Session III - Monday, August 31 - late afternoon

PL3

APERIODIC STRUCTURES AT HIGH PRESSURE

C. Hejny

University of Innsbruck, Institute for Mineralogy and Petrography, Innrain 52, A-6020 Innsbruck, Austria
clivia.hejny@uibk.ac.at

High-pressure studies of aperiodic materials still represent a great challenge and have been rare until recently. The combination of high-pressure science and aperiodic crystallography demands special expertise for sample preparation, data collection and data processing. The analysis of in-situ high-pressure datasets measured from aperiodic crystal structures within a diamond anvil cell with limited access to reciprocal space has only become possible due to the development of easy-to-use software for the routine analysis of modulated crystal structures, e.g. JANA2006 [1], which also implements tools for the analysis of high-pressure data sets. The superspace approach not only allows the analysis of crystal structures with an incommensurate modulation, but is also of special interest for the processing of high-pressure data measured from commensurately modulated structures, because of the reduction in the number of parameters in the refinement process [2].

High-pressure studies of aperiodic structure were sparked by the striking discovery of incommensurate composite and incommensurately modulated crystal structures of the elements at high pressures [3]. This was followed by a growing number of structural investigations of the high-pressure dependence of aperiodic structures. Recently a notable accumulation of incommensurately modulated structures in conjunction with magnetism and superconductivity causes the interest in investigating the temperature- and also pressure stability of these phases and their phase transitions, e.g. [4]. In contrast to this, quasicrystalline material has been demonstrated to be stable over a considerable range of pressure and temperature and also over cosmic timescales [5].

1. V. Petricek, M. Dusek, L. Palatinus, *Z. Kristallogr*., **229** (2014), 345.

2. M. Bykov, E. Bykova, M. Hanfland, HP. Liermann, S. van Smaalen (2013) *High Pressure Res.,* **33** (2013), 501.

3. MI. McMahon, RJ. Nelmes, *Chem Soc Rev.* **35** (2006), 943.

4. M. Bykov, E. Bykova, L. Dubrovinsky, M. Hanfland, H. Liermann, R. Kremer, S. van Smaalen, *Acta Cryst.* **A70** (2014), C263.

5. V. Stagno, L. Bindi, Y. Shibauaki, Y. Tange, Y. Higo, HK. Mao, PJ. Steinhardt, Y. Fei, *Sci. Rep.* **4** (2014), 5869.

S3-L1

DESIGNING FUNCTIONAL MATERIALS IN SUPERSPACE

John Bleddyn Claridge

University of Liverpool, Department of Chemistry, Crown Street, L69 7ZD Liverpool, UK

The area of improper ferroelectrics and potentially multiferroics has recently received significant attention do the prediction that a combination of $a^-a^-c^+$ tilting and layered ordering of the A site cations along $[001]_{perov}$ in perovskite ABX_3 systems or in the even n Ruddleston Popper (RP) phases $(A_{n+1}B_nX_{3n+1})$, leads to noncentrosymmetric structures which are predicted to have significant switchable polarisations.

The oxide heterostructure $[(YFeO_3)_5(LaFeO_3)_5]_{40}$, which is magnetically ordered and piezoelectric at room temperature, has been constructed from two weak ferromagnetic $AFeO_3$ perovskites with different A cations using RHEED-monitored pulsed laser deposition. Here we elaborate a superspace description of cation ordering in tilted perovskites that allows the prediction of the symmetry of arbitrary cation ordered superlattices, along $<100>_{perov}$, $<110>_{perov}$ and $<111>_{perov}$ and ordering of both A and B cations, of the various tilted perovskites, which also rationalizes the observed domain structures. This approach is futher expaned to include magnetic symmetry and the potential for finding other suitable structural distortions in non-perovskite systems such as rutile superlattices where the metal insulator transition in VO_2 plays the role of the tilt transition.

S3-L2

NEUTRON LAUE AND X-RAY DIFFRACTION STUDY OF A NEW CRYSTALLOGRAPHIC SUPERSPACE PHASE IN N-NONADECANE/UREA

P. Rabiller[1], S. Zerdane[1], C. Mariette[1], G.J. McIntyre[2], M.-H. Lemée-Cailleau[3], L. Guérin[1], J.C. Ameline[1], and B. Toudic[1]

[1] *Institut de Physique de Rennes, UMR UR1-CNRS 6251, Université de Rennes 1, 35042 Rennes, France*
[2] *Australian Nuclear Science and Technology Organisation, New Illawarra Road, Lucas Heights NSW 2234 Australia*
[3] *Institut Laue-Langevin, 71 avenue des Martyrs, 38042 Grenoble cedex 9, France*
philippe.rabiller@univ-rennes1.fr

Aperiodic composite crystals, such as *n*-alkane/urea inclusion compounds present long-range order without translation symmetry. For such host/guest [1] intergrowth nanotubular structures, which have a sole incommensurate direction *c*, a four-dimensional superspace [2-3] description usually gives the positions of the complete set of Bragg peaks. In such materials, symmetry breakings must be described as structural changes within crystallographic superspaces and the increase of the number of superspace groups with the increase of the dimension of the superspace allows many more structural solutions. We recently reported a sequence of phases in *n*-nonadecane/urea which involves at atmospheric pressure such structural degrees of freedom [4]. The study of the (T, P) phase diagram, through single crystal X-ray and neutron diffraction experiments, clearly evidenced the increase of structural solutions within this formalism [5]. With no evident reason at the time to suspect that further transitions would occur at lower temperature, these studies were limited to 80K. In fact this assumption was unfounded, and here we present a study down to 4K, making use of modern neutron Laue diffraction technique at atmospheric pressure, in which we evidence a supplementary phase transition within the crystallographic superspaces of dimension five.

1. Hollingsworth M.D. & Harris K.D.M. (1996), *Urea, Thiourea, and Selenourea* In *Comprehensive Supramolecular Chemistry*, Edited by D.D. MacNicol, F. Toda & R. Bishop, p. 177-237. Oxford: Elsevier Science Ltd.

2. Janssen, T., Chapuis, G. & de Boissieu, M. (2007). *Aperiodic Crystals: From Modulated Phases to Quasicrystals*. Oxford: Oxford University Press.

3. van Smaalen, S. (2007). *Incommensurate Crystallography*. Oxford: Oxford University Press.

4. Toudic, B., Garcia, P., Odin, C., Rabiller, P., Ecolivet, C., Collet, E., Bourges, P., McIntyre, G.J., Hollingsworth, M.D. & Breczewski, T. (2008). *Science* **319**, 69-71.

5. Toudic, B., Rabiller, P., Bourgeois, L., Huard, M., Ecolivet, C., McIntyre, G.J., Bourges, P., Breczewski, T. & Janssen, T. (2011). *Europhys. Lett.* **93,** 16003.
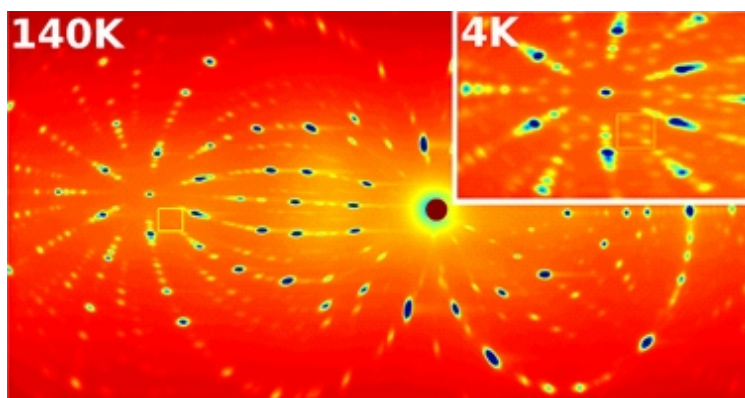
Figure 1. Neutron Laue pattern obtained at the OPAL reactor (Australian Nuclear Science and Technology Organisation) evidencing a new phase below liquid N_2 temperature in *n*-nonadecane/urea.

S3-L3

OXYGEN EXCESS AND OXYGEN DEFICIENT L-Ta$_2$O$_5$ RELATED COMPOSITE STRUCTURES

S. Schmid, V. Fung

School of Chemistry, The University of Sydney, Sydney NSW 2006, Australia
siegbert.schmid@sydney.edu.au

The low temperature structure of tantalum pentoxide, L-Ta$_2$O$_5$, has been the subject of many investigations. Although Ta$_2$O$_5$ has been widely utilised in tantalum capacitors the structure of this compound is still not completely understood. A range of other metal oxides can be doped into Ta$_2$O$_5$ resulting in stable high temperature phases isostructural to L-Ta$_2$O$_5$. The range of possible metal oxides includes those leading to structures with oxygen excess (*e.g.* WO$_3$) as well as oxygen deficient structures (*e.g.* Al$_2$O$_3$) [1].

Members of the $(1-x)$Ta$_2$O$_5\cdot x$GeO$_2$ and $(1-x)$Ta$_2$O$_5$ $\cdot x$Al$_2$O$_3$ solid solutions were synthesised, and the structures were investigated using synchrotron X-ray powder diffraction and neutron powder diffraction data [2]. Structural models were developed and refined using using a [3+1] dimensional incommensurate composite structure approach.

It was found that the structures of all members of the $(1-x)$Ta$_2$O$_5\cdot x$GeO$_2$ and $(1-x)$Ta$_2$O$_5\cdot x$Al$_2$O$_3$ series synthesised could be described with the *Xmmm*(0　s00) superspace group and a composition dependent modulation vector $\boldsymbol{q}$, similar to both L-Ta$_2$O$_5$ and $(1-x)$Ta$_2$O$_5$ $\cdot x$WO$_3$ [3]. Introduction of the modulation to the structural models resulted in generally more favourable bond valence sum values and bond distances compared to the basic structure.

Atomic modulation functions for displacements across both the $(1-x)$Ta$_2$O$_5\cdot x$GeO$_2$ and $(1-x)$Ta$_2$O$_5\cdot x$Al$_2$O$_3$ series, and for pure L-Ta$_2$O$_5$, were found to be very similar, and also strongly resemble the AMFs found in previous work done on the Ta$_2$O$_5$-WO$_3$ system [4]. This points to an extraordinary compositional flexibility of the L-Ta$_2$O$_5$ structure type, considering the variable oxygen-to-metal ratio.

The similarity of the AMFs demonstrates that although these structures in 3D space would require descriptions with different space groups and multiplicities, in 4D superspace they are closely related. This brings about the possibility of considering the L-Ta$_2$O$_5$ composite structure as a general structure type in higher dimensional space, similar to structure types for conventional 3D structures.

1. R. S. Roth, J. L. Waring, *J. Res. Nat. Bureau of Standards A* **74**, (1970), 485.

2. S. Schmid, V. Fung., *Aust. J. Chem.* **65,** (2012), 851.

3. R. L. Withers, S. Schmid. J. G. Thompson, *Prog. Solid State Chem.* **26,** (1998), 1.

4. S. Schmid, J. G. Thompson, A. D. Rae, B. D. Butler, R. L. Withers, N. Ishizawa, S. Kishimoto, *Acta Crystallogr.* B**51**, (1995), 698.

S3-L4

P$_4$W$_{20}$O$_{68}$: SUCCESSIVE PHASE TRANSITIONS TOWARD CHARGE DENSITY WAVE STATES

E. Duverger-Nédellec, K. Kolincio, A. Pautrat, O. Pérez,

CRISMAT ENSICAEN/ CNRS, 6 Boulevard du Maréchal Juin - F-14050 CAEN cedex 4 FRANCE
olivier.perez@ensicaen.fr

Monophosphate tungsten bronzes (MPTBp) of general formula (PO$_2$)$_4$(WO$_3$)$_{2m}$ (with 4　m　14) can be described as the regular stacking of WO$_3$ slabs of ReO$_3$–type structure and slices PO$_4$ of groups [1]. MPTBp are low dimensionality oxides exhibiting successive transitions toward charge density (CDW) and/or spin density wave (SDW) states. These transitions lead to structural distortions associated to the appearance of satellite reflections. This family is relevant to analyse CDW and SDW states and their competition since by changing the m value the

electronic anisotropy and the density of carriers can be tuned. An investigation of the phase transitions *versus* temperature as well as the structure determination of the different states has to be done for several members. The relationship between physical and structural properties could be then performed.

We decided to focus our attention on the MPTBp m = 10: P$_4$W$_{20}$O$_{68}$. This member is exhibiting a CDW state at room temperature (RT) and the solution of the modulated structure associated to the CDW state proposed by Roussel

et al [2] is providing us a cornerstone for our study. Owing to the technical limits of the "old-fashion diffractometer" used by these authors, a few number of satellite reflections was collected and consequently only the atomic displacements of the tungsten species was modelled; an improvement of the description could be expected with a modern diffractometer (Apex2 CCD detector and high brilliance micro focus X-ray source).

The diffraction patterns observed by Roussel *et al* [2] were fully indexed using the following cell parameters $a = 5.30$ Å, $b = 6.55$ Å, $c = 35.82$ Å,   = $= 90°$, $= 90.6°$, **q** = 0.43 **a*** and the superspace group $P112_1(_100)0$. Surprisingly, our measurements at RT are revealing a different pattern: the basic cell is also monoclinic but with **b** as unique axis and two wave vectors $\mathbf{q_1} = 0.5$ **a*** and $\mathbf{q_2} = 0.39$ **a*** are observed. The experiments performed *versus* temperature evidenced the ground state structure above 400 °C with no more evidence of satellite reflections. Cooling the crystal up to RT different features can be observed (see fig-1): for T close to 210 °C diffuse scattering with V shape is observed, reflections condense within the diffuse scattering around 200 °C then the diffuse phenomenon fully disappears and at RT we are back to the CDW state with satellite reflections. However this CDW state is now

the one observed by Roussel *et al* [2]. The present work is then evidencing the possibility to stabilize two different CDW states at RT for the *m*=10 MPTBp. The temperatures of the different transitions are accurately determined by monitoring the intensity of the satellite compared to the main reflections. Then a full data collection was performed for both states with a high resolution strategy (sample-detector distance larger than 10cm and fine slicing scanning mode) to limit the reflections overlapping and a structure solution is proposed. Finally the modifications of the WO_6 environments are analysed *via* bond valence calculations to evidence electronic ordering within the WO_3 slabs for the different states and these results are discussed in regards to electronic transport measurements.

1. Phosphate tungsten bronze series: crystallographic and structural properties of low-dimensional conductors; P.Roussel, O.Pérez and Ph.Labbé; Acta Cryst. B57, pp. 603-632 (2001).

2. $P_4W_{20}O_{68}$: A complex charge-density-wave modulated structure with an antiferroelectric-like lattice distortion; P.Roussel, Ph.Labbé, H.Leligny, D.Groult, P.Foury-Leylekian, J.P.Pouget, Physical Review B 62, pp. 176-188 (2000).
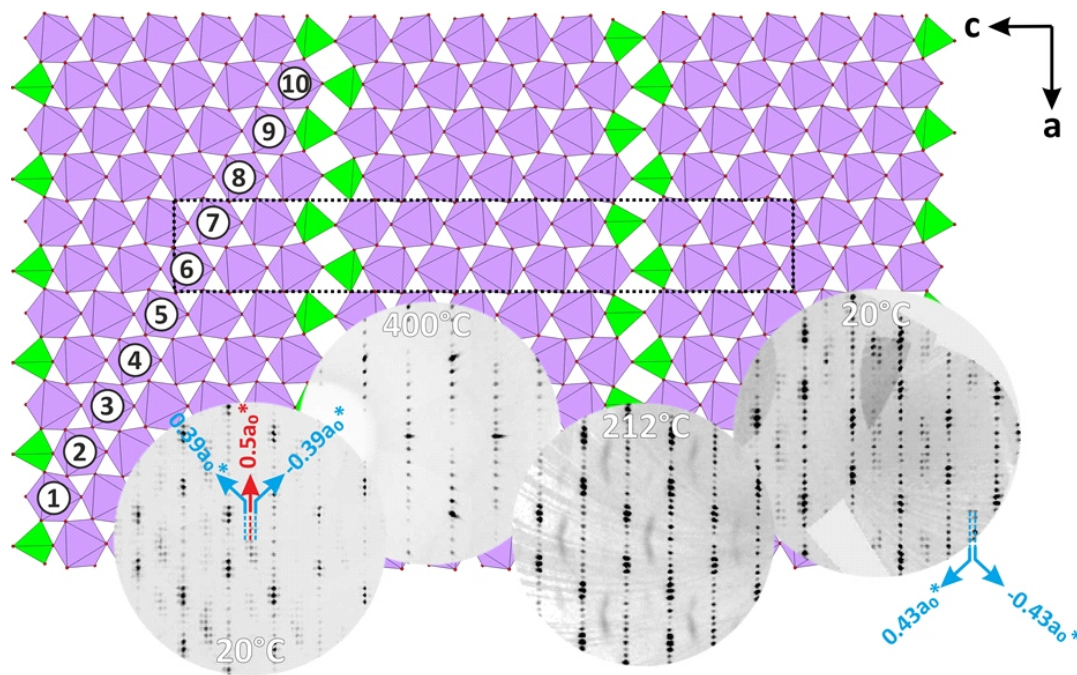
Figure 1. Ground state structure of $P_4W_{20}O_{68}$ (green and violet colours are used for PO_4 and WO_6) and (h0l)* diffraction planes measured during the thermal cycle 20°C ⇨ 400°C ⇨ 20°C.