EUROPEAN **S**YNCHROTRON **R**ADIATION **F**ACILITY

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ESRF	**Experiment title:** **Unravelling the Half Metallic Ferromagnetism of Metal/Oxide epitaxial interfaces**	**Experiment number**: HE1237bis
Beamline: ID8	**Date of experiment**: from: 09/07/03 to: 10/07/03	**Date of report**: 15/09/2003
Shifts: 6	**Local contact(s)**: Céline De Nadai and Nicholas Brookes	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Susana GOTA and Martine GAUTIER-SOYER

C.E.A. Saclay - DSM-DRECAM-SPCSI Service de Physique et Chimie des Surfaces F-91191 Gif-sur-Yvette Cedex France

Céline DE NADAI and Nicholas BROOKES

ESRF, BP 220, F-38043 Grenoble Cedex, France

Alberto TAGLIAFERRI

Dipartimento di Fisica, Politecnico de Milano. Piazza Leonardo da Vinci 32 I-20133 Milano Italy

Report:

The scientific committee allowed 18 shifts for the proposal HE1237 entitled "Unravelling the Half Metallic Ferromagnetism of Metal/Oxide Epitaxial Interfaces".
The SR-XPS measurements concerning the NiMnSb/MgO and the Fe/MgO interfaces have been performed (see experimental report 1237).

Because of the ESRF breakdown on the 11th and 12th of May 2002, we did not measure the bare $Fe_3O_4(111)$ layer and the $Fe_3O_4(111)/Al_2O_3(111)$ interface.

Recently (July 2003), ID08 team granted us 6 shifts of "in house" time to compensate the shifts lost due to the ESRF breakdown. This report (HE1237bis) accounts for the SR-XPS and XMCD measurements done during this period.

Two 25 nm-thick $Fe_3O_4(111)$ layers were studied: one exhibiting a free surface and the another one covered with a thin layer of Al_2O_3 (3nm) epitaxially grown on it. The samples

were grown by MBE (molecular beam epitaxy) without exposing the Fe_3O_4/Al_2O_3 interface to air.

a. Previous magnetic characterization.

A macroscopic magnetic characterization of the samples was done in our laboratory before the ESRF beamtime. The hysteresis loops measured with a VSM (vibrating sample magnetometer) are shown in Figure 1. As shown in the insert, a magnetic field of at least 1kOe is required to close the hysteresis loop.

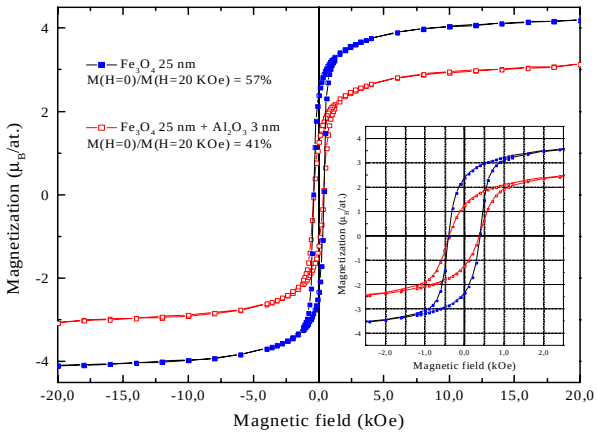

Figure 1

In the following M_S^{VSM} refers to the magnetic moment at saturation, as measured with the VSM (applied field of 20 kOe, which is the maximum field supplied by the apparatus). Also, the magnetic moment at remanence (M_R^{VSM}) is the one measured when the magnetic field is switched off.

For a given thickness, the macroscopic magnetic properties of the bare layer are more satisfactory than those of the film covered with the alumina barrier. The M_S of the bare layer is that expected for standard Fe_3O_4, whereas that of the Fe_3O_4/Al_2O_3 sample is ~25% lower. Besides, the remanence ratio (M_R^{VSM}/M_S^{VSM}) is 57% for the bare layer and 41% for the Fe_3O_4/Al_2O_3 bilayer.

b. SR-XPS experiments

The procedure to restore the surface cleanliness after the passage through air of the bare $Fe_3O_4(111)$ layer consists in an annealing *in situ* at 800 K ($P_{O2} = 10^{-6}$ Torr). We didn't have time enough to fully complete this essential step, and the SR-XPS experiments were thus carried out on a surface that was not completely carbon free (as probed by XPS). The SR-XPS spectrum shown in Fig. 2.a shows a negative polarization at the Fermi level in agreement with precedent published work [1][2][3]. The acquisition time was roughly 8 hours and the energy resolution 0.5 eV.

No cleaning procedure was applied to the Fe_3O_4/Al_2O_3 sample. The topmost layers of Fe_3O_4 are protected by the Al_2O_3 barrier. Figure 2.b show a SR-XPS spectrum of this sample, recorded during 8 hours with an energy resolution of 0.5 eV. Due to the thickness of the Al_2O_3 layer (3nm) and the residual carbon contamination, the spin resolved signal coming from the upmost layers of Fe_3O_4 is rather weak. However, experimental report 1237 demonstrates the feasibility of this kind of measurements (spin polarisation of the occupied states near the Fermi energy through an insulating barrier) for the Fe/MgO interface, and so

does the spectrum of figure 2.b for the Fe_3O_4/Al_2O_3 interface. Unfortunately, the low statistics doesn't allow to draw up more precise conclusions than an almost certainly negative polarization. The acquisition time should be highly increased in this case in future SR-XPS experiments.

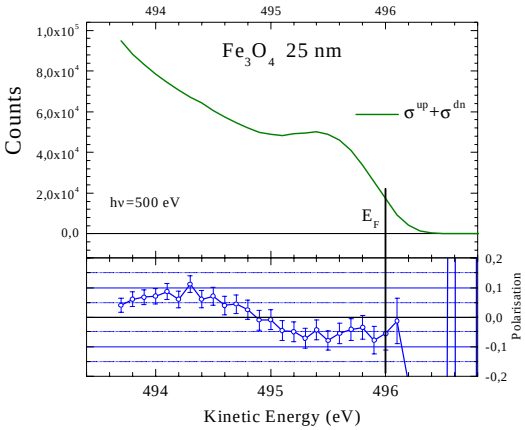

Figure 2.a

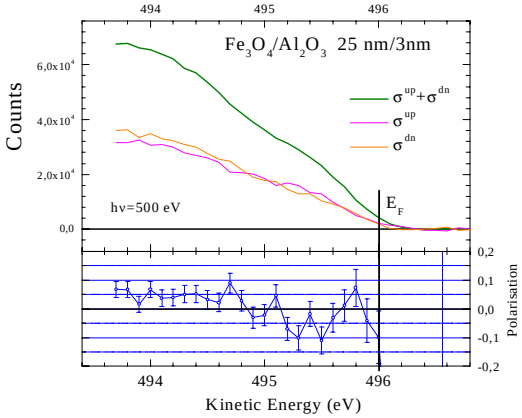

Figure 2.b

In the experimental set-up, a coil applies a magnetic pulse in order to magnetize the samples, but the SR-XPS acquisition takes place with the magnetic field switched off (electron detection). The value of the SP at the Fermi level shown in figures 2.a and 2.b must be corrected by the value of the M_R/M_S ratio. As we explain below in this report, the knowledge of the exact value of this correction is essential.

During the july 2003 experiments, we realised that the pulsed magnetic field applied during the SP measurements is not sufficient to saturate typical Fe_3O_4 layers.

Using a VSM in our laboratory, we made a careful estimation of the pulsed field actually applied in the ID08 XPS endstation. In figure 3, an IRM (Initial Remanence Magnetization) curve of the 25 nm Fe_3O_4 bare layer is shown. It represents the magnetic moment at remanence (H= 0) as a function of the magnetic field applied to the sample before switching off the field. The value of the remanent magnetization of thes samples after the pulse is given by the horizontal line.

This comparison permits us to estimate the pulsed field applied just before SR-XPS measurements at the ESRF to be about 500-600 Oe.

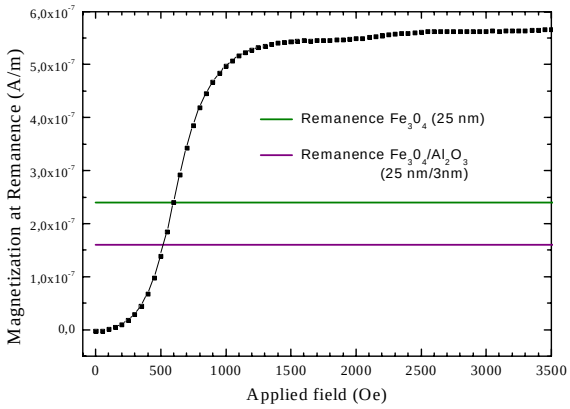

Figure 3

c. XMCD experiments

XMCD experiments have also been performed using the High Field Magnet XMCD endstation at ID08. On the one hand XMCD allowed us to study the local magnetic moment of the Fe cations in our layers. On the other hand, they gave us an additional and independent confirmation of the low value of the magnetic field applied before the SR-XPS experiments.

Figure 4 summarizes our XMCD results.

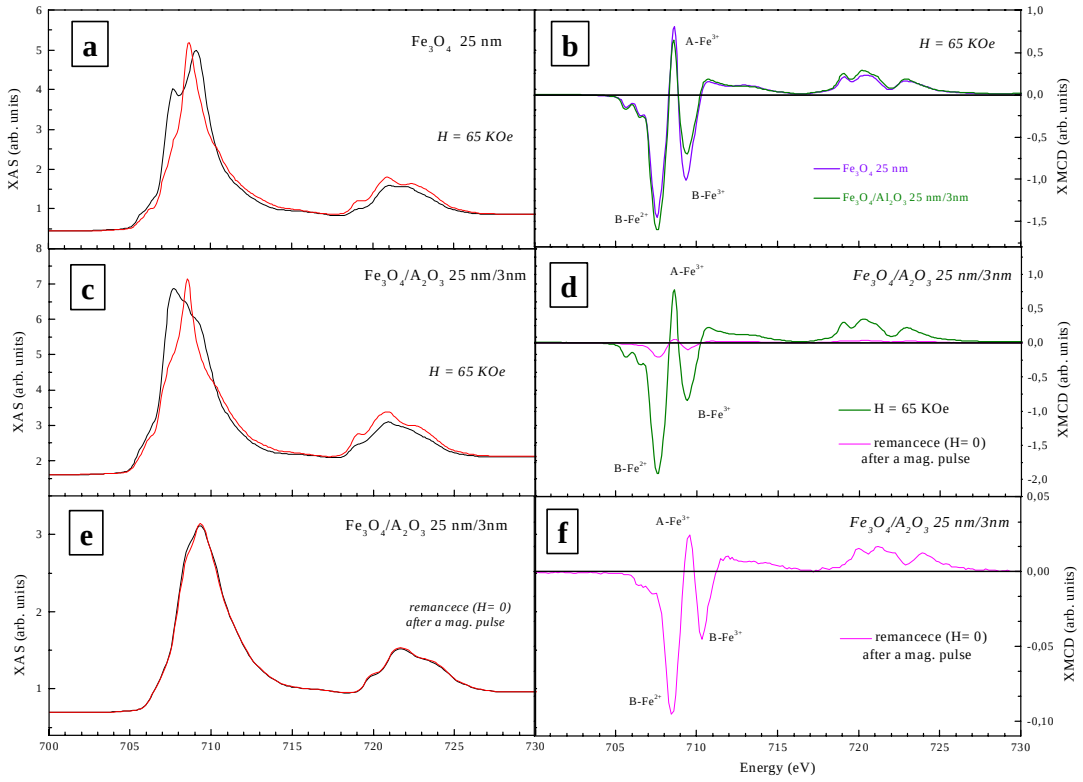

Figure 4

The features of both the XAS and the XMCD of the Fe_3O_4 layer measured with an applied field of 65 kOe (figures 4.a and b) are typical of standard magnetite [4,5], whereas those of the Fe_3O_4/Al_2O_3 interface (figures 4.c and d) are quite different.

A comparison of the normalized XMCD signals (with and without barrier) is shown in figure 4.b. In particular, the ratio between the XMCD negative peaks related to the Fe^{2+} and Fe^{3+} cations in octahedral sites is altered with respect to standard magnetite. Fe 2p-XPS measurements performed in our laboratory with a standard X source (not shown here) are consistent with an increased number of the Fe^{2+} cations at the Fe_3O_4/Al_2O_3 interface.

Figures 4.e and 4.f show the XAS and XMCD spectra recorded for the Fe_3O_4/Al_2O_3 sample in the XPS endstation of ID08 at remanence after the magnetic pulse. XMCD intensity is about 10% of that obtained when applying 65 kOe (see comparison of the normalized spectra in figure 4.d).

In conclusion, the magnitude of the pulse is not sufficient in two ways: the reliability and precision of the final value of the spin polarisation is compromised since the correction due to the M_R/M_S ratio becomes too large. The field is also lower than the value required to close the major hysteresis loop. Hence the subsequent field reversals performed during the

measurement (about 15 per shift) produce a decreasing net magnetization as monitored by XMCD measurements (not shown here). As a consequence the samples were not appropriately magnetized before the SR-XPS measurements. We particularly emphasize this point since knowing remanence exactly is critical for obtaining the accurate spin polarisarion rate.

Conclusions and outlook of this work

The XMCD and VSM results strongly indicate that the magnetic and electronic properties of a Fe_3O_4 layer are affected by the presence of the Al_2O_3 barrier. The measurement of the spin polarization at the Fermi level of the Fe_3O_4/Al_2O_3 interface appears as the key experiment in order to investigate this point. We have demonstrated the possibility to measure the spin polarisation of the occupied states near the Fermi energy through an insulating barrier, an information which is of crucial importance for the understanding and improvement of MTJ devices.

The results reported here are highly encouraging. Nevertheless, accurate SR-XPS experiments at Fe_3O_4/Al_2O_3 will be possible if a number of experimental conditions are improved.

1-The magnetic pulse before the SR-XPS acquisition should be enhanced. We need that the coil supplies at least 1.5-2 kOe in order to saturate magnetite-based samples properly. This action is compulsory to succeed in the future SR-XPS experiments. A new set up is planned by ID08 to solve this problem.

2- SR-XPS measurements have to be recorded with better energy resolution and counting rate. The 100% spin polarization has been predicted by band structure calculations at the Fermi level. The extension in energy of the negative full spin polarization is not given by the calculations. At room temperature, the natural width of the Fermi level is about 40 meV. Using a resolution of 500 meV, we average a rather extended region above the Fermi level. If the spin polarization is lower or if it becomes positive in an energy range inside the energy resolution, the spin polarization measured will be always inferior to that at the Fermi level itself.

[1]Morton et al. Surf. Sci. 513 L457 (2002)

[2]Huang et al J. Magn. Magn. Mater, 239, 261 (2002)

[3] Dedkov et al. Phys. Rev. B 65, 64417 (2002)

[4] P. Kuiper et al., J. Electron. Spectrosc. Relat. Phenom. 86 p. 107 (1997).

[5] L. Stichauer et al. JAP 90, p. 2511 (2001).