Heavyweight Meets Flyweight: An Experimental Platform

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An unique experimental platform: the laboratory for high safety standards (LHS), proved to be a versatile setup for investigating solid state sciences of actinides- and beryllium-based intermetallics. Such compounds of uranium, thorium, beryllium and magnesium with late transition metals can give rise to materials exhibiting unusual physical properties based on intriguing structural and chemical bonding characteristics. We highlight here a selection of recent research achievements.

Starting from investigations of the chemical physics of rare-earth compounds, the corresponding actinide and beryllium-based systems promised considerable insight into unconventional electronic behavior. Due to a subtle interplay between the constituting elements with respect to their electronic configuration and their physical properties especially uranium and its compounds represent a wide research area of solid-state sciences.

Experimental studies of such compounds require special safety precautions which are met in a laboratory of high safety standards (LHS). Since elements like osmium, thallium, other heavy metals as well as beryllium are used, inhalation of metals dusts and their escape into the environment has to be prevented. Therefore, all experiments with a latent danger of exposition are performed in closed set-ups under an atmosphere of argon gas. In addition, this concept guarantees that contamination of the samples with oxygen and moisture is prevented. For this purpose, a safety and experimental regime beyond the current standards was developed and proved to be highly successful. In the LHS interconnected inert gas gloveboxes are installed for carrying out experiments (see Figure 1).

Fig. 1: A view along the glove box system in the LHS.

Each glove-box module is dedicated to specific scientific experiments: preparation, synthesis, depot for samples and chemicals, X-ray and metallographic analysis, and crystal growth. Such experimental and technical concept guarantees that synthesis and characterization of scientific samples can be performed in a closed system under a protective atmosphere.

Careful characterization of synthesis products was the key for explaining the superconducting behavior of single crystals of the uranium heavy fermion – **UBe_{13}** [1]. The manufacturing of single crystals of this compound is practically possible only from aluminum melt. The role of aluminum in this process was not clear. The incorporation of Al into the crystal structure of as-cast polycrystalline samples $UBe_{13-x}Al_x$ is shown to be of the order 1-2 at.% by means of X-ray single-crystal structure determination, HRTEM and ^{27}Al NMR. Aluminum replaces Be atoms at the vertices of the Be_{12} icosahedrons, a basic structural unit of UBe_{13}. The aluminum solubility is strongly dependent on the temperature, it can diffuse and leave the structure upon annealing. Annealing strongly influences the low-temperature behavior of $UBe_{13-x}Al_x$ single crystals (see Figure 2).

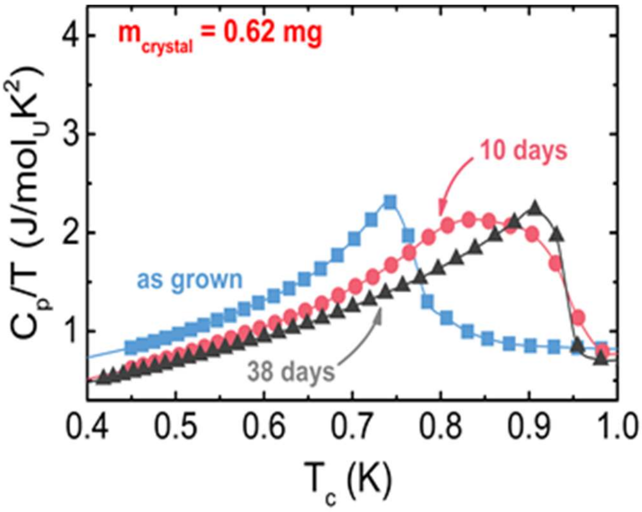

Fig. 2: Specific heat capacity (C_p/T) as function of temperature (T) and annealing time.

The crystal chemistry of beryllium intermetallic compounds is barely investigated, its binary and ternary phase diagrams are scarcely studied and only the few industrially relevant ones have been explored. This is mostly due to the toxicity of beryllium itself and the challenges associated with the synthesis due to the relatively high melting temperature and high vapor pressure of Be melts. The structural chemistry of Be-rich compounds is mostly dominated by the covalent character of Be, the low valence electron count, the small size, and the ability to coordinate larger atoms with high coordination numbers.

$Be_{21}Pt_5$ [2] is a rare γ-brass-type phase formed by a main-group element. Its crystal structure with 416 atoms per unit cell belongs to the complex metallic alloys (CMA). The structural pattern of $Be_{21}Pt_5$ is described as a 2×2×2 superstructure of the γ-brass structure or 6×6×6 superstructure to the simple bcc structure with a distinct distribution of defects. The main building blocks of the crystal structure are four types of polyhedral nested units (clusters) with compositions $Be_{22}Pt_4$ and $Be_{20}Pt_6$ (see Figure 3). Analysis of chemical bonding applying the electron localizability approach revealed strongly polar polyatomic and multi-center bonding, in accordance with the low valence electron count per atom in $Be_{21}Pt_5$. A new type of atomic interaction in intermetallic compounds – cluster bonds involving 8 or even 14 atoms – is found in this compound. Polyatomic interactions within the polyhedral nested units and three-center polar inter-cluster bonds result in a three-dimensional framework resembling the structural arrangement of NaCl.

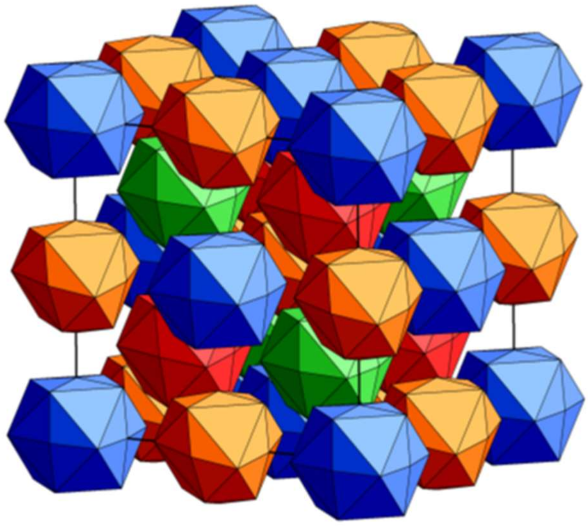

Fig. 3: Crystal structure of $Be_{21}Pt_5$, as composed of $Be_{22}Pt_4$ and $Be_{20}Pt_6$ clusters, respectively.

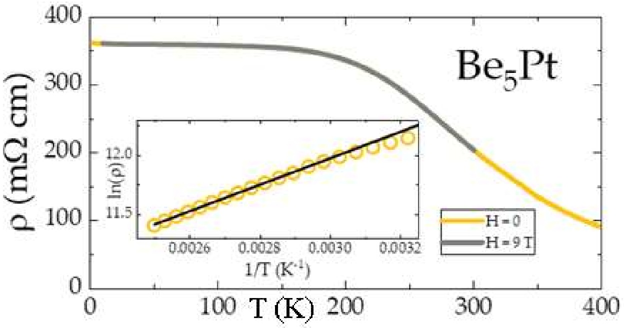

Fig. 4: Semiconducting-like behavior of Be_5Pt.

The question of how semiconducting phases may result from the union of exclusively metallic elements is an interesting and highly relevant one that furthers our understanding of bonding and valence in intermetallic compounds. Indeed, by combining an elaborated experimental characterization with a theoretical analysis of the chemical bonding, we find semiconducting behavior (bandgap of 190 meV) for the intermetallic compound **Be_5Pt** [3] at a very low valence electron count (see Figure 4). The appearance of the gap in the band structure is a consequence of relativistic effects and the unique chemical bonding picture of the compound characterized by polar two-atomic Pt-Be1 and multiatomic Pt-Be2 bonds. Quantum chemical analysis shows strong charge transfer from Be to Pt.

In the last period, in the course of joint experimental and quantum chemical investigations of the binary system Be-Ru, new phases – Be_3Ru, Be_2Ru, Be_7Ru_4 and $Be_{12}Ru_7$ with close composition were discovered. The intermetallic compound **Be_3Ru** [4] is one of the rare representatives of the $TiCu_3$-type structure, formed by the valence electron-poor element as a majority component. From the geometric point of view, the crystal structure of Be_3Ru can be derived by ‘coloring’ the hexagonal closest packing of spheres characteristic for large groups of intermetallic compounds. The closest packing in Be_3Ru is jointly formed by cationic and anionic components. This is in contrast to traditional inorganic compounds where one of the components forms the closest-packing motif, while the other one is located in the voids of the previous one. The binary beryllium compound **Be_2Ru** [5], adopts the crystal structure of the Fe_2P-type. Combined studies by X-ray single crystal diffraction and atomic-resolution electron microscopy reveal minor inclusions of orthorhombic motives dispersed into the hexagonal Fe_2P-type. All atomic arrangements are varieties of structural layers of the same kind.

Be_3Ru_2, **$Be_{12}Ru_7$**, and **Be_7Ru_4** [6] together with Be_2Ru, comprise a series of two-dimensional 'intergrowth' structures containing building blocks from U_3Si_2 (Be_3Ru_2) and Fe_2P (Be_2Ru) types (see Figure 5). Chemical bonding in all three compounds is realized by three- and four-atomic polar bonds involving ruthenium, which participates in all of them. The effective QTAIM charges of Be and Ru increase with Ru concentration, whereby for Ru a kind of saturation may be observed. The charge transfer stabilizes the atomic arrangements (see Figure 6). With increasing Ru content, the available electrons from Be are distributed among more Ru acceptors.

Thus the effective charge of the Ru species is not constant, but increases continously with increasing ruthenium content. However, the effective charge of beryllium reaches a maximum for B_2Ru, limiting the number of electrons available for bonding.

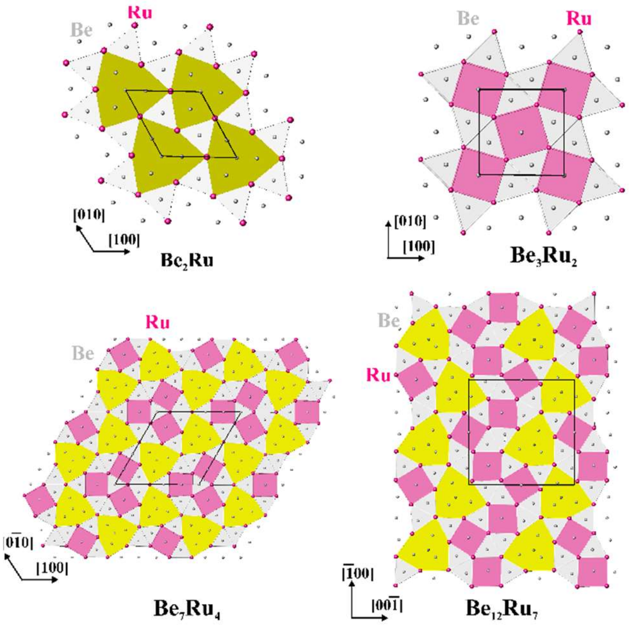

Fig. 5: Projections of Be_3Ru, and two-dimensional Be_2Ru-Be_3Ru_2 "intergrowth" structures of Be_7Ru_4 and $Be_{12}Ru_7$. Crystal structure of: (top left) Be_2Ru (Fe_2P type); (top right) Be_3Ru_2 (U_3Si_2 type); (bottom left) Be_7Ru_4; (bottom right) $Be_{12}Ru_7$. In red and white are highlighted the columns of tetragonal [Be@Ru_8] and trigonal [Be@Ru_6] prisms, typical for the U_3Si_2-type structural pattern. In yellow are highlighted the trigonal bi-prismatic columnar segments bearing columns of [Be@Be_6] trigonal prisms, typical for the Fe_2P-type motif. Ru and Be atoms are represented as pink and gray spheres, respectively.

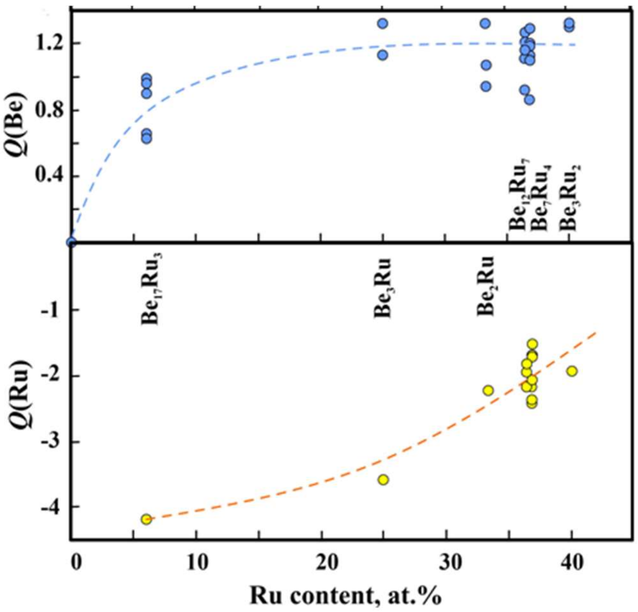

Fig. 6: QTAIM charges Q of beryllium (top) and ruthenium (bottom) in binary compounds vs. composition.

As another example of the rich structural chemistry of intermetallic Be-containing compounds, the binary **Be_2Fe** [7], which crystallizes in the C14-structure type hexagonal Laves phase can dissolve a large amount of Os as a third element without changing the crystal structure. When Ru substitutes Fe in Be_2Fe, a temperature- and composition-dependent transformation from the C14 to the cubic C15 Laves phase is observed, with narrow homogeneity range. Multiatomic bonds accompanied with charge transfer from Be to Fe/Ru/Os dominate also in these systems the electronic structure of compounds.

From these systematic studies we conclude that one of the possible reasons for the complex behaviour of Be rich compounds may be the usually low valence electron concentration in these materials, which (i) does not allow to use traditional electron counting schemes for understanding the composition and the crystal structure, and (ii) leads to multi-centre atomic interactions in the structures. The charge transfer observed in all of these compounds does not only play a crucial role in stabilizing the atomic architectures, but contributes also to the formation of distinctive features – in rare cases a gap at, or well pronounced dips near the Fermi level – in the calculated electronic density of states.

Besides their technological importance, exploring intermetallic compounds of Mg, their phase equilibria, and their structure-property relationships have been of general interest. The high affinity of Mg to Pt metals gives rise to a variable structural chemistry which was investigated for $\mathbf{Mg_3Pt_2}$ [8] and cubic $\mathbf{Mg_{29-x}Pt_{4+y}}$ [9] which belongs to the family of complex intermetallic compounds (CMA) (see Figure 7). Chemical bonding analysis reveals for $Mg_{29-x}Pt_{4+y}$ rather unexpected for a crystal structure of this size space-separated regions of hetero- and homoatomic bonds involving three to six partners (bonding inhomogeneity). Spatial separation of the regions with different bonding features is the key difference between the title compound and other CMAs, which are characterized by a predominantly homogeneous distribution of heteroatomic bonds.

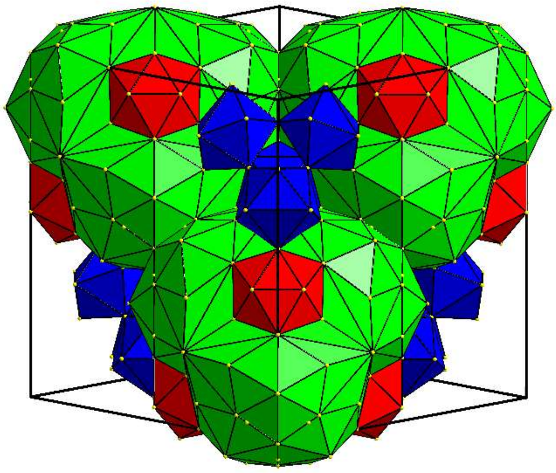

Fig. 7. Crystal structure of cubic $Mg_{29-x}Pt_{4+y}$ as a packing of crystallographic Mg-based Mackay clusters (green), tetrahedral units of four $PtMg_9$ tricapped trigonal prisms (blue) and the Pearce clusters (red).

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