s1.m1.p7 **The incommensurate modulated structure of $Sr_{14-x}Ca_xCu_{24}O_{41}$ as a function of temperature and composition** C. Bougerol-Chaillout, P. Bordet, J.F. Bérar, C. Darie, S. Pachot. *Laboratoire de Cristallographie, CNRS, BP 166 38042 Grenoble cedex 9, France.*
Keywords: spin ladders, incommensurate structure.

The interest for the spin-ladder compound $Sr_{14-x}Ca_xCu_{24}O_{41}$ has been stimulated by the report of superconductivity (T_c=12K) under pressure (3-6 GPa) in Ca-rich samples [1,2] whereas the Sr-rich compounds present a semiconducting-like behavior of the resistivity. On the crystallographic point of view, $Sr_{14-x}Ca_xCu_{24}O_{41}$ has an incommensurate modulated structure which can be described as the stacking along the b-axis of two sublattices: one consisting of CuO_2 chains, one of Cu_2O_3 ladders and a Sr layer. In order to correlate the change in the electrical properties to the modifications of the structure, we have prepared samples with different contents of various substituting elements. We report here the structural investigation of Ca-doped samples with x=6 (semiconducting) and x=13.6 (metallic) carried out by synchrotron powder x-ray diffraction on the ESRF BM16 beam line between 10 and 300K.

The lattice parameters have been determined at all temperatures and the structure refined at 10 and 300K using the XND software adapted for misfit structures [3]. The description was done in the Fmmm(00γ) space group with γ defined by $\gamma = c_{chain}^*/c_{ladders}^*$. We have calculated the variations of the atomic coordinates and the main bond distances over a period of the modulation t corresponding to the coincidence unit cell having a c parameter of about 27Å.

Concerning the atomic coordinates, the modulation amplitude is generally larger for the x=6 than the x=13.6 sample. From the interatomic distances, the valence of the Cu cations of the ladders (Cu1) and the chains (Cu2) were calculated for both samples along the modulation. The average valence of Cu2 is larger for x=6 (+2.67) than for x=13.66 (+2.27), whereas it is the opposite for Cu1. This indicates a charge transfer from the chains to the ladders as Ca substitution increases. Furthermore, v(Cu1) is almost flat for x=13.6 but varies strongly for x=6. This reveals that the charges are delocalized on the ladder sublattice for x=13.6, in agreement with its metallic properties, but are localized in the case of the semiconducting x=6 sample. The localization is very likely related to the presence, in almost equal proportion, of cations of different ionic radius (Sr and Ca) in the adjacent layer inducing large variations in the O1 positions along the stacking direction. In this respect, the x=13.6 sample is much more homogeneous, which is probably favorable for charges delocalization.

s1.m1.p8 **A multidisciplinary approach to the structures and properties of some chalcogenide misfit layered compounds**. W. Depmeier, *University of Kiel, IfG, Mineralogy-Crystallography, D-24098 Kiel, Germany.*
Keywords: chalcogenides, misfit compounds, multidisciplinary.

In the frame of a multidisciplinary project (DFG-Forschergruppe "Wachstum und Grenzflächen-eigenschaften von Sulfid- und Selenid-Schicht-Strukturen") a group of Theoretical and Experimental Physicists, Inorganic Chemists, Materials Scientists and Crystallographers (chair) of our university has started an investigation of chalcogenide layered structures with regard to the growth mechanisms, the geometric and electronic characteristics of the evolving surfaces and interfaces, and also of their high pressure behaviour.

Our group is particularly interested in misfit layered compounds $(MX)_{1+x}(TX_2)_n$ (n=1,2; $M=Pb^{2+}$, Sn^{2+}, RE; X=S; and T a 3d transition metal) and their high pressure behaviour. The particularities of their chemical composition and structures (e.g., lone pairs, low dimensionality, the topology with van-der-Waals-type gaps, effects of coupled cation ordering, electronic transitions, intrinsic aperiodicity) make high pressure studies on these compounds, and their component structures, a potentially rewarding topic.

In addition to crystal growth experiments (CVT), our group uses mainly x-ray diffraction techniques under high pressure (DAC, up to 15 Gpa; K. Knorr, L. Ehm), and methods of computational crystallography on the ab initio level (DFT, GGA; B. Winkler, M. Hytha). Both lines of research collaborate closely on jointly defined problems.

The contribution will focus on our own high pressure work, but the "Forschergruppe" and some new results of its research will be presented as well.

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