MS21-01 **Modulations and short range order in perovskites with lone pair A-cations.** Artem Abakumov, *EMAT, Department of Physics, University of Antwerp, Belgium*
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Transition metal perovskites with the A-positions occupied by the cations with lone electron pair (Bi^{3+}, Pb^{2+}) offer a wide playground for condensed matter physics due to potential combination of different ferroic properties. Incommensurate structural modulations and short range order easily arise in these materials due to a) progressive changes in oxygen vacancy concentration upon heterovalent $A^{3+} \rightarrow A^{2+}$ replacement; b) a competition between lone pair driven off-center displacements and cooperative nature of tilting distortion of the perovskite octahedral framework. Systematic evolution of the oxygen vacancy ordering in $BiFeO_3$ upon substitution of Bi by divalent cations (Pb, Sr) will be presented, starting from short-range ordered anion deficient planes towards long range ordered incommensurately modulated structures with crystallographic shear planes and back to disordered "$Pb_2Fe_2O_5$" phase [1 - 4]. Coupling of octahedral tilting distortion, octahedral deformation and strong covalent Bi-O bonding resulting in antiferrodistortive modulated structures will be demonstrated using examples of isovalent A- and B-site substituted $BiFeO_3$ [5, 6]. Particular focus will be made on a combination of transmission electron microscopy (TEM) with the bulk diffraction techniques (synchrotron X-ray and neutron powder diffaction) to unravel the complex structures of these materials. The ability of modern scanning TEM techniques to directly visualize discplacive and occupational modulations in complex oxides will be demonstrated.

[1] Abakumov, A.M., Hadermann, J., Bals, S., Nikolaev, I.V., Antipov, E.V., Van Tendeloo, G. (2006) *Angew. Chem.* **45**, 6697-6700.
[2] Abakumov, A.M., Batuk, D., Hadermann, J., Rozova, M.G., Sheptyakov, D.V., Tsirlin, A.A., Niermann, D., Waschkowski, F., Hemberger, J., Van Tendeloo, G., Antipov, E.V. (2011) *Chem. Mater*. **23**, 255–265.
[3] Dachraoui, W., Hadermann, J., Abakumov, A.M., Tsirlin, A.A., Batuk, D., Glazyrin, K., McCammon, C., Dubrovinsky, L., Van Tendeloo, G. (2012) *Chem. Mater.* **24**, 1378-1385.
[4] Pachoud, E., Bréard, Y., Martin, C., Maignan, A., Abakumov, A.M., Suard, E., Smith, R.I., Suchomel, R.M. (2012) Solid State Comm. **152**, 331–336.
[5] Rusakov, D.A., Abakumov, A.M., Yamaura, K., Belik, A.A., Van Tendeloo, G., Takayama-Muromachi, E. (2011) *Chem. Mater*. 23, 285–292.
[6] Belik, A.A., Abakumov, A.M., Tsirlin, A.A., Hadermann, J., Kim, J., Van Tendeloo, G., Takayama-Muromachi, E. (2011) *Chem. Mater*., 23, 4505–4514.

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MS21-02 **Modulated structure and magnetic order in *M*OCl (*M* = Ti, V, Cr, Fe) at low temperatures.** Andreas Schönleber,[a] Jian Zhang,[a] Sander van Smaalen,[a] Anatoliy Senyshyn,[b] [a]*Laboratory of Crystallography, University of Bayreuth, 95440 Bayreuth, Germany,* [b]*Forschungs–Neutronen–quelle Heinz Maier–Leibnitz (FRM2), 85747 Garching, Germany*
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The title compounds are isostructural with FeOCl at room temperature [1] but show a multitude of phase transition sequences and magnetic order at low temperatures. This difference occurs due to the different numbers of 3*d* electrons of the metal atoms in their three–valent states. We have performed low–temperature neutron powder diffraction experiments at instrument SPODI (FRM2, Garching, Germany) and low–temperature single crystal X–ray diffraction at beamline D3 (Hasylab/DESY, Hamburg, Germany) to explore the magnetic and nuclear superstructures: TiOCl exhibits a [1**a**×2**b**×1**c**] nuclear superstructure in the spin–Peierls state at low temperatures and an intermediate phase which is incommensurately modulated [2–4], while VOCl undergoes a phase transition towards a [2**a**×2**b**×2**c**] antiferromagnetic superstructure [5,6]. CrOCl shows two phase transitions towards a [1**a**×4**b**×1**c**] antiferromagnetic superstructure with the intermediate phase being a magnetic incommensurate structure [7,8]. The low–temperature behavior of FeOCl is still not clear [9,10] and will be discussed in this contribution. VOCl and CrOCl feature a strong magnetoelastic coupling resulting in monoclinic-distorted lattices in the antiferromagnetic phases [6,8]. The magnetic ordering is described by magnetic superspace group symmetry. The additional symmetry operator (1', *s*) in the extended symbol stands for the time inversion operator combined with an additional shift of ½ of the modulation function to describe antiferromagnetic order [11]. Structural distortions and magnetic superstructures are discussed in context of the symmetries of the filled 3*d* orbitals and the frustration of the magnetic exchange interactions in the crystal structures [6,8].

[1] Goldsztaub, S. (1934). *C. R. Hebd. Seances Acad. Sci.* **198**, 667–669.
[2] Seidel, A., Marianetti, C. A., Chou, F. C., Ceder, G. & Lee, P. A. (2003). *Phys. Rev. B* **67**, 020405.
[3] Schönleber, A., van Smaalen, S. & Palatinus, L. (2006). *Phys. Rev. B* **73**, 214410.
[4] Schönleber, A., Shcheka, G. & van Smaalen, S. (2008). *Phys. Rev. B* **77**, 094117.
[5] Wiedenmann, A., Vénien, J. P., Palvadeau, P., Rossat–Mignod, J. (1983). *J. Phys. C: Solid State Phys.* **16**, 5339–5350.
[6] Schönleber, A., Angelkort, J., van Smaalen, S., Palatinus, L., Senyshyn, A. & Morgenroth, W. (2009). *Phys. Rev. B* **80**, 064426.
[7] Nørlund Christensen, A., Johansson, T. & Quézel, S. (1975). *Acta Chem. Scand A* **28**, 1171–1174.
[8] Angelkort, J., Wölfel, A., Schönleber, A., van Smaalen, S. & Kremer, R. K. (2009). *Phys. Rev. B* **80**, 144416.
[9] Grant, R. W. (1971). *J. Appl. Phys.* **42**, 1619–1620.
[10] Adam, A. & Buisson, G. (1975). *Phys. Stat. Sol. A* **30**, 323–329.
[11] Petříček, V., Fuksa, J. & Dušek, M. (2010). *Acta Cryst.* A**66**, 649–655.

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