ESRF	**Experiment title:** XMCD study of pressure induced magnetic phase transitions in $La_{0.5}Ba_{0.5}CoO_{2.75}$	**Experiment number:** **HE-4142**
Beamline: **ID-12**	**Date of experiment:** from: **18.01.2022** to: **24.01.2022**	**Date of report:** 01.03.2022
Shifts: 18	**Local contact(s):** **Dr. Fabrice Wilhelm**	
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The cobaltites with perovskite structure are systems with fascinating transport and magnetic properties [1-11]. Compared to manganites, they have one extra degree of freedom: the Co ion spin state. The parent compound $LaCoO_3$ (LCO) is a paramagnetic (PM) insulator at low temperature (LT). As temperature increases a gradual spin transition (ST) from a low spin (LS, $t_{2g}^6e_g^0$) to an intermediate (IS, $t_{2g}^5e_g^1$) or high spin-state (HS, $t_{2g}^4e_g^2$) [1-5]. The insulator-metal transition occurs at ~550 K [1,2]. Previous studies showed that chemical substitutions in LCO can induce ferromagnetism (FM), presumably due to Zener double-exchange [1,2]. Low doped $La_{1-x}Ba_xCoO_{3-\delta}$ ($LBCO_{3-\delta}$) are AFM insulators [3]. The data specific to $LBCO_{3-\delta}$ can be understood considering a stabilization of the HS. Surprisingly, the T_c at these compositions increases under pressure [7,8,10]. The origin of the magnetostructural phase transition is unknown.

In $La_{0.5}Ba_{0.5}CoO_{2.75}$ all cobalt atoms have a 3+ configuration. The long-range FM ordering is gradually suppressed upon metallization. It leads a large magnetic anisotropy (Fig.1a) and giant magnetoresistance (Fig.1b). At LT the stabilization of AFM phase was found by our neutron diffraction result (Fig. 1c).

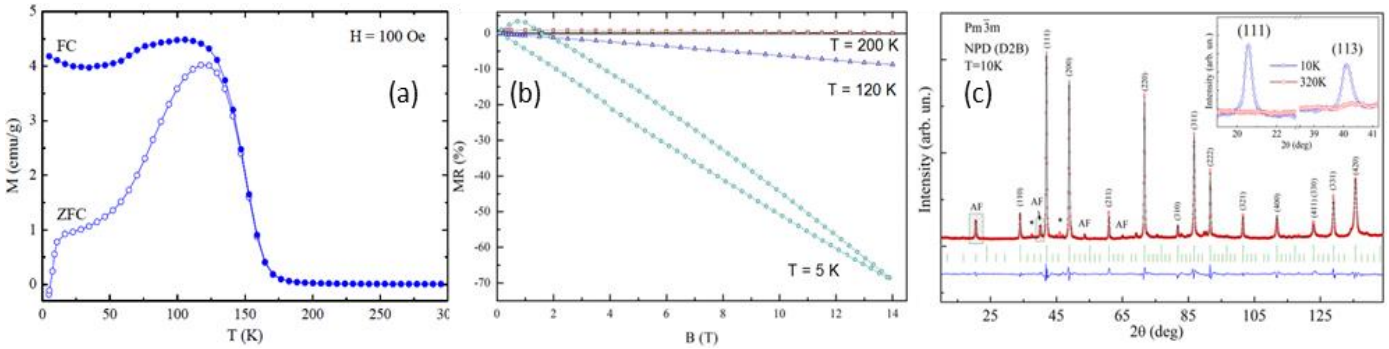

Fig. 1. (**a**) M vs T magnetization showing T_C=190 K. (**b**) MR vs H at 5, 120 and 200 K. (**c**) The neutron powder diffraction (D2B, ILL) pattern obtained for $La_{0.5}Ba_{0.5}CoO_{2.75}$ compound at 10 K. Bragg reflections are indicated by the vertical green ticks (the upper row denotes structural phase, the bottom one magnetic phase). The inset shows the peaks specific for G-type antiferromagnetic structure at 10 K, the parts of the 320 K pattern demonstrate a nearly disordered magnetic state.

The temperature-dependent magnetization can be understood assuming a gradual change in the spin-state of cobalt ions with temperature decrease. The ST is accompanied by a decrease of the FM component and a growth of the AFM one as seen in Fig. 1(a and c). An enhancement of the AFM interactions below 120 K is likely due to stabilization of the HS of the Co^{3+} ions.

Our previous high-resolution neutron powder diffraction studies on non-stoichiometric $LBCO_{3-\delta}$ showed that an oxygen content decrease is responsible for FM to AFM (G-type) transition [7,8]. In the intermediate composition region macroscopic phase separation into different structural and magnetic phases occurs. The FM–AFM transition and ST were induced by lowering temperature. It agrees well with the anomalous growth of Co and O isotropic ADPs around 100 K. The unit cell expansion is accompanied by a decrease of the average Co oxidation state and possibly by a transition into Co^{3+} HS state, with an ionic radius larger than the IS or LS states. Both AFM and FM phases have a cubic structure with different unit cell volume. The fraction of AFM phase increases gradually with cooling. The estimated magnetic moment in the AFM (FM) phase is around ±2(1.60) μ_B/Co. The strongly reduced $LBCO_{2.6}$ is pure AFM.

Several microscopic characteristics (including orbital, spin, and total magnetic moments on Co^{3+} atoms) will be computed with first-principle DFT + DMFT approach [4,6] and compared with experimental data. It will be possible to define statistical weights of Co magnetic states for a given temperature and crystal structure within the DFT + DMFT method.

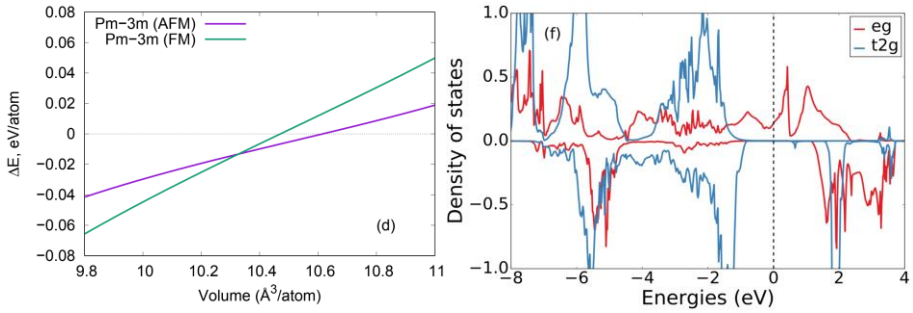

Fig. 2. Left panel: The difference of total energies on the volume between Pm-3m (AFM, FM) and R-3c (AFM) (d), zero level corresponds R-3c (AFM). Right panel: Total and partial densities of states for Pm-3m (FM) at V = 10.18 Å^3 (intermediate-spin state). The presented results were obtained by DFT+U method for $La_{0.75}Ba_{0.25}CoO_{2.9}$ system.

Figure 3 shows the temperature dependence of the normalized XANES and XMCD spectra for a $La_{0.5}Ba_{0.5}CoO_{2.75}$ recorded at Co *K*-edge in total fluorescence yield with electric field vector of X-ray perpendicular to the magnetic *c*-axis. A quite clear dichroic signal of the order of 0.005 % at T = 10 K with respect to the edge jump is visible at preedge feature of Co.

Co 3*d* and 4*p orbital* magnetic moments obtained from integrated XMCD singal shown in Fig. 3. Predictably, both moments grow up in the *P*-range of 0 – 5 GPa and decrease at the 10 GPa.

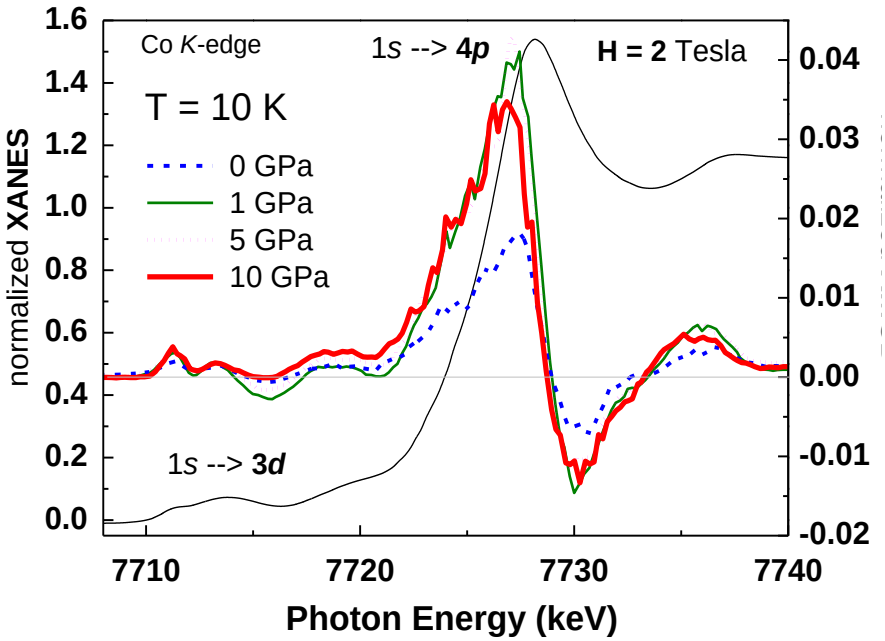

Fig. 3: Normalized XANES and XMCD spectra for $La_{0.5}Ba_{0.5}CoO_{2.75}$ at the Co *K*-edge under applied pressure.

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