ESRF	**Experiment title:** Cobalt spin states at the coupled Valence and Spin State Transition of (Pr,Sm,Ca)CoO_3 probed by XANES/XMCD at Co $L_{2,3}$ edges	**Experiment number:** **HC-2110**
Beamline: ID32	**Date of experiment:** from: 18/11/2015 to: 21/11/2015	**Date of report:** 23/02/2016
Shifts: 9	**Local contact(s):** K. Kummer	*Received at ESRF:*

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Report:

$(Pr_{1-y}Sm_y)_{0.7}Ca_{0.3}CoO_3$ belong to the class of Pr/Co oxides presenting a simultaneous Valence (charge transfer between Pr and Co ions) and Spin State (of the Co^{3+}) Transition. The purpose of the experiment HC-2110 was to determine the nature of the different species at play and their evolution as a function of the temperature by using XAS/XMCD. This work has been carried out on y= 0, used as a reference without VSST (instead a $T_c \sim 50$ K), and y= 0.36, showing the VSST at T*~ 110 K.

♦ The first step to analyse the Co XAS/XMCD spectra is an independent determination of the Co^{3+}/Co^{4+} ratio; this was here inferred from the Pr^{4+}/Pr^{3+} ratio derived from analysis of the XAS Pr $M_{4,5}$ edges. As shown in **Fig.1(a)**, there is no evolution of the spectra vs. T for y= 0, which are found to be typical of pure Pr^{3+} over the whole T range. In contrast, a clear variation with T is observed for y=0.36, revealing the development of Pr^{4+} at low temperatures. **Fig. 1(b)** shows this evolution based on linear combination fitting of $M_{4,5}$ XAS spectra representative for Pr^{3+} and Pr^{4+}, as in ref. [1]. One observes a sudden appearance of Pr^{4+} below the VSST, as systematically occuring in this type of transition [1-3]; Moreover, there is a striking quantitative agreement with previous results derived from analysis of the L_3 edge (bulk technique).

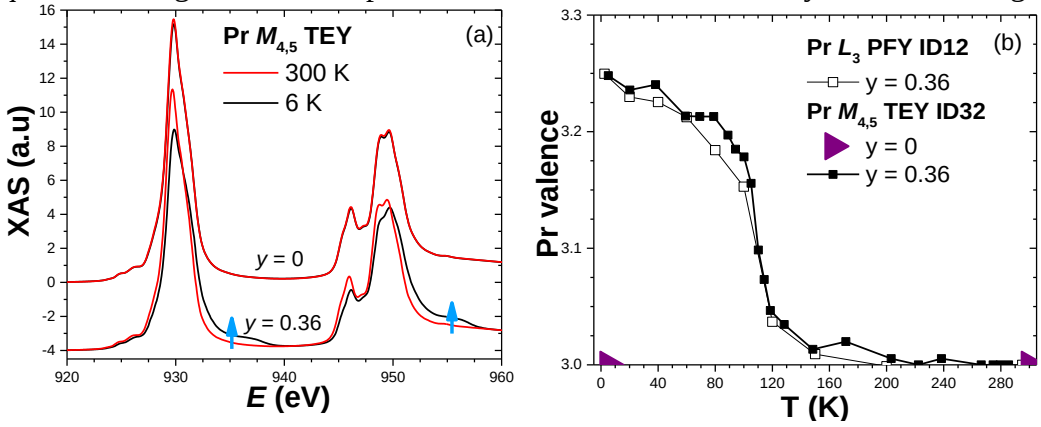
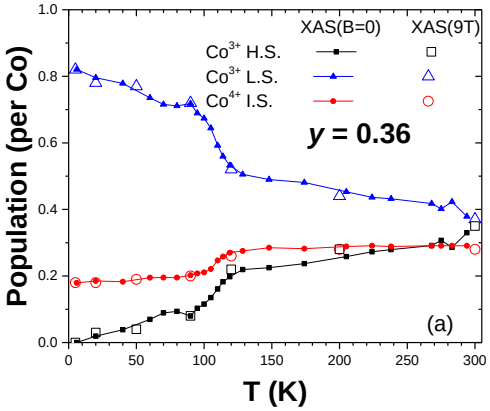


Fig.1
(a) Pr $M_{4,5}$ spectra for y = 0 and 0.36 measured in total electron yield mode.
(b) Temperature dependence of the Pr valence (ID12 measurements made in fluorescence with an energy resolved detector).

♦ Isotropic XAS spectra at the Co $L_{2,3}$ edges were recorded as a function of T for y= 0 and 0.36. They were analyzed in terms of populations of Co^{3+} LS, Co^{3+} HS and Co^{4+} IS, following an approach based on linear combination fitting of calculated reference spectra as in ref. [1]. For y= 0.36, **Fig. 2 (a)** exhibits the close interplay between the spin-state and valence degrees of freedom around T*. Owing to a better resolution than previous results, this data also clearly emphasizes small but significant temperature dependences of the Co^{3+}HS/Co^{3+}LS ratio on both sides of the transition.

♦ One also observed a striking similarity of the room temperature (RT) Co XAS spectra for the two y values [see **Fig. 2(b)**]. This suggests that the same scheme for the Co^{3+} spin-state at high T (i.e., either IS or mixed HS/LS, as presently done) should be considered for all y values. Including previous data for y=0.3, a

quantitative analysis yields Co^{3+} HS fractions at RT equal to 42%, 37% and 34%, for y=0, 0.3 and 0.36, respectively. On the one hand, such a trend would be in line with the expectation that an increase in Sm^{3+} can favor the Co^{3+} LS state. On an other hand, this contradicts the evolution inferred from a simple Curie-Weiss analysis of the magnetic susceptibility. Therefore, we feel that few additional measurements (Co XAS/XMCD at 300 K for typically 2 extra y values) would be highly welcome to clarify this important issue.



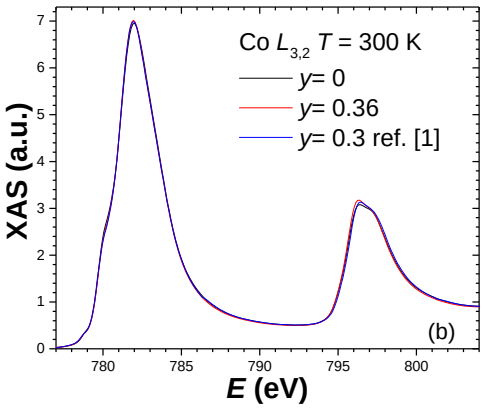
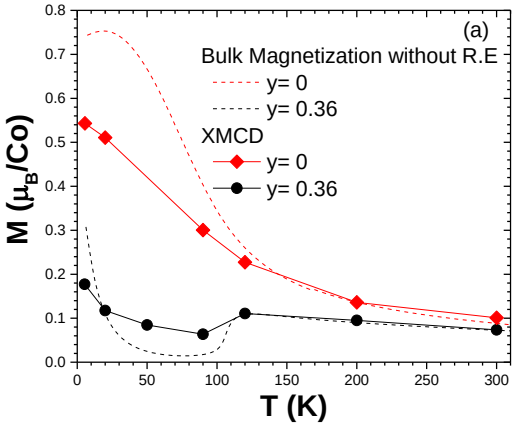


Fig.2
(a) Temperature dependence of Co species from XAS analysis at the Co $L_{2,3}$ edges of y= 0.36. **(b)** XAS spectra at the Co $L_{3,2}$ edges at 300 K for various y values.

♦ The heart of the experiment was to use XMCD measurements at the Co $L_{2,3}$ edge to get direct insight into the Co species at low T. XMCD measurements were performed for y= 0 and 0.36, at selected magnetic fields (up to 9T) and temperatures (between 5 and 300K). XMCD is clearly the most suitable tool for our purpose, since the XAS analysis relies on –sometimes questionable– reference spectra, while the analysis of bulk magnetometry data is made difficult by the various rare-earth contributions. Up to now, the Co *3d* magnetic moments were derived by the sum-rules analysis (using Co N_h determined from Pr data). **Fig. 3(a)** compares, for each y value, the Co magnetization derived from XMCD to that obtained after subtracting the Pr^{3+} and Sm^{3+} contributions from a standard magnetization curve. One observes a good consistency in the high T regime, which lends strong support to the accuracy of our XMCD analysis (the discrepancies at low T can be ascribed to the appearance of Pr^{4+} for y=0.36, and to the probable polarization of Pr^{3+} below the T_c for y=0). Let us now focus on the XMCD versus field at our base temperature of ~5 K [see **Fig. 3(b)**]. For y=0.36, there is a consensus about the fact that Co^{3+} is LS, implying that the XMCD only reflects Co^{4+} and can thus elucidate its spin state. Clearly, it appears that the XMCD data is hardly compatible with a IS state, whereas it can be well consistent with Co^{4+} LS within a mean field approach. This result is at odds with our previous conlusions derived from the adjustements of XAS spectra. The problem probably involves the reliability of the calculated reference spectrum of Co^{4+} IS; Reconsideration of the XAS analysis with Co^{4+} LS instead of IS is presently at work. For y=0, we emphasize that these XMCD results also contradict the two scenarii that are presently in competion; indeed the Co moments are found to be neither compatible with a Co^{3+}LS/Co^{4+}LS scheme (saturation expected around 0.3 μ_B/Co) nor Co^{3+} IS/Co^{4+} LS (saturation expected around 1.7 μ_B/Co) [4-5]. In conclusion, these results highlight the interest of XMCD to bring direct element selective information on the magnetism of this class of cobalt oxides.



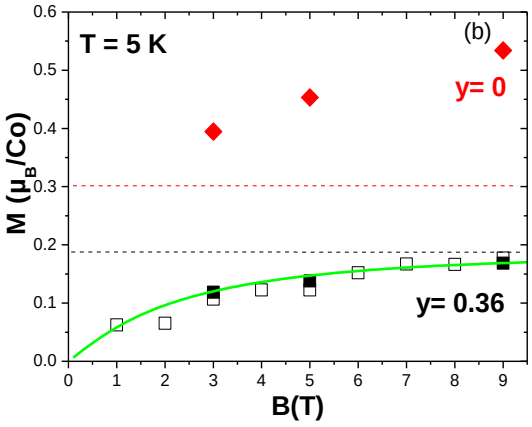


Fig.3
(a) Co Magnetic moments derived from bulk magnetic data with substracted rare-earth contributions (dashed lines) and from XMCD (symbols) at B = 9 T. **(b)** Field dependence of Co moments from XMCD (symbols) in comparison to expected values for Co^{4+} LS at saturation (dashed lines), and its field dependence for y= 0.36 within a mean field model (green line).

References: [1] F. Guillou et al., Phys. Rev. B 87, 115114 (2013) ; [2] J. Herrero-Martín et al., Phys. Rev. B 84, 115131 (2011) ; [3] H. Fujishiro et al., Phys Rev. B 87, 155153 (2013) ; [4] D. Phelan et al., Phys. 89, 184427 (2014) ; [5] K. Knížek et al., Phys. Rev. B 88, 224412 (2013).