## FA3-MS23-T01

### 2D-noncommensurate modulated misfit layer structures of franckeite and cylindrite.

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Crystal structures of these triclinic Pb-Sn-Sb-Fe-S compounds have a pronounced one-dimensional transversal wave-like modulation and a non-commensurate layer match in two dimensions. They consist of alternating pseudohexagonal (H) and pseudotetragonal (Q) layers and form a homologous pair: cylindrite with thinner Q layers and franckeite with Q layers of double thickness. The Q layer of a newly refined franckeite structure from the mine of San José, Bolivia, $Pb_{5.2}Ag_{0.2}Sn_{2.4}Sb_{2.2}Fe_{1.0}S_{14.5}$, is an MS layer (M = $Pb^{2+}$, $Sn^{2+}$, $Sb^{3+}$..) four atomic planes thick, with $a$ 5.815 Å, $b$ 5.873 Å, and the layer-stacking vector $c$ 17.366 Å. The lattice angles are α 94.98°, β 88.43°, γ 89.97°; the modulation vector q = -0.001 $a^*$ + 0.1282 $b^*$ - 0.0295 $c^*$. The H layer is a single-octahedron $MS_2$ layer (M = $Sn^{4+}$, $Fe^{2+}$, $Fe^{3+}$..) with $a$ 3.672 Å, $b$ 6.275 Å, $c$ 17.447 Å, α 95.26°, β 95.45°, γ 89.97°; the modulation vector is q = -0.001 $a^*$ + 0.1374 $b^*$ - 0.031 $c^*$. Length of the wave derived from the modulation vector is 45.80 Å; the match of centred (sub)cells in this $b$ direction, 15.5 Q : 14.5 H, occurs at 91.01 Å, a double of the modulation vector minus a structurally important difference Δ = 0.59 Å. The $a$ and $b$ vectors of both subsystems are parallel; the $c$ vectors diverge. 5D superspace refinement was performed in the superspace group C-1, using 7397 observed reflections. It resulted in the overall R(obs) value equal to 0.094. The Q layers are composed of two tightly-bonded double-layers, separated by an interspace hosting lone electron pairs. Average composition of cations on the outer surface was refined as $Pb_{0.74}(Sn,Sb)_{0.26}$ whereas that of cations covering the interspace with lone electron pairs, with a typical configuration analogous to that observed in orthorhombic SnS, corresponds to $(Sn,Sb)_{0.74}Pb_{0.26}$. Iron is dispersed over $Sn^{4+}$ sites in the H layer. Transversal modulation of the Q layer is achieved by the local variations in the Pb:(Sn,Sb) ratios at the Q-layer surface. Its purpose is to re-establish a one-dimensional commensurate contact along [010] between the *curved Q and H surfaces* to the greatest extent possible. Layer-stacking disorder and divergence of the Q and H stacking directions are typical for these composite structures as is the divergence between modulation wave-front and these stacking directions. Cylindrite forms cylindrical aggregates several millimetres thick with (in principle) hollow cores. The modulated $b$ direction becomes a cylinder axis and the unmodulated non-commensurate $a$ direction a cylinder tangent. Because of the increased rigidity of the Q layer, franckeite usually forms masses of curved crystals rather than cylindrical aggregates. The existence of this family depends critically on the radius ratios of the cations involved, especially those involving ($Pb^{2+}$, $Sn^{2+}$) and $Sn^{4+}$. Their replacement by a $Pb^{2+}$: $Bi^{3+}$ combination leads to misfit layer structures of a very different type (cannizzarite).

**Keywords: modulated structure, misfit layer structure, franckeite**

## FA3-MS23-T02

### Modulation functions of aperiodic crystals.

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The crystal structures of incommensurate composite crystals and incommensurately modulated crystals are described by average positions and modulation functions for the atoms in the unit cell of the basic structure. The latter is periodic for modulated structures and it comprises two interpenetrating, mutually incommensurate periodic structures for composite crystals. Established methods exist for the determination of modulated structures from diffraction data [1,2]. Nevertheless, it is accepted that often only approximate modulation functions can be determined, *e.g.* functions described by a few low-order harmonics or comprising a block-wave or saw-tooth function. The failure to obtain accurate descriptions of the modulations has the immediate consequence of a limited validity of any crystal-chemical analysis concerning chemical and physical properties.

Here we discuss the true nature of the modulations in aperiodic crystals. The analysis is based on structure refinements and applications of the maximum-entropy method (MEM) to diffraction data of several incommensurate composite crystals and incommensurately modulated crystals [3].

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## FA3-MS23-T03

### Periodic and aperiodic ordering in composition flexible square lattices

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There are many materials that exhibit ordered patterns of some atomic species (or vacancies) within a common structural framework. The variable atomic proportions, instead of implying a solid solution, introduce composition-dependent ordered configurations. They are generally superstructures. If the composition flexibility of the compound is strong, incommensurate arrangements also exist. These composition-driven ordered arrangements can be considered as occupation-modulated structures, and this viewpoint has been applied with much success to mixed layered compounds with ordering along a single direction. The efficiency of the approach lies on the fact that these 1D orderings are uniform or pseudo-uniform in the sense of distributing one specific motif as uniformly as possible [1,2]. These arrangements, following typical hierarchical structures, are specially simple when described in superspace.