Structural Complexity without Pentagonal Symmetry: New Binary Gallides and Aluminides Prepared by High-Temperature Centrifugation-Aided Filtration

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Local pentagonal or pseudo-pentagonal symmetry is one of the basic characteristics for the complexity of the crystal structures of approximants of quasicrystals (e.g., built of Mackay or Bergman clusters). Several binary and ternary transition metal compounds with aluminium and gallium in the concentration region close to quasicrystalline phases and their approximants (called complex metallic alloys, CMA) reveal this feature resulting in a strong structural complexity in different variations [1]. Recent detailed investigations on the intermetallic clathrate $Ba_8Ge_{43}\square_2$ (see *Advances in Clathrate Research*) showed that a similar level of the structural complexity (in the sense of the large unit cell parameters with hundreds of atoms per cell) can be achieved also without pentagonal or pseudo-pentagonal arrangement of atoms. In particular, it was shown that the kinetic factors play an important role in the formation of the complex ordered clathrate structures [2]. These findings stimulated our interest to synthesize new intermetallic phases with complex crystal structures in the binary systems of transition metals with aluminium and gallium investigated with appropriate preparation techniques.

In the beginning of 2003 equipment for high temperature centrifugation aided filtration technique (HTCAF) [3,4] was set up at the institute. With this technique compounds are synthesized in equilibrium with their melts, which are subsequently removed by filtration at elevated temperatures, as high as 1100 ºC. In this way, single-phase material consisting of crystals suitable for single-crystal X-ray diffraction is easily prepared. Several millimeter large single crystals and quantities up to several grams have been produced. The method relies on a large capacity centrifuge and steel “thermoses” that maintain the temperature during the centrifugation. The synthesis mixtures are located in quartz or tantalum ampoules fitted with appropriate filters (Fig.1).

The HTCAF method is especially powerful in explorative synthesis of peritectically forming compounds with a small temperature interval of equilibrium field between a solid binary phase and a melt. The application of the method has resulted in the discovery and crystallographic characterization of several novel compounds with complex crystal structures. Detailed investigations were performed in binary systems of 4*d* and 5*d* transition metals (i.e., rhodium and iridium) with aluminium and gallium. Several new compounds showing crystal structures with large unit cells and different levels of complexity were found in the aluminium- and gallium-rich regions. Here, the complexity appears without local pentagonal or pseudo pentagonal symmetry.

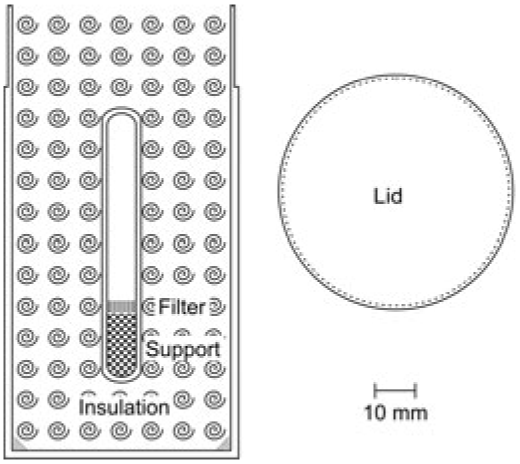

Fig. 1: Experimental setup for HTCAF with insulating “thermos” and quartz ampoule.

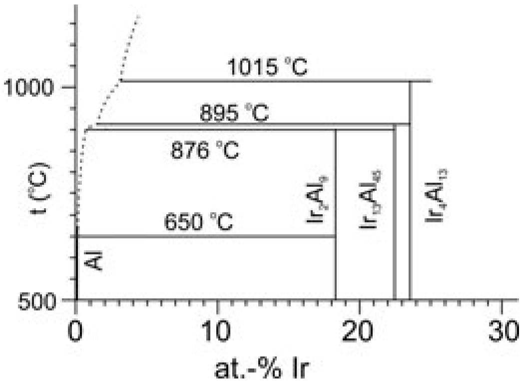

Fig. 2: Aluminum-rich part of the Ir-Al phase diagram.

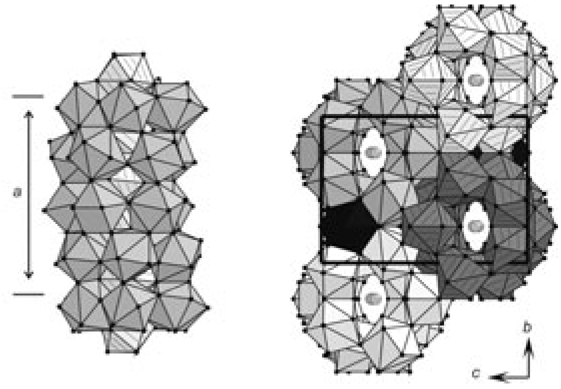

Fig. 3: Crystal structure of $Ir_{13}Al_{45}$. The rods are accentuated with different shading of grey. Al atoms are represented by black spheres, Ir atoms - with light grey spheres.

This is exemplified by $Ir_{13}Al_{45}$, where the temperature interval of the two-phase region with the melt is only 19 ºC (Fig. 2). The crystal structure of $Ir_{13}Al_{45}$ (Pearson symbol *oP*232, space group *Pnma*, a = 16.760 (2) Å, b = 12.321(1) Å, c = 17.425(2) Å) [5] belongs formally to the class of complex intermetallic compounds (CMA) [1], but merely shows a pseudo-fivefold arrangement of the transition metal centered irregular polyhedra, while the polyhedra themselves do not exhibit any pentagonality characteristic for a CMA (Fig. 3).

Another case of structural complexity is exhibited by the binary gallide $Ir_{112}Ga_{386}$ (Pearson symbol *cP*498-29, space group $Pm\bar{3}$, a = 19.8471(8) Å, Fig. 4).

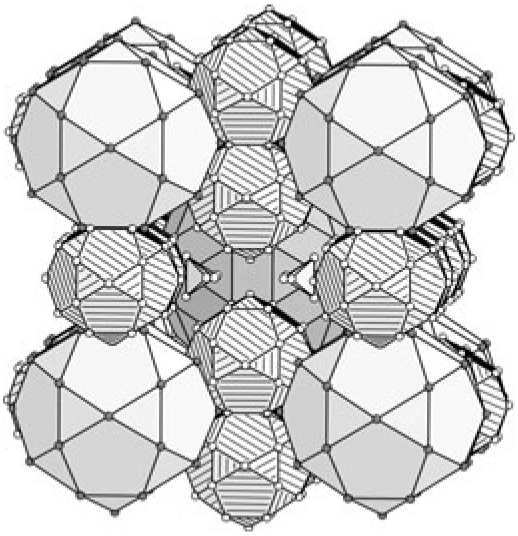

Fig. 4: Crystal structure of $Ir_{112}Ga_{386}$. Ga atoms are represented by light grey spheres. Ir atoms are not shown.

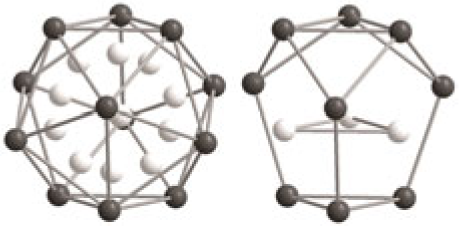

Fig. 5: Global averaged (left) and local (right) structure of the two innermost shells of the central cluster of $Ir_{112}Ga_{386}$. Distance restrictions allow simultaneous occupation of only three of the 12 positions in the inner shell. Ga atoms are represented by light grey spheres, Ir atoms - with dark grey spheres.

Its crystal structure shows globally nearly perfect average icosahedral symmetry in its two largest constituent clusters. However, the local symmetry is not at all icosahedral. One example is found in the core of the large cluster in the centre of the unit cell. What globally looks like two mutually exclusive icosahedral shells is in fact a triangle of gallium atoms inside an $[Ir_9]$ polyhedron in different orientations due to distance restrictions (Fig. 5).

The two new compounds Rh_4Ga_{21} (Pearson symbol *oC*136, space group *Cmca*, a = 40.135(6) Å, b = 6.470(2) Å, c = 6.473(1) Å) and Rh_3Ga_{16} (Pearson symbol *oC*76, space group *Ccca*, a = 30.424(7) Å, b = 6.476(2) Å, c = 6.468(2) Å) connect to previous theoretical investigations on the chemical bonding in the $PdGa_5$ structure [6]. From a topological point of view, both of these new crystal structures, and the crystal structure of $PdGa_5$, can be described either as inhomogeneous intergrowth structures containing three different kinds of segments (in particular of the more simple structural motifs of $CuAl_2$ and U_3Si_2), or as built up by layers of capped square antiprisms condensed via their capping atoms (Fig. 6).

The bonding analysis with the electron localizability indicator (ELI [7], see also *Chemical Bonding and the Correlation of Electronic Motion*) revealed that the crystal structures of Rh_4Ga_{21} and Rh_3Ga_{16} have to be considered as framework polyanions formed by covalently bonded gallium atoms with rhodium cations embedded into the cavities (Fig. 7). This variation of the bonding results again in crystal structures that belongs to the group of CMA, but do not show any pseudo-pentagonal symmetry.

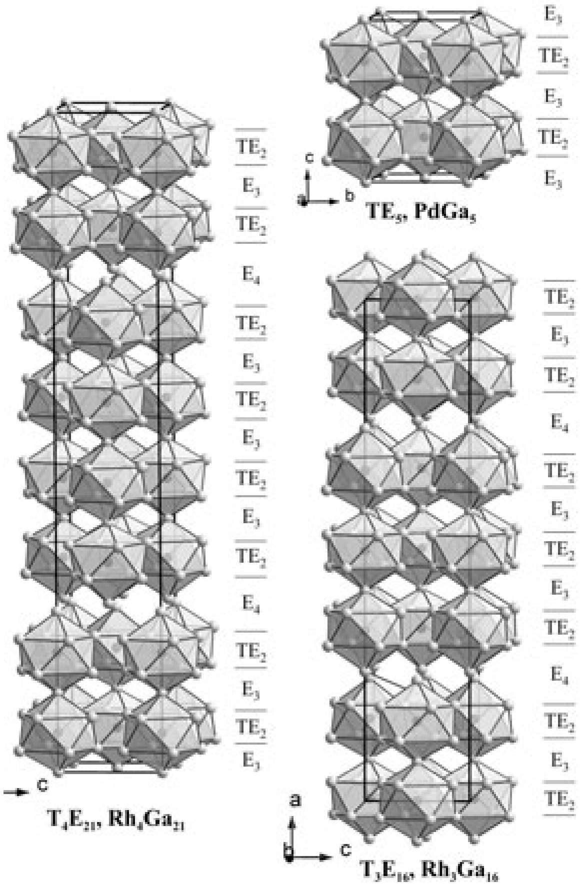

Fig. 6: Crystal structures Rh_4Ga_{21} and Rh_3Ga_{16} as intergrowth variants related to $PdGa_5$. Ga atoms are represented by light grey spheres, Ir atoms - with dark grey spheres.

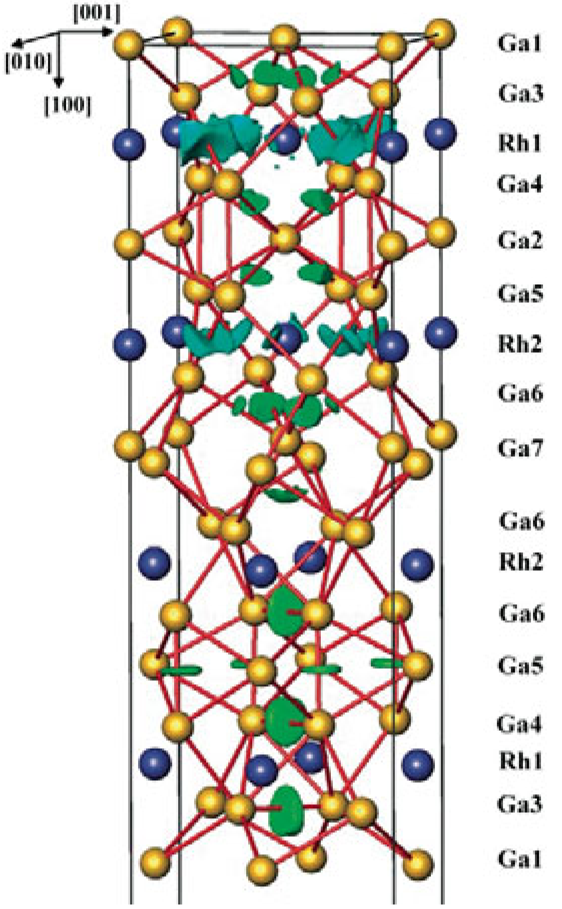

Fig. 7: ELI representing the chemical bonding in Rh_3Ga_{16}. Isosurfaces of ELI reveal the localization of the maxima only close to the Ga-Ga contacts in the crystal structure revealing the covalent interaction. No extra attractors were found on the (very short) Rh-Ga contacts suggesting the rather ionic interaction.

References

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