Fe$_3$O$_4$(111)/Fe(110) magnetic bilayer: Electronic and magnetic properties at the surface and interface

H.-J. Kim, J.-H. Park, and E. Vescovo

National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973

(Received 16 November 1999)

The surface and interface properties of the magnetic bilayer Fe$_3$O$_4$(111)/Fe(110) have been studied by low-energy electron diffraction, spin-polarized photoemission spectroscopy, and magnetic linear dichroism. The electronic structure at the surface region of the oxide departs considerably from the one of the underlying bulk layer. Correspondingly, the surface spin polarization is found to be lower than expected for pure Fe$_3$O$_4$. The magnetic bilayer coupling is driven by the formation of a specific Fe$_3$O$_4$(111)/Fe(110) interface. The same interface is also formed when an Fe metal overlayer is deposited on the oxide surface.

I. INTRODUCTION

Transition-metal oxide (TMO) materials have long been a subject of active research.[1] Their rich physical phenomenology is an ideal benchmark to test solid-state physics models.[2] Technologically, these materials are employed in important industrial processes as catalysts as well as anticorrosives and furthermore, they are used extensively in magnetic memories.

Until recently, spectroscopic studies of TMO were limited to bulk properties: the problem of preparing thin films of TMO with well-defined stoichiometry (and even more so their surfaces) seemed unsurmountable. However, recent works have demonstrated that it is possible to stabilize a few of these complex structures in the form of ultrathin films, by epitaxial growth on appropriate crystalline substrates. Particularly, thin films of Fe oxides have been successfully grown on different substrates, using different techniques: FeO has been reported to grow on Pt(111) (Refs. 3 and 4) and on Fe(110);[5,6] Fe$_3$O$_4$ has been grown on Pt(111) (Refs. 3 and 7) and on Fe(110) (Ref. 8) as well as on MgO(110) (Refs. 9 and 10) and NiO,[11] thin films of α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$ have been stabilized on Al$_2$O$_3$(0001) (Ref. 9) and MgO(100),[12,10] respectively.

These progresses are remarkable, considering the complex structures of TMO, and open new possibilities to investigate their electronic properties. This is particularly true in the case of *ferromagnetic* TMO, which, as bulk materials, were essentially out of reach of the most valuable magnetic spectroscopies such as spin-resolved photoemission and spin-resolved inverse photoemission.

In a recent related paper, we reported on the bulk properties of epitaxial Fe oxide films formed on the Fe(110) surface.[13] It was shown that the oxidation reaction proceeds through two distinguished phases: an initial (paramagnetic) FeO(111) layer is transformed into a stable Fe$_3$O$_4$(111) overlayer at high oxygen doses [>600 L (1 L=10^{-6} Torr s)]. In the resultant Fe$_3$O$_4$(111)/Fe(110) bilayer, the magnetizations of the two materials are coupled antiparallel.

Here we reconsider the same system but we focus on the electronic and magnetic properties at the surface and interface. We study them by means of low-energy electron diffraction (LEED), spin-polarized photoemission spectroscopy from the valence band, and magnetic linear dichroism (MLD) in photoemission from the Fe 3p core level. These results indicate that the surface of the thick oxide film does not resemble a simple, bulk-terminated Fe$_3$O$_4$ surface. The valence-band spectra are considerably different from those of cleaved Fe$_3$O$_4$ samples. Additionally, the surface spin polarization is smaller than expected in Fe$_3$O$_4$ (magnetite). The Fe$_3$O$_4$/Fe(110) antiparallel magnetic coupling is related to the formation of a unique Fe$_3$O$_4$(111)/Fe(110) interface. Interestingly, an antiparallel magnetic coupling is also found by preparing the opposite interface—Fe/Fe$_3$O$_4$(111).

II. EXPERIMENTAL RESULTS

The experiments have been performed at the U5UA undulator beamline at the National Synchrotron Light Source located at the Brookhaven National Laboratory.[14] Spin- and angle-resolved photoemission spectra have been collected with a commercial VSW 50-mm spherical analyzer coupled with a low-energy diffuse scattering spin polarimeter. The total energy resolution (light plus electron spectrometer) was set to 100 meV and the angular resolution was about 2°. The base pressure in the measurement chamber was about 5×10^{-11} Torr. Fe films have been prepared via *e*-beam evaporation on a W(110) substrate kept at room temperature. The total pressure increased to about 2×10^{-10} Torr during film depositions. After a short post-annealing (approximately 1 min long) to about 400 °C, the Fe films exhibit a sharp (1×1) LEED pattern.

Here we will consider the oxidation of thick Fe(110) films (>100 ML), whose behavior should, therefore, be comparable to Fe(110) single crystal.

The spin-resolved measurement have been performed in magnetic remanence with the sample magnetized along the in-plane [001] axis, which corresponds to the easy axis for thick Fe film.[15] All oxygen exposures have been performed at $p_{O_2} = 5 \times 10^{-7}$ Torr, with the sample annealed to 250 °C.

A. Atomic structure: LEED

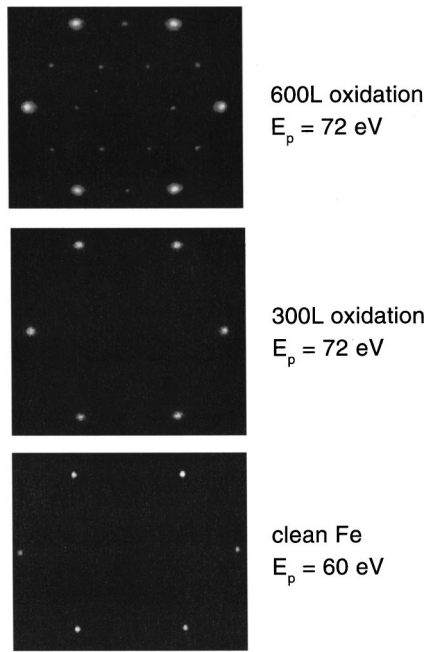The LEED patterns corresponding to the different stages of the oxidation are displayed in Fig. 1.

FIG. 1. LEED pattern from clean Fe(110) (bottom), and after oxygen exposure to 300 L (middle) and 600 L (top).

The Fe(110) LEED (bottom, rectangular pattern) undergoes a first modification after exposure to 300 L of oxygen (middle, hexagonal pattern) and a second one after additional 300 L (top, hexagonal 2×2 pattern). Further increase of the oxygen exposure (up to 1500 L) does not produce any appreciable modification of the LEED.

The appearance of the hexagonal symmetry in the LEED suggests the formation of a (111) surface. In the (111) direction, the three Fe oxides, stable in normal conditions—FeO, Fe₃O₄, and αFe₂O₃—have similar atomic structures, consisting of pure (hexagonal) oxygen planes separated by pure Fe planes. The lateral dimensions of the hexagonal oxygen lattice are very close in the three cases (see Fig. 2). There is a good lattice match along the substrate [100] direction (−1%, 1.7%, and −1.3% for FeO, Fe₃O₄ and α-Fe₂O₃, respectively). Along the substrate $[1\bar{1}0]$ direction, the oxygen hexagon is slightly expanded with respect to the Fe lattice (21.2%, 24.6%, 7.1%, respectively). Indeed, upon oxygen
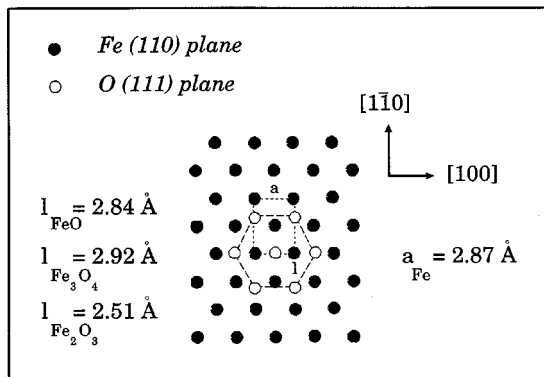

FIG. 2. Schematic representation of the lattice match conditions between the Fe(110) surface plane (full circles) and the (111) (hexagonal) oxygen planes in the Fe oxides stable at normal conditions.
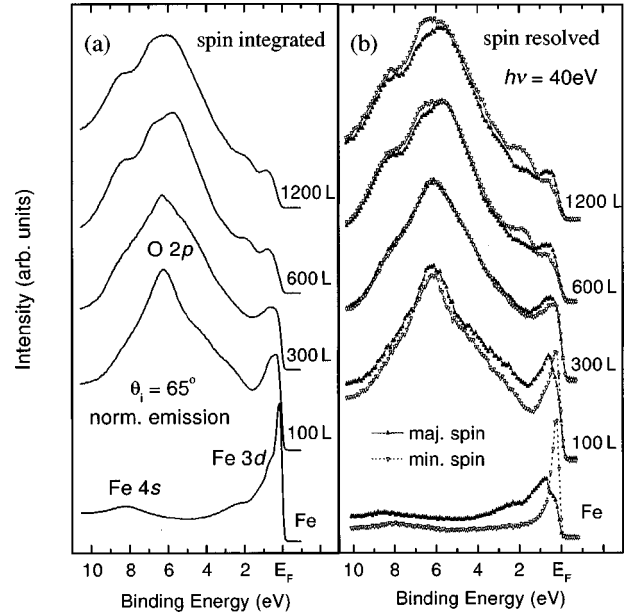

FIG. 3. (a) Spin-summed and (b) spin-resolved valence band photoemission spectra taken in normal emission with 40 eV photon energy, as a function of oxygen exposure.

exposures, one can directly observe a sort of contraction of the LEED picture (with respect to the Fe spots), corresponding to the *in-plane* lattice expansion, needed to accommodate the oxide layer.

This favorable epitaxial condition explains the growth of well-ordered (111) Fe oxide layers on the Fe(110) substrate but does not give any clear preference to any of the three stable Fe oxides mentioned above. However, in the hypothesis of ideal bulk-terminated (111) surfaces, previous studies suggest that one should find a hexagonal (1×1), a (2×2), and a $(\sqrt{3}\times\sqrt{3})R30°$ LEED pattern corresponding to the formation of FeO, Fe₃O₄, and α Fe₂O₃, respectively.[3] These considerations would then lead us to attribute the FeO stoichiometry to the first oxide phase (between 100 and 300 L oxygen exposures) and the Fe₃O₄ to the second phase (>600 L). In other words, the initial layer of FeO is forced to oxidize to Fe₃O₄ by additional oxygen exposure.

B. Electronic structure: Valence band

The presence of two distinct phases can be clearly distinguished also in the photoemission data. Representative valence-band spectra are reported in Fig. 3 as a function of oxygen exposure.

The Fe(110) spectrum (bottom left) shows the 3d emission, extended over the first 3 eV below the Fermi level and a small feature at about 8 eV, due to the 4s states.[16] The first oxidation stage is characterized by the development of the O 2p-derived emission at about 6 eV below E_F, accompanied by a smooth decrease in the intensity of the Fe 3d states. A pronounced modification in the electronic structure takes place above 600 L (second stage), as indicated by the appearance of a new feature in the spectra, at about 2 eV binding energy.

The two reaction stages are even more apparent in the spin-resolved spectra [Fig. 3(b)]. These spectra contain information about the magnetic ordering and the spin character of
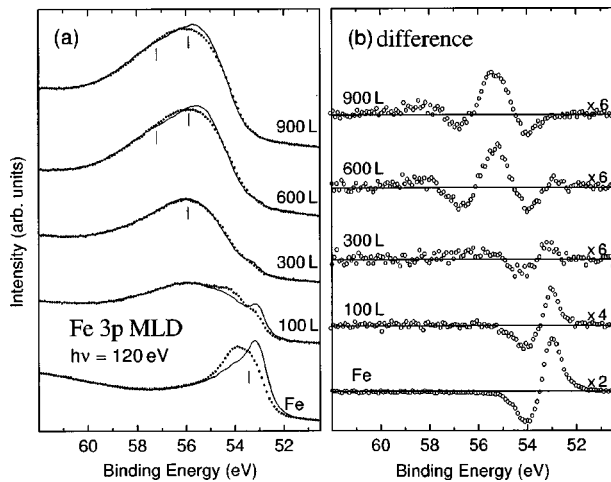
FIG. 4. Fe $3p$ photoemission spectra as a function of oxygen exposure. The light incidence angle is 56°, and the photon energy 120 eV. (a) Spectra taken with opposite magnetization (continuous lines and dots). (b) Corresponding difference spectra (i.e., MLD signals).

FIG. 5. Fe $3p$ spectra and MLD signals from the thick oxide film and after deposition of 1.2 and 4.8 Fe ML.

the electronic states. The Fe spectrum (bottom right) displays various features, which can be interpreted in terms of the Fe bulk and surface bands.[16] Initially, the oxygen exposure effectively reduces the spin polarization. The entire spectrum is essentially not polarized at 300 L. The small polarization near E_F is probably due to a residual contribution from the Fe metal underneath. The first Fe oxide is then not ferromagnetic—at least on its surface. Surprisingly, an appreciable polarization reappears in the spin-resolved spectra above 600 L. In the second stage, the oxide overlayer—or at least its surface—has regained a long-range magnetic order.

However, notice that the reappearance of a spin polarization is accompanied by a change of its sign: i.e., the Fe metal and the thick oxide overlayer have opposite magnetization. In other words, there is an antiparallel magnetic coupling in the $Fe_3O_4(111)/Fe(110)$ bilayer.

This antiparallel coupling appears to be independent from the thickness of the oxide layer. The spectra simply maintains the same overall ("negative") spin polarization during the growth of a thicker oxide layer (oxygen doses from 600 to 1200 L).[18] This behavior suggests that the origin of this coupling is related to the interface between the Fe metal and the oxide overlayer.

C. Electronic structure: Fe 3p core level

Additional information on the surface electronic structure of this system can be obtained from the Fe $3p$ core-level spectra and its MLD spectra (see Fig. 4).

The $3p$ spectrum of Fe shows the well-known, strong MLD effect.[17] After 300 L, the emission from the Fe metal is already reduced to only a weak shoulder. The intensity of Fe $3p$ spectrum is dominated by the broad oxide component, peaked about 2.5 eV below the main Fe feature. No dichroism signal is detected under this oxide component [Fig. 4(b)]. By increasing the oxygen doses above 300 L, the Fe $3p$ feature becomes even broader and a new shoulder appears about 4.2 eV below the Fe metal. Furthermore, as already seen from the spin-resolved valence-band spectra, at
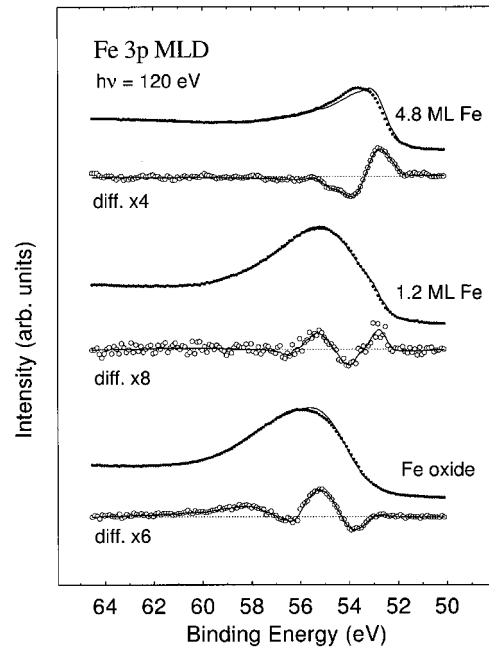
this stage the long-range ferromagnetic order is recovered in the oxide. In the MLD spectra, we can now clearly distinguish a magnetic signal under the oxide region.

The Fe $3p$ spectra confirm the picture we already introduced for the oxidation stages of the Fe(110) surface: $Fe(110)+300$ L $O_2 \rightarrow FeO(111)+300$ L $O_2 \rightarrow Fe_3O_4(111)$. In FeO, Fe is present only in one oxidation state (Fe^{2+}) while Fe_3O_4 contains both Fe^{2+} and Fe^{3+} sites.[19] The observed broadening of the core-level spectra with increasing oxygen exposures is then consistent with the initial formation of FeO followed by Fe_3O_4. Furthermore, at room temperature, FeO is paramagnetic and accordingly, no MLD signal is detected in the first stage. In the second stage instead, with the formation of ferrimagnetic Fe_3O_4, a magnetic signal has to be expected.

It is interesting to note that as a result of the core level shifts during the oxide formation, the MLD spectra of the TMO/TM bilayers can be used to detect the sign of the magnetic coupling. In the case of Fe_3O_4/Fe, the antiparallel coupling is reflected in the opposite signs of the MLD spectra at the lowest binding energy side: positive for Fe [see Fig. 4(b) bottom, about 53 eV] and negative for Fe_3O_4 [Fig. 4(b) top, about 54 eV]. In Fe_3O_4 the net magnetic moment is carried by the Fe^{2+} ions, which are located at the lowest binding energy among the three inequivalent Fe ions of this oxide.

As already mentioned, the photoemission data and our previous work[13] suggest that the antiparallel coupling is closely related to the $Fe_3O_4(111)/Fe(110)$ interface. In order to further explore this sort of interface effect, we have also prepared the opposite interface—namely, $Fe/Fe_3O_4(111)$—by evaporating a thin Fe film on top of the thick oxide. The corresponding Fe $3p$ spectra are shown in Fig. 5. The onset of the MLD signal changes sign when evaporating Fe, i.e., the magnetization of the Fe overlayer is coupled antiparallel to the underlying oxide layer. We conclude that the antiparallel coupling is a property associated to

the Fe-Fe$_3$O$_4$ interface, independently from the way in which it is formed, Fe$_3$O$_4$/Fe or Fe/Fe$_3$O$_4$.

III. DISCUSSION

The preparation of thin films of TM oxides by epitaxial growth on a metal substrate has been a subject of considerable research in recent years, driven by fundamental as well as technological reasons. Various groups have studied the oxidation reaction of the Fe(110) surface, with different experimental techniques.[5,6,8,20] Their findings should, therefore, be compared to ours.

Smentkowsky and Yates studied the Fe(110)-O$_2$ reaction in the temperature range 90–920 K using Auger spectroscopy.[8] In good agreement with our data, they also concluded that for oxidation at 600 K and at high oxygen doses, Fe$_3$O$_4$ is the stable oxide formed on the Fe(110) surface.

More recently Cappus and co-workers reexamined the oxidation of the Fe(110).[5] They obtained a (2×2) LEED pattern, similar to the one shown in Fig. 1 (top), by exposing the Fe(110) surface to 4000 L O$_2$ at 600 K followed by 4 min annealing at 870 K. On the basis of x-ray photoemission spectroscopy $2p$ data, they concluded that this (2×2) pattern did not indicate a bulk-terminated Fe$_3$O$_4$(111) surface but rather a reconstructed FeO(111) surface. Furthermore, they suggested that the product of the oxidation should depend on the thickness of the metal substrate. Particularly, a different output should be expected whether oxidizing a thin film or a single crystal. In the case of an Fe single crystal, the Fe supply is larger than in thin films and consequently it could shift to the right the equilibrium of the reaction Fe$_3$O$_4$+Fe$\rightleftarrows$FeO. Although their argument sounds sensible, it does not seem appropriate for the oxidation of our thick Fe films ($>$100 ML). In our case, the Fe metal layer is always thick; indeed, the spin polarization and the MLD signal remain ''negative,'' even at the highest oxygen absorptions (see Figs. 3 and 4). Therefore, we tend to attribute the differences—formation of FeO in Ref. 5 and of Fe$_3$O$_4$ in our case—to the specific conditions (temperature and oxygen pressure) used in the two experiments. It is well known that the various stable Fe oxides can easily transform into one another by varying the preparation conditions.

The magnetic properties of the oxide formed on the Fe(110) surface have been recently examined by Koike and Furukawa,[6] using LEED and spin-polarized secondary electron spectroscopy (SPSES). Their experimental results are in good agreement with ours. They observed the (1×1) to (2×2) evolution of the hexagonal LEED pattern as a function of oxygen exposure and the SPSES measurements indicated the antiparallel magnetic coupling. However their conclusions were considerably different from ours. They also interpreted the (2×2) LEED pattern as a surface reconstruction of bulk FeO(111). Accordingly, they had to conclude that the reappearance of the magnetic ordering at high oxygen exposures, was confined only to the (reconstructed) surface layer. FeO is paramagnetic at room temperature (T_N^{FeO} $= 198$ K). Furthermore, they had to suppose that this reconstructed FeO surface was for some reasons (i) ferromagnetic and (ii) magnetically coupled through the paramagnetic (insulator) FeO to the Fe metal substrate. Naturally all these

hypotheses are not necessary, if the oxide overlayer is Fe$_3$O$_4$.[13]

As already mentioned, the valence-band data from the surface of our oxide on Fe(110) are quite different from what one would expect from the bulk-terminated Fe$_3$O$_4$ surface. Various groups have measured spin-integrated valence-band spectra from bulk Fe$_3$O$_4$ cleaved *in situ* to expose a [110] or a [100] surface.[21,22] In spite of the different surface orientations, the intensity at the Fermi level in the photoemission spectra is consistently lower in the bulk samples than in our films. A larger intensity at E_F, even at the highest oxygen exposures, cannot be attributed to the signal from the Fe metal underneath, as it is demonstrated by the absence of Fe metal in the $3p$ spectra (see Fig. 4). Therefore, the higher photoemission intensity at E_F seems to be an intrinsic feature of the films prepared on the Fe(110) surface. Probably, it indicates the formation of an oxygen deficient Fe$_3$O$_4$ surface. Note that although we performed several attempts exposing the sample to additional oxygen in a variety of conditions of both temperature (within the range 100–600 K) and pressure (within the range between 10^{-6}–10^{-10} Torr), we did not succeed in obtaining a reduced emission at E_F.

The fact that the surface of these films does not have the pure Fe$_3$O$_4$ stoichiometry is also apparent from the small polarization (16%) observed close to E_F. Alvarado and co-workers studied bulk Fe$_3$O$_4$ by spin-polarized threshold spectroscopy.[23,24] They found a polarization between 40% and 60% for the first state near E_F ($^6A_{1g}$), in good agreement with the value $\frac{2}{3}$ predicted by theoretical considerations.[25]

Note that the reduced polarization is confined only at the surface region. Our previous measurements showed that the bulk magnetization of the oxide overlayer is as high as 80% the value for pure Fe$_3$O$_4$.[13] This suggests that the small surface polarization could partially be due to inequivalent terraces on the Fe$_3$O$_4$(111) surface. As already mentioned, along the [111] direction the Fe$_3$O$_4$ crystal consists of pure oxygen planes separated by pure Fe planes. Therefore, if different terraces of Fe atoms (and/or of oxygen planes in contact with different Fe planes[4]) are exposed on the surface, the polarization measured by photoemission is effectively reduced, due to the ferrimagnetic ordering of Fe$_3$O$_4$. This view is supported by recent scanning tunnel microscope images showing that on the (111) surface of bulk Fe$_3$O$_4$ samples two inequivalent Fe planes are indeed present.[26]

The [111]-stacking alternating pure-Fe and pure-O planes has also an interesting consequence for the magnetic behavior of this bilayer. In Fe$_3$O$_4$, the stacking is of the type $\cdots$-Fe$_1$-O-Fe$_2$-O-Fe$_1$-$\cdots$, where Fe$_1$ is an Fe plane containing Fe$^{3+}_{\text{octh}}$ and Fe$_2$ an Fe layer containing both Fe$^{2+}_{\text{octh}}$ and Fe$^{3+}_{\text{teth}}$ (see Fig. 6). The magnetic moments of the Fe^{3+} ions ($5\mu_B$) localized on Fe$_1$ and Fe$_2$ planes[27] are aligned antiparallel and cancel each other. Therefore, Fe^{2+} sites ($4\mu_B$) alone support the net magnetization. Furthermore, inside the Fe$_2$ planes, Fe^{2+} and Fe^{3+} ions are also coupled antiparallel. It follows that the observed antiparallel magnetic coupling implies that between the two possible interfaces—namely, Fe$_{\text{met}}$-O-Fe$_1$-O-$\cdots$ and Fe$_{\text{met}}$-O-Fe$_2$-O-$\cdots$—only the first one is actually (or preferably) realized (see Fig. 6).

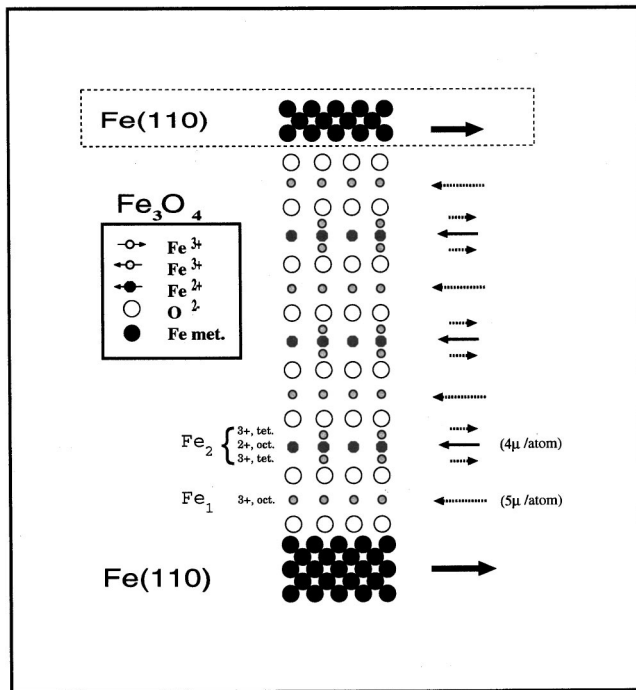It is difficult to indicate a unique cause of this preference.

FIG. 6. Schematic representation of the $Fe_3O_4(111)/Fe(110)$ structure. The arrows indicate the local direction of magnetization in the Fe planes. In Fe_3O_4 the magnetization is supported by the Fe^{2+} ions (continuous arrows), while the Fe^{3+} magnetic moments cancel (dashed arrows).

However, it seems plausible that an interface with a uniform Fe metal surface tends to prefer another uniform Fe layer close to it: i.e., the Fe_1 type containing only $Fe_{octh}^{3+;\uparrow}$ rather than the Fe_2 type containing both $Fe_{octh}^{2+;\uparrow}$ and $Fe_{teth}^{3+;\downarrow}$. Furthermore the formation of a complex Fe layer like the Fe_2 would require the development of a full three-dimensional structure and would consequently be unfavored in the formation of an interface.

One can also notice that if one would cut the oxide layer only to contain the first Fe plane (i.e., Fe_{met}-O-Fe_1-O), one would actually look at an oxide layer closely resembling FeO. Indeed the Fe atoms would all have the same octahedral symmetry as in FeO. The fact that the first phase of the oxide looks like FeO becomes then quite understandable also from this point of view. Indeed it seems to be quite a general fact that the first monolayer of Fe_3O_4 grown on metal (111) surfaces looks like FeO. It has also been found on Pt(111).[3] A quantitative analysis has shown that this 1 ML FeO is, however, quite particular, in that the Fe to O distance is nearly half of the one found in bulk FeO.[4]

IV. CONCLUSION

We have investigated the electronic and magnetic properties at the surface and interface of epitaxial Fe oxide films grown on Fe(110). Two distinct oxide phases as a function of the oxygen exposure, are clearly marked by the modification of the atomic [LEED, (1×1) to (2×2)] and the electronic structure (photoelectron spectroscopy, valence-band and core-level spectra). The first one (between 100 and 300 L O_2) is identified as FeO(111); the second as Fe_3O_4 (111).

The photoemission data suggest that the surface of these Fe_3O_4 (111) thick films are oxygen deficient with respect to a bulk-terminated surface. This oxygen deficiency together with the exposure of inequivalent (111) terraces is possibly at the origin of the small surface polarization found on these films.

The antiparallel magnetic coupling does not depend on the thickness of the oxide layer or the direction of the interface—Fe/Fe_3O_4 (111) or Fe_3O_4 /Fe (110). This antiparallel coupling implies the formation of the Fe_1-Fe (110) interface.

These results should be important in all applications making use of the surface and/or interface properties of TMO thin films and/or TMO/TM based multilayers.[28]

ACKNOWLEDGMENTS

[1] See, for example, S. Hüfner, in *Photoelectron Spectroscopy*, edited by M. Cardona, Springer Series in Solid-State Science (Springer, Berlin, 1995).

[2] A recent extensive review on the subject is M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998).

[3] A. Barbieri, W. Weiss, M. A. Van Hove, and G. A. Somorjai, Surf. Sci. **302**, 259 (1994).

[4] C. S. Fadley, M. A. Van Hove, Z. Hussain, and A. P. Kaduwela, J. Electron Spectrosc. Relat. Phenom. **75**, 273 (1995).

[5] D. Cappus, M. Hassel, E. Neuhaus, M. Heber, F. Rohr, and H.-J. Freund, Surf. Sci. **337**, 268 (1994).

[6] K. Koike and T. Furukawa, Phys. Rev. Lett. **77**, 3921 (1996).

[7] W. Weiss, A. Barbieri, M. A. Van Hove, and G. A. Samorjai, Phys. Rev. Lett. **71**, 1848 (1993).

[8] V. S. Smentkowsky and J. T. Yates, Surf. Sci. **232**, 113 (1990).

[9] Y. J. Kim, Y. Gao, and S. A. Chambers, Surf. Sci. **371**, 358 (1997).

[10] F. C. Voogt, T. Fujii, P. J. M. Smulders, L. Niesen, M. A. James, and T. Hibma, Phys. Rev. B **60**, 11 193 (1999).

[11] D. M. Lind, S. D. Berry, G. Chern, H. Mathias, and L. R. Testardi, Phys. Rev. B **45**, 1838 (1992).

[12] Y. Gao, Y. J. Kim, S. Thevuthasan, S. A. Chambers, and P. Lubitz, J. Appl. Phys. **81**, 3253 (1997).

[13] H.-J. Kim, J.-H. Park, and E. Vescovo, this issue, Phys. Rev. B **61**, 15 284 (2000).

[14] E. Vescovo, H.-J. Kim, Q.-Y. Dong, G. Nintzel, D. Carlson, S. L. Hulbert, and N. V. Smith, Synchrotron Radiation News **12**, 10 (1999).

[15] H. J. Elmers and U. Gradmann, Appl. Phys. A: Solids Surf. **51**, 255 (1990).

[16] H.-J. Kim and E. Vescovo, Phys. Rev. B **58**, 14 047 (1998).

[17] Ch. Roth, F. U. Hillebrecht, H. B. Rose, and E. Kisker, Phys. Rev. Lett. **70**, 3479 (1993).

[18] The thickness of the oxide layer cannot be obtained from the

photoemission data. A qualitative estimate (within approximately a factor of 2) can be obtained from the x-ray absorption data discussed in Ref. 13. We found an oxide thickness x of 17, 31, 41, and 68 Å for the 300, 600, 900, and 1500 L oxygen exposures, respectively.

[19] In Fe$_3$O$_4$—inverse spinel structure—the Fe is found into two different oxygen environments: tetrahedral (A sites, 8 per unit cell) and octahedral (B sites, 16 per unit cell). A sites are occupied by Fe^{3+} ions, while B sites are half occupied by Fe^{3+} and half by Fe^{2+} ions. Inside both A and B sublattice the moments ($5\mu_B$ for Fe^{3+} and $4\mu_B$ for Fe^{2+}) are ferromagnetically aligned but the two sublattices are antiferromagnetically coupled.

[20] E. Vescovo, C. Carbone, W. Eberhardt, O. Rader, T. Kachel, and W. Gudat, Phys. Rev. B **48**, 285 (1992).

[21] A. Chainani, T. Yokoya, T. Morimoto, T. Takahashi, and S. Todo, Phys. Rev. B **51**, 17 976 (1995).

[22] J.-H. Park, L. H. Tjeng, J. W. Allen, P. Metcalf, and C. T. Chen, Phys. Rev. B **55**, 1 (1997).

[23] S. F. Alvarado, W. Eib, F. Meier, D. T. Pierce, K. Sattler, H. C. Siegmann, and J. P. Remeika, Phys. Rev. Lett. **34**, 319 (1975).

[24] S. F. Alvarado, M. Erbudak, and P. Munz, Phys. Rev. B **14**, 2740 (1976).

[25] S. F. Alvarado and P. S. Bagus, Phys. Lett. **67A**, 397 (1978); P. S. Bagus, J. L. Freepuf, and D. E. Eastman, Phys. Rev. B **15**, 3661 (1977).

[26] A. R. Lennie, N. G. Condon, F. M. Leibsle, P. W. Murray, G. Thornton, and D. J. Vaughan, Phys. Rev. B **53**, 10 244 (1996); N. G. Condon, F. M. Leibsle, T. Parker, A. R. Lennie, D. J. Vaughan, and G. Thornton, *ibid.* **55**, 15 885 (1997).

[27] Strictly, the Fe$_2$ is not a plane but an Fe layer containing three closely spaced Fe planes Fe$_{teth}^{3+}$-Fe$_{octh}^{2+}$-Fe$_{teth}^{3+}$.

[28] See, for example, P. J. van der Zaag, A. R. Ball, L. F. Feiner, R. M. Wolf, and P. A. A. van der Heijden, J. Appl. Phys. **79**, 5103 (1996); P. Seneor, A. Fert, J.-L. Maurice, F. Montaigne, F. Petroff, and A. Vaures, Appl. Phys. Lett. **79**, 4017 (1999).