From Zintl to Wade: diversity of [Ga_n**] clusters in ternary intermetallic compounds** *Yurii Prots[#], Matthias Kotsch, Alim Ormeci, Matej Bobnar, Frank R. Wagner, Miroslav Kohout and Yuri Grin*

Studies of the correlation between crystal structure, electronegativity difference between the constituent components and valence electron concentration in intermetallic compounds of gallium led to the discovery of a series of new materials consisting of interconnected pyramidal [Ga₅] and bell-like [Ga₅] clusters as building units.

Intermetallic compounds containing discrete gallium cluster units are mainly found in systems with alkali or alkaline-earth metals, europium or uranium [1]. A systematic analysis of the yttrium-gallium compounds revealed a charge transfer and valence electron concentrations as the main characteristics of atomic interactions [2]. Applying such an approach to the gallium connectivity in MGa_n compounds allows to highlight the ranges of existence for the different gallium arrangements in terms of the electronegativity difference between the constituent components (ΔEN) and the number of valence electrons per gallium atom (VEC_{Ga}). The isolated clusters form in the region with 5-6 valence electrons per Ga atom (Fig. 1). The number of reported phases with isolated $[Ga_n]$ units is limited, and the number of atoms in $[Ga_n]$ does not exceed n = 5. To expand this series, the investigation of ternary M-Li-Ga systems (M = Sr, Ba, Eu) was performed in the selected regions of VEC_{Ga}, where the formation of [Ga_n] clusters is expected. The introduction of Li enables fine-tuning of the VEC_{Ga} in the system as well as an optimal spatial separation of the cluster units due to the size difference between Li^+ and M^{2+} . The study resulted in several ternary compounds with various, and often unique, atomic arrangements.

The synthesis of the new compounds was performed by reaction of the mixtures of the respective constituent elements in sealed tantalum crucibles with a built-in sieve. While alkali earth elements (Sr or Ba) and Ga were used in a stoichiometric ratio, a small excess of lithium was applied to improve the crystal growth. The excess lithium was removed by high-temperature centrifugation-aided filtration (HTCAF). An important part of the synthesis was the almost exact control of the temperature regime, since most compounds form peritectically.

Crystal structure determination of the investigated phases was conducted by a combination of X-ray single crystal, X-ray powder and neutron powder diffraction, whereby the atom distribution was correctly established, especially for Li species.

The central recurring motif in Ba₃LiGa₅ [3] (space group *Immm*, a = 6.2720(2) Å, b = 6.5872(2) Å,



Fig. 1: Gallium arrangements in MGa_n phases in dependence on the number of valence electrons per gallium atom VEC_{Ga} and the electronegativity difference between the components ΔEN [3].

c = 12.6878(8) Å) is a tetragonal pyramid [Ga₅]. This cluster is capped on top of the quadrangular face by a lithium atom (Fig. 2*a*). The orientation of the [Ga₅] pyramids is random, resulting in the equal occupation of Li and Ga at the 4*g* position above and below the quadrangular plane. The pyramids are interconnected into chains via Ga–Ga contacts at opposing corners of the base along [100]. Quantum chemical calculations on ordered variants clearly showed that structural arrangements without homonuclear Ga–Ga contacts between the chains are favorable, which indicates the 1D character of the Ga substructure in Ba₃LiGa₅.

Ba₃LiGa₅ can be understood formally within the Zintl– Klemm concept considering the electronic balance $[Ba^{2+}]_3[Li^{1+}]_1[(3b)Ga^{2-}]_2[(4b)Ga^{1-}]_3$. Alternatively, the structure can also be described using the Wade–Mingos rules. According to the latter, the twofold connected pyramidal nido-cluster $[Ga_5]^{7-}$ requires 14 skeletal electrons for stabilization, 2 electrons for two inter-cluster Ga–Ga bonds and 6 electrons for three lone pairs on the gallium atoms, which do not participate in homoatomic inter-cluster bonds. In total, the formula unit Ba₃LiGa₅ possesses 22 valence electrons, i.e. this counting scheme is also charge-balanced. The Wadelike description of the pyramidal $[Ga_5]$ cluster is



Fig. 2: $[Ga_n]$ clusters in Ba_3LiGa_5 (a) and $Sr_3Li_5Ga_5$ (b). Positions of the ELI–D maxima shown by the ELI-D isosurfaces in and around the bell-like $[Ga_5]$ anion and $[Sr_6]$ polycation in $Sr_3Li_5Ga_5$ (c).

favored by chemical bonding analysis due to the presence of the lone-pair on threefold-bonded Ga atoms together with the inter-cluster bonds.

The remarkable structural feature of $Sr_3Li_5Ga_5$ ($R\overline{3}m$, a = 9.6040(5) Å and c = 22.061(1) Å) is an isolated bell-like [Ga5] cluster - the first five-membered nonconvex Ga unit observed in intermetallic phases [4]. While the strontium compound is fully ordered, the europium phase $Eu_3Li_{5+x}Ga_{5-x}$ [5] shows mixed occupancy of one position by Li and Ga. The latter is possibly a result of the equivocal valency of europium. The replacement of Eu by a divalent cation without forbitals (Sr) is a good starting point for quantum chemical calculations. The clusters are comprised of three triple-bonded and one four-bonded gallium atom forming a tetrahedron with an additional single-bonded pendant gallium atom. The suggested electron counting $[Sr^{2+}]_{3}[Li^{+}]_{5}[(1b)Ga^{4-}]_{1}[(3b)Ga^{2-}]_{3}[(4b)Ga^{1-}]_{1}$ implies an interpretation of this unit as a Zintl anion. The latter was generally confirmed by chemical bonding analysis. Assigning all populations of the ELI-D basins, ascribed to the Ga anion, 26.73 electrons are obtained, which is remarkably close to the 26e⁻ necessary for an ideal Zintl anion [Ga₅]¹¹⁻. Nevertheless, the low markedness of the Ga-Ga bonding between atoms forming the base of the tetrahedron in the ELI-D picture may hint toward a rearrangement as a (Wade-like) cluster anion, where less electrons are necessary for stabilization. This would explain the formation of the polycation $[Sr_6]^{n_+}$ (1.22 e⁻ in the ELI-D basin) using the 'excess' electrons and support the closing of the gap in the electronic density of state.

The peculiarities of the crystal structures discussed here agree well with the estimated regions for the existence of different gallium arrangements, which are deduced as a function of the VEC_{Ga} and the electronegativity difference of the components (Fig. 1). Ba₃LiGa₅ with the lowest number of the electrons per Ga atoms $(\text{VEC}_{\text{Ga}} = 4.4)$ in the investigated series and the pyramidal cluster chains $-[\text{Ga}_5]_n$ can be considered as an intermediate between structures with 2D nets, like in BaGa₂ (VEC_{Ga} = 4), and structures with isolated [Ga_n] clusters. Sr₃Li₅Ga₅ (VEC_{Ga} = 5.2) with [Ga₅] bell-like units, however, belongs to the latter family.

In our further work, the investigations and analysis of chemical bonding in Ga clusters are to be extended to the three-valent M^{3+} rare earth metals. Furthermore, it should be interesting to incorporate In and Sn into the cluster units.

External Cooperation Partners

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