ESRF	**Experiment title:** **XAFS study of a local atomic and electronic strusture of $Pr_{1-x}Sr(Ba)_xCoO_3$ perovskites**	**Experiment number:** **HE-2791**
Beamline: **BM29**	**Date of experiment:** from: **16.04.2008** to: **22.04.2008**	**Date of report:** 01.09.2008
Shifts: 18	**Local contact(s):** **Dr. Sakura PASCARELLI**	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists)

Dr. Anatoli POPOV -Institut Laue Langevin 38042 GRENOBLE, France

Dr. Vadim SIKOLENKO* - Laboratory for Neutron Scattering PSI & ETHZ CH-5232, Switzerland

Dr. Sergei VOITEKHOVICH - Institute of Physical Chemistry, University of Hamburg, Germany,
Prof. I. O. TROYANCHUK - Joint Institute of Solid State and Semiconductor Physics, Belarus

Mr. Vadim EFIMOV*- Joint Institute for Nuclear Research, Dubna, Moscow region, Russia

The cobalt-based solid solutions with perovskite structure have attracted much research attention in recent years [1] due to a variety of magnetic and transport properties. Thus the most exciting cobaltites properties are the "colossal" magnetoresistance, possibility of the spin state transition and a high catalytic activity [2]. More interesting cobaltites properties were observed in the compound with chemical composition $R_{0.5}A_{0.5}CoO_3$ (Ln notes Pr, Nd, Tb, Sm; A - Sr, Ba). The Ba-doped cobaltites exhibit a number of phase transitions - antiferromagnet-ferromagnet, ferromagnet-paramagnet, spin-state and insulator-to-metal, which depend on oxygen content and *R* ionic radius [3]. The Sr-doped cobaltites have entirely different properties, probably connected with other crystal structure features. Thus the metallic behaviour was observed in resistivity-temperature curves below 300 K. The ferromagnet-paramagnet transition occurs between T_1 ~230 and T_2 ~175 K and depends on lanthanide ionic radius. Among the mentioned Sr-doped cobaltites the $Pr_{0.5}Sr_{0.5}CoO_{3-d}$ compound has drawn a great attention. Our recent SQUID magnetization curves (see Fig. 1) revealed two unusual features observed on the M(T) dependence, which were not found in the similar cobaltites. First, there was a clear hysteresis between FC (field cooling) and ZFC (zero field cooling) magnetization curves. Second, there was a downward step around T ~ 100 K. It is note that the second feature causes a particular interest. This ***anomaly*** cannot be attributed to a transition into an anti-ferromagnetic state because the M(H) curve at 5 K clearly indicates ferromagnetism.

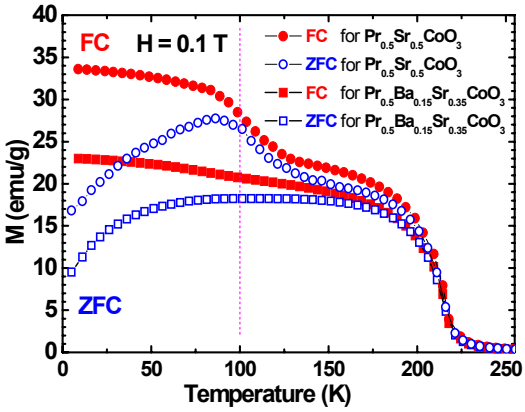

Fig. 1: Temperature dependence of the field cooling (FC) and zero field cooling (ZFC) magnetization of $Pr_{0.5}Sr_{0.5}CoO_3$ and $Pr_{0.5}Ba_{0.35}Sr_{0.15}CoO_3$.

In this work we have performed the combination XAFS and neutron powder diffraction (NPD) measurements in order to study the correlations between a local geometric distortion of the CoO_6 octahedron and the spin states transition of the cobalt ions in order to elucidate the origin of such anomaly in $R_{1-x}A_xCoO_3$ (*R* notes Pr, La; A notes Sr and Ba; x = 0.0 and 0.5).

The experiments were carried out at beamline **BM29** (Co *K*-edge) and diffractometer **D2B** (ILL).

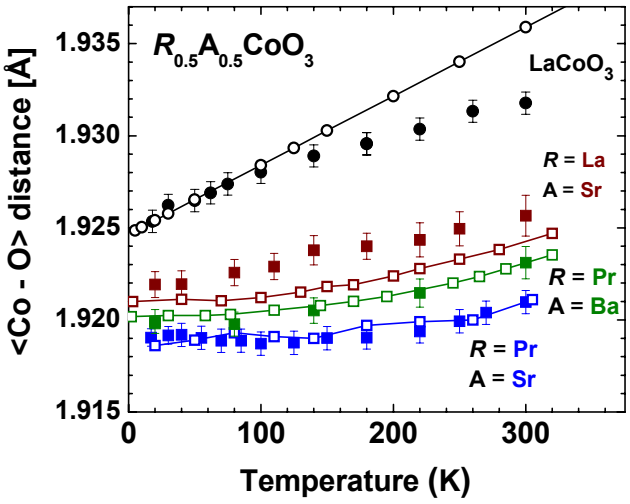

Fig. 2: The temperature dependence of the average Co–O distances obtained by EXAFS (full circles) and NPD (empty squares) for $R_{1-x}A_xCoO_3$.

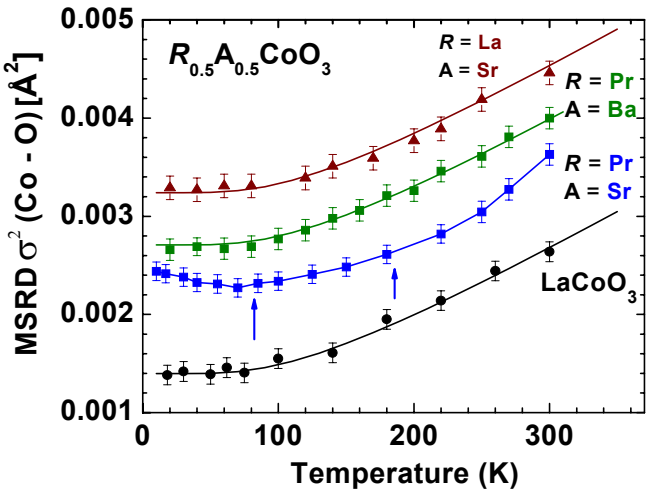

Fig. 3: The temperature dependence of the Co–O mean square relative displacement for $R_{1-x}A_xCoO_3$.

Figures 2 and 3 show the evolution of the average temperature dependance Co–O distances obtained by EXAFS and NPD as well as mean square relative displacement MSRD values in the $R_{1-x}A_xCoO_3$. The obtained results have established that in the case of $La_{0.5}Sr_{0.5}CoO_3$ in contrast to $Pr_{0.5}Sr_{0.5}CoO_3$ and $Pr_{0.5}Ba_{0.5}CoO_3$ the Co–O distances determined from EXAFS analysis are longer than that obtained by NPD studies and also a significant growth of the Co–O MSRD of $La_{0.5}Sr_{0.5}CoO_3$ is observed. It should be noted that the two-anomaly behavior near 90 K and 180 K of the Co–O MSRD in $Pr_{0.5}Sr_{0.5}CoO_3$ was found (see arrows in Fig. 3). Such unusual behavior could be explained by local distortion appearance from our NDP data which could be attributed to a structural transition from tetragonal space group *I4/mcm* to the orthorhombic space group *Imma* and into the rhombohedral phase *R-3c* (i.e. *reentrant* structure phase transition) or transformation of an electronic configuration 4*f*-orbitals Pr^{3+} ions due to the formation new stable covalence 4*f* (Pr^{3+})–2*p* (O) bonds, which may be attributed to a local Jahn-Teller distortion. To clirify relible the origin of these unexpected structural phase transitions in $Pr_{0.5}Sr_{0.5}CoO_3$ we are going to carry out EXAFS study of the local distortion around Pr^{3+} ions at the Pr *K*-edge from 20 K to 300 K.

Moreover, figures 2 and 3 clearly indicate a new unusual effect in $LaCoO_3$: first of all an nonlinearaty of MSRD curve near 100 K and second that Co–O distances determined from EXAFS analysis are shorter than that obtained by NPD studies, especially at higher temperatures (see Fig. 2). At the same time, one expects opposite behavior, i.e. the distances from EXAFS should be longer than that provided by NPD due to the motion of the oxygen atoms in the direction perpendicular to the Co–O bonds [4]. The observed unusual behaviour can be in general explained ether in a model of highly anisotropic oxygen displacements parallel and perpendicular to the Co–O bonds or of the spin-state transition which can be well described by an inhomogeneous mixed LS ground state and a HS excited one.

In order to estimate the contribution of these models to the observed effect we plan to carry out the neutron single-crystal diffraction study on $LaCoO_3$ below and above phase transition temperature. These measurements will also help us to check the exictance of the Jahn-Teller distortions.

An increase of local distortion in *A*-sublattice of perovskite structure ABO_3 by means of a substitution of the rare-earth ions with strontium and barium ones, having the size larger than that of rare-earth ions, lead also to an essential growth of the MSRD σ^2(Co–O) (see Fig. 3), which reflects mainly the amplitude of the oxygen atoms vibrations in the direction along the Co–O bond. Thus, considering both the interatomic distances, observed by EXAFS and diffraction (see Fig. 2), as well as the changes in the MSRD (see Fig. 3), one can conclude that introduction of strontium and especially barium ions modifies significantly the anisotropy of thermal vibrations of the oxygen atoms. The amplitude of oxygens vibrations is the largest in the direction perpendicular to the Co-O bonds in $LaCoO_3$, but in the direction along the bonds in $R_{0.5}A_{0.5}CoO_3$.

References

[1] M. Haverkort, J. Cezar, T. Lorenz, N.B. Brookes, L.H. Tjeng, et.al., *Phys. Rev. Lett.* **97**, 176405 (2006).
[2] P.M. Raccah, J.B. Goodenough, *Phys. Rev*. **155**, 932 (1967); G. Briceno et.al. *Science* **270**, 273 (1995).
[3] M.A. Senaris-Rodriguez and J.B. Goodenough, *J. Solid State Chem*. **118**(2), 323 (1995).
[4] A. Sanson, F. Rocca, G. Dalba, P. Fornasini, R. Grisenti, G. Artioli., *Phys. Rev B* **73**, 214305 (2006).