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Experimental Report ESRF beam time HE-3261

In our beam time HE-3261 we have successfully performed soft x-ray absorption (XAS) and x-ray magnetic circular dichroism (XMCD) experiments at the Mn L_{23} edge on c(4x2) Mn_3O_4/Pd monolayer phase which bring promise of new exciting properties in view of the strongly compressive strain state and the presence of a rhombic array of regularly distributed Mn vacancies.

The goals of experiment HE-3261 were: a) verify recent theoretical predictions [1] of a ferromagnetic ground state in this intriguing monolayer system; b) search for possible new magnetic anisotropy phenomena; c) spectroscopically establish the Mn ion valence and spin character, and orbital and spin contribution to the ground state magnetic moment, i.e. the basic elements determining electronic structure and underlying magnetic properties of *3d* magnetic oxides. To this purpose, we have successfully prepared the c(4x2) Mn_3O_4 monolayer phase on a Pd(1,1,19) surface using the MBE and LEED/STM set-up at ID08 and we have thus performed XAS and XMCD experiments in-situ at the beam line at different sample temperatures in the range from 8 K to 300 K. The temperature dependent XMCD spectra, in particular, have been recorded as a function of an applied magnetic field up to 5 T in different experimental dichroic geometries (Fig.1 (a–b). Standard manganese oxide thin films such as MnO were also prepared and measured in-situ at ID08 for spectroscopic reference purposes.

We have found that the Mn L_{23} edge isotropic XAS spectra of the c(4x2) Mn_3O_4/Pd monolayer phase measured at ID08 are strongly different from those of MnO, $LaMnO_3$, $SrMnO_3$ and Mn_3O_4 reference standards in which Mn ions have a 2+, 3+, 4+ and mixed 2+ and 3+ oxidation state, respectively, and we found not possible to fit the measured Mn L_{23} isotropic XAS spectra of the c(4x2) Mn_3O_4/Pd monolayer phase with any linear combination of Mn 2+, 3+, 4+ reference standard spectra. This indicates that the electronic structure of the c(4x2) Mn_3O_4/Pd monolayer phase is indeed strongly different from that of other to date known manganese oxide compounds. Very likely the c(4x2) Mn_3O_4/Pd monolayer phase is a peculiar mixed valence system and, in order to verify this hypothesis, theoretical simulations of the measured XAS spectra based on cluster model and multiplet calculations are presently in progress.

We also found that the XMCD spectra measured at low temperature in high magnetic field exhibit a strong magnetic dichroism effect which vanishes at increasing temperatures (Fig.1 c–d). This provided us with a suitable probe to study the temperature dependent field induced magnetization of the c(4x2) Mn_3O_4/Pd monolayer phase as shown in Fig.1 (e) reporting the XMCD dichroism signal measured as a function of temperature and magnetic field at $\theta = 0$ photon beam incidence. The plots in Fig.1 (e) show that in the 8 K to 300 K temperature range there is no opening of an hysteresis loop thus showing that, at least above 8 K, the c(4x2) Mn_3O_4/Pd monolayer phase is in a paramagnetic state. Nevertheless, from a mean field analysis of the magnetization curves (solid fitting line in Fig.1 e) we find indication that local magnetic correlations at Mn ion may actually be ferromagnetic, so that ferromagnetic long range magnetic ordering below 8 K remains a possible scenario.

In addition to the above findings, two major conclusions can be drawn based on the temperature and field dependent XMCD spectra recorded during beam time HE-3261. First, the c(4x2) Mn_3O_4/Pd monolayer phase is more easily magnetized when the magnetic field is set parallel rather than perpendicular to the sample surface normal, as shown in Fig.1 (f). Second, based on XMCD sum rules analysis [2], the orbital to spin magnetic moment ratio in the studied manganese oxide monolayer phase turns out to be $m_{orb}/m_{spin} = 0.08$, i.e. at least one order of magnitude larger than in ordinary 2+ and 4+ manganese oxides such as MnO ($m_{orb}/m_{spin} = 0$) and Ca_3CoMnO_6 ($m_{orb}/m_{spin} = 0.007$) [3], thus clearly indicating the existence of a strongly unquenched Mn orbital moment in the studied c(4x2) Mn_3O_4/Pd monolayer phase. Moreover, the XMCD experiments showed that the value of the ratio m_{orb}/m_{spin} is substantially reduced from 0.08 to 0.05 when the magnetizing external field is flipped from perpendicular ($\theta=0$) to parallel ($\theta=70^0$) to the sample surface.

This interesting result correlates nicely with the discovery of the strong magnetic anisotropy phenomenon reported above and displayed in Fig.1 (f), since the onset of a giant orbital moment may very likely be connected to the presence of an easy magnetization axis perpendicular to the sample surface.

A complete understanding of the origin and nature of the observed strong magnetic anisotropy phenomena and the onset of giant orbital moment in the studied manganese oxide monolayer phase requires detailed forthcoming theoretical calculations. Nevertheless, the available XAS and XMCD data recorded at ID08 in our beam time HE-3261 are sufficient to disclose the existence of new and unexpected electronic and magnetic properties in *3d* oxide nanostructures.

We expect that these results will foster renewed interest in the search for atomically engineered *3d* oxide nanostructures and in designing new experiments to more deeply explore the electric and magnetic properties of this intriguing class of materials.

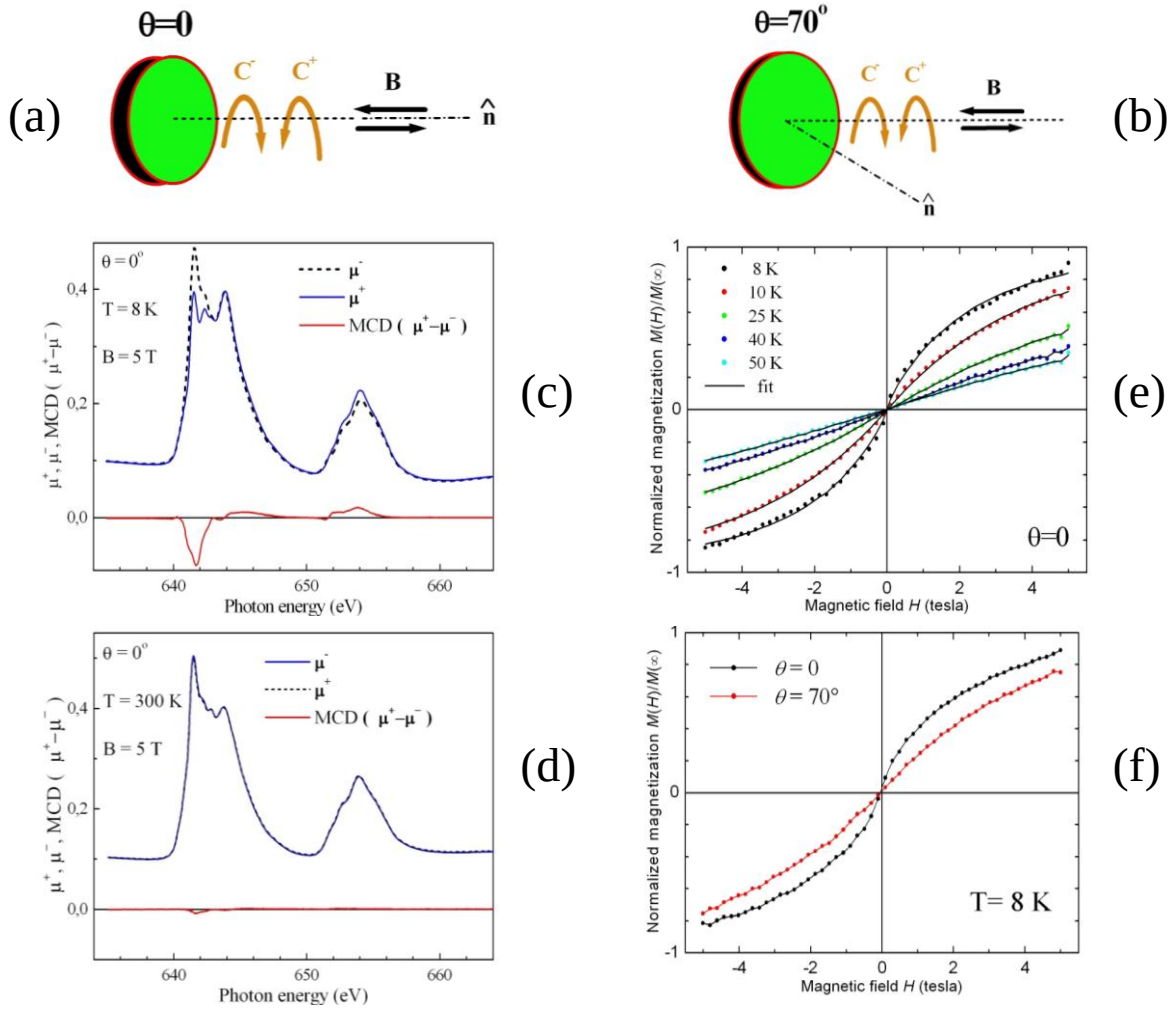

Fig.1: (a–b) experimental XMCD geometry: photon wave vector and magnetic field (**B**) direction parallel (θ=0) and almost perpendicular (θ=70°) to the sample surface normal; (c–d) θ=0 MCD spectra with parallel (μ^+) and antiparallel (μ^-) alignment of photon spin and magnetic field and relative MCD signal ($\mu^+ - \mu^-$) at T=8K (c) and at T=300K (d); (e) temperature and magnetic field dependence of MCD signal (sample magnetization) measured at θ=0: dots are experimental points, solid lines are Brillouin function fitting lines in mean field approximation; (f): sample magnetization measured at T=8 K at θ=0 and θ=70° i.e. with the magnetic field lying perpendicular and almost parallel to the sample surface, respectively.

References

[1] C. Franchini, J. Zabloudil, R. Podlousky, F. Allegretti, F. Li, S. Surnev and F.P. Netzer, *J. Chem. Phys.* **130** (2009) 124707

[2] S. Agnoli, M. Sambi, G. Granozzi, S. Surnev and F.P. Netzer *et al.*, *J. Phys Chem. B* **109** (2005) 17197

[3] Y. Zhang, H.J. Xiang and M.-H. Whangbo, *Phys Rev. B* 7**9** (2009) 54432