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

Emil Makovicky[a], Václav Petříček[b], Michal Dušek[b], Dan Topa[c]. [a]University of Copenhagen, Denmark. [b]Czech Academy of Sciences Prague, Czech Republic. [c]University of Salzburg, Austria.
E-mail: emilm@geo.ku.dk

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 = 0.59Å. 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

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Modulation functions of aperiodic crystals.

Sander van Smaalen, Liang Li. *Laboratory of Crystallography, University of Bayreuth, Bayreuth, Germany.*
E-mail: smash@uni-bayreuth.de

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].

[1] van Smaalen S.: *Incommensurate Crystallography* (Oxford University Press, Oxford, 2007). [2] Petricek, V.; Dusek, M., *Z. Kristallogr.* 2004, 219, 692. [3] Li, L.; Schönleber, A.; van Smaalen, S., *Acta Crystallogr. B* 2010, 66, 130.

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Periodic and aperiodic ordering in composition flexible square lattices

J.M. Perez-Mato[a], S. Gonzalez de la Torre[a], L. Elcoro[a], Alberto Garcia[b]
[a]*Dept. de Fisica de la Materia Condensada. Facultad de Ciencia y Tecnologia. Universidad del Pais Vasco (UPV-EHU), Apdo. 644, 48080 Bilbao, Spain.*
[b]*Inst. de Ciencia de Materiales de Barcelona, CSIC, Campus de la UAB, E-08193 Bellaterra, Spain*
E-mail: jm.perez-mato@ehu.es

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.

Here we explore the generalization of this approach to systems where ordering is active in 2D. We have investigated the most uniform ordered configurations of two atomic species, A and B, lying on a two dimensional square lattice of composition $A_{1-x}B_x$, as a function of x. By simulated-annealing optimization of a lattice gas model with repulsive pair interactions we show that the pseudo-uniform 2D orderings most commonly favoured are stripe or checkerboard arrangements [3]. Exceptionally, more complex configurations such as 2D tilings, with tiles defined by distinct supercells of different composition, are observed. General rules underlying these orderings treated as modulated structures can be derived. Their description (and prediction!) within the superspace formalism, using occupation step-like modulations and composition-dependent wave vectors, are specially simple, with a *closeness* condition being fulfilled by some superspace atomic domains. The rules obtained generalize the hierarchical (Farey-tree) rules that govern 1D uniform orderings [1,2].

The hierarchical intensities in the Fourier spectrum of these pseudo-uniform arrangements distinguish two basic modulation wave vectors that define in direct space a specific lattice. This lattice is not generally a superlattice of the basic square lattice and can be considered an *average* monoatomic lattice of B atoms (with a node density consistent with the B composition). The observed pseudo-uniform ordering can then be interpreted as a modulated configuration of a composite system formed by this average lattice of B atoms and the square lattice, their misfit being controlled by the composition x. The possibility of regarding modulated structures as composites and vice versa is characteristic of uniform or pseudo-uniform orderings, where a closeness condition between some atomic domains exists [4].

[1] Perez-Mato, J.M.; Zakhour-Nakhl, M.; Weill, F.; Darriet, *J. Mater. Chem.* 1999, 9, 2795. [2] Darriet, J.; Elcoro, L.; El Abed, A.; Gaudin, E., Perez-Mato, J.M. *Chem Mat.* 200214, 3349. [3] Watson, G.I.; *Physica A* 1997, 246, 253. [4] Perez-Mato, J.M.; Etrillard, J.; Kiat, J.M.; Liang, B.; Lin, C.T. *Phys. Rev.* 2003, 67, 024504.

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Cation composition dependence of superlattice reflections in $(Sr/Ca/La)_{14}Cu_{24}O_{41}$,. Ognjen Milat
Institute of Physics, Zagreb, Croatia.
E-mail: milat@ifs.hr

Crystallographic structure of the $(Sr/La/Ca)_{14}Cu_{24}O_{41}$ "chain-ladder" compounds is complex [1] due to being composed of two interpenetrated subsystems with lattice parameters mutually incommensurate along one direction. "Ladder"-subsystem is formed by the $(Sr/La/Ca)_2Cu_2O_3$ layers on an orthorhombic (*Fmmm*) lattice, and "chain"-subsystem consists of the CuO_2 interleaved layers on an (*Amma*) lattice [2]. While cell parameters a ($\approx 1.14nm$) and b ($\approx 1.34nm$) are common for both lattices regardless of the cation composition, the misfit between the c-parameters is found to depend on substitution and doping. The c_{Ld}/c_{Ch} ratio is always close to $\sqrt{2}$, but varies from 1.45 to 1.41 [3] for pure $Sr_{14}Cu_{24}O_{41}$, to $Sr_2Ca_{12}Cu_{24}O_{41}$, respectively, being roughly 1.43 in La/Ca for Sr substituted $La_6Ca_8Cu_{24}O_{41}$. In addition, partial substitution of La for Sr affects electronic structure by reducing hole-doping on $Cu^{2+\delta}$.

A lot of doubt has recently emerged about doped hole ordering into Wigner crystal (WC) on the $5c_{Ld}$ or $3c_{Ld}$ superlattice cells, as found by RXS [4]. This ordering is allocated onto "ladder" subsystem due to observation of weak RXS spots at reciprocal positions commensurate with "ladder", but not with "chain" basic spots. Here, we present detailed electron diffraction study of the corresponding 4-dim reciprocal lattice, and prove that all spots can be indexed: $H = ha* + kb* + lc_{Ld}* + mc_{Ch}*$. Spot`s intensity depends more on local imaging conditions and degree of order, then on nominal composition. By varying the Sr/La/Ca composition and the corresponding c_{Ld}/c_{Ch} ratio, all reciprocal lattice points shift in positions along $c*$; the range $(^1/_5c_{Ld}*- ^1/_3c_{Ld}*)$, coinciding to $(^1/_{7.1}c_{Ch}*- ^1/_{4.3}c_{Ch}*)$, is swept by the weak spot 00-46. Therefore, the peaks observed in that range should be assigned as *00-46* reflection, and could not be exclusively related to "hole" superlattice formation in "ladder" subsystem only, as claimed for $5c_{Ld}$ WC in $Sr_{14}Cu_{24}O_{41}$ [4].

[1] Milat O., Van Tendeloo G., Amelinckx S., Mebhod M., Deltour R., *Acta. Cryst.* 1992, A48, 618. [2] Siegrist T., Schneemeyer L.F., Shunnsine S.A., Waszeck J.V., Roth R.S., *Mat. Ress. Bull.* 1988, 23, 1429. [3] Hiroi Z., Amelinckx S., Van Tendeloo G., Phys. Rev. 1996, B54, 15849. [4] Rusydi A., Abbamonte P., Eisaki H., Fujimaki Y., Blumberg G., Uchida S., Sawatzky G.A., PRL 97, 2006, 016403.

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The composite structure of $Ag_{0.5}Cu_{0.5}V_2O_5$. W. Hermes[a], M. Dollé[b,c], J. Galy[b,c], S. Lidin[b], P. Rozier[b,c]. [a]*Department of Chemistry, Polymer & Materials Chemistry, Lund University, P.O. Box 124, SE-22100 Lund, Sweden.* [b,c]*Centre d'Elaborationde Matériaux et d'Etudes Structurales CNRS 29, rue Jeanne Marvig, BP 94347, 31055 Toulouse cedex 4, France.* [b,c]*Université de Toulouse, UPS, 118 route de Narbonne, 31062 Toulouse, France.*

The structure of $Ag_{0.5}Cu_{0.5}V_2O_5$ was determined on the base of X-ray single crystal data and compared to the pure Cu and Ag compounds. $Ag_{0.5}Cu_{0.5}V_2O_5$ is polymorph and the room-temperature (RT) phase as well as the low-temperature phase can be described as composite structures. The phase transition occurs at around 140 K and was detected by heat capacity measurements. The average structure of the RT-phase crystallizes in the space group *C2/m*, and was described by *P. Rozier et al* [1]. An account of the synthesis procedure can be found here as well. At RT the structure is only partially ordered. Between the vanadate blocks, there are two different types of channels hosting Cu/Ag positions. In the smaller channels, the Ag/Cu positions order to give a composite type arrangement with $c_{Vandate} = 3.74$ Å and $c_{Ag2/Cu2} = 4.06$ Å, while in the larger channels, the Ag/Cu positions are less well determined. The symmetry of the composite structure is $C2(0\beta 1/2)0$, b≈0.92, the breaking of the mirror symmetry perpendicular to c being very important for the convergence of the model.

Below the transition temperature, two phenomena occur. First, the modulation vector changes from (0 0.92 1/2) to (0.006 0.88 0.47), the deviation from 0 of the component along a* is not statistically significant, but that along c* is, and the symmetry of the structure is reduced to triclinic. Simultaneously, a secondary q vector appears at (0.065 0.95 0.33). Because of twinning according to the underlying monoclinic cell, the resulting diffraction pattern is somewhat complex.