



	Experiment title: EXAFS/XANES study of the layered cobaltites RBaCo₂O_{5+d} (R = Y, Pr) at the d = 0 ÷ 0.5	Experiment number: HE-2643
Beamline: BM29	Date of experiment: from: 03.10.2007 to: 09.10.2007	Date of report: 17.02.2008
Shifts: 18	Local contact(s): Dr. Marco VACCARI	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists)		
Dr. Andrey PODLESNYAK - Hahn-Meitner-Institut, Glienicker str. 100 Berlin D-14109 Germany		
Dr. Vadim SIKOLENKO* - Hahn-Meitner-Institut, Glienicker str. 100 Berlin D-14109 Germany		
Mr. Vadim EFIMOV* - Joint Institute for Nuclear Research, 141980 Dubna, Moscow region, Russia		
Mr. Andrew SAZONOV* - Institute of Crystallography, Jaegerstr. 17-19, D-52066 Aachen, Germany		

The discovery of the giant magnetoresistance in the manganites with perovskite structure [1] has stimulated the research of the compounds exhibiting large magnetoresistance. In LnCoO₃ oxides (Ln - lanthanide) Co ions in the ground state are characterized by the low spin electronic configuration $t_{2g}^6 e_g^0$. This state (LS: $S = 0$) gradually passes to intermediate spin one (IS: $S = 1$; $t_{2g}^5 e_g^1$) with temperature enhancement. For example, the spin state of cobalt ions in LaCoO₃ gradually changes from LS to IS with temperature increment in the temperature range of 20 ÷ 100 K [3].

Recently cobaltite oxides with perovskite-like structure have attracted a considerable interest of many researchers because of their specific properties making them promising materials in SOFC, chemical reactors catalysis, gas separation membranes and many other applications. An especially interesting feature observed for these materials is an ordering of oxygen vacancies which can drastically change the physical properties [4] of such compounds in comparison with stoichiometric ones.

The oxygen deficient layered double perovskites RBaCo₂O_{5+d} (where R - rare earth element) are being increasingly studied because of their interesting magnetic and transport properties. In particular, the materials with d = 0.5 exhibit a paramagnetic, ferromagnetic and antiferromagnetic transitions, which are related to an interplay between spin, charge and orbital degrees of freedom of the cobalt ions [5]. In RBaCo₂O_{5.5} only Co³⁺ ions are present, which are sited in ideally alternating octahedral CoO₆ and pyramidal CoO₅ environments. Depending on the ratio of the crystal field and the intra-atomic exchange energies, Co³⁺ ions can be stabilized either in low-spin (LS) state ($t_{2g}^6 e_g^0$, $S = 0$), intermediate-spin (IS) state ($t_{2g}^5 e_g^1$, $S = 1$) or high-spin (HS) state ($t_{2g}^4 e_g^2$, $S = 2$). The IS state of Co³⁺ leads to a Jahn–Teller (JT) distortion of the oxygen octahedra in the structure [6]. It was shown in the past that perovskites containing JT cations show oxygen isotope effects on many physical properties. These were intensively studied in the case of superconducting cuprates but also for GMR manganates and nickelates.

EXAFS spectra were treated using the EDA software package following the standard procedure [7]. The energy position E_0 , used in the definition of the photoelectron wave number $k = [(2m_e/\hbar^2)(E - E_0)]^{1/2}$, was set at the threshold energy of 7714 eV.

The Fourier transforms (FTs) of the EXAFS $\chi(k)k^2$ spectra were calculated in the wave number interval $k = 0.5 \div 19 \text{ \AA}^{-1}$ with a Gaussian-type window function. A curve fitting procedure [7] was used in the same wave number interval to determine the Co-O distance for the first coordination shell of cobalt and the mean

square relative displacement (MSRD). The input file for FEFF8 was constructed using the ATOMS code based on structural data from the results of Rietveld refinement of our neutron diffraction spectra [8].

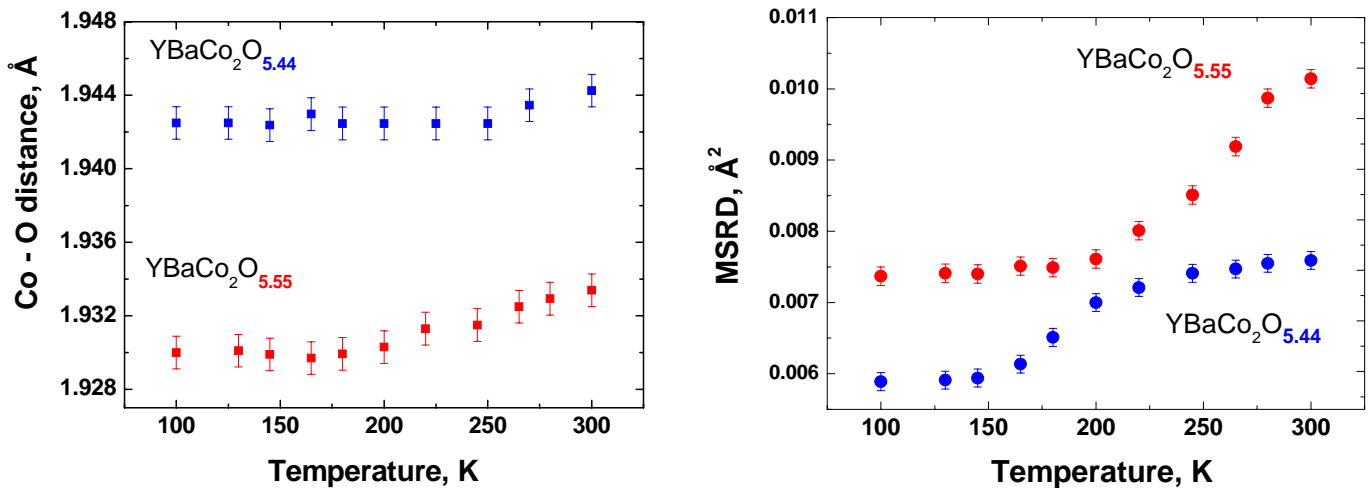


Figure 1: (a) the temperature dependence of the Co–O distances and (b) the Co–O MSRD for YBaCo₂O_{5.5} and YBaCo₂O_{5.44}.

Figures 1a, b clearly indicate unusual behavior in layered cobaltites: first Co–O distances for YBaCo₂O_{5.5} are shorter than in YBaCo₂O_{5.44} in the all temperature range (see **figure 1a**) and second the nonlinear increase of mean square relative displacement (MSRD) curve near 200 K. The observed unusual behaviour can be in general explained either in a model of highly anisotropic oxygen displacements parallel and perpendicular to the two different Co–O bonds because of crystal structure transition (crossover $P4/nmm \rightarrow I4/mmm$) or in the spin-state transition (see **figure 2**) which can be well described by an inhomogeneous mixed LS ground state and a IS excited Co³⁺ ions (in case of YBaCo₂O_{5.5}) and mixed LS Co⁴⁺ and a IS state of Co³⁺ ions (in case of YBaCo₂O_{5.44}) which leads to a Jahn–Teller distortion of oxygen octahedra in this crystal structure [8].

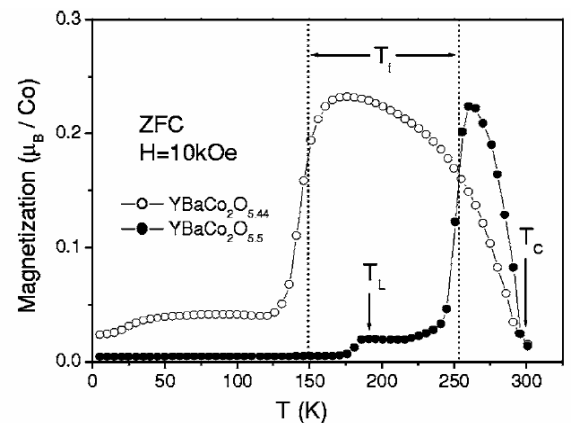


Figure 2: Temperature dependence of the field cooling (FC) and zero field cooling (ZFC) magnetization of YBaCo₂O_{5.5} and YBaCo₂O_{5.44}

References

- [1] P.M. Raccah and J.B. Goodenough, Phys. Rev. **155**, 932 (1967).
- [2] I. O. Troyanchuk, N. Kasper, D. D. Khalyavin, Szymczak, Phys. Rev. Lett. **80**, 3380 (1998).
- [3] A. A. Taskin, A. N. Lavrov, Y. Ando. Phys. Rev. B **71**, 134414 (2005).
- [4] D. Khalyavin, I.O. Troyanchuk, N.V. Kasper, Szymczak, Phys. Rev. Lett. **80**, 3380 (1998).
- [5] T. Vogt, P.M. Woodward, P. Karen, B.A. Hunter, Phys. Rev. Lett. **84**, 2969 (2000).
- [6] A. Podlesnyak, K Conder, V Pomjakushin, M Stingaciu, S Streule J. Phys.: Condens. Matter **17** (2005) 5813–5820.
- [7] A. Kuzmin, Physica B **208/209**, 175 (1995).
- [8] D. D. Khalyavin, D. N. Argyriou and U. Amann, A. A. Yaremchenko and V. V. Kharton, Phys. Rev. B **75**, 134407 (2007).