

MS29-P2 Complex cubic structures: mixed zincides/cadmides/mercurides CaM_{16} and SrM_{16}

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In a systematic synthetic, crystallographic and bond theoretical study, the stability ranges as well as the distribution of the isoelectronic late *p*-block elements Zn, Cd and Hg in the polyanions ('coloring') of the recently reported new mercurides (Sr/BaHg_6) [1] and the prominent YCd_6 -type phases (Ca/SrCd_6) [2] have been investigated.

The stability range of the YCd_6 -type structure of CaCd_6 and SrCd_6 ($Im-3$, $a \approx 1500\text{-}1600$ pm) could be continuously extended to considerable high Hg contents of $\text{CaCd}_{0.89}\text{Hg}_{5.11}$ and $\text{SrCd}_{0.83}\text{Hg}_{5.17}$, respectively. All Ca compounds of this series form the original stoichiometric YCd_6 -type structure with a type 2 triple split disorder (d2) of the $M(2)$ tetrahedra in the pentagondodecahedra (cf. figure top right).

For SrCd_6Hg_x a cubic $2 \times 2 \times 2$ superstructure of the YCd_6 -type ($Fd-3$, $a \approx 3200$ pm, $\text{Eu}_4\text{Cd}_{25}$ -type [3]) appears. Herein, the $[M(2)_4]$ tetrahedra are no longer disordered, but $\frac{3}{4}$ of the cubes, which are not occupied in the aristotype and partially occupied in the new Hg-rich ternary Ca-Zn mercurides like e.g. $\text{CaZn}_{1.74}\text{Hg}_{4.40}$, are filled in an ordered fashion. The shape and filling of the cubes is essentially connected with the orientation of the $[M(2)_4]$ tetrahedra inside the pentagondodecahedra (cf. figure).

At the section $\text{CaZn}_{6-x}\text{Cd}_x$, larger amounts of smaller Zn atoms cause the formation of ternary variants of the cubic $\text{Mg}_7\text{Zn}_{11}$ -type structure [4] ($\text{Ca}_7\text{Zn}_{5.2}\text{Cd}_{3.8}$: $Pm-3$ $a=918.1$ pm; $R1=0.035$). For Ca-Zn-Hg, the new likewise complex cubic 1:5 (20:100) phase $\text{CaZn}_{1.3}\text{Hg}_{3.7}$ ($F-43m$, $a=2145.4$ pm, $R1=0.0704$), which is closely related to $\text{Ba}_{20}\text{Hg}_{103}$ and its ternary Zn/Cd derivatives [5], is formed in addition.

The results of the FP-LAPW DFT bandstructure calculations like the *Bader* charges and volumes are used to rationalize the Zn/Cd/Hg distribution in the new mixed metallides. For the calculation of an YCd_6 -type representative, a model compound 'CaHg₆' was set up using the crystal data of $\text{CaCd}_{0.89}\text{Hg}_{5.11}$, which has been transformed into the subgroup $I23$ to resolve the disorder of the $[M(2)_4]$ tetrahedra (fig. bottom right).

[1] M. Wendorff, C. Röhr, *J. Alloys Compd.* **546**, 320 (2013).

[2] G. Bruzzone, *Gazz. Chim. Ital.* **102**, 234 (1972).

[3] C. P. Gomez, S. Lidin, *Chem. Eur. J.* **10**, 3279 (2004).

[4] V. Mihajlov, C. Röhr, *Z. Anorg. Allg. Chem.* **636**, 1792 (2010).

[5] M. Wendorff, C. Röhr, *Z. Naturforsch.* **67b**, 893 (2012).

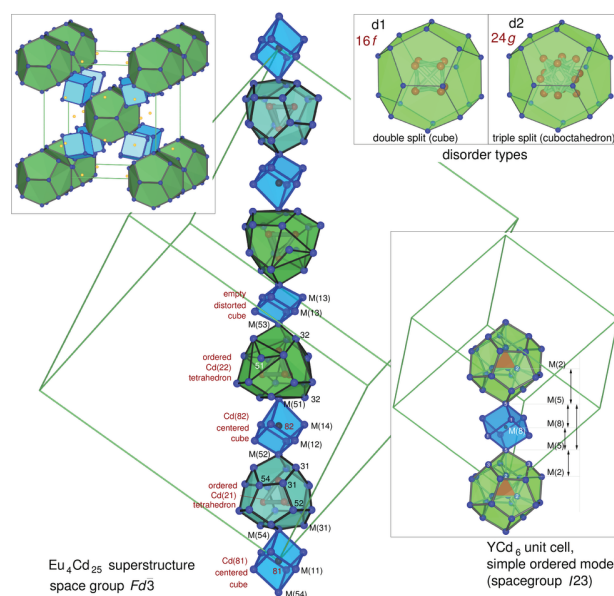


Figure 1. Details of the disorder (top right) and several ordered variants of the cubic YCd_6 -type structure in mixed calcium and strontium Zn/Cd/Hg compounds.

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