ESRF	**Experiment title:** **XAFS study of local structural distortions in $R_{1-x}Sr_xCoO_3$ at the R *K*-edge in the range of unusual phase transitions**	**Experiment number**: **HS-3232**
Beamline: **BM29**	**Date of experiment**: from: **17.02.2010** to: **23.02.2010**	**Date of report**: 23.03.2010
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The peculiar properties of $LaCoO_3$ have been intensively studied since 1950's and a lot of controversial explanations appeared. In the ground state the Co^{3+} ions are found to be in the low-spin electronic configuration (LS; $t^6_{2g}e^0_g$, S=0). With temperature increase the spin state of Co ions changes gradually in the range of 40-100 K followed by a transition into a metallic state at 400-500 K. The original interpretation of the low-temperature transition was done in terms of thermally-induced population of the low-lying high-spin state (HS; $t^4_{2g}\ e^2_g$, S=2). Later, especially after LDA+U band structure calculations, another interpretation was put forward: the first transition near 100 K could be due to a thermal activation of an intermediate-spin state (IS; $t^5_{2g}\ e^1_g$, S=1) of Co^{3+} ions. This is probably due to an orbital ordering induced by a cooperative Jahn-Teller distortion of Co^{3+} ions in IS state. Very recent soft X-ray absorption spectroscopy and magnetic circular dichroism (MCD) at the Co $L_{2,3}$ edge as well as theoretical calculations for a CoO_6 clusters have shown that the spin-state transition in $LaCoO_3$ can be well described by a LS ground state and a triply degenerate HS excited state [1].

More interesting properties of cobaltites were observed in the perovskite solid solution series $R_{1-x}A_xCoO_{3-\delta}$ (R= La, Pr, Nd; A= Sr, Ba, Ca). Among of these compounds the Sr-doped cobaltites exhibit a number of phase transitions - antiferromagnet-ferromagnet, ferromagnet-paramagnet, spin-state and insulator-to-metal, which depend mainly on oxygen content and A ionic radius [2]. Thus the metallic behaviour was observed in resistivity-temperature curves below 300 K. The ferromagnet-paramagnet transition occurs between T_1 ~225 and T_2 ~110 K and depends on rare-earth ionic radius. It should be noted that among above-mentioned Sr-doped cobaltites the $Pr_{0.5}Sr_{0.5}CoO_{3-\delta}$ compound has drawn a great attention.

One of the explanations would be a change in the nature of the ferromagnetic coupling associated with charge or orbital ordering among the some part of the Co ions, e.g. a long range Jahn-Teller ordering of e_g orbitals of the IS Co^{3+} ion ($t_{2g}{}^5e_g{}^1$). The cooperative orbital ordering within the ferromagnetic state can lead to a change of the magnetic anisotropy that indeed was observed in $Pr_{0.5}Sr_{0.5}CoO_3$ [3].

The second possible explanation of the observed unusual behaviour of magnetic properties and crystal structure in the $Pr_{0.5}Sr_{0.5}CoO_3$ is the 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. It is expected that 4*f*-orbitals of rare-earth ions do not participate actively in formation of chemical bonds. However, an anomaly superconducting properties in the $PrBa_2Cu_3O_7$ have been explained in model of strong hybridization between 4*f*-orbitals of Pr^{3+} and 2*p*-orbitals of oxygen ions [4].

In this work we have performed the XAFS study of the $R_{1-x}Sr_xCoO_3$ (R = Pr, La, Nd) at the R *K*-edge in order to find most probable model explaining the nature of the small local and long-range structural distortions in the range of unusual spin-state and phase transitions.

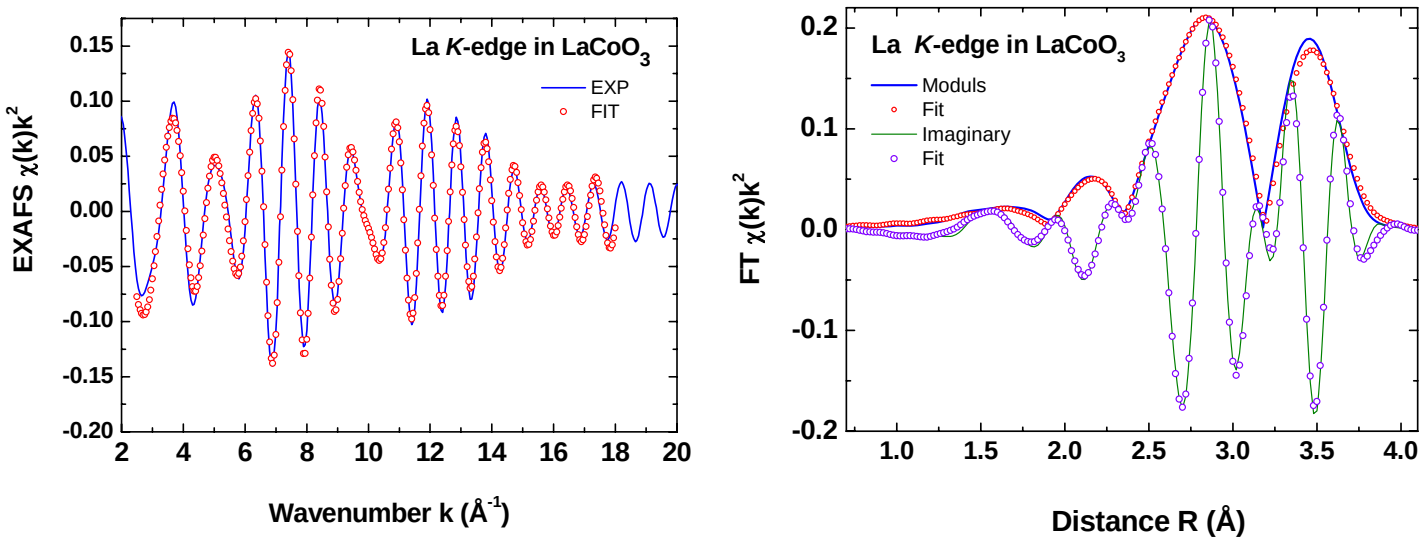
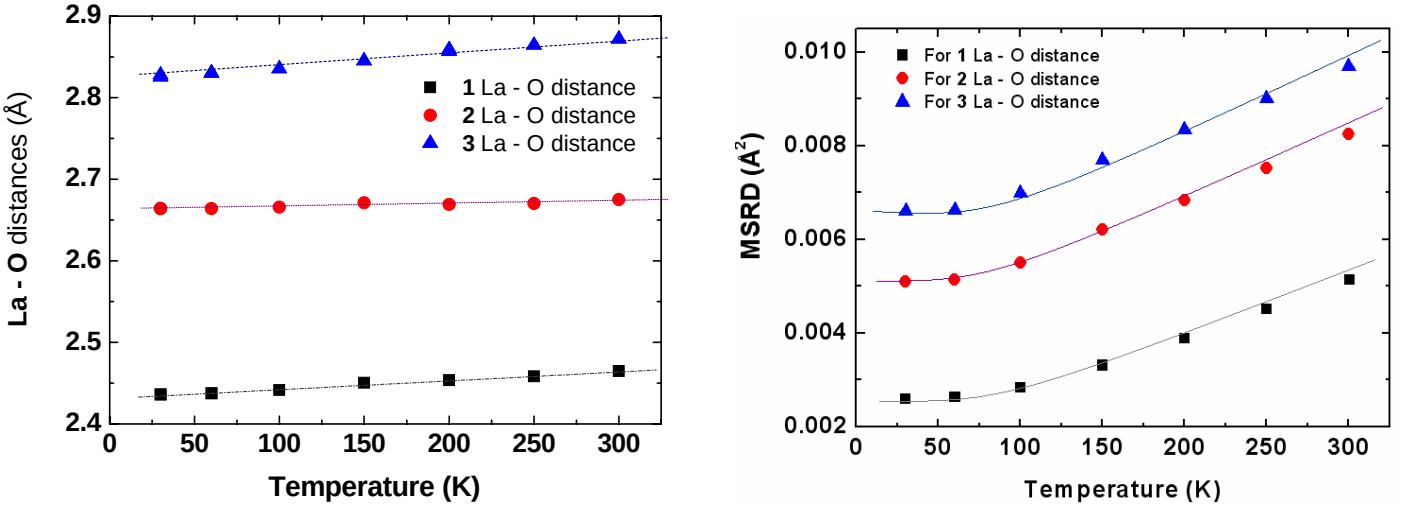


Fig. 1. Experimental La *K*-edge EXAFS signals $\chi(k)k^2$ and their Fourier Transforms (modulus and imaginary parts) for $LaCoO_3$. (Only one spectrum is shown for clarity).

For $LaCoO_3$ solid solutions an experimental and culculated EXAFS χ $(k)k^2$ signals at the La *K*-edge and their FTs at T = 10 K are shown in Fig. 1. The FTs signals are typical for perovskite-type structure and show well-resolved peaks up to 9 Å. In our case we will consider only analysis of the broad peak in the range 2.3÷3.2 Å, corresponding to the first coordination shell which consists of three La - O distances composed of six and two times on three oxygen atoms around absorbing lanthanum atom. One should note that all EXAFS χ $(k)k^2$ signals are of very good quality up to about 25 $Å^{-1}$.



a) **b)**

Fig. 2: The temperature dependence of the culculated La–O distances (**a**) and their mean square relative displacement (MSRD) (**b**) for $LaCoO_3$. Lines are guides for eyes.

Figure 2 shows the evolution of the temperature dependance La–O distances (**a**) and their MSRD values (**b**) in the $LaCoO_3$. The obtained results have established an nonlinearaty of MSRD curves for the three distances in the range of spin-state transition near 100 K as well as growth MSRD curves value with increase of La–O distance (see Fig. 2). It is noted that such small change of MSRD value (see Fig. 2) for 3 distances in the region of spin-state transition can probably not be interpreted in terms of local lattice distortion arising from the *static* Jahn-Teller effect. In order to estimate the contribution of these models to the observed effect we plan to carry out the neutron diffraction and inelastic neutron scattering study below and above spin-state transition temperature. Combined EXAFS and neutron scattering data on $LaCoO_3$ single crystal will also help us to check the existence of unusual behavior in the temperature range near spin-state transition.

References

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