EUROPEAN SYNCHROTRON RADIATION FACILITY
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Experiment Report Form

	Experiment title: On the spin-state transitions in $LaCoO_3$: Revising a revision ??	**Experiment number**: HE-1755
Beamline: ID08	**Date of experiment**: from: 08-12-2004 to: 15-12-2004	**Date of report**: 17-02-2005
Shifts: 22	**Local contact(s)**: Nick Brookes, Júlio Criginski Cezar	*Received at ESRF:*

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The spin state, the spin state transition and their impact on the electronic properties in $LaCoO_3$ have been a long-standing issue [1-3]. Various early studies based on magnetic measurements attributed the low-temperature spin-state transition to a change from the low-spin (LS) $^1A_1$ ground state to the high-spin (HS) $^5T_2$ thermally excited state [1-3]. This classic picture has been *revised* in 1996 by the work of Korotin *et al.* [4], in which they found from LDA+U calculations that band formation substantially lowers the energy of the intermediate-spin state (IS) $^3T_1$, while it does not affect the HS state. At temperatures above 150 K the IS becomes lower in energy than the LS. Many studies in the last decade put a lot of effort to confirm this LS-IS scenario [5-8]. So far, electron spectroscopic studies indicated only an insignificant temperature dependence of the spectra below 300 K [5]. From detailed theoretical simulations on the valence-band XPS spectrum of $LaCoO_3$ (taken with $h\nu$ = 1253.6eV), Saitoh *et al.* concluded that the 80 K spectrum can be reproduced by assuming a mixing of 70% $^1A_1$ + 30% $^3T_1$ [6]. From the insignificant temperature dependence they excluded a $^1A_1 - {}^5T_2$ mixture since the $^5T_2$ spectrum, which is spread over a wide energy range, is completely different from the $^1A_1$ spectrum, while the $^3T_1$ spectrum is more similar to the $^1A_1$ spectrum. Nevertheless, the insignificant temperature depenence obviously contradicts the magnetic susceptibility measurements [6,7].

In order to resolve the $LaCoO_3$ problem we carried out detailed temperature- and emission-angle-dependent valence-band XPS measurements on $LaCoO_3$ single crystals during the 08-12-2004 to 15-12-2004 period. The valence-band XPS spectra of $LaCoO_3$ taken at $h\nu$ = 700eV presented in Fig. 1 show a predominant peak A at 1 eV binding energy, which is twice as high as peaks B at 3.1 eV and C at 5.7 eV. In contrast, the XPS data from Saitoh *et al.* [6] presented in Fig. 2 show nearly the same height for these three peaks. Since the peak at 1 eV is expected to be related to the LS ground state, the large spectral weight at peak A indicates that our $LaCoO_3$ sample has a much larger LS contribution than found by Saitoh *et al*. In order to clarify this difference we measured spectra at grazing emission (60° off normal). We observe a strong decrease of spectral weight of peak A from normal to grazing emission. This indicates

that the spin state of the Co^{3+} ions at the surface is not LS. Therefore the weakness of peak A observed by Saitoh *et al.* might be due to the poor quality of the powder sample or mishandling of the sample surface.

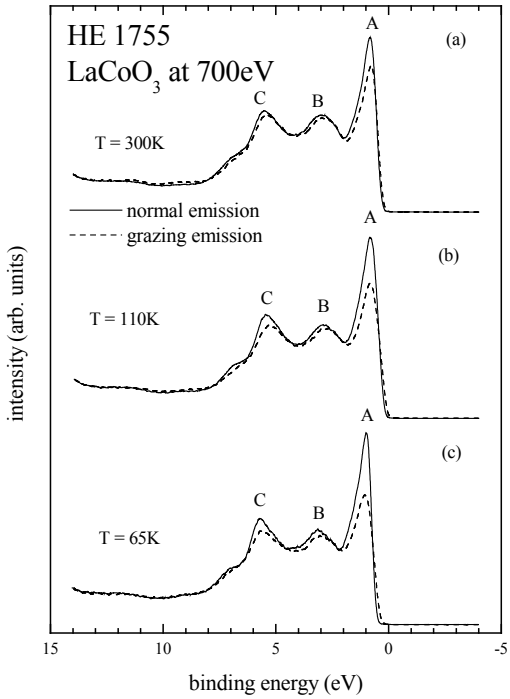

Fig. 1. XPS Spectra of $LaCoO_3$ taken with 700 eV photon energy in normal emission (solid lines) and 60° off normal (dashed) at (a) T=300K, (b) T=110K and (c) T=65K

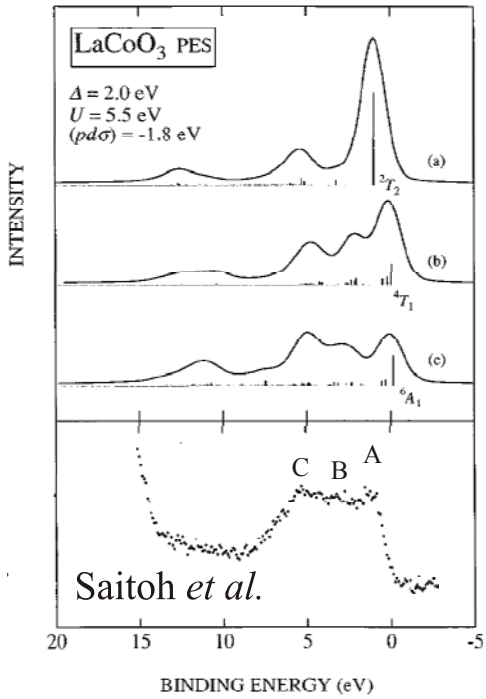

Fig. 2. XPS spectra of polycrystalline $LaCoO_3$ at T = 80K (bottom) and cluster calculation of Co 3d spectral weight in LS (a), IS (b), and HS (c). [6]

We have carried out x-ray magnetic circular dichroism (XMCD) measurements at the Co-$L_{2,3}$ edges of $LaCoO_3$ with a magnetic field of 6 Tesla. Since $LaCoO_3$ is not FM, i.e. non-magnetic at low temperatures and only paramagnetic at higher temperatures, the XMCD is very weak as shown in Fig. 3. Therefore a high accuracy of the energy calibration (error < 0.005 eV) was required and was achieved by measuring simultaneously a CoO reference upstream. Open circles in Fig. 3 is XMCD spectrum (× 20) taken at 110 K, i.e. at maximum in magnetic susceptibility. From 110 K to 300 K (filled circles) the XMCD (× 20) signal

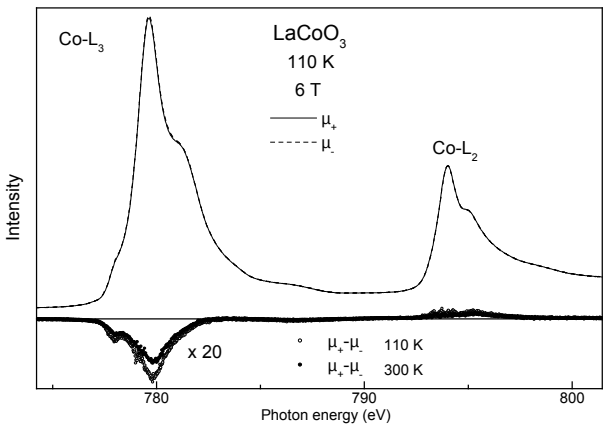

Fig. 3. Co 2*p* XAS spectra μ_+ (dashed line), μ_- (solid line) and μ_+–μ_- (open circles) of $LaCoO_3$, where μ_+ and μ_- refer to photo helicity parallel and antiparallel to the magnetic field ***B***, respectively. The μ_+–μ_- taken at 300 K (filled circles) is also presented for comparison.

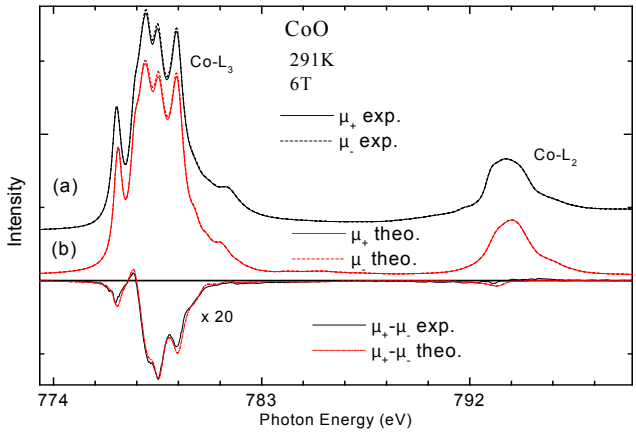

Fig. 4. (a) Experimental Co-$L_{2,3}$ XMCD spectra of CoO taken at 291K and 6T. (b) Theoretical simulation.

decreases to 70% in a similar way as the magnetic susceptibility. According to the orbital sum rule [9], $M_{orb}/M_{spin}=2[\Delta I(L_3)+\Delta I(L_2)]/3[\Delta I(L_3)-\Delta I(L_2)]$, we deduce $L_z/2S_z \approx 1/4$. This indicates that the thermally excited state has a large orbital moment and can be either HS or IS. For the IS scenario, we can exclude both the orbital-ordered x^2-y^2/xy case proposed by Korotin *et al.* [4] as well as the strong JT $3z^2$-r^2/xy case (xy denotes a xy hole), since both cases have $L_Z=0$. So we are left with a HS scenario or an IS scenario of $3z^2$-r^2/xz-yz (xz-yz refers to the linear combination of *xz* and yz holes). The theoretical simulation of the XMCD spectrum of $LaCoO_3$ is in progress, with which we expect to distinguish which of the two scenarios is correct.

As a test to double check the reliability of XMCD measurements on paramagnetics systems at high temperatures, we set out ot do an experiment on CoO in the paramagnetics phase. The XMCD signal is proportional to the induced magnetization of the Co ion. CoO has the largest susceptibility of about 5.3 emu mol^{-1} at its Neel temperature (291K). The spectra, measured at 291K and a magnetic field of 6 Tesla are shown in Fig. 4(a). The XMCD of CoO can be well reproduced by a cluster calculation as shown in Fig. 4(b). From this cluster we also calculate that the spin orbit signal $\Sigma_i\langle l_i \cdot s_i\rangle$ is about $1.00\mu_B^2$, in very close agreement with spin-resolved photoemission data [10].

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