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

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

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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 $Eu_3Al_{1.8}Ge_{2.2}$, $Eu_3Al_2Ge_4$, Yb_2AlGe_3, and $Yb_{17}Al_8Ge_{19}$ 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 $Eu_3Al_{1.8}Ge_{2.2}$ (Ta_3B_4 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 $Eu_3Al_2Ge_4$ ($Sr_3Al_2Ge_4$ 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 $[Al_2^- Ge_4^-]^{6-}$ in $Eu_3Al_2Ge_4$ with four-bonded Al and three-bonded Ge atoms can be interpreted as electron-precise Zintl anions. In contrast, the planar ribbons $^1_\infty[Al_{2/2}Ge_2Al_{2/2}]$ of condensed six-membered rings in $Eu_3Al_{1.8}Ge_{2.2}$ exhibit considerably shorter Al-Ge bonds and an Al-Al bond length of only 251 pm. Yb_2AlGe_3 (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 Y_2AlGe_3 structure type. Folded $[Al_2Ge_2]$ ladders, also found in $Eu_3Al_2Ge_4$ and the known compound $Yb_7Al_5Ge_8$, 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 $Eu_3Al_2Ge_4$, whereas π-bonding contributions are evident from the band structures of $Eu_3Al_2Ge_2$ and Yb_2AlGe_3. In full accordance, the tDOS of both compounds exhibits no minimum at E_F, small phase widths are possible for $Eu_3Al_2Ge_2$ and related alkaline earth compounds, and Yb_2AlGe_3 is isotypic with several other more electron-rich Ln^{III} compounds. The complicated structure of the new compound $Yb_{17}Al_8Ge_{19}$ (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 $[Al_4Ge_4]$ 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, Ge_2 dumbbells are interspersed as a third structural element.

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