmstead M M, Kauzlarich S M and Webb D J 1998 Structure and ferromagnetism of the rare-earth Zintl compounds: Yb$_4$MnSb$_{11}$ and Yb$_4$MnBi$_{11}$ Chem. Mater. 10 3583–8

Young D M, Torardi C C, Olmstead M M and Kauzlarich S M 1995 Exploring the limits of the Zintl concept for the A$_{14}$MnP$_{11}$ structure type with M = Zn, Cd Chem. Mater. 7 93–101

Helm A O, Ozawa T C, Wahlstrom S M, Morton S A, Dan Waddill G and Tobin J G 2003 X-ray photoelectron spectroscopy studies of Yb$_{14}$MnSb$_{11}$ and Yb$_{14}$SnSb$_{11}$ J. Solid State Chem. 176 262–75

Baranets S and Bobev S 2019 From the ternary phase to quantum liquid solid solutions Ca$_{14}$Zn$_{1-x}$Sb$_{11}$ (δ ≈ 0.4) to the quaternary solid solutions Ca$_{14}$RE$_{x}$Zn$_{1-x}$Sb$_{11}$ (RE = La–Nd, Sm, Gd, x ≈ 0.9). A tale of electron doping via rare-earth metal substitutions and the concomitant structural transformations Inorg. Chem. 58 8506–16

Makongo J P A, Darone G M, Xia S-Q and Bobev S 2015 Non-stoichiometric compositions arising from synergistic electronic and size effects. Synthesis, crystal chemistry and electronic properties of A$_4$Cd$_{1-x}$P$_{11}$ compounds (0 ≤ x ≤ 0.3). A = Sr, Eu; Pn = As, Sb) J. Mater. Chem. C 3 10388–400

Baranets S, Voss L, Stoyko S and Bobev S 2019 Synthesis, crystal structure and physical properties of the solid solutions Ca$_{14}$RE$_x$CdSb$_{11}$ (RE = La–Nd, Sm, Gd–Yb, x ≈ 0.85 ± 0.15) J. Appl. Phys. 125 245101

Kazem N and Kauzlarich S M 2016 Handbook on the Physics and Chemistry of Rare Earths ed J C G Bünzli and V K Pecharsky (New York: Elsevier) pp 177–208

Liu K F and Xia S Q 2019 Recent progresses on thermoelectric Zintl phases: structures, materials and optimization J. Solid State Chem. 270 252–64

Chan J Y, Kauzlarich S M, Klavins P, Shelton R N and Webb D J 1997 Colossal magnetoresistance in the...
transition-metal Zintl compound Eu14MnSb11 Chem. Mater. 9 3132–5

[352] Kim H, Huang Q, Lynn J W and Kauzlarich S M 2002 Neutron diffraction study of the ternary transition metal Zintl compound Ca14MnSb11 J. Solid State Chem. 168 162–8

[353] Webb D J, Cohen R, Klavins P, Shelton R N, Chan J Y and Kauzlarich S M 1998 Magnetism and colossal magnetoresistance in the compound Sr14MnSb11 J. Appl. Phys. 83 7192–4

[354] Sánchez-Portal D, Martin R M, Kauzlarich S M and Pickett W E 2002 Bonding, moment formation, and magnetic interactions in Ca14MnBi11 and Ba14MnBi11 Phys. Rev. B 65 144414

[355] Kim H, Klavins P and Kauzlarich S M 2002 Structure, magnetism, and magnetoresistance of the rare-earth transition metal compounds Eu13AMnSb11 (A = Ca, Sr, Ba, and Yb) Chem. Mater. 14 2308–16

[356] Prakash J, Stoyko S, Voss L and Bobev S 2016 On the extended series of quaternary Zintl phases Ca13REMnSb11 (RE = La–Nd, Sm, Gd–Dy) Eur. J. Inorg. Chem. 2016 2912–22

[357] Xia S-Q and Bobev S 2008 Zintl phase variations through cation selection. Synthesis and structure of A22Cd4Pn18 (A = Eu, Sr, Ba; Pn = Sb, Bi) Inorg. Chem. 47 1919–21

[358] Suen N-T, Wang Y and Bobev S 2015 Synthesis, crystal structures, and physical properties of the new Zintl phases A21Zn4Pn16 (A = Ca, Eu; Pn = As, Sb)—versatile arrangements of [ZnPn4] tetrahedra J. Solid State Chem. 227 204–11

[359] Gascoin F and Sevov S C 2002 Synthesis and characterization of K18Nb7As14 and Cs6Nb2As6: the first mixed-valence transition-metal Zintl phases Inorg. Chem. 41 5920–4

[360] Pivan J-Y, Guérin R, Pena O, Padiou J and Sergent M 1988 Crystal structures and properties of new rare earth rhodium phosphides: La8Rh13P17 and Ce8Rh13P17 Mater. Res. Bull. 23 513–20

[361] Chykhrij S I, Babizhetskys V S and Kuz’m a Y B 2001 New ternary phosphides Ln23Ni48P17 (Ln = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er) Z. Anorg. Allg. Chem. 627 1319–24

[362] Stoyko S S, Blanchard P E R and Mar A 2010 Ternary rare-earth iron arsenides RE12Fe57.5As41 (RE = La, Ce) Inorg. Chem. 49 2325–33

[363] Ovchinnikov A, Saparov B, Xia S-Q and Bobev S 2017 The ternary alkaline-earth metal manganese bismuthides Sr2MnBi2 and Ba2Mn1−xAux (x ≈ 0.15) Inorg. Chem. 56 12369–78

[364] Grin Y 2019 Inhomogeneity and anisotropy of chemical bonding and thermoelectric properties of materials J. Solid State Chem. 274 329–36

[365] Blatov V A and Ilyushin G D 2010 New method for computer analysis of complex intermetallic compounds and nanocluster model of the samson phase Cd3Cu4 Crystallogr. Rep. 55 1100–5