

FA4-MS01-O1

Structural Hidden Degrees of Freedom in Aperiodic Materials. Mickaël Huard. *I.P.R. UMR CNRS 6251, Université de Rennes 1, 35042 Rennes, France.*

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Self-assembly underlies the formation of a wide variety of biological and supramolecular tubular structures [1]. One feature of these materials is to present the ultimate one-dimensional confinement for the guest molecules giving uni-axial composite crystals. Aperiodicity in these materials may appear rather naturally due to the misfit of host and guest parameters along the channels or the tubes [2]. Superspace crystallography is required to correctly describe these aperiodic structures where no translation symmetry exists in the physical three dimensions world [3,4]. These structures may present new structural and dynamical properties related to the infinite degeneracy of their ground state [5,6]. This presentation focuses on original sequences of phase transitions found in the host-guest prototype alkane urea inclusion compounds. Very high-resolution neutron diffraction recently allowed us to reveal such a phase transitions sequence in nonadecane-urea, which can only be interpreted in terms of internal dimension of the superspace [7]. We will present new results, concerning different compounds within the urea-alkane family, which illustrate the way nature may explore all the hidden degrees of freedom allowed in higher dimensional spaces.

[1] G.M. Whitesides and B. Grzybowski Self-assembly at all scales. *Science*, 295, 2418, **2002**. [2] M. D. Hollingsworth and K. D. M. Harris, *Comprehensive Supramolecular Chemistry* (Vol. 6; Solid State Supramolecular Chemistry: Crystal Engineering), pp. 177-237, **1996**. [3] S. Van Smaalen and K.D.M. Harris, *Proc. Roy. Soc. London Ser. A*, 452, 677, **1996**. [4] T. Janssen, G. Chapuis, M. de Boissieu, *Aperiodic Crystals: From Modulated Phases to Quasicrystals* (Oxford Univ. Press, Oxford, **2007**). [5] J. Marti-Rujas, A. Desmedt, K.D.M. Harris, F. Guillaume *J. Am. Chem. Soc.* 126 11124, **2004**. [6] B. Toudic, F. Aubert, C. Ecolivet, P. Bourges, T. Brezczewski, *Phys. Rev. Lett.* 96 145503, **2006**. [7] B. Toudic et al., *Science* 319, 5859, 69 - 71 **2008**.

Keywords: guest-host structures; aperiodic crystallography; phase transitions

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On the Structures of the Dense Alkali Metals. Eugene Gregoryanz^a, Christophe Guillaume^a, Lars Lars Lundegaard^a, Olga Degtyareva^a, Malcolm McMahon^a, Stas Sinogeikin^b, Malcolm Guthrie^b. ^a*CSEC and School of Physics, University of Edinburgh.* ^b*HPCAT, APS, Argon, USA.*

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The alkali group elements are considered as textbook examples of free electron metals because of the single s electron in the valence band. However, when these metals are subjected to compression these simple systems exhibit unexpected complexity departing from the free-

electron behaviour at high densities. The pressure-induced complexity is attributed to the increased role of the core electrons becoming more appreciable with decreased volume [1]. Due to the difficulties associated with the high reactivity and chemistry of the alkalis and limited set of tools available to study them at extreme conditions until very recently only the behaviour of caesium was known up to 200 GPa at 300 K. Lately the melting curve of Na measured by the x-ray diffraction techniques was shown to have unexpected minimum at 118 GPa [2] and the plethora of the new phases associated with this minimum was discovered [3] owing to the development of the single crystal techniques in the diamond anvil cell [4]. In this presentation I will discuss the common traits and differences between Na and other alkali metals at extreme compressions and make a comparison with theoretical studies.

[1] J. Neaton and N. Ashcroft, *Phys. Rev. Lett.*, 86, 2830, **2001**
[2] E. Gregoryanz et al., *Phys. Rev. Lett.*, 94, 185502, **2006** [3] E. Gregoryanz et al., *Science*, 230, 1054, **2008** [4] L. Lundegaard, *PhD Thesis*, U. of Edinburgh, Edinburgh, **2008**.

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On the Application of the Fibre Bundle Approach to the Description of the Symmetry of Magnetic Structures and Other Aperiodic Structures. Jerzy Warczewski^a, Paweł Gusin^a, Tamara Śliwińska^a, Józef Krok-Kowalski^a. ^a*Institute of Physics, University of Silesia, ul. Uniwersytecka 4, 40-007 Katowice, Poland.*

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We present a description of the magnetic structures in terms of fibre bundles [1]. Such an approach turns out to be the most general, because it is based on the most general product of two arbitrary spaces, namely the Cartesian product, which is very suitable to the combination of two “worlds”, e.g. the “world of positions” (R^3) and the “world of spins” (V_3). Thus the description of crystal structures is to be carried out in R^3 , whereas the description of spin structures is to be carried out in V_3 . This approach equates the symmetry analysis of magnetic structures with the method of the higher dimensional embeddings of the modulated structures. The symmetry groups appearing in the symmetry analysis become structural groups of the bundles. From the other side a higher dimensional space needed to the description of a modulated structure makes here the total space of the bundle E_6 . Thus these three methods, namely the symmetry analysis, the higher dimensional embeddings and the fibre bundles are equivalent. We introduce the Gaussian factor which will play a double role: it makes the magnetization vector \mathbf{M} to be a field and simultaneously makes the description of the magnetic structures more physical. The total magnetic group TG_m in the space E_6 is the tensor product of the magnetic group G_m and the space group G_Λ of the crystal structure, where m is the index which enumerates magnetic ordering (ferromagnetic, antiferromagnetic, simple spiral, ferromagnetic spiral, skew spiral and both transverse and longitudinal spin waves). It is worthwhile to mention here

that these different magnetic structures have been found by the authors to be related with the values of certain topological invariants [2]. It seems that the above approach could serve also for the description of the symmetry groups of all the other aperiodic structures, like e.g. the modulated nonmagnetic structures, quasicrystals (nonmagnetic and magnetic) etc.

[1] J. Warczewski, P. Gusin, T. Śliwińska, G. Urban, J. Krok-Kowalski, *Central European Journal of Physics*, 5(3) 2007 377-384. [2] P. Gusin, and J. Warczewski, *Journal of Magnetism and Magnetic Materials*, 281/2-3 2004 178-187.

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FA4-MS01-O4

Giant Unit Cell Structures in the System Al-Cu-Ta. Thomas Weber^a, Julia Dshemuchadse^a, Matthias Conrad^b, Bernd Harbrecht^b, Walter Steurer^a. ^aLaboratory of Crystallography, ETH Zurich, Switzerland. ^bFachbereich Chemie, Philipps-Universität Marburg, Germany.

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Three cluster-based structures of unprecedented complexity have been observed in the system Al-Cu-Ta [1, 2]: $cF432$ -Al₆₉Ta₃₉ (AT-19), $a = 19.153 \text{ \AA}$, $V = 7,026 \text{ \AA}^3$, $cF(5,928-x)$ -Al_{56.6}Cu_{3.9}Ta_{39.5}, $x = 33$ (ACT-45), $a = 45.376 \text{ \AA}$, $V = 93,428 \text{ \AA}^3$ and $cF(23,256-x)$ -Al_{55.4}Cu_{5.4}Ta_{39.1}, $x = 98$ (ACT-71), $a = 71.490 \text{ \AA}$, $V = 365,372 \text{ \AA}^3$. The space group is $F 3m$ in all three cases. Despite the complexity of the structures, usage of cutting edge X-ray diffraction technology allowed to collect high quality diffraction data suitable for precise structure determination. There are two complementary approaches to the understanding of the structures. First, the crystals can be seen as cluster-based compounds. The common fundamental building unit is a triple-shell Al₁₀₂Ta₅₇ fullerene cluster with a diameter of about 13.5 Å. In the case of AT-19 the fullerenes form a distorted *fcc* packing, where the empty spaces are filled by Friauf or CN15 Frank-Kasper polyhedra. ACT-45 and ACT-71 host super clusters built of four or ten fullerenes, respectively, *i.e.* fragments of the AT-19 structure. The super clusters are separated by extended blocks, which are related to Laves phases. An alternative approach to the understanding of the structures is describing them as modulated structures. The common basic structure is a 6.5 Å sized cubic Laves phase. AT-19, ACT-45 and ACT-71 are 3-fold, 7-fold and 11-fold commensurate super structures, respectively. The lattice of the basic structure can clearly be identified in the diffraction pattern, however, many satellite reflections show intensities, which are comparable or even stronger than main intensities. An interesting and quite exceptional aspect of the structures investigated in this work is that they show self-templating properties: when shifting the along a main axis projected structure by 1/4 unit translation it is found that densely filled regions are systematically superimposed to loosely filled regions and *vice versa*.

[1] Weber, T., Dshemuchadse, J., Kobas, M., Conrad, M., Harbrecht,

B., Steurer, W., *Acta Cryst. B*, accepted for publication. [2] Conrad, M., Harbrecht, B., Weber, T., Jung, D.Y., Steurer, W., *Acta Cryst B*, accepted for publication.

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FA4-MS01-O5

K₄CoMo₃O₁₂ at Low Temperatures: Phase Transitions and Modulated Structures. J.M. Engel^a, H. Ehrenberg^b. ^aInstitut für Werkstoffwissenschaft, Technische Universität Dresden, Helmholtzstrasse 7, D-01069, Dresden. ^bInstitute for Complex Materials, IFW Dresden, Helmholtzstrasse 20, D-01069 Dresden, Germany.

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K₄CoMo₃O₁₂ shows a large variety of different polymorphic modifications from a high-temperature phase till several high-pressure phases [1]. Consequently low-temperature single-crystal experiments on α -K₄Co(MoO₄)₃ at 200, 150 and 101K were performed. All data were collected with a Xcalibur system from Oxford-Diffraction equipped with a Sapphire2 detector using ω - and ϕ -scans. The cooling was performed with a cryo system also from Oxford-Diffraction.

The structural changes at low temperatures were indicated by additional reflections detected in the projection of the reciprocal space. In the case of the data at 200K the superstructure reflections bisect the a^* -axis. However in the data at 150K and 101K occur satellite reflections with modulation vectors close to $q = 1/2 a^* + 1/3 b^* + 1/3 c^*$. The refinement of the q -vector leads to $q = 0.501 a^* + 0.350 b^* + 0.318 c^*$ at 150K and to $q = 0.501 a^* + 0.343 b^* + 0.328 c^*$ at 101K, respectively. Therefore we are dealing here with incommensurately modulated structures.

The first low-temperature modification at 200K has also the space group P-1 with four formula units per unit cell and the lattice dimensions $a = 15.3637(6)$, $b = 9.8492(4)$, $c = 10.0014(4) \text{ \AA}$ as well as $\alpha = 92.819(3)$, $\beta = 106.588(4)$ and $\gamma = 105.772(3)^\circ$. The significant alteration in the structure is a fractional change of the coordination of Co from six to five.

Ignoring the superstructure reflections from the data of 150K and 101K, the average structures exhibit again exclusively six-fold coordinated Co atoms.

We will present the results of the data analysis and compare the structures with each other.

[1] Solodovnikov S.F., Klevtsov P.V., Solodovnikova Z.A., Glinskaya L.A., Klevtsova R.F., *J. Struct. Chem.*, 1998, 39, 230-237.

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