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Adsorbate-induced spin-polarization enhancement of Fe₃O₄(001)

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Abstract

Using a spin-polarized metastable helium beam, we have investigated the remanent spin polarization at the surface of clean, hydrogen-terminated and benzene-adsorbed Fe₃O₄(001) thin films prepared on MgO(001) substrates. For the clean surface, a small negative asymmetry is detected in the ejected electron yields for helium-electron spins aligned parallel and anti-parallel to the sample magnetization direction. This confirms earlier experimental results from less surface-sensitive techniques which show that the spin polarization at the surface of Fe₃O₄(001) is much reduced from the bulk value and, furthermore, implies that majority-spin states actually dominate at the Fermi level. However, when hydrogen-terminated, the asymmetry is considerably enhanced and positive highlighting the important role that surface adsorption and passivation will play in the development of spintronic materials. This is further demonstrated for the adsorption of the simplest π -conjugated molecule, benzene, at the clean Fe₃O₄(001) surface where a similar enhancement in the spin polarization is observed, an effect that could prove beneficial to the design and fabrication of organic spintronic devices.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Magnetite Fe₃O₄ has attracted a great deal of attention recently due to its classification as a half-metallic ferromagnet (HMF) and the prediction of a -100% spin polarization at the Fermi level, $P(E_{\rm F})$, for the bulk material [1]. This property renders Fe₃O₄ and other HMFs as attractive candidates for spintronic devices in which spin-dependent transport is key to their operation [2]. To exploit fully the potential of these systems and ensure that efficient spin injection occurs, a thorough understanding of surface and interface effects is essential. This is especially true when considering the large reduction in spin polarization from the bulk value that occurs when Fe₃O₄ films are incorporated into multi-layered samples, as necessary for a practical device application [3].

Density functional theory (DFT) calculations have convincingly shown that bulk-truncated Fe₃O₄(001) stabilizes to form a modified *B*-terminated polar surface consisting of oxygen and octahedral Fe(B) atoms (see the inset of figure 2(a)) [4]. This is associated with a Jahn-Teller distortion of surface atoms into a wave-like structure along the [110] direction to give a $(\sqrt{2} \times \sqrt{2}) R45^\circ$ surface reconstruction, as consistently observed with LEED [5, 6]. X-ray diffraction [4] and scanning tunnelling microscopy [6, 7] experiments provide further evidence for the validity of this model whilst spinpolarized photoemission spectroscopy (SPPES) has been used to observe the reduction in $P(E_{\rm F})$ predicted to occur due to the presence of surface states in the majority-spin band gap. This change in the electronic structure arising due to the truncation of the bulk leads to a loss of half-metallicity and a large reduction in $P(E_{\rm F})$. Specifically, $P(E_{\rm F})$ values of -80% for the (1 1 1) orientation [8] and -55% [9] and -40%[10] for the (001) orientation have been reported although their interpretation has been subject to some debate [11]. Additionally, although considered to be a surface-sensitive technique, the information depth of SPPES means that a significant contribution from the bulk is included in the signal so that the nature of $P(E_{\rm F})$ at the outermost surface remains uncertain. In any case, it is clear that at the $Fe_3O_4(001)$ surface

 $P(E_{\rm F})$ is much reduced when compared with the bulk and that recovery to a higher value would be highly beneficial to spintronics research.

Recently, a dramatic increase in $P(E_{\rm F})$ due to the adsorption of atomic hydrogen was observed at the surface of $Fe_3O_4(001)$ using a spin-polarized metastable helium (He^{*}) beam operating in fields of up to 5 T [12]. Supporting DFT calculations showed that the enhancement was mainly due to a modification of oxygen surface states when dangling bonds at O1 sites are eliminated through bonding with hydrogen atoms, in turn resulting in a recovery of half-metallicity. In this work we have used the related technique of spin-polarized metastable de-excitation spectroscopy (SPMDS) to show that an enhancement in $P(E_{\rm F})$ also occurs at room temperature for hydrogen-terminated Fe₃O₄(001) films prepared in the remanent state. This is an important result as it shows that adsorbate-induced changes to the surface electronic structure of $Fe_3O_4(001)$ may lead to improved interfacial magnetic properties that could benefit incorporation into spintronic devices.

Hydrogen termination of Fe₃O₄(001) results in the simplest adsorbate structure and as such is a good test system for a study of more advanced, functional molecular adsorbates that are commonly employed in organic spintronics research [13]. Typical molecules used in this rapidly expanding field are π -conjugated organic semiconductors (OSCs) such as Alq₃ [14]. We demonstrate here that the adsorption of benzene (C₆H₆)—the simplest π -conjugated molecule—on Fe₃O₄(001) also leads to a large enhancement in $P(E_F)$.

2. Experimental

Fe₃O₄(001) thin films ~25 nm thick were epitaxially grown on single-crystal MgO(001) substrates that were cleaned by annealing at 700 °C in an O₂ partial pressure of ~3 × 10⁻⁴ Pa for up to 30 min. Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) were used to ensure that a surface free of contamination and with good structural order was obtained. Fe was deposited using 99.99%-purity Fe rods heated using an electron-beam evaporation source (Omicron EFM3). Deposition was carried out at rates of ~1 Å min⁻¹ in an O₂ atmosphere of ~3 × 10⁻⁴ Pa and with the substrate held at 350 °C. A doser was used to deliver a high local O₂-gas load at the sample in order to reduce the residual pressure of the UHV preparation chamber (base pressure <2 × 10⁻¹⁰ mbar) during deposition.

The effectiveness of the growth procedure has been well characterized with a number of techniques. Quantitative analysis of AES spectra (not shown) illustrates that the oxide phase produced is Fe₃O₄ [15] and LEED indicates a clear $(\sqrt{2} \times \sqrt{2})R45^{\circ}$ reconstruction at the surface of the films, as seen in figure 1(*a*). Hysteresis curves measured using an *ex situ* magneto-optical Kerr effect (MOKE) set-up with a magnetic field applied in the in-plane [0 0 1] direction show a high degree of squareness and a coercivity of ~300 Oe, in agreement with previous studies (figure 1(*b*)) [16]. High-quality epitaxial growth in the bulk of the thin films was confirmed using transmission electron microscopy (TEM) and selected-area



Figure 1. (*a*) LEED pattern of a clean Fe₃O₄(001) surface showing a $(\sqrt{2} \times \sqrt{2})R45^{\circ}$ reconstruction. (*b*) MOKE hysteresis loop for a magnetic field applied in-plane along the [001] direction of a 25 nm Fe₃O₄(001) film. (c) Schematic of the SPMDS set-up used to probe $P(E_{\rm F})$.

diffraction (SAD). Additionally, magnetoresistance results (not shown) agree with previous measurements of similar $Fe_3O_4(001)$ thin films prepared on MgO(001) [17].

To hydrogen-terminate the Fe₃O₄(001) films, thermal dissociation of H₂ gas with a cracking filament was used. When fully hydrogen-passivated, the clean Fe₃O₄(001) $(\sqrt{2} \times \sqrt{2})R45^{\circ}$ surface reconstruction changes to (1×1) , as indicated by the corresponding LEED pattern. For experiments investigating benzene adsorption, the sample was cooled to 100 K before being exposed to purified benzene vapour by backfilling the specimen chamber via a leak valve [18]. The total exposures reported here do not account for the sensitivity of the ion gauge. Before SPMDS experiments were performed, the films were pulse-magnetized in-plane using an *in situ* coreless coil. Magnetic saturation was confirmed with a simple *in situ* MOKE set-up to observe the Kerr rotation on switching the direction of magnetization.

The apparatus used to produce a spin-polarized beam of metastable helium atoms has been described in detail elsewhere [19], and is schematically shown in figure 1(*c*). Optical pumping with 1083 nm circularly polarized radiation from a laser diode was used to spin polarize the He* atoms, and a weak external magnetic field used to avoid degeneracy and align the spins either parallel or anti-parallel to the sample magnetization direction. The spin polarity was switched by simply altering the helicity of the pumping radiation. After interacting with the Fe₃O₄(001) films, the yield of electrons ejected from the surface as a result of He* atom de-excitation was measured as a function of their energy using a simple retarding-field analyser. The asymmetry, *A*, between spectra for He* atom spins aligned parallel, I_{\uparrow} , and anti-parallel, I_{\downarrow} , to the majority spins of the magnetized sample, was



Figure 2. (*a*) Spin-summed MDS spectra measured for a clean and hydrogen-terminated $Fe_3O_4(001)$ surface. (*b*) The asymmetry calculated from spin-resolved MDS data such as that shown in (*a*). In both (*a*) and (*b*), data are smoothed over 10 points. The inset of (*a*) shows a schematic of the clean $Fe_3O_4(001)$ surface adapted from [4].

then calculated using the standard definition $A(\%) = (I_{\uparrow} - I_{\downarrow})/(I_{\uparrow} + I_{\downarrow}) \times 100$. Note that in our previous investigation of the spin polarization at the Fe₃O₄(001) surface [12], a separate experimental set-up was used [20].

3. Results and discussion

Figure 2(a) shows the spin-summed MDS spectra for a clean and hydrogen-terminated $Fe_3O_4(001)$ surface. The integrated electron yields obtained directly from the retarding field analyser have been differentiated and smoothed to produce spectra which show features due to the dynamics of He* de-excitation. At the metallic $Fe_3O_4(001)$ surface, He* atoms de-excite via resonance ionization (RI) followed by Auger neutralization (AN) causing the ejection of an electron from the surface [21]. As two electrons are involved in this latter process, which takes place $\sim 2-5$ Å from the surface, the measured MDS spectra reflect a self-convolution of the surface density of states (DOS) that spill furthest into the vacuum meaning that only the electronic states of the outermost atoms are probed by the incoming He* beam. The kinetic energy maximum, $E_{k,\max}$, occurs when both electrons involved in the AN process originate from the Fermi level.

The clean Fe₃O₄(001) surface is terminated with a modified *B* layer consisting of O and octahedral Fe(*B*) atoms (see the inset of figure 2(*a*)). DFT calculations have shown that the absence of Fe(A) atoms results in the confinement of hybridized O $2p_{x,y}$ -Fe $d_{x^2-y^2}$ states at the surface yielding a significant DOS energetically located in the bulk Fe₃O₄ majority band gap at around E_F [4, 22]. At low kinetic energies, the clean spectrum is dominated by emission due to secondary electrons although a shoulder is visible at a kinetic energy of ~6 eV. In their study of oxygen adsorption on an Fe(110) surface, Förster *et al* have previously observed a peak in an MDS spectrum at a kinetic energy of ~5.5 eV and assigned this to emission from O 2*p* states [23]. In fact, the overall form of the MDS spectrum presented by those authors for high O exposures agrees very well with that shown in figure 2(a) suggesting that at the clean Fe₃O₄(001) He* de-excitation is predominantly caused by O states. Further evidence for the assignment of this shoulder as being due to O 2*p* emission is provided by spin-polarized ultraviolet photoemission spectroscopy (SPUPS) of Fe₃O₄(111)/Fe(110) magnetic bilayers [24].

The MDS spectrum for the hydrogen-terminated $Fe_3O_4(001)$ surface shows several distinct changes from that of the clean surface with increased emission in the energy region just below $E_{\rm F}$ and a more pronounced shoulder at ~6 eV. Previous DFT calculations by the authors have shown that hydrogen preferentially adsorbs onto oxygen atoms located at O1 sites which, in contrast to the O2 site, have no subsurface Fe(A) neighbour [12, 22]. Upon adsorption, the oxygen dangling bonds present at the clean surface are saturated by O-H bond formation causing a large modification to the surface electronic properties, in particular a shift of the surface states to a higher binding energy. Electronic charge is transferred from the chemisorbed H atoms to surface O1 atoms and then to surrounding Fe(B) atoms [22]. LDOS calculations show that this process shifts the O 2p states downward from $E_{\rm F}$ accompanied by an increase in the Fe(B) density in this region. The shoulder in the hydrogen-terminated MDS spectrum can therefore be attributed to the increased LDOS of O 2p states at the surface, and the increased intensity at higher kinetic energies to emission from Fe(B) d states. Both of these changes are due to hydrogen-induced weakening of the hybridization between O $2p_{x,y}$ and Fe $d_{x^2-y^2}$ states. Consequently, the contribution of Fe states to the MDS spectrum has increased so that it is now more reminiscent to that for a clean Fe surface exposed to a low dose of oxygen [23].

Figure 2(*b*) shows the asymmetry, *A*, for a clean and hydrogen-terminated Fe₃O₄(001) surface at kinetic energies approaching $E_{k,\text{max}}$ which represents emission at around the Fermi level. The data have been smoothed over 10



Figure 3. (*a*) Spin-summed MDS spectra for a clean $\text{Fe}_3\text{O}_4(001)$ surface before and after exposure to 48 L of C_6H_6 . (*b*) The asymmetry corresponding to the data shown in (*a*). In both (*a*) and (*b*), data are smoothed over 10 points.

points to account for the rapidly decreasing count rate as the kinetic energy increases. Due to the dynamics of He* atom de-excitation, a positive asymmetry results from a surface spin polarization that is negative reflecting the dominance of minority spin states. In the case of the clean surface, the asymmetry declines sharply towards E_F to a value less than 0% indicating that the spin polarization at the Fermi level of the clean Fe₃O₄(001) surface is very low and has a positive polarity, in sharp contrast to the $-100\% P(E_F)$ predicted for the bulk material. Due to difficulties in precisely determining the kinetic energy cut-off associated with the reduced count rate, the maximum negative asymmetry reported in figure 2(*b*) represents a lower limit for the value at the Fermi level. However the qualitative trend is clear with the spin polarization reducing drastically and changing polarity toward E_F .

The half-metallic nature of bulk Fe₃O₄ arises due to a band gap in the majority-spin channel and the presence of Fe(B) minority spin states at $E_{\rm F}$ [1]. For the clean modified-Bterminated $Fe_3O_4(001)$ surface, DFT calculations have shown that the presence of the surface states discussed earlier leads to a significant spin-up (majority) DOS at $E_{\rm F}$ and therefore a corresponding decrease in $P(E_{\rm F})$ [4, 22]. In fact, these calculations suggest that there is a dominance of majorityspin states at $E_{\rm F}$ which would concur with the experimental result observed here. The observation of a positive $P(E_{\rm F})$ has not been reported before although reduced negative values have been recorded in previous SPPES experiments [9, 10, 24]. Also, our previous work showed $P(E_{\rm F})$ to approach zero for high sample biases although measurements close to $E_{\rm F}$ were hindered by a low signal [12]. Additionally, this was for a sample in a 5 T magnetic field and not the more technologically relevant remanent state.

The asymmetry for a hydrogen-terminated $Fe_3O_4(001)$ surface (figure 2(*b*)) displays opposite behaviour to the clean surface and increases to a much higher positive value on approaching E_F . DFT calculations show that unoccupied minority spin-down states of the clean surface cross the Fermi level and become partially occupied upon hydrogen adsorption [12, 22]. O p-state energies are also displaced and a metal-to-half-metal transition is predicted to occur leading to a reconfiguration of the surface electronic structure and a massive enhancement of $P(E_{\rm F})$. The result here goes some way to confirming such a situation and it should be noted that due to a low count rate at very high kinetic energies, the value reported for A at $E_{\rm F}$ in figure 2(b), and therefore $P(E_{\rm F})$, is a conservative estimate. The spectrum is similar to that obtained using a spin-polarized metastable He beam in a 5 T magnetic field although in that case a larger maximum value for A of >50% was recorded [12]. The difference is primarily attributed to the influence of anti-phase boundaries in the remanent films studied here [25].

The value of $P(E_F)$ is particularly important in spintronics applications as it is electrons located near the Fermi level that determine the spin transport properties of a material. The low, positive value reported here for the clean Fe₃O₄(001) surface supports previous SPPES studies [9, 10, 24] and lends evidence to the assertion that spin flip processes at the interface of Fe₃O₄-based devices explains the unexpectedly low magnetoresistance values observed [26]. The dramatic polarity reversal and enhancement of $P(E_F)$ upon hydrogenpassivation suggests that these undesirable effects can be avoided through careful consideration and control of the interfacial electronic structure. This will be particularly important in the very new field of organic spintronics which seeks to make use of the advantageous properties of π -conjugated OSCs in device design and fabrication.

Figure 3 shows the MDS spectrum and asymmetry for an Fe₃O₄(001) surface exposed to a relatively high dose of benzene, C₆H₆. In contrast to clean and hydrogen-terminated Fe₃O₄(001), He* atoms now undergo Auger de-excitation, a one-electron process similar to photoemission occurring at insulating and low-work-function surfaces. As a result, the MDS spectrum is more featured than for the clean surface (figure 3(*a*)) showing peaks that correspond to the molecular orbitals of the benzene molecule with the highest occupied molecular orbital (HOMO) at the highest kinetic energy, similar to the case for benzene adsorption on Fe(100) [27]. In similarity to hydrogen termination, the asymmetry for the benzene-adsorbed surface again shows marked changes from the clean spectrum (figure 3(b)), in particular a polarity change and enhancement at around $E_{\rm F}$. However, it is likely that the origin of the sharp rise in the asymmetry close to $E_{\rm F}$ is different in the two cases. In contrast to hydrogen termination where the formation of chemical O-H bonds leads to a large downward shift in binding energy of O p states, benzene is expected to physisorb on the $Fe_3O_4(001)$ surface with limited interaction between molecule and substrate. The observed asymmetry around $E_{\rm F}$ is then expected to arise due to a weak adsorbate-induced state. Further experimental and theoretical work is underway to clarify the exact mechanism behind the polarization enhancement for the case of benzene adsorption.

4. Conclusions

We have used the technique of SPMDS to investigate the surface electronic and magnetic properties of clean and hydrogen-terminated $Fe_3O_4(001)$ films prepared in the remanent state. For the clean surface, the asymmetry A is slightly negative indicating the dominance of majority electrons and a positive spin polarization at the Fermi level, as predicted by DFT calculations. However, when terminated with hydrogen, the polarity of A becomes highly positive indicating that $P(E_{\rm F})$ is reversed and considerably enhanced for hydrogen-terminated $Fe_3O_4(001)$ films in the remanent state. This inversion and increase are associated with the elimination of surface dangling bonds and the corresponding shift in O p-state energies at around $E_{\rm F}$. A similar situation also occurs for the adsorption of a simple π -conjugated molecule, in this case benzene, at the clean $Fe_3O_4(001)$ surface. Such observations suggest that adsorption-induced changes in electronic and magnetic properties will play a vital role in developing interfaces for spintronic devices, and that surface passivation is a route to retaining high spin-polarization values at the surface of HMFs. As magnetotunnelling across an interface is largely dependent on $P(E_{\rm F})$, it may be expected that selective and controlled adsorption in OSC/HMF hybrid devices will lead to an improvement in device properties, particularly magnetoresistance.

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