Segregation of Calcium and Magnesium into Different Substructures. $Ca_4Ag_{0.948}Mg$ and Other Compounds with Gd_4RhIn-type Structure

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The metal-rich compounds R_4PdMg (R = Ca, Eu, Tb–Lu), R_4AgMg (R = Ca, Yb), R_4PtMg (R = Eu, Tb–Lu), and R_4AuMg (R = Ca, Eu, Yb) were synthesized by induction melting of the elements in sealed tantalum tubes in a water-cooled sample chamber. All samples were characterized by powder X-ray diffraction. The structures of $Ca_4Ag_{0.948}Mg$ and Yb_4PdMg were refined on the basis of single-crystal X-ray diffractometer data: Gd_4RhIn type, $F\bar{4}3m$, a = 1434.6(1) pm, $wR2$ = 0.0269, 523 F^2 values, 18 variables for Yb_4PdMg and a = 1485.78(7) pm, $wR2$ = 0.0188, 617 F^2 values, 20 variables for $Ca_4Ag_{0.948}Mg$. For the first time small defects on the 16*e* transition metal site of a Gd_4RhIn-type compound have been observed, and the first compounds of this structure type with the divalent rare earth elements europium and ytterbium as well as with calcium are reported. The striking structural motif of these compounds (exemplary for $Ca_4Ag_{0.948}Mg$) is the clear segregation of two alkaline earth elements into two different substructures, calcium forming trigonal prisms around the silver atoms and magnesium forming covalently bonded tetrahedra (Mg–Mg 328 pm). The latter are embedded in larger cavities of the adamantane-like three-dimensional network of edge- and corner-sharing $AgCa_6$ trigonal prisms. This is evident from the chemical bonding analysis of the electronic structure by *ab initio* calculations. The density of states shows *s*-like metallic conductivity with an active role played by the Ag *d* states within the valence band and for the bonding with calcium. Temperature-dependent magnetic susceptibility data of Eu_4PdMg and Eu_4PtMg show Curie-Weiss behavior above 230 K with experimental magnetic moments of 7.94(1) and 8.00(1) μ_B per Eu atom for the palladium and platinum compound, respectively. Ferromagnetic ordering is detected at the comparatively high Curie temperatures of 150.1(5) (Eu_4PdMg) and 139.1(5) (Eu_4PtMg) K. Magnetization measurements at 3 K show full parallel spin alignment and the typical behavior of soft ferromagnets.

Key words: Crystal Structure, Alkaline Earth Metals, Magnesium, Ferromagnetic Ordering