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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].

In nonmagnetic insulator $LaCoO_3$ the substitution of La^{3+} with divalent Sr^{2+} ion creates paramagnetic to ferromagnetic (x>0.2) transition as the dopant concentration is increased [2]. The Sr^{2+} ionic radius is significantly larger than that of the La^{3+} ion, so it is possible to expect stabilization of the intermediate spin (IS) state of cobalt ions upon substitution. In addition, an appearance of Co^{4+} ions upon such heterovalent substitution leads to the ferromagnetic metallic ground state [3]. To prevent the Co^{4+} ion appearance, it is possible to introduce both Sr^{2+} and Nb^{5+} ions, which at the presence of Co^{3+} ions, will be in oxidizing state 5+. By simultaneously introducing Sr and Nb, the cobalt ions keep their valence state and the electroconductivity of $La_{1-x}Sr_xCo_{1-y}Nb_yO_3$ solid solutions decreases with increasing of dopant concentration. Thus, the different nature of ferromagnetic interactions formation in these systems is obvious [4].

In this work we have performed the combination X-ray Absorbtion Fine structure (XAFS) and neutron powder diffraction (NPD) measurements in order to study the correlation of local and long-range structural distortions on CoO_6 octahedra in the $LaCoO_3$ and $La_{0.5}Sr_{0.5}Co_{1-y}Nb_yO_3$ (x = 0.0; 0.10; 0.25) below and above magnetic phase transition.

The experiments were carried out at beamline **BM29** (Co *K*-edge) and spectrometers **D1A/D1B** (ILL).

Figures 1 and **2** clearly indicate a new unusual effect in $LaCoO_3$ [5]: first of all an nonlinearaty of mean square relative displacement (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 **figure 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 [6]. 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 triply degenerate HS excited one [1].
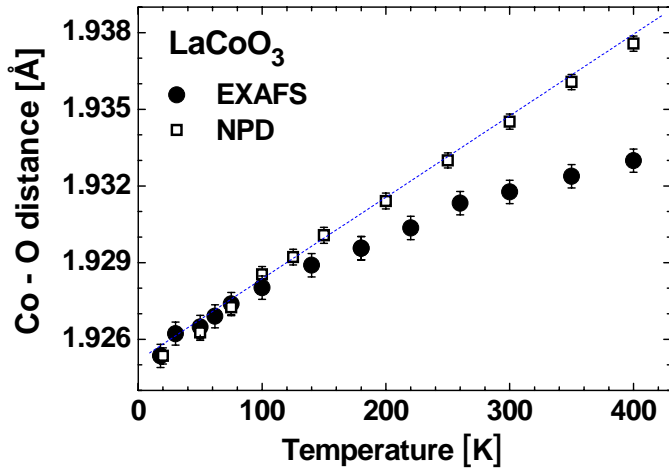
Fig. 1: The temperature dependence of the Co–O distances obtained by EXAFS (full circles) and NPD (empty squares) for $LaCoO_3$.
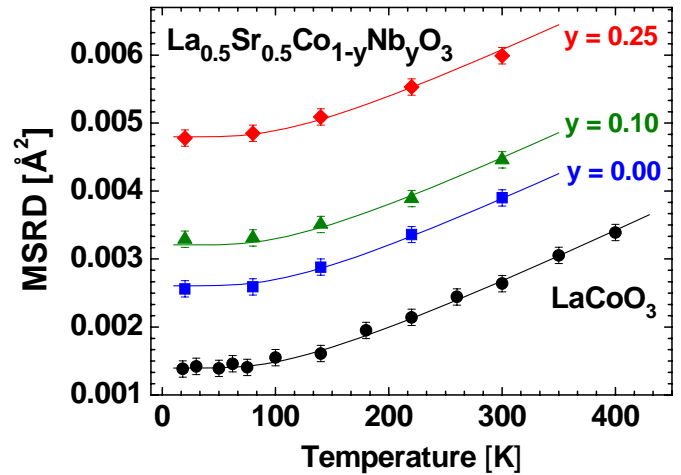

Fig. 2: The temperature dependence of the Co–O mean square relative displacement (MSRD) for $La_{0.5}Sr_{0.5}Co_{1-y}Nb_yO_3$.

Moreover, we may conclude that such small change of MSRD value (see **Figure 1**) in the region of phase transition can probably not be interpreted in terms of local lattice distortion arising from the Jahn-Teller effect. In order to estimate the contribution of these models to the observed effect we plan to carry out the 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.

Figures 2 and **3** show the evolution of the temperature dependance Co–O distances obtained by EXAFS and NPD as well as MSRD values in the $La_{0.5}Sr_{0.5}Co_{1-y}Nb_yO_3$ [7]. The obtained results have established that in the case of $La_{0.5}Sr_{0.5}CoO_3$ in contrast to $LaCoO_3$ the Co–O distances determined from EXAFS analysis are longer than that obtained by NPD studies. A gradual substitution of Co by Nb in the $La_{0.5}Sr_{0.5}Co_{1-y}Nb_yO_3$ exhibits both a significant growth of the Co–O MSRD and the inverse behavior of Co–O distances similar to the $LaCoO_3$, especially for the sample $La_{0.5}Sr_{0.5}Co_{0.75}Nb_{0.25}O_3$ where all cobalt ions are in three-valence IS state (see **Figure 3**). Such unusual behavior could be explained by local distortion appearance which could be attributed to a Jahn-Teller lattice distortion around Co ions or an essential increase of the vibration amplitude of oxygen atoms parallel/perpendicular to Co–O bond.

Fig. 3: The temperature dependence of the Co–O distances obtained by EXAFS (full color symbols) and NPD (empty black symbols) for $La_{0.5}Sr_{0.5}Co_{1-y}Nb_yO_3$.

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] I.O. Troynchuk, R. Szymczak, et.al., *Phys. Stat. Sol.* (b) 242, No. 6, pp. 49-51 (2005).

[5] V. Sikolenko, A.Sazonov, A.Kuzmin, J.Purans, I.Troyanchuk, et.al., *J. Phys. Chem. Solids*, in press.

[6] A. Sanson, F. Rocca, G. Dalba, P. Fornasini, R. Grisenti, G. Artioli., *Phys. Rev B* **73**, 214305 (2006).

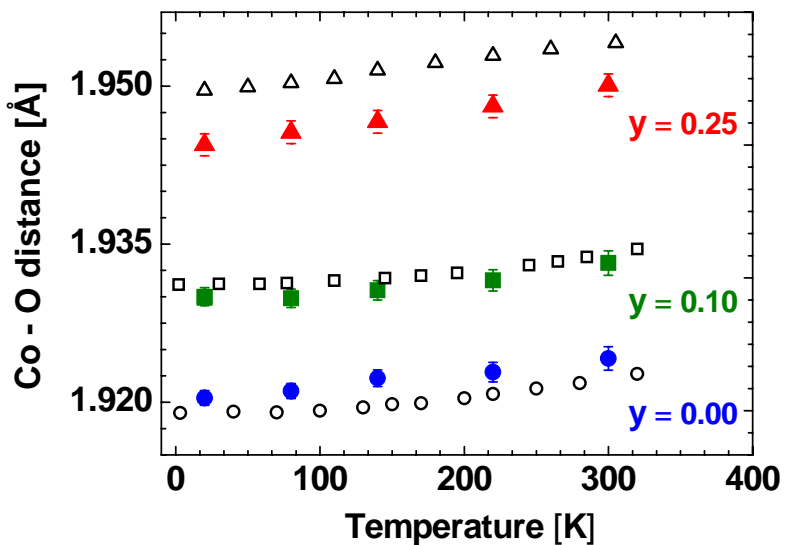[7] V. Sikolenko, J. Purans, A. Kuzmin, I.O. Troyanchuk, V.Efimov and A.Sazonov, *Phys. Rev B*, in press.