Aluminium-Germanide der zweiwertigen Lanthanoide Eu und Yb: Synthese, Strukturchemie und chemische Bindung

Aluminum Germanides of the Divalent Lanthanoids Eu and Yb: Synthesis, Structural Chemistry and Chemical Bonding

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Z. Naturforsch. 2011, 66b, 793–812; received July 4, 2011

In the course of attempts to substitute Ca by Yb and Sr by Eu in known alkaline earth Al-germanides, the four new ternary compounds Eu₃Al₁₈Ge₂₂, Eu₃Al₂Ge₄, Yb₂AlGe₃, and Yb₁₇Al₈Ge₁₉ have been synthesized from mixtures of the elements and their crystal structures determined by means of single-crystal X-ray data. The two europium compounds Eu₃Al₁₈Ge₂₂ (Ta₃B₄ structure type, orthorhombic, space group Immm, a = 417.68(3), b = 470.70(3), c = 1897.2(2) pm, Z = 2, R₁ = 0.0439) and Eu₃Al₂Ge₄ (Sr₃Al₂Ge₄ structure type, monoclinic, space group C2/m, a = 1235.9(6), b = 416.8(2), c = 878.4(4) pm, β = 110.615(13)°, Z = 2, R₁ = 0.0978) are isotypic with the corresponding strontium phases. After ionic decomposition, the layers [Al−₂Ge−₄]₆− in Eu₃Al₂Ge₄ with four-bonded Al and three-bonded Ge atoms can be interpreted as electron-precise Zintl anions. In contrast, the planar ribbons \( \infty [\text{Al}_2/2\text{Ge}_2\text{Al}_2/2] \) of condensed six-membered rings in Eu₃Al₁₈Ge₂₂ exhibit considerably shorter Al-Ge bonds and an Al-Al bond length of only 251 pm. Yb₂AlGe₃ (orthorhombic, space group Pnma, a = 682.20(10), b = 417.87(9), c = 1813.9(3) pm, Z = 4, R₁ = 0.0415) crystallizes with the Y₂AlGe₃ structure type. Folded [Al₂Ge₂] ladders, also found in Eu₃Al₂Ge₄ and the known compound Yb₇Al₅Ge₈, are connected by planar cis/trans chains of Ge atoms. The total density of states calculated within the FP-LAPW DFT band structure approach shows a distinct minimum at the Fermi level for the electron precise Zintl compound Eu₃Al₂Ge₄, whereas \( \pi \)-bonding contributions are evident from the band structures of Eu₃Al₂Ge₂ and Yb₂AlGe₃. In full accordance, the tDOS of both compounds exhibits no minimum at \( E_F \), small phase widths are possible for Eu₃Al₂Ge₂ and related alkaline earth compounds, and Yb₂AlGe₃ is isotypic with several other more electron-rich \( Ln_{III} \) compounds. The complicated structure of the new compound Yb₁₇Al₈Ge₁₉ (tetragonal, space group P4/nmm, a = 1542.50(2), c = 788.285(8) pm, Z = 2, R₁ = 0.0282) contains three different building blocks: distorted [Al₄Ge₄] heterocubane units are interconnected by four-bonded Ge atoms to form columns running along the c axis. Secondly, eight-membered rings are formed by alternating Al and Ge atoms, each being in a trigonal-planar Al/Ge coordination. The rings are terminated by Ge atoms (bonded to Ge of the ring) and linked to the first structural unit by a further Ge atom (bonded to Al of the ring). Thirdly, inside the large channels, which are formed by the packing of the eight-membered rings, Ge₂ dumbbells are interspersed as a third structural element.

Key words: Aluminum, Ytterbium, Europium, Germanides, Crystal Structure, Band Structure Calculation