Ternary $EuMg_{5+x}$-type structures: Challenges in refining channel occupancies

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The synthesis of polar intermetallic compounds and their structural chemistry is a key focus of our research. For the composition of approximately 1:5, the $EuMg_{5+x}$ structure type, besides the very common $CaCu_5$-type, also occurs quite frequently. As indicated by the "*x*" in the eponymous compound, the exact number of atoms in the unit cell can vary [1], leading to challenges in structure refinement. In this work, we provide a summary of our findings on this structure type, based on studies of the ternary systems *A*–*M*–*M*' (*A* = Ca, Sr, Ba; *M* = Mg, Zn; *M'* = Zn, Cd, In) [2].

In the $EuMg_{5+x}$-type structure of $Ba_3Mg_{5.2}Cd_{10.8}$ ($P6_3/mmc$, a=1023.10(5), c=1082.63(5) pm), the *A* atoms are arranged in rings of three, filling the voids within a topologically close-packed (*t.c.p.*) network of *M* atoms. The latter network is formed by vertex-sharing double tetrahedral stars (Fig. 1, red) leaving empty channels along [001]. The electron density distribution within these channels, which varies from compound to compound and even along an M:M' phase width [e.g. in $Ca(Mg_yZn_{1-y})_{5+x}$ (y = 0.1 - 0.9)], gives rise to many questions regarding the atomic distribution and it's crystal-chemical interpretation [3].

We describe the channels as strings of corner connected cubes. These cubes are also part of the *M* network. In the investigated systems the filling of these cubes varies leading to different models for the overall structure. For Zn containing compounds Zn_2 dumbbells can be observed. In the Sr–Mg–In system additional reflexes can be observed which could be indexed with a rhombohedral unit cell ($P6_3/mmc \rightarrow P31c \rightarrow R3c$, a = 1775.97(8), c = 3181.12(13) pm, Fig. 1). In this superstructure every third 'cube' is empty and heavily squeezed (Fig. 1, aquamarine), resembling less a cube and more a cluster consisting of six tetrahedra which share a common edge. Therewith, this structure motif fits the *t.c.p.* principle again.

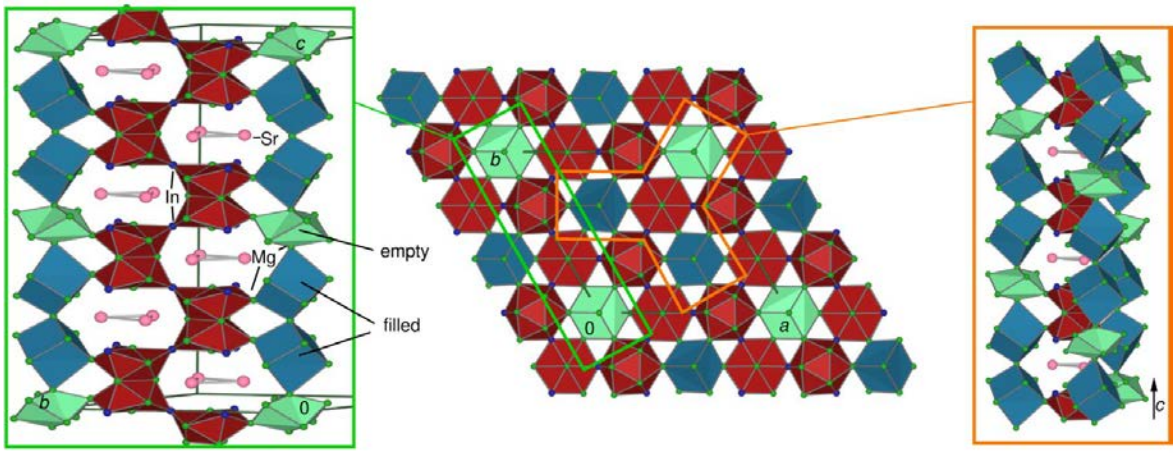

Figure 1. Structure of $Sr_3Mg_{12.5}In_{3.1}$, a superstructure of the $EuMg_{5+x}$-type.

[1] Mühlpfordt, W. (1997) *Z. Anorg. Allg. Chem.* **623**, 985-989.

[2] Köhler, K. (2022) *PhD thesis, University of Freiburg;* K. Köhler, C. Röhr. (2019) *Acta Cryst.* **A75**, 424.

[3] Fredrickson, R. T., Fredrickson, D. C. (2023). *Acta Cryst.* **B79**, 320-329.