ESRF	**Experiment title:** Room temperature ferromagnetism in pure and transition metal doped TiO_2 films	**Experiment number**: HE-2112
Beamline: ID08	**Date of experiment**: from: 12/4/2006 to: 18/4/2006	**Date of report**: 7/3/2009
Shifts: 18	**Local contact(s)**: Julio Criginski Cezar	*Received at ESRF:*

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Report:

The aim of experiment HE-2112 was to study room temperature ferromagnetism in films of pure and transition-metal-doped TiO_2, by means of x-ray magnetic circular dichroism at the Ti $L_{2,3}$ edges and at the O K edges.
Within the available shifts at ID08, two pure films of anatase TiO_2 were deeply studied with XMCD as a function of: film thickness (10 and 200-nm-thick films), temperature (300 and 10 K), orientation of the samples (magnetic field parallel or perpendicular to the films' surface), and magnetic field strength (between 0.01 and 5 T).
The two investigated films were capped with a thin layer of Au (~ 3 nm of thickness) in order to enhance the surface electrical conductivity necessary to perform clean total electron yield (TEY) measurements, on these otherwise insulating samples. Total fluorescence yield (TFY) measurements were attempted, but were abandoned due to the low efficiency of the used photodiode for the low energies of the Ti L (~ 450 eV) and O K (~530 eV) edges, resulting in a 10-times larger background in TFY as compared to TEY.
Figure 1 shows the XAS and XMCD data taken at room temperature on the 200-nm-thick film, with a magnetic field of 5 T applied both perpendicular and almost parallel to the film surface, i.e. parallel or almost perpendicular to the *c*-axis, respectively. As clearly shown in the figure, a clear though weak dichroism signal is present at both the O K edge and at the Ti $L_{2,3}$ edges. This signal is mostly concentrated on the first oxygen XAS pre-peak at 529 eV as well as on the low-energy features of both Ti L_2 and Ti L_3 edges. These features are all related to the $3d(e_g)$ electrons of Ti, either directly or through hybridization with the O 2p

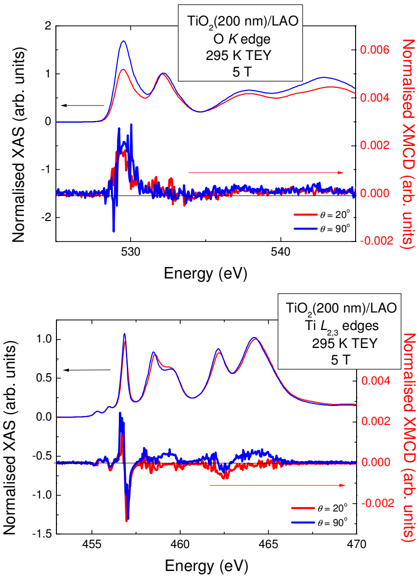

Figure 1 – Angular dependence of the XAS and XMCD of TiO_2 at 300 K and 5 T.

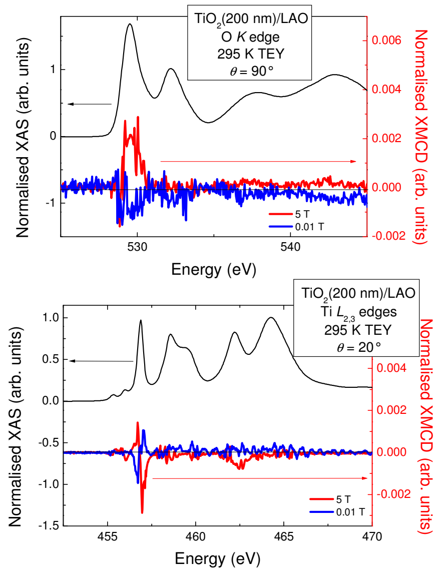

Figure 2 – Magnetic field dependence of the XMCD signal of TiO_2 films at 300 K.

electrons. The presence of this XMCD signal indicates therefore that these electronic shells are polarized by the applied magnetic field.

By comparison between the two measurement geometries in figure 1, a certain anisotropy of the magnetization (expected from SQUID magnetization measurements) appears at the O K edge, as the same XMCD intensity relates to a XAS feature (the first pre-peak at 529 eV) which is considerably weaker in grazing than in normal incidence. On the other hand, the Ti XMCD can be considered as almost isotropic within the current statistical accuracy.

The measurements at room temperature do not show any difference between the thick (200 nm) and thin (10 nm) sample. Both the shape and the magnitude of the XMCD at the Ti L and O K edges are identical within the statistical accuracy of the measurements (not shown here).

Figure 2 shows the O K and Ti $L_{2,3}$ edge measurements as a function of magnetic field (5 and 0.01 T). The measurements at +0.01 T have been performed after saturation in a field of -5 T (i.e. with a field of the opposite direction). Under these conditions, the sample should have a negative magnetization, as 0.01 T is slightly below the coercive field. In fact, at all measured edges, the XMCD signal at +0.01 T after saturation at -5 T has opposite sign as compared to the XMCD at +5 T, as expected. This is a first proof of the ferromagnetic origin of the measured XMCD signal. However, the magnitude of the XMCD at +0.01 T is fairly large (about 50% of its value at 5 T), whereas SQUID measurements suggest a considerably smaller magnetization for these low fields (~5 times lower at 0.01 T than at 5 T). Successive XMCD runs on the same samples showed irreproducible results for fields considerably lower than 1 T, while measurements above 1 T in different rounds are perfectly reproducible. We therefore tend to conclude that, for measurements in very low magnetic fields of the order of 0.01 T, the large-field superconducting magnet of ID08 is not perfectly suited: the magnetic field strength is not reproducible for small fields which are in the range of the remnant field of the magnet itself. The low field measurements should better be reattempted by using an

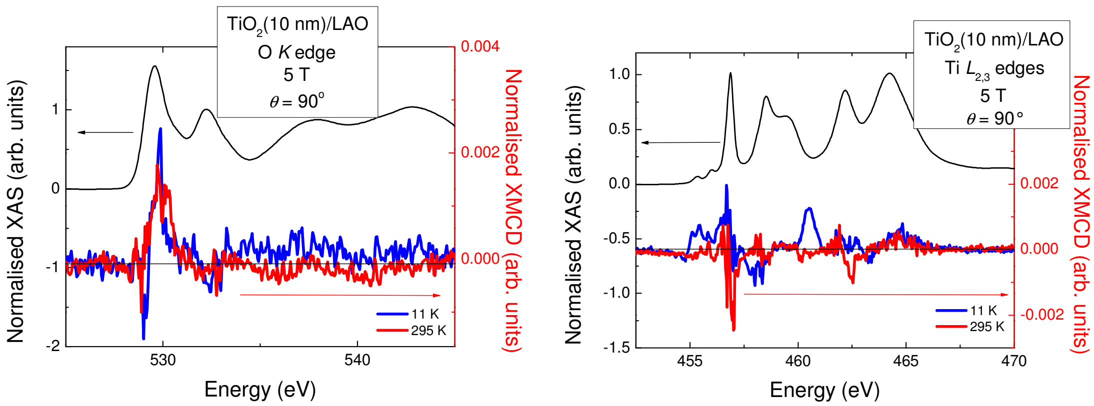

Figure 3 – Temperature dependence of the XMCD of TiO_2 for a field of 5 T.

electromagnet with a better control of the field for field magnitudes of the order of some hundred gauss.

Figure 3 shows the temperature dependence of the XMCD at the O K and Ti L edges. It is evident that at the O K edge, the intensity of the XMCD signal does not increase while decreasing the temperature from 300 K to 10 K, thus further supporting the ferromagnetic origin of the signal measured at this edge. However, at the Ti $L_{2,3}$ edges, a new component appears at 10 K, with characteristic energies clearly different from the component observed at room temperature. The low-temperature component has a clearly paramagnetic (i.e., approximately linear) dependence on the applied magnetic field. The origin of this new component is at the moment not clear.

Complementary measurements aimed at demonstrating the ferromagnetic origin of the XMCD signal measured at both the O K and the Ti $L_{2,3}$ edges were attempted, including measurements of element selective magnetization loops, and total electron yield measurements in exact remanence. However, due to the extreme weakness of the XMCD signal, none of these measurements has so far provided reliable results. We therefore propose to carry out further measurements in weak and zero magnetic fields by using the electromagnet available on ID08, which allows one for a careful regulation of the magnetic field for fields in the order of a few hundred gauss, which corresponds to the field region that could not be studied consistently with the superconducting magnet, but which is necessary to prove the ferromagnetic origin of the XMCD signal measured at room temperature on the studied anatase TiO_2 films.