

# Cadmium-Auride $A^{II}Cd_xAu_{2-x}$ ( $A^{II} = Ca, Sr$ ) Synthese, Kristallstruktur, chemische Bindung

Cadmium-Aurides  $A^{II}Cd_xAu_{2-x}$  ( $A^{II} = Ca, Sr$ ) – Synthesis, Crystal Structure, Chemical Bonding

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Following the observation that the binary dicadmides and diaurides of calcium and strontium ( $A$ ) both form the  $KHg_2$  structure type, the two sections  $A^{II}Cd_xAu_{2-x}$  have been studied systematically by means of synthetic, X-ray structural and theoretical investigations. The binary border compound  $CaCd_2$  is dimorphic forming the  $KHg_2$  structure at elevated temperatures (orthorhombic, space group  $Imma$ ,  $a = 488.63(9)$ ,  $b = 754.1(2)$ ,  $c = 851.3(2)$  pm,  $Z = 4$ ,  $R1 = 0.0498$ ) and the  $MgZn_2$ -type Laves phase at ambient conditions (hexagonal, space group  $P6_3/mmc$ ,  $a = 599.71(9)$ ,  $c = 962.7(2)$  pm,  $Z = 4$ ,  $R1 = 0.0309$ ). Starting from the known binary calcium auride  $CaAu_2$  only a very small amount of Au can be replaced by Cd. Around the 1:1 ratio of Au and Cd the  $TiNiSi$  structure type (orthorhombic, space group  $Pnma$ ), an ordered variant of the  $KHg_2$  type, has a small homogeneity range ( $CaCd_xAu_{2-x}$  with  $x = 1/0.76(2)$ :  $a = 735.0(1)/731.7(1)$ ,  $b = 433.66(6)/431.43(7)$ ,  $c = 873.7(2)/869.9(2)$  pm,  $Z = 4$ ,  $R1 = 0.0482/0.0539$ ). The analogous structure type is also observed in the Sr compounds with the difference that in this case a continuous transition from the  $KHg_2$  type of  $SrAu_2$  (*i.e.*  $x = 0$ ) towards the distorted  $TiNiSi$  structure type (up to  $x = 0.86$ ) is observed in the series  $SrCd_xAu_{2-x}$  (for  $x = 0.86(1)/0.45(1)$ :  $a = 764.0(1)/758.4(1)$ ,  $b = 458.07(7)/474.6(1)$ ,  $c = 872.16(12)/829.2(2)$  pm,  $Z = 4$ ,  $R1 = 0.0446/0.0410$ ). Attempts to prepare the Ca compounds of intermediate composition around a Cd content of  $x \approx 0.5$  resulted in the formation of the Au-rich phase  $Ca_5Cd_2Au_{10}$  crystallizing with the  $Zr_7Ni_{10}$  structure type (orthorhombic, space group  $Cmca$ ,  $a = 1390.6(4)$ ,  $b = 1015.7(3)$ ,  $c = 1025.6(2)$  pm,  $Z = 4$ ,  $R1 = 0.0657$ ). In this compound, Cd and Ca occupy common crystallographic sites, which are occupied by In in the isotopic ternary compound  $Ca_4In_3Au_{10}$ . Similarly, at the Cd-rich parts of the sections  $A^{II}Cd_xAu_{2-x}$  no simple phase width of the  $KHg_2$  structure type exists. In the case of the calcium series the new compound  $Ca_{11}Cd_{18}Au_4$ , which shows only a very small phase width, is formed instead. This compound crystallizes with a new structure type ( $Ca_{11}Cd_{18+x}Au_{4-x}$  with  $x = 0.6/0$ : tetragonal, space group  $I4_1/amd$ ,  $a = 1030.83(6)/1029.39(6)$ ,  $c = 3062.5(3)/3051.0(3)$  pm,  $Z = 4$ ,  $R1 = 0.0475/0.0379$ ) exhibiting a complicated Cd/Au polyanion with four-, five- and six-bonded Cd/Au atoms. The results of FP-LAPW band structure calculations are used to explain the electronic stability of the compounds. The calculated Bader charges of cadmium and gold atoms (and In and Au atoms for comparison) are used to discuss the transition between Cd-rich cadmides (like  $CaCd_2$  and  $Ca_{11}Cd_{18}Au_4$ ), auridocadmates (like  $CaCdAu$ ) and the Cd-poor cadmium aurides (like  $Ca_5Cd_2Au_{10}$ ).

**Key words:** Aurides, Cadmium, Laves Phases, Band Structure Calculation