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The incommensurate structure of the binary thallides *A*$^*_4$Tl$_{13}$ (*A* = Rb, Cs).The solution of an old problem.

In the course of our studies on alkali trielides with mixed triel positions (Ga/In) [1] and (In/Tl), analysis of the binary phase diagrams Rb-Tl and Cs-Tl [2] show incongruent melting behaviour at the composition *A* Tl~3 (*A* = Rb, Cs). A complete structural description of those phases has not been published to this day, even though *Corbett* and *Dong* [3] were able to determine the composition 'A_4Tl_{13}', as well as one of the structural elements of those phases. In our work, due to the incongruent melting behaviour, the alkali poorer composition *A* Tl_4 was chosen for the synthesis of the two isotypic title compounds. X-Ray single crystal data were used to solve the structure.
The main reflections of the modulated structure were indexed with a *C*-centered orthorhombic lattice. The basic structure was solved in the space group *Cmca* using the *charge-flipping* method (Basic structure of Rb_4Tl_{13}: *Cmca*, *Z* = 1, *a* = 545.75(3), *b* = 3909.95(20), *c* = 2148.90(11) pm).All satellite reflections could be indexed with a primitive orthorhombic lattice and the *q*-vector ***q*** = (0 0 0.2996(1)), allowing the refinement of the (3+1) D modulated structure. The model was obtained by $k2$ symmetry reduction from *Cmca* to *Pbcm* (Rb_4Tl_{13}: *Pbcm*(0 0 γ)*s*00, ***q*** =(0 0 0.2996(1)), *Z* = 1 , *a* = 3907.80(20), *b* = 2147.61(11), *c* = 545.63(3) pm, $R1$=0.083, $R1_{\mathrm{mr}}$=0.063, $R1_{\mathrm{sr}+-(1)}$ = 0.168). The structure exhibits as one structural element isolated chains of interpenetrating icosahedra
(Fig. 1b). These chains are coordinated by cations only. They are embedded between complex 2D thallide layers (Fig. 1a), similar to those observed in the structure of K_6Tl_{17} [4]. Both positions in the centre of the chains as well as two atoms in the layer exhibit a strong positional modulation, which is refined using the *saw-tooth* function (Fig. 2). The positions of the remaining atoms affected by this modulation can be refined using harmonic modulation functions. The modulation is probably caused by the size of the thallium atoms, which are too large to fit into the structure in a way compatible with the periodicity of the lattice.

Figure 1: a) Unit cell of the basic structre of Rb_4Tl_{13}. The thallium atoms refined with a saw-tooth function in the final model (Tl(19) and Tl(29)) are represented as blue spheres. All remaining atomic positions are shown as red (Rubidium) resp. green (Thallium) ellipsoids (Probability: 90%).
b) Detailed view of one chain of interpenetrating icosahedra with 90% probability ellipsoids and atomic labels from the model of the basic structure (projection along [001]).

Figure 2: De Wolff's sections from the final structure of Rb_4Tl_{13}. a) $x3$-$x4$-section at the Tl(191) site. b) $x3$-$x4$-section at the Tl(292) site (Contour lines at intervals of 30 e^- x $10^{-6}pm^{-3}$).
The difference between the atomic labels of the final and the basic structure (Fig.1) results from the symmetry reduction from *Cmca* to *Pbcm*. The Tl(19) site splits up to Tl(191) and Tl(192) and the Tl(29) site splits up to Tl(291) and Tl(292).

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