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Oxidation of the Fe(110) surface: An $Fe_3O_4(111)/Fe(110)$ bilayer

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The oxidation state and magnetic behavior of *in situ* oxidized Fe(110) surfaces has been studied using x-ray absorption spectroscopy and magnetic circular dichroism (MCD). Low-energy electron diffraction has been used to monitor the surface atomic structure. At high oxygen exposures, the system is unambiguously identified as an $Fe_3O_4(111)/Fe(110)$ bilayer. The MCD results show that the Fe_3O_4 overlayer is magnetically coupled (antiparallel) to the Fe substrate. This picture is in contrast to a previous report, which claims the formation of an FeO(111) overlayer with a reconstructed magnetic surface [Phys. Rev. Lett. **77**, 3921 (1996)].

Recent years have seen great development in the research on magnetic thin films and multilayers, due to potential technical applications in magnetic devices such as magnetic memories and sensors. The two-dimensional geometry of these systems is at the origin of various unusual magnetic phenomena,[1–3] such as, for example, magnetic size effects and magnetic couplings in multilayers.

This research has been chiefly confined to ''simple'' superstructures in which the building blocks are single-element materials. However, it has often been suggested that by using compounds, one could perhaps take advantage of their complex properties to engineer new magnetic structures. Confining the discussion to the important subcategory of transition metal oxide (TMO) systems, various interesting magnetic behaviors can be expected. Most of the TM oxides have the antiferromagnetic ground state. However, along a certain crystallographic direction, these oxides are often magnetically polar: i.e., the magnetic moment is aligned ferromagnetically within a plane but antiferromagnetically between adjacent (oxygen separated) TM planes. Often the magnetic polarity is accompanied by a chemical polarity, due to the sequence of TM-layer/O-layer. Magnetism and chemistry may then be combined to produce unusual situations.

For example, in an antiferromagnetic TMO, chemical polarity could induce a surface reconstruction such that the ground state of the reconstructed surface becomes ferromagnetic. In this case, above the Néel temperature, the oxide layer could become paramagnetic in the bulk, yet maintaining a (reconstructed) ferromagnetic surface. Obviously the situation can become even more interesting when such a TMO material is used inside a multilayer structure containing pieces of the type $\cdots$TMO/TM$\cdots$, thus allowing both surface and interfaces effects.

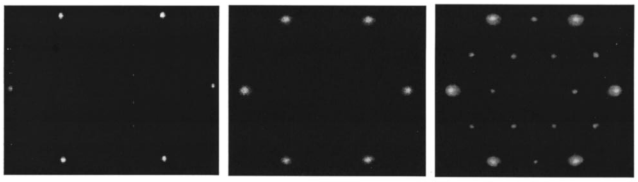
Some TMO/TM systems can be obtained by directly oxidizing clean TM surfaces. Recently, one such case has been reported on an Fe-oxide/Fe system, obtained by exposure to oxygen of an Fe(110) surface.[4] By a combination of structural low-energy electron diffraction (LEED) and magnetic (secondary electron spin-polarization) measurements, it was found that the formation of this oxide layer proceeds via two distinct stages. The first stage, identified as an FeO(111) layer, was not magnetic. However, the second stage, reached at higher oxygen exposures, was interpreted as a surface reconstruction of the FeO layer, leading to a *ferromagnetic* surface, a sort of $Fe_3O_4(111)$ surface termination. Surprisingly, this surface was found to be (antiferro)magnetically coupled to the underlying Fe substrate, suggesting a new indirect magnetic coupling mechanism between two different magnetic materials—$Fe_3O_4^{surf}$ and Fe^{subst}—via a nonmagnetic insulating spacer (FeO^{spacer}).

Unfortunately, none of the previous measurements provide direct information on either the oxidation state or the oxygen stoichiometry, in spite of the fact that these are most critical for understanding of the magnetic coupling mechanism. Indeed some of the oxides can be transformed into a ferromagnetic or ferrimagnetic or even antiferromagnetic state by varying the oxygen stoichiometry.[5]

Here we report on a detailed study of the oxidation of Fe(110) performed with a combination of surface sensitive (LEED) and rather bulk sensitive x-ray absorption spectroscopy (XAS) with magnetic circular dichroism (MCD) techniques. The XAS spectra (at both the Fe $L_{2,3}$ and the O K edges) display a characteristic multiplet structure[6,7] which reflects the ionic state. The MCD spectra instead uniquely provide the element-specific magnetic information.[8] Thus XAS with MCD measurements is a powerful tool to determine the ionic state and the magnetic information. Furthermore, this technique has a comparable probing depth to the typical thickness of oxidized Fe, and thus provides information on the whole oxide layer.

The XAS and MCD results unambiguously identify the magnetic oxide overlayer as Fe_3O_4. In the second oxidation stage, the entire oxide overlayer is (ferrimagnetic) Fe_3O_4—not only its surface layer, as previously proposed.[4] The whole Fe_3O_4 overlayer is coupled antiferromagnetically to the underlying Fe substrate. Therefore, the magnetic coupling must be interpreted as a direct coupling at the interface, rather than a new type of indirect magnetic coupling through a nonmagnetic insulating spacer.

The experiments have been performed at the renewed U4B circular-polarized beamline at the National Synchrotron Light Source located at the Brookhaven National Laboratory. The base pressure in the measurement chamber was about 1×10^{-10} Torr. Thick Fe(110) films [>100 monolayers and therefore well representative of Fe(110) single crystal] have been obtained by epitaxial growth on a W(110) substrate.



(a) clean Fe
E_p = 60 eV

(b) 300 L oxidation
E_p = 72 eV

(c) 600 L oxidation
E_p = 72 eV

FIG. 1. LEED patterns during the oxidation of the Fe(110) surface.

The Fe films have been prepared by e-beam evaporation at room temperature, followed by 1 min annealing to about 400 °C. All the oxygen doses have been done at $p_{[O_2]}=5\times10^{-7}$ Torr with the sample annealed to 250 °C. The XAS spectra have been collected in the sample current mode. Sample current from a reference Fe was monitored simultaneously, and the photon energy uncertainty was minimized to be less than 20 meV. The MCD data were obtained by switching the sample magnetization at each photon energy relative to the fixed photon helicity. A 300 Oe pulse magnetic field, which is large enough to saturate the magnetization, was applied along the *in-plane* [001] magnetic easy axis of the thick Fe/W(110) film.[9] The photon helicity was set to be 85% at a 300 meV photon energy resolution, and the incident angle was off by 45° from the magnetization direction. The XAS spectra were normalized by the photon flux monitored with a gold mesh, and the experimental geometry and the degree of the helicity were taken into account for the MCD signal.

The LEED patterns corresponding to the different stages of the oxidation reaction are reported in Fig. 1. Figure 1(a) shows the (1×1) rectangular LEED pattern characteristic of the clean Fe(110) surface. After oxygen exposure to 300 L, the pattern is qualitatively modified. It is now hexagonal [Fig. 1(b)], indicating the formation of a (111) surface. By further exposing the system to additional 300 L of oxygen, the LEED undergoes a second transformation, marked by the appearance of half-order diffraction spots with respect to the primitive hexagonal lattice [Fig. 1(c)]. Further increase of the oxygen exposure (up to 1500 L) does not produce any appreciable modification of the LEED pattern.

As previously proposed,[10,4] the LEED patterns shown in Fig. 1 are consistent with the formation of an FeO(111) surface (first oxidation stage) followed by the formation of an Fe_3O_4(111) surface (second oxidation stage). However, due to the surface sensitivity, the LEED results cannot identify the oxidation state of the entire oxide layer. The question remains open if this second LEED pattern indicates a surface reconstruction of an underlying FeO(111) layer or rather the formation of a new oxide with a different stoichiometry. The XAS measurements, which are rather bulk sensitive and display spectroscopic fingerprints, provide a clear answer to this question.

Fe $L_{2,3}$-edge XAS and MCD spectra for this second oxidation stage of the Fe(110) are shown in Fig. 2. At 1500 L, the highest O_2 exposure examined in this work, the absorption spectrum (top, solid line) is dominated by the thick oxide overlayer. Yet the contribution from the underlying Fe substrate is considerable (top, dotted line), indicating that the measurement covers the entire oxide layer.

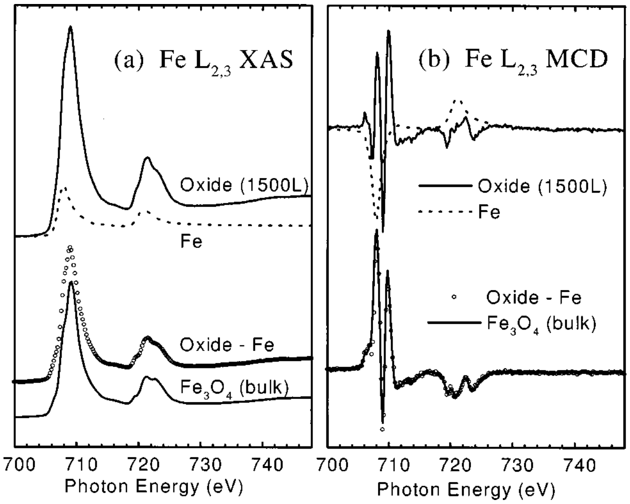


FIG. 2. (a) Fe $L_{2,3}$ XAS from 1500 L oxygen exposed Fe film (top, solid line) and from Fe metal (top, dotted line). The Fe-subtracted spectrum (bottom, open circles) is compared to the bulk Fe_3O_4 one (bottom, solid line). (b) Same as (a) for MCD curves. For convenience of comparison, the sign of the MCD of the Fe_3O_4 (bulk) has been inverted.

The spectra of the bare oxide layer are obtained by subtracting the Fe-metal contributions as estimated mainly from the MCD spectrum.[11] In the bottom of Figs. 2(a) and 2(b), these bare oxide spectra (circles) are directly compared to those of a bulk Fe_3O_4 sample (lines).[12] Even considering the small uncertainty in the estimation of the Fe-metal contribution, the agreement for both XAS and MCD spectra is apparently so good over the entire energy range that the oxidation state can be obviously identified as Fe_3O_4.

Indeed the Fe_3O_4 XAS exhibits a complicated line shape, and the MCD spectrum an even more complicated one. Fe_3O_4 is a mixed valent system with three different Fe sites, Fe^{3+} tetrahedral and octahedral sites and Fe^{2+} (octahedral) sites. Hence, the XAS and MCD spectra correspond to an overlap of three different sets of multiplet structures. At this high oxidation stage, the estimated MCD anisotropy of the oxide layer is as high as $80\pm5\%$ of the bulk Fe_3O_4. This result suggests that the ferrimagnetic Fe_3O_4 oxidation state is present nearly in the entire oxide layer. Indeed one has to consider that even if this oxide layer was pure Fe_3O_4, there still remain regions at the Fe-oxide/Fe interface and the oxide surface where departures from the ideal Fe_3O_4 stoichiometry are likely.

Furthermore, the sign of the MCD spectrum of the oxide layer is inverted with respect to that of the bulk Fe_3O_4 sample; i.e., it is coupled antiferromagnetically to the underlying Fe metal, whose magnetization direction is determined by the applied field direction. This implies that the energetics at the interface favors an antiparallel coupling between the two magnetic layers.

The evolution of the oxidation reaction is shown in Fig. 3 and Fig. 4. The XAS and MCD spectra are presented as measured (left panels, solid lines) and after subtraction of the Fe-metal contributions (right panels, open circles). Clearly the Fe-metal contribution decreases with oxygen exposure, showing that the thickness of the oxide layer continuously increases up to 1500 L.[13]

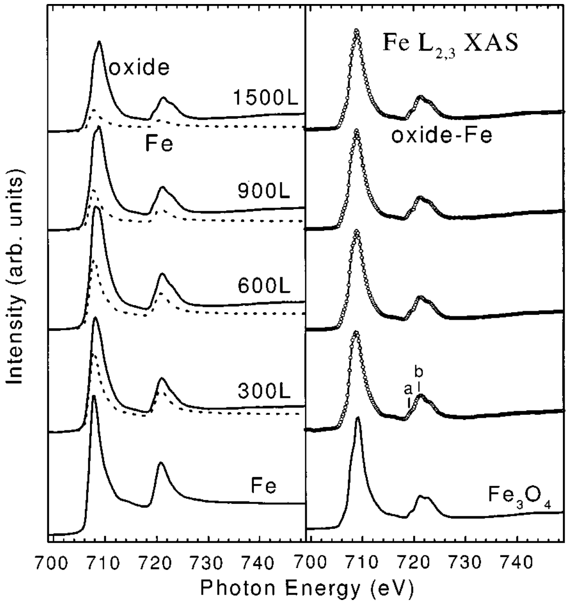


FIG. 3. Left: Fe $L_{2,3}$ XAS spectra as a function of the oxygen exposures (solid lines) and corresponding estimated metallic Fe contributions (dotted lines). Right: Fe-subtracted spectra. The spectrum from a bulk Fe_3O_4 sample is also reported for comparison (bottom spectra, solid line).

Up to about 300 L (first oxidation stage), the XAS spectrum displays a line shape corresponding to something in between FeO and Fe_3O_4, indicating that, at this stage, the oxide layer is a mixture of these oxides. For example, the intensity of feature *a* is ~35% intensity of feature *b* (see Fig. 3), while FeO exhibits about 52% intensity,[14] and in Fe_3O_4, the feature *a* is 26% intensity of the feature *b*. At this first stage, the MCD spectrum is dominated by the Fe MCD, and the contribution of the oxide layer is negligible. Thus, in agreement with the results of Ref. 4, we conclude that the oxide overlayer is nonmagnetic at this stage. The small residual MCD signal is probably induced from the interface, where the Fe metal is expected to contribute a different MCD spectrum.

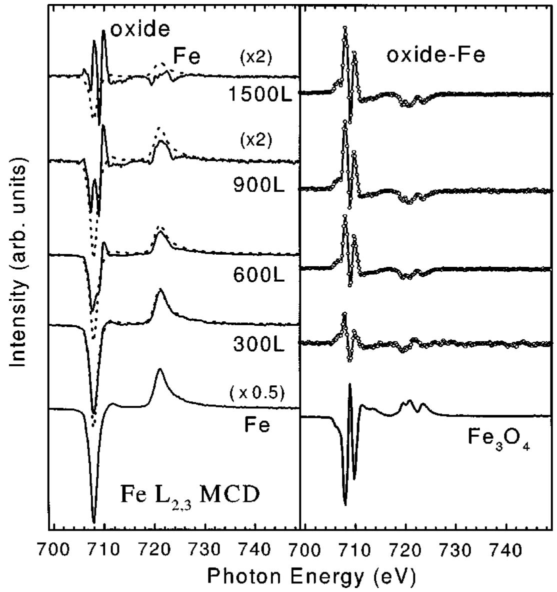


FIG. 4. Same as Fig. 3 for MCD curves.

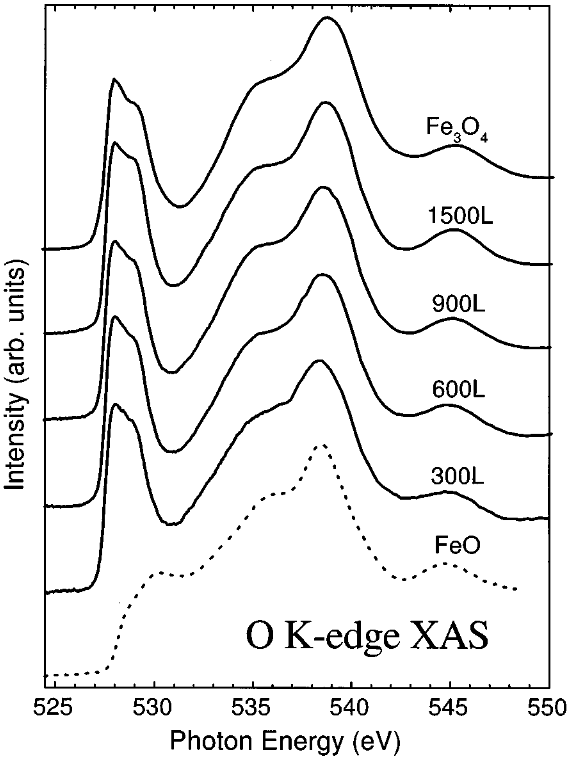


FIG. 5. O *K*-edge XAS spectra during the oxidation reaction of the Fe(110) surface. For comparison the XAS spectra from the Fe_3O_4 (top) and FeO (bottom) are also shown.

At the second oxidation stage (above 600 L), the extracted XAS and MCD spectra of the Fe-oxide layer are instead very comparable to those of Fe_3O_4. One may notice that there are some disagreements, especially in the MCD spectrum. Possibly, at 600 L the thickness of the oxide layer is still small such that the contributions at the interface and/or surface are important. However, the relative contributions from the interface/surface diminishes at higher oxygen exposures. At 900 L and 1500 L, the XAS and MCD spectra of the oxide layer are nominally identical to those of Fe_3O_4. The continuous evolution of the XAS/MCD spectra as a function of oxygen exposure clearly indicates that during the second stage the entire oxide layer transforms into a ferrimagnetic Fe_3O_4. Indeed the Fe_3O_4 layer grows up at each O_2 exposure.[15]

A similar behavior is also observed in the O *K*-edge XAS measurements. In Fig. 5 these spectra are presented in comparison with those from pure Fe_3O_4 and FeO (top and bottom, respectively). The spectra are normalized to the same intensity at the high-photon-energy side. All the spectra in the second oxidation stage (600 L, 900 L, and 1500 L) are very similar to that of Fe_3O_4, while the 300 L spectrum is again more like something between those of Fe_3O_4 and FeO.

In conclusion, we have shown that a magnetically (antiparallel) coupled $Fe_3O_4(111)/Fe(110)$ bilayer is obtained by *in situ* oxidation of Fe(110). Only the initial stage (up to about 300 L) contains appreciable amounts of FeO. At higher oxygen exposures (600, 900 L), the oxide overlayer is gradually converted into ferrimagnetic $Fe_3O_4(111)$. Further increase of the oxygen exposure only results in the formation of a thicker $Fe_3O_4(111)$ overlayer. The observed antiparallel magnetic coupling therefore originates from the direct contact of the two magnetic materials: Fe metal and $Fe_3O_4(111)$ overlayer. It appears that the energetics of the Fe(110)/Fe_3O_4 interface favors an antiparallel coupling between the two magnetic layers.

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[5] For example, there are three stable Fe oxides in normal conditions with different oxidation states FeO, Fe_3O_4, α-Fe_2O_3 and different magnetic ordering, antiferromagnetic FeO and ferrimagnetic the other two.

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

[10] A. Barbieri *et al.*, Surf. Sci. **302**, 259 (1994).

[11] The MCD spectrum can be decomposed only to Fe-metal and Fe_3O_4 contributions; any residual FeO does not contribute to this magnetic spectrum.

[12] The spectrum from the bulk Fe_3O_4 has been taken in a separate run with the same experimental apparatus and in the same experimental conditions.

[13] The thickness of the oxide layer cannot be quantitatively obtained from the XAS data. A qualitative estimate (within approximately a factor of 2) can be done assuming that the total yield spectra are dominated by the secondary emission and applying to the Fe contribution the formula: $I = I_0 \times e^{-x/\lambda}$. Assuming $\lambda = \lambda(4\ \mathrm{eV}) = 35$ Å, one obtains an oxide thickness x of 17, 31, 41, 68 Å for the 300, 600, 900, 1500 L oxygen exposures, respectively.

[14] J.-H. Park, Ph.D. thesis, University of Michigan, 1994.

[15] A quantitative estimate of the amount of Fe_3O_4 present in the system can be obtained under the ideal hypothesis that the oxide layer is a mixture of pure FeO and Fe_3O_4. In this case one can derive the relative ratio between Fe metal and Fe_3O_4 from the MCD signal (Ref. 11). Using the ratio between MCD and XAS signals in pure Fe and Fe_3O_4 bulk samples, one can then reconstruct the XAS spectra as a combination of Fe metal and the Fe_3O_4 components of the oxide layer. Comparing these spectra with the measured ones, one can estimate the relative amount of Fe_3O_4 and FeO present in the oxide layer at the various oxidation stages. We find that the Fe_3O_4 contribution accounts for 28%, 58%, 75%, 80% of the oxide signal for the 300, 600, 900, 1500 L oxygen exposures, respectively.