ESRF	**Experiment title:** XMCD study of the behavior of Co orbital magnetization of the $La_{1-x}Sr_xCo_{1-y}Nb_yO_3$ single crystals in the range of spin-state and ferromagnetic phase transitions	**Experiment number:** **HE-3677**
Beamline: **ID12**	**Date of experiment:** from: **31.08.2011** to: **06.09.2011**	**Date of report:** 01.09.2013
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A perovskite-like lanthanum cobalt oxide $LaCoO_3$ belongs to a family of perovskites that attracts a lot of interest because of their rich variety of physical properties. In the ground state the Co^{3+} ions are found to be in the low-spin state (LS; $t^6_{2g}e^0_g$, $S = 0$). The transition ~120 K was ascribed to the thermal activation of the intermediate-spin state (IS; $t^5_{2g}\,e^1_g$, $S = 1$) or high-spin state (HS; $t^4_{2g}\,e^2_g$, $S = 2$) of Co^{3+} [1-9].

Soft X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) at the Co $L_{2,3}$-edges as well as theoretical calculations for a CoO_6 clusters [2] 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. The authors [2] argue that large orbital momentum revealed by the Co $L_{2,3}$-edges XMCD measurements invalidates existing LS-IS scenarios [1].

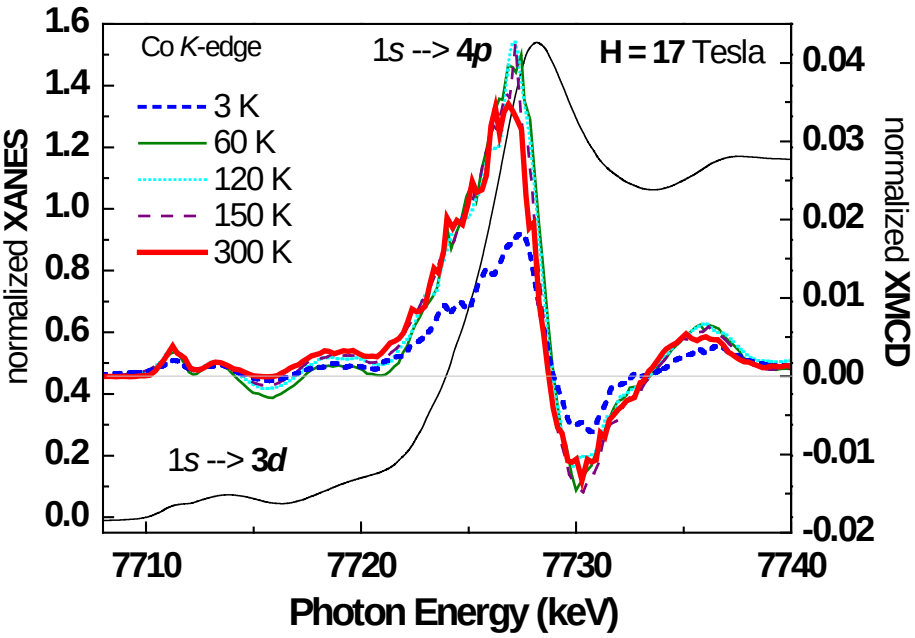

Fig. 1: Co *K*-edge XANES and temperatue-dependent XMCD spectra under external magnetic field of 17 Tesla for a $LaCoO_3$ single crystal parallel to the *c*-axis.

It is worth noticing that recent Co $L_{2,3}$ XMCD data by Burnus *et. al.* [6] showed that Co^{2+} ions in $LaMn_{0.5}Co_{0.5}O_3$ have a large orbital moment, $L_z/S_z \sim 0.47$. The L_z/S_z is surpisingly similar to one reported by Haverkort *et. al.* [2] in $LaCoO_3$ single crystal. Clearly, one need to be concirned about strain field and vacancies on the $LaCoO_3$ surface [7-9]. The present study was undertaken to provide a essentially buld probe of Co spins states, by making use of hard x-ray XMCD at the Co *K*-edge.

Figure 1 shows the temperature dependence of the normalized XANES and XMCD spectra for a $LaCoO_3$ single crystal 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 0.02 % at T = 3 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. 1 following the prescription in Ref. [10] are depicted in Fig. 2(a) and 2(b), respectively. Predictably, both moments grow up in the *T*-range of 3 K – 120 K and decrease in the range of 150 K – 300 K. The absolue values of the derived orbital moments are quite small, and most importantly, the 3*d* and 4*p* moments gain only factors of ~2 and 3, respectively, as temperature increases from 3 K to 120 K. Magnetic moment obtained by the bulk SQUID-magnetization measurement at 14 Tesla, shown in Fig. 3, increses by factor of 10 as T grows from 3 K – 25 K to 120 K. Recalling that SQUID-magnetization provides the total magnetic moment of Co ions (the sum of orbital and spin moments) the following two conclusions are in order: (i) Major contribution to the total magnetc moment gain between 3 K and 120 K ought to come from the ***spin*** moment change; and (ii) about 10 times 3*d* total moment change and 2 times orbital moment change implied by the LS ->HS transition scenario [2] is not observed in the present study, Fig.3 and Fig 2(a). We would like to point out that the IS state implies smaller than HS state 3*d* orbital moment value. The observed less than factor of 2 gain appears to be a good argument for the LS ->IS transition model [1].

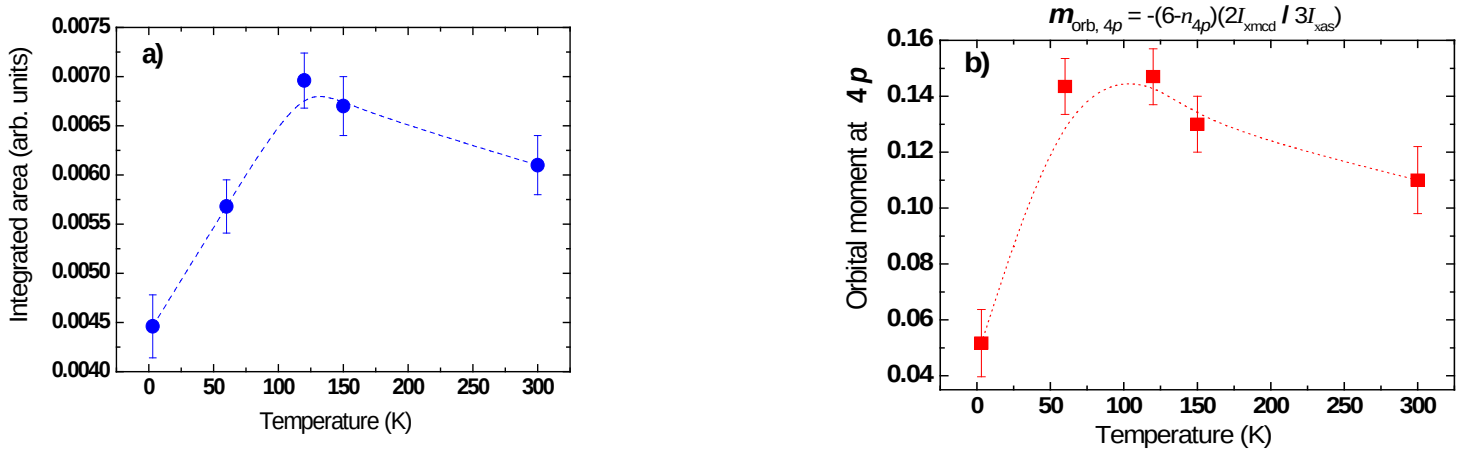

Fig. 2: Temperature-dependent 3*d* orbital magnetic moment (**a**) as a integrated area from 7709 eV to 7714 eV of the XMCD spectra at the Fig.1 and 4*p* orbital moment (**b**) calculated from Ref.10 per Co ion for $LaCoO_3$ single crystal.

The previous soft X-ray XMCD data at the Co $L_{2,3}$-edges [2], which reflect mainly the surface contribution, do not correlate with our hard X-ray XMCD at the Co *K*-edge (i.e. bulk contribution). The disagreement could probably be attributed to a significant influence of crystal surface (tansile strain, vacansies) [5, 7-9], which results in a stabilization of higher spin states Co^{3+}.

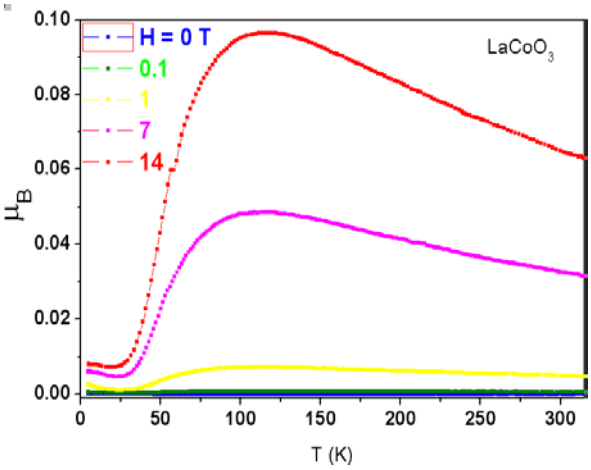

Fig. 3: SQUID magnetization curves for $LaCoO_3$ single crystal at different external magnetic fields.

References

[1] M. Korotin, *et.al*, *Phys. Rev.* B **68** 235113 (2003).
[2] M. Haverkort,*et.al*. *Phys. Rev. Lett.* **97,** 176405 (2006).
[3] P.G. Radaelli, S.W. Cheong, *Phys. Rev.* B **66**, 094408 (2002).
[4] G. Maris, V.Volotchaev,*et.al*,*Phys. Rev*. B **67**, 224423 (2003).
[5] K. Knížek, J. Hejtmánek, Z. Jirák, Petr Tomeš, P. Henry, G. André, *Phys. Rev*. B **79**, 134103 (2009).
[6] T. Burnus, M. W. Haverkort, V. L. J. Joly, L. H. Tjeng, et.al, *Phys. Rev*. B **77**, 125124 (2008).
[7] D. Fuchs, E. Arac, C. Pinta, et.al, *Phys. Rev*. B **77**, 014434 (2008); Phys. Rev. B **75**, 144402 (2007).
[8] J.-Q. Yan, J.-S. Zhou and J.B. Goodenough, *Phys. Rev*. B **70**, 014402 (2004).
[9] A. Herklotz, A.D. Rata, L. Schultz, K.D¨orr, *Eur. Phys. J. B* **76**, 215–219 (2010); *Phys. Rev. B* **79**, 092409 (2009).
[10] B. T. Thole, P. Carra, F. Sette, and G. van der Laan, *Phys. Rev.Lett.* **68**, 1943 (1992).