ESRF	**Experiment title:** High-field XMCD study of the nature of the spin-state polarons in hole-doped LaCoO3	**Experiment number**: HE-3391
Beamline: ID08	**Date of experiment**: from: 27/10/2010 to: 01/11/2010	**Date of report**: 28/12/2012
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Names and affiliations of applicants (* indicates experimentalists):

Stefano Agrestini

Zhiwei Hu

Martin Rotter

Yi-Ying Chin

Report:

Among transition-metal oxides some cobaltites are very remarkable because they possess the so-called spin-state degree of freedom, i.e. the possibility of the Co^{3+} ion to be in different spin states: it can be in a low spin (LS, S=0), in a high spin (HS, S=2) and even in an intermediate spin (IS, S=1) state. $LaCoO_3$ in particular has attracted considerable interest, because it shows a thermally induced spin state transition from a nonmagnetic LS ground state to a paramagnetic HS state [1].

In our experiment we investigated a related spectacular magnetic phenomenon occurring when a small fraction of La is substituted by Sr in $LaCoO_3$: a susceptibility study [2] reported that holes introduced by this substitution in the nonmagnetic LS Co^{3+} matrix behave as localized magnetic impurities with unusually large spin values (S=10-16) [2]. A very recent joint inelastic-neutron-scattering, electron–spin-resonance and NMR investigation [3] has given strong experimental support for the presence of spin clusters with a big moment and it has been proposed that the each doped hole is not localized on a single Co^{4+} site, but is actually extended over the neighbouring Co^{3+} sites forming a magnetic seven-site (heptamer) polaron, where all the involved Co^{3+} ions are transformed from LS to IS state [3].

The aims of our experiment were to shed light on the nature (HS or IS) of the spin state of the Co^{3+} and Co^{4+} sites taking part in these magnetic polarons and to clarify whether these polarons can be described in terms of Co^{3+} and Co^{4+} sites or rather in terms of a coherent Co intermediate-valence state. In order to address these issues, we investigated the spin state of the Co ions in $La_{1-x}Sr_xCoO_3$ by using soft X-ray MCD at the Co-$L_{2,3}$ edge in applied field of 5 Tesla. This technique is a powerful tool to obtain information about the magnetic states at each atomic site. With the use of magneto-optical sum rules, it gives the orbital magnetic moment and the spin magnetic moment on each atomic site.

For the present investigation several single crystals with Sr concentrations x = 0.002, 0.004, 0.005, 0.0075 and 0.008 were grown by floating zone method. For each single crystal Co-$L_{2,3}$ XAS spectra at T=300 K were carefully examined for possible Co^{2+} impurity contributions, which were found in the samples with x=0.0075 and 0.008. For this reason we measured the XMCD signal only on the crystals with x=0.002, 0.004 and 0.005 at several temperatures: T = 200, 110, 60, 20 K for x = 0.004, 0.005 and T = 300, 60 K for x = 0.002. As the MCD signal is quite small many XAS spectra were collected for each temperature and sample in order to have a good signal to noise ratio. The XAS spectra were collected in both H = 5 T and –5 T applied fields and in groups of four or quartet (*paap* or *appa*, where *a* and *p* indicate photon spin parallel or

antiparallel to the applied field, respectively) in order to minimize the effect of any time dependence in the X-ray beam on the measured spectra. XAS spectra of CoO were recorded simultaneously as energy calibration for the Co-$L_{2,3}$ edge.

Typical Co-$L_{2,3}$ XAS spectra are shown in Fig. 1 (top) for x=0.004. In Fig. 2 (bottom) the XMCD spectra of the three investigated samples at 60 K are displayed. For comparison we show also the XMCD spectrum of a pure $LaCoO_3$ crystal (black curve) taken from ref [1]. Our data shows that a very light doping in Sr can produce a strong enhancement of the XMCD signal, which is in agreement with the huge increase of the paramagnetic signal observed by susceptibility [2]. The shape of the measured XMCD spectra seems to be rather similar to that of the pure $LaCoO_3$ except for a scale factor. This similarity was observed for all temperatures (not shown). Because the multiplet structure of a XMCD spectrum is characteristic for the spin state of the ion, our data may suggest that the magnetic signal in $La_{1-x}Sr_xCoO_3$ is mainly due to Co^{3+} ions in a HS state and may suggest that the holes introduced in the LS Co^{3+} matrix would induce locally a LS-to-HS state transition of the neighbouring Co^{3+} ions and not a LS-to-IS state transition as proposed in literature [3-5]. Unfortunately, the beam was very unstable during the beamtime of our experiment (the beam was lost several times every day), which in turn produced an instability of the optics of the beamline. As a consequence of the instability, not only the spectra were showing often energy shifts, but also we observed irregular flux variation of the beam impinging on the sample, which could not be compensated by dividing the measured XAS spectrum by the beam flux I0 given by the monitor. Hence the background of the spectra of each quartet was never parallel, affecting the XMCD signal. This is especially bad when the XMCD signal is small as in $La_{1-x}Sr_xCoO_3$ for low Sr doping and actually prevented a reliable quantitative analysis of the data. If we can believe the data from the sample with x=0.004 we get the ratio L_z/S_z = 0.6(1) μ_B at T = 60 K and 300 K with the use of magneto-optical sum rule. The value is surprisingly close to the one (0.50 μ_B) obtained for the pure $LaCoO_3$ and may indicate the presence of a large orbital moment, which is characteristic of HS Co^{3+} [1].

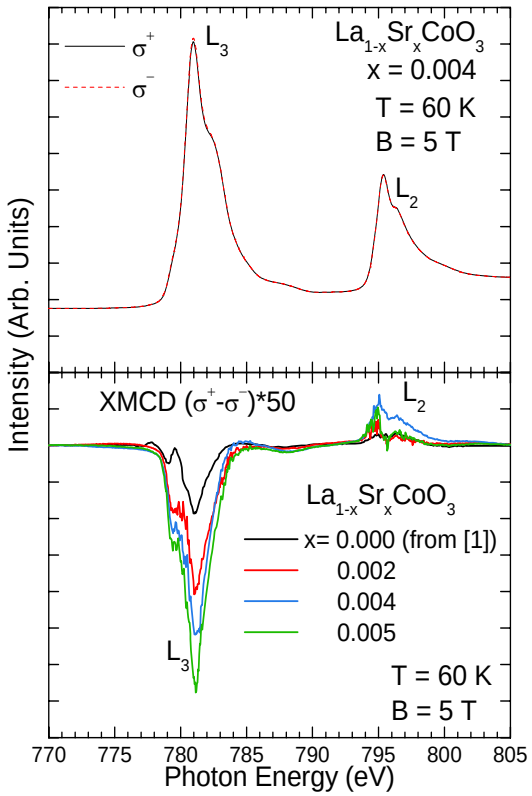

Fig.1. Top: Representative Co-$L_{2,3}$ XAS spectra measured on x=0.004 sample at T=60 K at ID08 in ESRF with circular polarized soft X-rays. Bottom: XMCD spectra measured on $La_{1-x}Sr_xCoO_3$ for different dopings at T=60 K. The black curve is taken from [1].

In summary, the results of the present experiment are very promising as they provide indications that in hole-doped $LaCoO_3$ the main contribution to the magnetic signal of the magnetic polarons is associated to Co^{3+} ions in a HS state. However, beam instability hampered a reliable quantitative interpretation of the data. Repeating the experiment under more stable conditions would be decisive for a better understanding of the nature of the polarons (estimation of the number of HS Co^{3+} ions participating in the formation of the polarons, spin state of the Co^{4+} ion, etc). We would like to stress that our results are indicating a new view on how the Co magnetic moment is formed in cobaltates. We would like also to remind that in a previous work [1] by employing this technique we were able unravel the HS/IS state dilemma in pure $LaCoO_3$.

References

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