

s3.m11.o3 **Superspace Approach Applied to the Y Series of Hexagonal Ferrites.** Ivan Orlov, Alla Arakcheeva and Gervais Chapuis, *Ecole Polytechnique Fédérale de Lausanne, CH-1015, Switzerland. E-mail: Ivan.Orlov@epfl.ch*

Keywords: Superspace Approach; Layered Structures; Ferrites

Hexagonal ferrites, a group of ferromagnetic layered structures with exceptional diversity, is based on six compounds which are closely related to $\text{BaFe}_{12}\text{O}_{19}$ (magnetoplumbite) [1]. They can all be derived by stacking three building blocks S, R and T, having 2, 3 and 4 oxygen layers respectively. These blocks behave as rigid structural units and stack along the *c* axis in a variety of ratios and permutations, often rising to structures of 'biological magnitude' [2]. We succeeded to describe the structures built by all combinations of T and S blocks by a single structural model in 4-dimensional superspace with single composition-dependent parameter. This model is supported by electron diffraction simulation where the continuously variable character of the diffraction diagram indicates that various stacking sequences might be interpreted as modulations applied to a common basic structure.

- [1] P.B.Braun, *Philips Res. Rept.* **12**, 491 (1957)
 [2] J.A.Kohn, *et al. Science*, **172**, 3983, 519-525 (1971)

s3.m11.o4 **Modulated Charge or Orbital Ordering in 2d or 3d Manganites.** Olivier Pérez, Dominique Grebille, Nicolas Guiblin, Premysl Beran, Christine Martin, Maryvonne Hervieu and Richard Retoux, *Lab. CRISMAT (UMR CNRS 6508) ENSICAEN, 14050 CAEN Cedex, France. E-mail: perez@ismra.fr*

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Perovskite 3D or Ruddlesden-Popper 2D manganites have been the subject of a lot of controversies in recent years, concerning the appearance of ordering phenomena involving electronic localization and associated with very fascinating physical properties, such as magnetoresistance [1]. The corresponding transitions were interpreted as charge or orbital ordering, resulting from the existence of a mixed valence for manganese, according to the global stoichiometry of the compounds, which can be tuned by an appropriate ratio of lanthanide +3 and alkaline earth +2 cations. Accurate structure refinements in the appropriate formalism for modulated structures were developed using single crystal X-ray or neutron diffraction data. A particular attention has been paid to the local distortion of the MnO_6 octahedra which could be the consequence of Jahn-Teller e_g electronic localization of Mn^{3+} cations.

In particular, $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ presents below 150K a commensurate 2-fold superstructure ($\text{Pbnm}(\text{O}\beta 0)$) which is better described by the $\text{P2}_1\text{nm}$ symmetry rather than a $\text{P2}_1/\text{m}$ one, and which was refined using both single crystal neutron and X-ray diffraction data. This symmetry is compatible with two Mn atomic sites, but the respective distortion of the corresponding octahedra appear very similar and small, with no clear evidence for pure Mn^{3+} or Mn^{4+} sites. It rather supports the assumption of a polaronic ordering [2]. In the Bi-Sr-Mn-O and Bi-Ca-Mn-O systems, charge order transitions to 2 fold superstructures are also observed at temperatures close to room temperature. The structure of $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{Bi}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ have been solved using neutron powder diffraction and X-ray single crystal diffraction. In both cases, two independent Mn sites are evidenced, but in the first case only, a significant difference in the octahedral distortion was found and this result is clearly confirmed by the different contrasts of stripes observed by HRTEM.

The Ruddlesden-Popper ($n=1$) phase $\text{Pr}_{0.5}\text{Ca}_{1.5}\text{MnO}_4$ has been studied by single crystal X-Ray diffraction and TEM. The charge ordered state is already stabilized at room temperature and is characterized by an incommensurate modulation ($q^*=0.412b^*$) in the Aema setting of the average structure. The modulated displacements are almost purely transverse et lead to a small distortion which evolves continuously in the modulation direction, still without clear evidence for a Mn^{3+} or Mn^{4+} localization.

- [1] for example, Mori, S., Chen, C. H. & Cheong, S.W. (1998). *Nature*. **392**, 473-476; Autret, C. Retoux, R., Hervieu, M. & Raveau, B. (2001) *Chem. Mater.*, **13**, 4745-4752.
 [2] Daoud-Aladine, A., Rodriguez-Carvajal, J., Pinsart-Gaudart, L., Fernandez-Diaz, M.T. & Revcolevschi, A. (2002) *Phys. Rev. Lett.* **89**, 097205