Giant magnetic moment in epitaxial Fe_3O_4 thin films on MgO(100)

S. K. Arora,[1,*] Han-Chun Wu,[1] R. J. Choudhary,[1,†] I. V. Shvets,[1] O. N. Mryasov,[2] Hongzhi Yao,[3] and W. Y. Ching[3]
[1]*Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), School of Physics, Trinity College Dublin, Dublin 2, Ireland*
[2]*Seagate Research Center, Seagate Technology, 1251, Waterfront Place, Pittsburgh, Pennsylvania 15222, USA*
[3]*Department of Physics, University of Missouri-Kansas City, Kansas City, Missouri 64110, USA*
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Magnetization studies on well characterized epitaxial magnetite (Fe_3O_4) thin films grown on MgO(100) show that the ultrathin films (<5 nm thickness) are ferromagnetic and their magnetic moments are much greater than those of bulk magnetite, particularly at a thickness of 20 nm or below. The observation of a ferromagnetic nature in ultrathin magnetite films (<5 nm) is in contrast to the previously accepted dead layer interface model or a superparamagnetic behavior for ultrathin films of magnetite. From detailed spin-polarized density functional theory based calculations of Fe_3O_4-MgO interface, we calculate a deviation in spin moment of the Fe atoms in the vicinity of the interface from their bulk values, which is insufficient to explain the observed results. Orbital moment contribution for the surface Fe atoms was found to be quite small. The noncompensation of spin moments between the tetrahedral (*A*) and octahedral (*B*) sublattices at the surface and antiphase-domain boundaries are inferred to be the main factor contributing to the observed enhanced magnetic moment.

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Magnetite Fe_3O_4 is one of the most important transition metal oxides and is being actively investigated due to its half metallic ferromagnetic nature, high Curie temperature (858 K), and the presence of a metal-insulator transition at 120 K (Verwey transition).[1–4] These properties make Fe_3O_4 a potential candidate for spin electronic devices such as spin valves or spin tunnel junctions and microwave resonant circuits. It has a cubic inverse spinel structure, where Fe^{3+} ions occupy tetrahedral sites (*A* sites), whereas octahedral sites (*B* sites) are occupied by both Fe^{3+} and Fe^{2+} ions. The spin of Fe^{3+} ions at octahedral and tetrahedral sites are aligned antiparallel to each other leading to a net magnetic moment of $4\mu_B$/f.u. Transport and magnetic properties of epitaxial magnetite films have been investigated in detail.[5–13] Epitaxial Fe_3O_4 films grown on MgO substrate are reported to contain antiphase boundaries (APBs).[5–7,9] The presence of APBs leads to unusual magnetic properties of epitaxial Fe_3O_4 films, such as nonsaturation of magnetization in high magnetic fields[5] and superparamagnetic behavior[10] for ultrathin (<5 nm) epitaxial magnetite films. From these studies, it is evident that the magnetic property of magnetite thin film depends on the method of preparation nature of defects and their density.[5–12]

The effect of intrinsic defects on the magnetic properties of ultrathin films of Fe_3O_4 is still a controversial topic. In a previous report, Zhou *et al.*[14] found that ultrathin Fe_3O_4 films are ferromagnetic but their magnetization is reduced in comparison with the bulk values. They reported a magnetically inactive and/or dead layer of about 0.42 nm. In these investigations, no emphasis was given to the surface and interface magnetism, which is expected to strongly influence the magnetic properties. In fact, the theoretical predictions on (001) Fe_3O_4 surface using first principles calculations suggest either an increase or decrease in the magnetic moment of the surface layer, which strongly depends on the surface reconstruction.[15] It prompted us to carefully look at the magnetic response of the films at smaller thicknesses. In this paper, we report a systematic study of the magnetic properties of well characterized Fe_3O_4 films (2–55 nm).

Thin films of Fe_3O_4 were grown on (001) oriented MgO single crystal substrates by using an oxygen plasma assisted molecular beam epitaxy (MBE) (DCA MBE M600, Finland) with a base pressure of 5×10^{-10} Torr. Details of the growth procedure are given elsewhere.[16] The MgO substrates used in the present investigations were those having a rms roughness of 0.2–0.4 nm over a 5×5 μm^2 area, as determined using an atomic force microscope. The single phase structural and epitaxial nature of the Fe_3O_4 films was characterized by using a multicrystal high-resolution x-ray diffractometer (Bede-D1, Bede, U.K.).[17] X-ray reflectivity (XRR) investigations in these films revealed a small interface roughness (0.3–0.5 nm) between the Fe_3O_4-MgO interface.

The magnetic properties of the films were examined by using a vibrating sample magnetometer (Quantum Design-14T Physical Property Measurements System) with a sensitivity of 5×10^{-7} emu. The magnetization versus field (*M-H*) loops were measured by applying the magnetic field in the film plane along the ⟨001⟩ direction. In order to subtract the diamagnetic contribution from the measured data and rule out possibility of any additional contribution from the magnetic impurities within the substrate, *M-H* loops from the piece of substrate used for each film were subtracted from the corresponding *M-H* loop of the film. Uncertainty in the film volume determination is ~2% as the film thickness was determined from *in situ* reflection high energy electron diffraction and *ex situ* XRR. The uncertainty in measuring the absolute value of magnetization for the films is about 3%.

Figure 1 shows the representative magnetic hysteresis loops (HLs) of Fe_3O_4 films (5 and 20 nm thicknesses) and of a (100) oriented single crystal slice of Fe_3O_4 measured at 300 K with an applied in-plane magnetic field. Low field HLs of 5 and 20 nm films are also shown in the inset of Fig. 1. From the data, we find that the magnetic moment of the

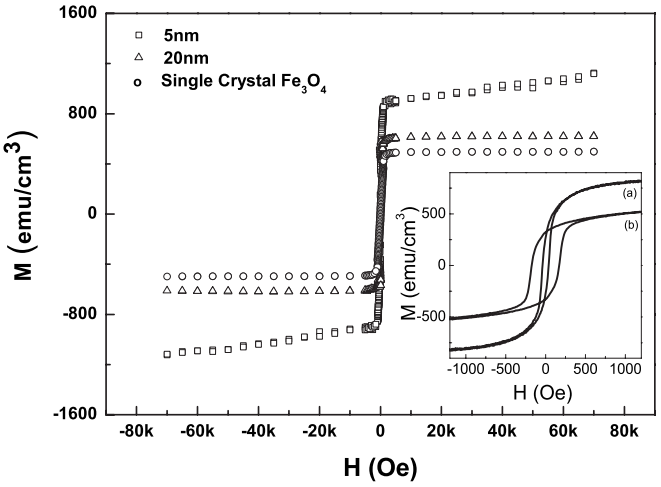

FIG. 1. Magnetization HLs of 5 and 20 nm Fe_3O_4 films measured at 300 K with an in-plane magnetic field applied along the ⟨001⟩ direction. Magnetization values are normalized to the volume of Fe_3O_4. The magnetization hysteresis loop of a slice of Fe_3O_4 single crystal measured at 300 K, which is also shown for comparison. The inset shows the low field HL for (a) 5 and (b) 20 nm films measured at 300 K.

Fe_3O_4 single crystal is 498 emu/cm^3 at 10 kOe field. This value is in good agreement with earlier studies. The 20 nm Fe_3O_4 films show a saturation behavior with a moderate magnetic field (>8 kOe). For the 5 nm film, magnetization exhibited a finite slope with magnetic field. The magnetic moment values for the 5 and 20 nm Fe_3O_4 films are found to be 922 and 613 emu/cm^3, respectively. The coercivity (H_c) values for the same films are 30 and 172 Oe, respectively. For film thickness greater than 20 nm, we find that the magnetic moment values are quite close to the values for bulk Fe_3O_4 (509 emu/cm^3 for the 55 nm film). For the 5 nm film, the magnetic moment value (922 emu/cm^3 or 7.7 μ_B/f.u.) at 10 kOe field strength is significantly larger than the bulk magnetic moment value of 4 μ_B/f.u. This behavior was repeatedly observed for the films of small thickness (2–20 nm). All of the films down to 2 nm thickness exhibit a ferromagnetic behavior. However, for a 2 nm film, we find a reduced moment (955 emu/cm^3) in comparison with a 3 nm film (1000 emu/cm^3). As will be explained in detail later, the noncompensation of spin moments between the *A*- and *B*-type Fe-O planes is one of the major factors for the observed enhancement of magnetization in Fe_3O_4 thin films. A small reduction in the magnetic moment of the 2 nm sample, as compared to the 3 nm sample, is possibly related to the partial noncompensation. The 2 nm thickness corresponds to 9.5 magnetic unit cells (one magnetic unit cell corresponds to a 0.21 nm thickness consisting of one *A*- and one *B*-type Fe-O plane) representing a completely noncompensated scenario. However, small uncertainty in the film thickness (of the order of 0.04 nm in our case) can lead to a partial noncompensation and a reduced magnetic moment. It should also be mentioned that the results presented here are not from a single point measurement (for each thickness, two or more samples were checked). The scatter in the magnetization values (10 kOe) was within 3%–7% for $t<10$ nm and less than 4% for $t\geq 20$ nm. Observation of a substantial (giant) increase in the magnetic moment of Fe_3O_4 films is in stark contrast to the earlier notion of a reduction in magnetic moment, which relies on the magnetic frustration caused by the APBs.[5,9,11] This is a curious observation in the sense that much of the earlier published work related to ultrathin magnetite films suggested either the formation of a magnetically dead layer or the presence of superparamagnetism.[10,11,14] In these earlier investigations, reduction in the moment was ascribed to the frustrated exchange at the APBs. The absence of an interfacial magnetically dead layer in the current set of films as opposed to the one reported in an earlier study[14] is due to the difference in the surface roughness of the two sets of samples. Substrates having a rms roughness of ≤0.4 nm over a 5×5 μm^2 area were used for this study. Fe_3O_4 films deposited on substrates with greater roughness showed a reduced magnetic moment, which is likely to be related to the influence of roughness on interface properties and increased density of APBs in the films.

Temperature dependence studies of HL on these samples (not shown) demonstrated that the coercivity H_c of all the films increases with a decrease in temperature, in particular, across the Verwey transition. For example, H_c of a 5 nm thick Fe_3O_4 film increases from 30 Oe at 300 K to 220 Oe at 100 K. Although the H_c of the films of <5 nm thickness is small at 300 K, their remanence moment (M_R) is significant (40%–48%). Similar values of M_R are obtained at lower temperatures. The small H_c of the magnetite films observed for thin films (2–5 nm) at 300 K is representative of a weak pinning of the magnetic domains. The sharp change in H_c across the Verwey transition temperature (T_V) has been related to the changes in magnetic properties associated with the structural phase transition.[18]

In addition to the above for ultrathin films, one needs to consider the effect of surface and interface magnetism on magnetic properties. We model our Fe_3O_4 films as consisting of a bulklike Fe_3O_4 layer with a bulk saturation magnetization M_s and interface plus surface contribution of moment M_i at the Fe_3O_4-MgO and Fe_3O_4-air interfaces. The magnetization M is given by

$$M = M_s + \frac{M_i}{t}. \tag{1}$$

Figure 2 shows the thickness (t) dependence of M(10 kOe) multiplied by the Fe_3O_4 film thickness. In the inset, M(10 kOe) values as a function of film thickness for $t<20$ nm are shown. The solid line is a straight line fit to the data according to Eq. (1). The slope of the fit is 482 emu/cm^3, which within experimental errors agrees with the value of magnetic moment of bulk Fe_3O_4 (480 emu/cm^3). The positive intercept on the y axis (1475 nm emu/cm^3) is the magnetic contribution to the film arising from the surface and/or interface. Our data suggest that the earlier proposition of a dead layer model for the Fe_3O_4-MgO interface was an oversimplification.[14] The inverse thickness dependence of effective magnetization (M) given by the model [Eq. (1)] to separate out distinct bulk M_s and interface M_i contributions is questionable, in particular, for the case of Fe_3O_4 films on MgO(100). Apart from the

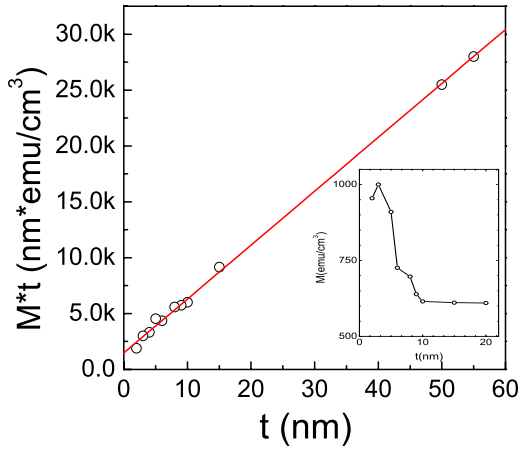

FIG. 2. (Color online) Magnetization (10 kOe) multiplied by the Fe_3O_4 film thickness as a function of film thickness. The solid line represents a straight line fit to the data. The linear regression fits well to the data (*chi-square* parameter being 0.9992). The magnetization (300 K, 10 kOe) values as a function of film thickness in the low thickness regime are shown in the inset.

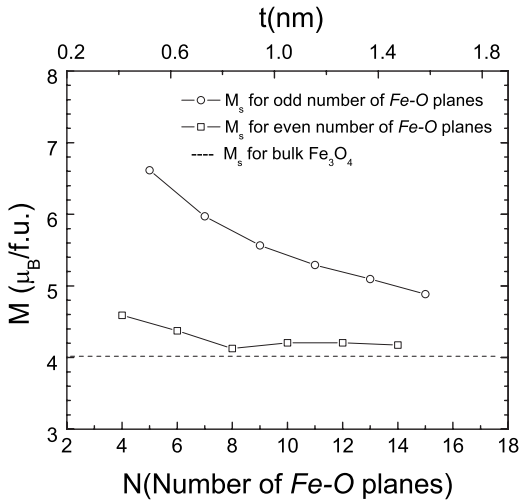

FIG. 3. Layer-resolved saturation magnetization as function of layer number for a 50 Fe-O layer thick Fe_3O_4 slab estimated by using a spin-polarized DFT calculation. The circle and square symbols represent the cases of noncompensated (odd number of Fe-O planes) and compensated (even number of Fe-O planes) structures, respectively. The horizontal dashed line shows the magnetic moment value for a Fe_3O_4 magnetic f.u. The separation between adjacent *A*- and *B*-type Fe-O planes is 0.105 nm.

interface and surface-related contribution for ultrathin films, an additional thickness dependent magnetization contribution could result from a totally different origin, i.e., from the thickness dependence of the antiphase-domain size. It prompts us to carefully look at the complex layered structure of Fe_3O_4. In the layered structure of Fe_3O_4, for the completion of a magnetic unit cell (f.u.), the formation of a complete pair of atomic sublayers is vital. For example, if we consider that the Fe_3O_4 growth on MgO starts either with the *A*- or *B*-plane atomic layer, then for the completion of the magnetic unit cell, a subsequent deposition of *B* and *A* layers is needed. If the growth is terminated at an atomic plane which does not lead to the completion of a magnetic f.u. of the Fe_3O_4, one expects an increase in the magnetic moment due to the noncancelation of the magnetic moments between *A*- and *B*-site Fe^{3+} ions. We will call this mechanism a noncompensation effect.

In order to gain additional insights into noncompensation vs surface/interface contributions, we carried out spin-polarized density functional theoretical calculations for a series of Fe_3O_4 slabs and Fe_3O_4-MgO(001) interfaces based on *A*- or *B*-layer nucleation and their relative positions on the MgO(001) surface. All calculations were performed by using the VASP code with the projector augmented plane wave method using generalized gradient approximation.[19] From the calculations for the Fe_3O_4-MgO interface, we infer that the interface of Fe_3O_4 with *B*-site nucleation is energetically most stable. The magnetic moments of Fe atoms in the Fe-O layers in the vicinity of the Fe_3O_4-MgO interface are comparable to that obtained for bulk Fe_3O_4 from a similar calculation. However, an increase in polarization of some of the oxygen atoms (as large as 0.36 μ_B) in the vicinity of interface was noted. In these calculations, an even number of Fe-O layers were used in the slab. These calculations suggest that the spin moment contribution from the Fe_3O_4-MgO interface is not enough to explain our observation of the large magnetic moment.

We further consider the effect of noncompensation on the spin moment of magnetite. A supercell model with Fe_3O_4 slab thickness equivalent to 50 Fe-O planes was used to estimate the influence of noncompensation on the magnetic moment. The magnetic moment for an even number of Fe-O planes corresponds to complete compensation while for an odd number of Fe-O planes correspond to the simplest model of noncompensation. The Fe_3O_4 slab is surrounded by a 10 Å thick vacuum layer on either sides of the slab. The calculated layer-resolved spin moments per f.u. calculated for a Fe_3O_4 slab are shown in Fig. 3. It is clear that the noncompensation of spin moments due to an odd number of layers will enhance the magnetic moment for the surface layers and will vanish for larger thickness samples. We find that the spin moment per f.u. is substantially larger due to the noncompensated surface layer: being 6.6 μ_B/f.u. for the 5th Fe-O layer and 5 μ_B/f.u. for 15th Fe-O layer. The value of spin moments rapidly decreases for a thicker slab. For the 50th Fe-O layer, we find that the spin moments are comparable to the value of bulk Fe_3O_4, i.e., ~4 μ_B/f.u. For an even number of layers or fully compensated Fe_3O_4 slabs, magnetic moment per f.u. is only slightly larger than the bulk value 4 μ_B/f.u., indicating that surface effects due to reduced coordination are marginal or much smaller than miscompensation in this case. From these results, we infer that the noncompensation is the main factor for moment enhancement for thin Fe_3O_4 films. The orbital moment contribution (<1% of spin moment) was found to be quite small, as noted in our calculation and in other calculations.[15,20,21] The uncompensated spin and extra charge associated with the surface might lead to a much more profound change in the magnetic moment of the entire film. It may affect the antiferromagnetic exchange (J_{AB}) between the *A* and *B* layers underneath the surface, i.e., intersublattice exchange interaction.

A similar argument of noncompensation applies to the antiphase domains (APDs), provided that it is possible to overcome the antiferromagnetic exchange across the boundary[22] and the domain's lateral size is a noninteger multiple of the magnetic f.u. length, which is 0.21 nm along (010) and (001) directions, respectively. In a recent study, using off-axis electron holography measurements on a 25 nm thick magnetite film, Kasama *et al.*[22] showed that it is possible to overcome the antiferromagnetic coupling in the films for a majority of APB configurations with the application of a moderate magnetic field. Their study suggests that the linear increase in magnetic moment at moderate fields was not only related to the reduction in domain wall width but also to the disappearance of AFM coupling across APBs. In the above scenario, if we consider the noncompensation effect related to the APDs, then depending on the density of APBs, there will be a concomitant enhancement in the total magnetic moment. For example, for a square domain with size of 5×5 nm^2, we estimate that the domain's volume magnetization is enhanced by 16%. This may be an underestimate due to the fact that the modification in J_{AB} may not be limited to the layers in the vicinity of the boundary. This effect inversely scales with the domain area and will be significant for smaller domains rather than for the larger ones, which means that it will be more significant for the thinner films.

Further possibilities of any unreacted Fe and nonstoichiometry (cation or anion vacancies) are ruled out due to the fact that the volume of the magnetite unit cell in our films remains constant, as evident from our high-resolution x-ray diffraction and transmission electron microscopy (TEM) studies.[17] The presence of the Verwey transition was used as an additional evidence of support that the films are stoichiometric, where T_v is extremely sensitive to stoichiometry.[23] Remarkably, Verwey transition is visible down to a thickness of 2 nm, pointing to a very high quality of the Fe_3O_4 films (Fig. 4). Reduction in T_v with decreasing film thickness could suggest a small deviation from the perfect stoichiometry,[24] which may contribute to enhancement in the magnetic moment of the films. However, the reduction in T_v of thin films does not necessarily indicates deviation from perfect stoichiometry. Thin films of Fe_3O_4 are known to exhibit suppressed Verwey transition that could originate from a variety of other reasons, e.g., strain or antiphase boundaries.[8,12] Even if finite amounts of cation and anion vacancies are present in our films, their densities are not enough to explain the observed changes in magnetic moment for small thickness films. From the work of Shepherd *et al.*[24] we can estimate that if the entire reduction in T_v from 123 to 85 K (Fig. 4) could be accounted for by the deviations from the perfect stoichiometry ($Fe_{3(1-\delta)}O_4$, where δ is 0 for perfect stoichiometric magnetite), this would mean that δ is only 0.0108. This would then result in a change in the magnetic moment by 1.1%. The small value of change in the magnetic moment suggests that possible changes in the stoichiometry should be discarded as an explanation for the observed effect.

The possibility of Mg in-diffusion in Fe_3O_4 films[25] is also ruled out due to the low growth temperature and tendency of Mg^{+2} ion to substitute at B sites that will reduce the magnetic moment rather than enhancing it. This has been confirmed

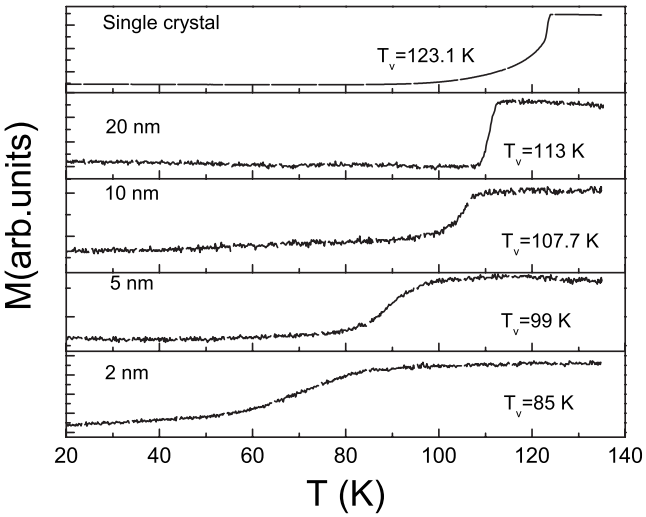

FIG. 4. Magnetization as a function of temperature for various thickness Fe_3O_4 films measured during the warming cycle in the presence of a 200 Oe field. Data for the single crystal magnetite sample are also shown for comparison. The samples were zero field cooled to 10 K prior to the M-T measurements.

through high-resolution TEM[17] and Auger electron spectroscopy (AES) depth profiles. Figure 5(a) shows an Auger electron spectrum taken *ex situ* for an as-deposited 3 nm Fe_3O_4 film at 300 K. The AES was performed in a separate chamber as the MBE growth chamber was not equipped with this facility. The carbon peak is seen in Fig. 5(a), as expected for any surface brought into the Auger chamber from the ambient. The curves in Figs. 5(b) and 5(c) show the spectra for the same film that has been subjected to Ar-ion bombardment so that the film left on the substrate is 1.5 and 0.8 nm thick, respectively. In the as-deposited and Ar-ion etched film (1.5 nm thick), the presence of Mg is not detected. A Mg peak is only barely seen when the films are etched further ($t<1$ nm). At this thickness, the sampling depth for AES be-

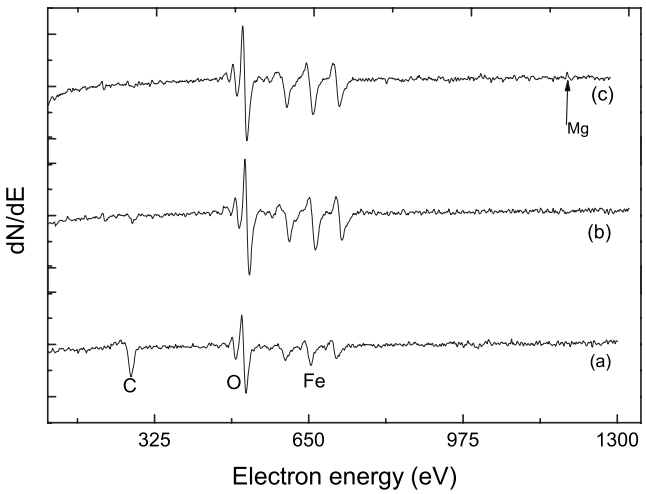

FIG. 5. Auger electron spectra of a 3 nm Fe_3O_4 film taken at 300 K for (a) as deposited, (b) after Ar-ion etching with the remaining film thickness of 1.5 nm, and (c) after second etching with remaining thickness of 0.8 nm.

comes comparable to the film thickness and we do expect to see a signal corresponding to Mg in the substrate. In addition to this, we would also like to point out that the MgO-Fe_3O_4 interface was found to be coherent and even with the high-resolution TEM image close to the atomic resolution, we could not find any signature of Mg in these films.[17] Hence, we can say that the presence of Mg in our films is ruled out. The Mg diffusion was considered by us as a possibility. However, from the TEM and AES studies, it turns out that the Mg in-film diffusion is not the reason for the observed effect.

From the above discussion, it is clear that if we add the contributions from the interface, noncompensation along the growth direction, as well as at the APBs, we can explain about 23% enhancement in the magnetic moment of a 5 nm thick magnetite film. At present, the origin of the giant magnetic moment observed for our films is not clear. It appears that the noncompensation at the surface may have profound effect on the intersublattice exchange in the layers underneath. Nevertheless, our results are of great significance from the application point of view, as they do not support the dead layer model and demonstrate that the precise control of surface and interfaces of Fe_3O_4 film is essential to control the magnetic properties of the epilayers.

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*Corresponding author; FAX+353-1-8963037; aroras@tcd
†Present address: UGC-DAE Consortium for Scientific Research, Indore, India.

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