Polarized neutron reflectivity study of NiFe$_2$O$_4$ films with very large saturation magnetization

F. Rigato, X. Martí, J. Fontcuberta
Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB s/n, 08193 Bellaterra, Spain
E-mail: rigatofr@yahoo.it

Abstract. Epitaxial (001)-oriented NiFe$_2$O$_4$ films have been grown by RF magnetron sputtering on (001)MgAl$_2$O$_4$ substrates. In agreement with previous reports, magnetization loops of the thinner films reveal a saturation magnetization up to 3 times larger than the thicker films, which display values in agreement with the bulk. Here we discuss polarized neutron reflectivity experiments which are able to disregard that the magnetization overshoot is caused at the early stages of the growth.

1. Introduction

Spinel ferrites (AB$_2$O$_4$, B = Fe) are ferrimagnetic compounds intensively studied nowadays due to their potential use in spintronics. They have been studied both as insulating barriers [1] or as conducting magnetic electrodes [2] in magnetic tunnel junctions (MTJ), and spin filtering effects have been demonstrated for tunnelling barriers [1, 3, 4]. Combined in nanocomposites with ferroelectric perovskites, they also showed the possibility of controlling the room temperature magnetization by the application of electrical field, which exploitation is of major interest [5, 6]. From a more fundamental perspective, spinel thin films still raise one long standing question: why the magnetization of ultrathin films (t < 10 nm) can be up to 3 times larger than in the thicker films or the bulk samples [7, 8]. It turns out that most approaches to exploit spinel thin films in MTJ heterostructures will require films with thicknesses below 10 nm, which is just the thickness range where magnetization enhancing has been repeatedly observed. Understanding of this anomalous behaviour calls for more studies in this subject.

The magnetization of ferrites arises from the unbalance of the magnetic moments at antiferromagnetically coupled A (tetrahedral) and B (octahedral) sites of the spinel unit cell. In thin films, the presence of antiphase boundaries [9] seems to be predominant in reducing the saturation magnetization, and their relevance increases with the film thickness. On the other hand, as the magnetization is sensitive to the cation occupancies at A and B sites, anomalous magnetization, compared to equilibrium one, can be obtained both in bulk materials and thin films provided that cation distribution is somehow quenched in a form distinct from the equilibrium distribution. Indeed it has been proposed that this could be the origin of the exceedingly large magnetization reported in NiFe$_2$O$_4$ and CoFe$_2$O$_4$ thin films [8, 10, 11]. Cationic disorder could be produced by the out-of-equilibrium conditions associated with thin film growth and likely to be more important in thinner films as the growing time is typically shorter. Enhanced magnetization may also arise from the symmetry breaking at film surface or, most generally at any surface, as it is documented in antiferromagnetic systems [12]. In both cases, free surfaces may display magnetic properties distinct
than deep into the film. Last, enhanced magnetization could also originate by some sort of chemical interdiffusion of film/substrate species leading to a further enhancement of the unbalancing between magnetization of A and B sublattices. Indeed it had been proposed, at least in the case of MgO substrates, that interdiffusion may occur [7].

We recall that, in order to be able to account for the observed dependence of the saturation magnetization with thickness in NiFe$_2$O$_4$ and CoFe$_2$O$_4$, surface effects are expected to be relevant as in thick films the enhanced magnetization is gradually washed out. In early works [10], we have analyzed thin films grown on several substrates, displaying different strain and surface roughness; we have shown that the same trend is always observed thus disregarding the epitaxial strain and surface roughness as major causes of the additional magnetic moment. Therefore it is of relevance to explore the magnetization profile of ferrite thin films aiming to elucidate the eventual presence of distinctive magnetic characteristics at surface and deep into the film.

Here we report on the use of polarized neutron reflectivity (PNR) [13], a technique particularly sensitive to the magnetization depth profile along the direction perpendicular to the sample surface, in contrast to the similar X-ray reflectivity (XRR). We present here the PNR study of (001)NiFe$_2$O$_4$ films grown on (001)MgAl$_2$O$_4$ substrate and we compare the collected patterns to several models where the excess of magnetic moment has been located at different parts of the sample. We conclude that the magnetic-rich layer cannot be located at the substrate/film interface thus disregarding the possibility of non-equilibrium A/B cationic distribution or interdifussion between the film and the substrate at the interface.

2. Experimental details
Thin films discussed here, with thickness $t$ of 6 and 10 nm, were grown by radio frequency magnetron sputtering using a stoichiometric NiFe$_2$O$_4$ (NFO) target. MgAl$_2$O$_4$ (MAO) substrates, (001)-oriented, were placed at 6 cm from the magnetron. The growth was performed at a total pressure of 250 mTorr in a mixed atmosphere of argon and oxygen, in ratio 10:1. The substrate temperature during deposition was kept at 600 ºC. The samples thickness was determined by regulating the deposition time, through a calibration of the growth rate ($0.28$ nm/min) constructed by measuring with XRR the thickness of analogous films with $t > 15$ nm. PNR experiments were performed at CRISP instrument at ISIS spallation neutron source [14]. PNR curves simulations were performed using POLLY software [15].

Samples’ structure was investigated by X-ray diffraction (XRD); magnetization data were collected using a superconducting quantum interference device (SQUID).

3. Results and discussion
XRD characterization revealed that the NFO films grown in this work are (001) textured and epitaxial on the MAO substrate. The reciprocal space map around the (206) NFO and MAO reflections for a typical sample (10 nm thick) is shown in Fig. 1a. The MAO(206) reflection is located just below the substrate maximum ($Q_x \sim 0.2460$ Å$^{-1}$) corresponding to a fully strained film and extends along a constant $Q_z \sim 0.7150$ Å$^{-1}$ up to $Q_x \sim Q_z/3 \sim 0.2380$ Å$^{-1}$ corresponding to a totally relaxed material. Although it may seem that strain may play a role in the first layers, in an early work [10] we have observed that fully relaxed thin films on STO substrates of similar thickness displayed the very same magnetization overshoot and hence we did not put the heading of this paper on an eventual strain-induced magnetization. Further details on identically prepared samples are available elsewhere [10].

Magnetization loops of two samples (6 and 10 nm thick) obtained at 10 K with the magnetic field applied along the [100] direction of the (001)MAO substrate are shown in Fig. 1b. The same linear diamagnetic contribution by the MAO substrate ($\chi_d = -1.09 \times 10^{-6}$ emu·Oe$^{-1}$·cm$^{-3}$), measured separately, has been removed in both cases from the rough data. The loops show a saturation magnetization well above the bulk expected value (signaled by a horizontal arrow), slightly larger for the thinnest sample in agreement with previous reports on similar ferrites [8, 10]. Importantly, the magnetization loops of the bare substrates do not show any measurable ferromagnetic contribution (see data in Inset of Fig 1b).
We now turn to the discussion on the preparation of the PNR experiment carried out in the mentioned samples. We first present PNR simulations corresponding to NFO samples, 10 nm thick, with three different distributions of magnetization along the depth of the film are considered. First, in Fig. 2(a) we shown two curves \( R^+ \) and \( R^- \) corresponding to the neutron reflectivity of a NFO film where an homogeneous distribution of magnetic moment (sketched in inset of Fig. 2 (a)) and using polarized neutrons with magnetic moments pointing in opposite directions perpendicular to the beam axis and parallel to the sample surface. The splitting of both curves stems from the presence of net magnetic moment in the material [13]. Their difference, better evidenced in the so-called spin asymmetry \( SA = (R^+ - R^-)/(R^+ + R^-) \), is shown also in inset of Fig. 2(a): the spin asymmetry is determined by the profile of the net magnetic moment along the sample depth, while the structural contributions are almost cancelled. The situations that we want to explore in detail in this manuscript does not correspond to the described homogeneous distribution of Fig. 2(a), but to a possible excess of magnetization confined either to the topmost region of thickness \( \Delta T \) (Top-rich model) or to a bottom layer of thickness \( \Delta B \) (Interface-rich model). Therefore we have also simulated the expected SA for these situations, considering several values of \( \Delta T \) and \( \Delta B \) in a range between 1 and 4 unit cells. Exemplary simulations of expected results for both models are presented in Fig. 2(b) (\( \Delta T = 2 \) u.c., \( \Delta B = 0 \) u.c.) and Fig. 2(c) (\( \Delta T = 0 \) u.c., \( \Delta B = 2 \) u.c.), respectively. Insets in Figs 2(b,c) sketch the profiles of magnetization in each case. Starting from a model of homogenous magnetization along the film thickness, the simulations were constructed by fixing two limiting conditions: (i) the total magnetic moment \( m \) of the film had to correspond to the value previously measured by SQUID at 3.5 kOe, the maximum field available in the PNR beamline, and 300 K, and (ii) the eventual regions with large magnetization are assumed to have a magnetization 4 times larger than the magnetization of the remaining part of the coating. This second condition arises because, within the picture of spinel inversion as source of the enhanced magnetization, the maximal magnetization of a normal NiFe\(_2\)O\(_4\)
spinel, having all Fe$^{3+}$ ions at B sites, would be four times larger (8 $\mu_B$) than that of a fully inverse structure with Fe$^{3+}$ equally populating A and B sites (2 $\mu_B$) per unit formula [10]. Resulting simulations are displayed in Fig. 2(b) and (c) respectively. In Fig 2(c) one first notice that a clear decay of SA parameter at larger Q values is expected, whereas the corresponding data in Fig. 2(b) displays a rather constant value even at larger Q. Therefore, an evident difference of SA should be observed experimentally in these two limiting cases. Notice that the SA curves cross the 0 value at very different Q’s: while the top-excess curve ($\Delta t_T = 2$ u.c., $\Delta t_B = 0$ u.c.) barely crosses it in the simulated range, the interface-excess ($\Delta t_T = 0$ u.c., $\Delta t_B = 2$ u.c.) model clearly predicts a change of sign of SA. In short, in the first case the $R^+$ and $R^-$ curves cross at much higher Q values than in the second.

Now we describe the PNR experimental results. As measurements were performed at relatively small magnetic field ($H_0 = 3.5$ kOe), in order to ensure the maximum magnetization possible of the NFO films and thus the largest possible contrast between $R^+$ and $R^-$ curves, the films were ex-situ saturated in a magnetic field of 50 kOe applied parallel to the films surface and transferred to the sample holder in the neutron beamline. During the experiment, the maximum magnetic field available in the beamline was applied also in-plane and along the same direction used in the magnetic preparation of the samples. The PNR curves collected for the 10 nm and 6 nm thick samples are presented in Fig. 3. Data show that in both cases, the $R^+$ and $R^-$ curves barely overlap in the analyzed
Q-range and accordingly, the SA does not vanish. Indeed, as best seen in the insets of Fig. 3, the experimental SA for the $t = 6$ nm film clearly departs from zero whereas for the $t = 10$ nm SA only approaches zero gradually at large Q values. According the results of the modeling described above, that would indicate that the bottom-rich model cannot describe the data, as in this model SA should vanish within the explored Q range.

The solid lines through the SA data in Figs. 3(a,b) are the results of the best fits obtained assuming the distinct magnetization profiles describe above, that is: a homogenous (1), 2 u.c. Top-rich (2) or 2 u.c. Interface-rich model (3) respectively. While simulations for $\Delta T_I$ or $\Delta T_B \leq 2$ u.c. lead to comparable results, both top and interface rich models considering thicker regions (not shown) result clearly inconsistent with the experimental data. Comparison of best fits with experimental data also points out that the Top-rich magnetization profile describes the data with much more accuracy. Detailed inspection of the homogeneous and Top rich models and the corresponding fits (lines (1) and (2)) in Figs. 3 shows that a clear distinction between these two situations cannot be achieved with the experimental sensitivity.

It thus follows that from the current set of data the possibility of a homogeneously distributed magnetic moment cannot be discriminated from the top-excess scenario. However, the PNR experiment presented here allows ruling out the possibility of an interface-excess scenario that could
be produced by an eventual interdiffusion of atoms at the interface or alternatively by a localized cationic only partial A/B (Ni/Fe) inversion.

Finally, we would like to point out that recently the origin of a giant magnetic moment in magnetite thin films has been also addressed by complementary magnetic techniques, including PNR. It was concluded from these studies that the excess magnetization is related to impurities (Fe) in the used MgO substrates [16]. Our results can not be interpreted in the same way as our substrates, which are MgAl$_2$O$_4$, do not reveal traces of any ferromagnetic impurity but a conventional diamagnetic behaviors as indicated above.

4. Conclusions
In summary, we have prepared (001)NFO//(001)MAO films to study the larger saturation magnetization reported for very thin films ($t$ approximately below 10 nm). After a standard X-ray diffraction and magnetic characterization the films were analyzed using the PNR technique. Experiments pretended to discriminate among two different scenarios where the excess of magnetization is confined at the topmost surface or at the film/substrate interface. Data revealed that the excess of magnetization, if it is not homogenous, must be located in the topmost surface of the films thus ruling out the possibility of interface, substrate-related, effects.

5. Acknowledgements
Support by the Spanish Government [Projects MAT2008-06761-C03 and NANOSELECT CSD2007-00041] and Generalitat de Catalunya (2009 SGR 00376) are acknowledged.

References
[1] Ramos A V, Guittet M J, Moussy J B, Mattana R, Deranlot C, Petroff F and Gatel C 2007 Appl. Phys. Lett. 91 12210
[2] Lüders U, Barthélémy A, Bipes M, Bouzehouane K, Fusil S, Jacquet E, Contour J P, Bobo J F, Fontcuberta J and Fert A. 2006 Adv. Mater. 18 1733
[3] Chen Y F and Ziese M 2007 Phys. Rev. B 76 014426
[4] Takahashi Y K., Kasai S, Furubayashi T, Mitani S, Inomata K, and Hono K 2010 Appl. Phys. Lett. 96 072512
[5] Zheng H, Wang J, Lofland S E, Ma Z, Mohaddes-Ardabili L, Zhao T, Salamanca-Riba L, Shinde S R, Ogale S B, Bai F, Viehland D, Jia Y, Schlom D G, Wuttig M, Roytburd A and Ramesh R, 2004 Science 303, 661
[6] Dix N, Muralidharan R, Guyonnet J, Warot-Fonrose B, Varela M, Paruch P, Sánchez F and Fontcuberta J 2009 Appl. Phys. Lett. 95 062907
[7] Venzke S, van Dover R B, Phillips J M, Gyorgy E M, Siegrist T, Chen C H, Werder D, Fleming R M, Felder R J, Coleman E and Opila J 1996 J. Mat. Res. 11 1187
[8] Lüders U, Bipes M, Bobo J F, Cantoni M, Bertacco R and Fontcuberta J, Phys. Rev. B 2005 71 134419
[9] Margulies D T, Parker F T, Spada F E, Goldman R S, Li J, Sinclair R and Berkowitz A E 1996 Phys. Rev. B 53 149175
[10] Rigato F, Estradé S, Arbiol J, Peiró F, Lüders U, Martí X, Sánchez F and Fontcuberta J 2007 Mater. Sci. Eng. B 144 43
[11] Rigato F, Geshev J, Skumryev V and Fontcuberta J 2009 J. Appl. Phys. 106 113924
[12] Kodama R H, Makhlof S H and Berkowitz A E 1997 Phys. Rev. Lett. 79 1393
[13] Ott F. 2007 C. R. Physique 8 763
[14] http://www.isis.stfc.ac.uk/instruments/crisp/
[15] Blundell S J and Bland J A C 1993 J. Mag. Mag. Mater. 121 185
[16] Orna J, Algarabel P A, Morellón L, Pardo J A, de Teresa J M, López Antón R, Bartolomé F, García L M, Bartolomé J, Cezar J C and Wildes A 2010 Phys. Rev. B 81 144420