# Magnetic Structure of Oxidized Fe(001)

B. Sinković,[a] P. D. Johnson, and N. B. Brookes
*Physics Department, Brookhaven National Laboratory, Upton, New York 11973*

A. Clarke and N. V. Smith
*AT&T Bell Laboratories, Murray Hill, New Jersey 07974*
(Received 4 May 1990)

The combination of spin-polarization detection with core-level photoemission to give spin-polarized electron spectroscopy for chemical analysis provides new information on the oxidation of an iron surface. During the initial stage of oxidation the predominant phase is of a ferrimagnetic $\gamma$-$Fe_2O_3$ form. An observed antiferromagnetic coupling of this oxide with the iron substrate is attributed to a superexchange interaction, providing evidence for a possible site-exchange mechanism during the initial oxidation. Annealing transforms this oxide into an antiferromagnetic $Fe_xO$ form which is also present at the initial stage.

PACS numbers: 75.25.+z, 75.50.Rr

Studies of the magnetic properties of surfaces and thin films with techniques involving spin-polarized electrons are becoming increasingly commonplace.[1,2] In particular, spin-polarized photoemission has been widely used to study the electronic structure of ferromagnetic materials[3] and their interaction with impurity atoms.[4] We describe here studies of the progressive oxidation of an iron surface using spin-polarized core-level photoemission spectroscopy. There have been a number of earlier studies of this oxidation[5-7] but no measurement of the magnetic properties. Iron exists in a number of different oxide forms. FeO and $\alpha$-$Fe_2O_3$ are antiferromagnetic, and $\gamma$-$Fe_2O_3$ and $Fe_3O_4$ are ferrimagnetic, the magnetization in the latter being determined by the distribution of iron ions between the octahedral and tetrahedral sites. Thus, in $\gamma$-$Fe_2O_3$ the net magnetization reflects the $Fe^{3+}$ ions in the octahedral sites; in $Fe_3O_4$ the magnetization reflects the $Fe^{2+}$ ions in the octahedral sites. An electron energy-loss spectroscopy[6] (EELS) study of the oxidation of an iron surface indicated the possibility of a distinct oxide phase following chemisorption and preceding the final oxide formation. It was proposed that the phase represented a two-dimensional oxide formed by oxygen incorporation into the Fe lattice. However, its exact composition, structure, and magnetic properties were unknown. By combining spin-polarization analysis with the chemical specificity of core-level photoemission we develop a new probe, spin-polarized electron spectroscopy for chemical analysis (or SPESCA), and demonstrate its capability for the study of magnetic compound formation. Two oxidation states are again clearly resolved and show interesting changes in spin polarization as we proceed from the initial adsorption to the beginning of true oxidation. Within the initial oxidation, the experiment reveals evidence for a ferromagnetic or ferrimagnetic oxide, which couples antiferromagnetically to the iron substrate. Annealing the surface leads to the formation of an oxide showing a smaller core-level shift and a loss of polarization. The latter observation suggests that the final oxidation state is either paramagnetic or antiferromagnetic.

The experiments were carried out on a system that has been described extensively elsewhere.[8] Briefly, photons are provided by the UV undulator installed on the vacuum-ultraviolet ring at the National Synchrotron Light Source. The photoemitted electrons are detected by a hemispherical analyzer equipped with a low-energy spin detector, the latter described in more detail elsewhere.[9] Following cycles of argon-ion bombardment and annealing to produce a clean sample, the oxidation studies were performed by exposing the sample to oxygen and then subsequent annealing. Low-energy electron diffraction and Auger electron spectroscopy were provided to monitor the crystal order and surface cleanliness, respectively. All the photoelectron spectra shown here were recorded using photons of 90-eV energy.

We have first repeated an earlier spin-polarized photoemission study of the iron $3p$ core level.[10] Core-level photoemission reflects the local environment and as such the spin-polarized variety will reflect the local magnetic environment. Figure 1(a) shows the spin-resolved spectra obtained from the clean surface; Fig. 1(b) shows the same spectra after background subtraction. The spin polarization in the core level is $-23\%$. In contrast to the earlier study, we find evidence of an exchange splitting of 0.5 eV. The relative intensity of the two spin components, with the more intense minority peak at lower binding energy, is similar to that obtained in the earlier study and is consistent with naive multiplicity arguments for the respective final states $^5P$ and $^7P$.[11-13] The observation of the $^7P$-like final state at lower binding energy than the $^5P$ state is also consistent with a simple atomic picture. Thus the relative intensities and binding energies reflect the spin-dependent interaction of the final-

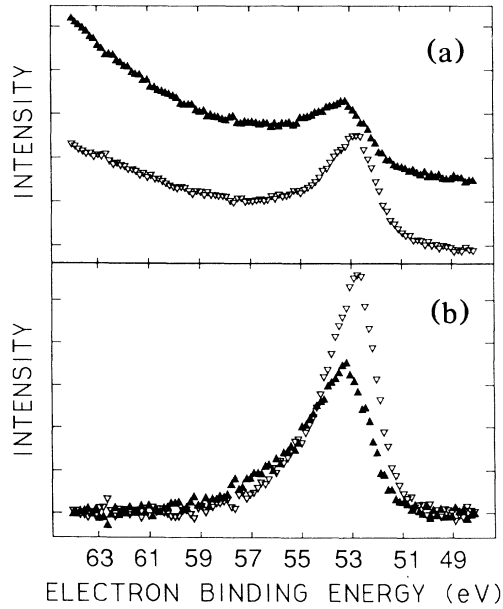


FIG. 1. (a) Spin-resolved Fe $3p$ photoemission spectra recorded from clean Fe(001) with 90-eV photons. In all figures, upward triangles indicate majority spin, downward triangles indicate minority spin. (b) The same as in (a) but with the background subtracted.

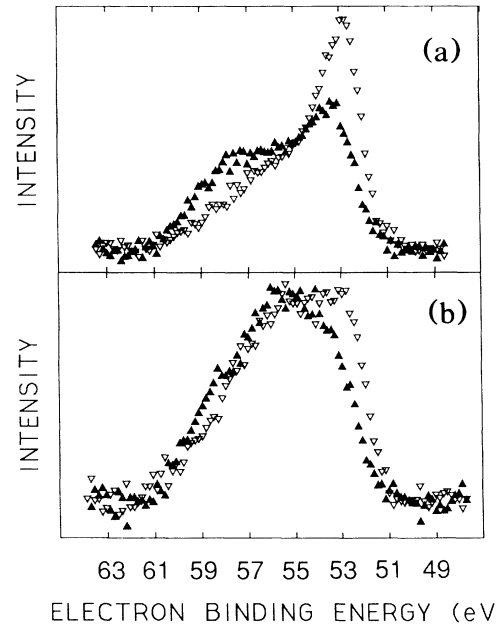


FIG. 2. (a) Spin-resolved Fe $3p$ spectra, $h\nu = 90$ eV, of the initial oxidation of Fe(001) after exposure to 16 L of $O_2$ with the background subtracted [1 L (langmuir) $= 10^{-6}$ Torr sec]. (b) The same as in (a) but after annealing to 650 °C.

state core hole with the net spin of the valence electrons. The two spin components show a similar line shape after background subtraction; they have a Doniach-Sunjić form[14] similar to that of the spin-integrated spectrum.

Initial exposure to oxygen produces a chemisorbed phase with no change in the Fe $3p$ spin-integrated spectrum. The spin analysis also shows no change in the polarization of the core level as compared to the clean metal. Such an observation indicates that the oxygen does not affect the magnetic properties of the surface layer and is consistent with our earlier study[4] of the valence bands for this system.

Further exposure to oxygen leads to the formation of an oxide layer as evidenced by a chemically shifted core level. The spin-resolved photoemission spectra from this system, after background subtraction, are shown in Fig. 2(a). There are two important observations that can be made; first, the oxide component of the $3p$ spectra has a net polarization, and second, the polarization is of the opposite sign (positive) to that of the substrate metal, which remains negative. Thus the new oxide phase clearly possesses a net magnetic moment, which, because of the reversed spin, couples antiferromagnetically to the iron substrate below. The spin-resolved components of this oxide phase can be seen more clearly when they are compared with equivalent spectra from the clean surface, as presented in Fig. 3. These spectra highlight the new peak in the majority component, shifted from the clean-surface peak by 4.5 eV. The minority component, on the other hand, shows a less well-resolved peak shifted approximately 3.5 eV from the equivalent clean-surface spectrum. It should be noted that the relative binding energy of these two components is reversed from that observed for the clean surface. As discussed earlier the

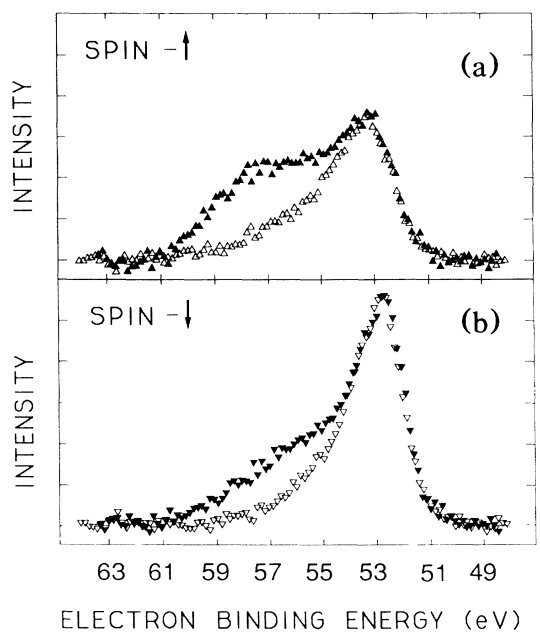


FIG. 3. (a) Majority-spin Fe $3p$ spectra, $h\nu = 90$ eV, from clean Fe(001) and after exposure to 16 L of $O_2$. (b) The same as in (a) but for minority-spin electrons.

atomic picture of multiplet states predicts the lower-binding-energy peak to have the strongest spectral weight, regardless of the orientation of the magnetic moment. Therefore the observation of the stronger of the two oxide-induced peaks being at higher binding energy cannot be interpreted as an exchange splitting but more likely indicates the presence of two different chemical states of iron in the initial oxide phase. This possibility is supported by the spectral width of the oxide component ($\sim$4.7 eV) which is much larger than the equivalent width in oxides containing only one oxidation state ($\leq$ 3.0 eV) and very similar to the width in an oxide with two oxidation states ($\sim$4.5 eV).[15]

In order to highlight the changes in the present Fe $3p$ spectra as a result of oxidation we show in Fig. 4(a) spin-resolved difference spectra. These are obtained from Fig. 2(a) by subtracting the clean-surface spectra of Fig. 1(b) to show the contribution from the initial oxide only. The binding energies of the substrate iron $Fe^0$ as well as the chemically shifted[16] $Fe^{2+}$ and $Fe^{3+}$ are indicated. It is evident from Fig. 4(a) that the majority-spin spectrum of the oxide shows the presence of predominantly $Fe^{3+}$ with some contribution from $Fe^{2+}$. The minority spin, on the contrary, indicates the presence of predominantly $Fe^{2+}$ and a small contribution from $Fe^{3+}$ ions. The relative intensity of the majority and minority components is such that there is no net polarization in the $Fe^{2+}$, and a substantial positive polarization in the $Fe^{3+}$ component of the oxide. There is no majority or minority intensity at the position of the iron metal, which, in these difference spectra, indicates that the magnetization of the iron substrate after the oxidation stays the same.

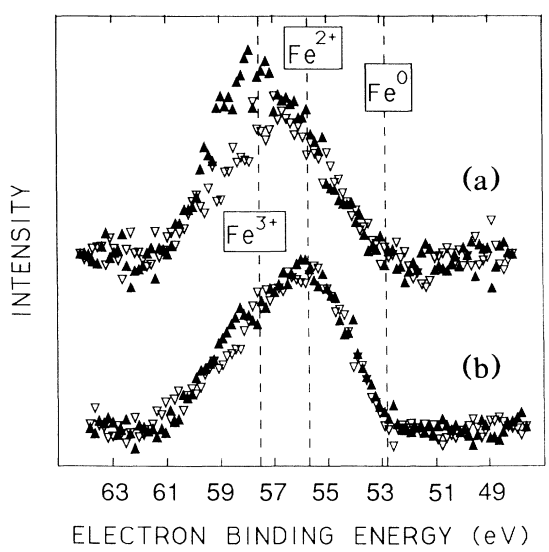


FIG. 4. Spin-resolved spectra of Fe $3p$ oxide component obtained by subtracting the clean-surface spectrum for (a) exposure of the surface to 16 L of $O_2$, and (b) the same as in (a) after subsequent annealing to 650 °C.

In Fig. 2(b) we show the spin-resolved spectra obtained from the oxygen-exposed surface after annealing to 650 °C. The spectra still show the presence of emission from the substrate core level, but they are now dominated by an unpolarized component shifted approximately 3.0 eV from the clean-surface core level. The lack of polarization in this new feature may be taken as evidence of either a paramagnetic or antiferromagnetic phase. The oxide contribution is highlighted in the difference spectra shown in Fig. 4(b). It is evident from this figure that the main contribution to the annealed oxide phase comes in $Fe^{2+}$ form with only a small $Fe^{3+}$ component.

The spin analysis in the present study provides important new information on the chemically shifted components and hence the oxide formation. For the initial oxide the $Fe^{3+}$ shows a net polarization whereas the $Fe^{2+}$ component shows no polarization. The opposite order of polarization would be expected for $Fe_3O_4$ since as discussed earlier the $Fe^{2+}$ octahedral sites carry the net moment.[17] Further, the presence of antiferromagnetic $\alpha$-$Fe_2O_3$ can also be ruled out on the basis that no polarization would be expected. Thus the polarization in the $Fe^{3+}$ component points to the presence of ions with the coordination appropriate to that found in ferrimagnetic $\gamma$-$Fe_2O_3$. $Fe^{3+}$ ions possess a high magnetic moment of $5\mu_B$. This should result in a large exchange-induced splitting for the multiplets in core-level photoemission with, as already noted, the dominant peak at lower binding energy being the minority-spin component on that site. This we believe is the component observed in the experiment, with no other exchange-split components being observed. This is probably a reflection of the relative intensities of the two components and, indeed, earlier spin-integrated Fe $3p$ photoemission spectra[18] of $Fe^{3+}$ ionic compounds have found that the $^5P$ final states at higher binding energy have much smaller spectral weight as compared to the $^7P$ component.

The initial oxide spectra shown in Fig. 4(a) contains in addition to the $Fe^{3+}$ peaks (reflecting $\gamma$-$Fe_2O_3$) a smaller unpolarized $Fe^{2+}$ component. This observation indicates the coexistence of an antiferromagnetic $Fe_xO$ phase. Following annealing, the spectra, shown in Fig. 4(b), indicate that the initial oxide converts almost completely to this $Fe_xO$ phase. This is supported by our observation of the unpolarized $Fe^{2+}$ component and is in agreement with the earlier EELS study.[6]

In summary, the polarization studies of the initial oxidation of Fe(001) indicate the presence of a mostly ferrimagnetic, $\gamma$-$Fe_2O_3$-like oxide with some contribution from an antiferromagnetic $Fe_xO$-like phase. However, this initial oxide represents only 1–2 atomic monolayers and it is therefore difficult to make direct comparison with the bulk iron oxides. It is more likely that the initial oxide in fact represents a unique oxide phase as was

suggested in the earlier EELS study.[6] This possibility is confirmed by our observation of an antiparallel alignment of the oxide and the metal substrate moments, an indication of strong coupling between the two. The most obvious way of inducing this antiferromagnetic coupling is a superexchange interaction between the outer $Fe^{3+}$ ions and the substrate atoms mediated by an oxygen ion between. Indeed such an interaction is responsible for the different magnetic structures found in the iron and other oxides.[19] Thus our observations are consistent with the suggestion that during the initial oxidation, following the chemisorption phase, there is a site reversal of an adsorbate oxygen atom with an underlying iron atom. Lanyon and Trapnell[20] proposed such a site exchange mechanism as the commencement of Mott-Cabrera-type[21] kinetics of the oxidation of iron. Our observation of antiparallel coupling between the oxide and substrate iron moments strongly supports this model.

In our study we have been able to characterize the magnetic properties of the unique iron oxide phase that follows the initial chemisorption stage by combining photoemission from core levels for chemical selectivity with spin analysis for probing the magnetic properties. In this way it proved possible to examine the magnetism of thin oxide layer as distinct from that of the metal substrate despite the fact that both involve the same element. Furthermore, we were able to differentiate between different phases of the oxides. Such a spin-polarized electron spectroscopy for chemical analysis should prove a useful tool for the examination of local magnetic properties.

This work was supported in part by U.S. Department of Energy Contract No. DE-AC02-76-CH00016 and National Science Foundation Materials Research Group Contract No. DMR-86-03304.

[a]Present address: Physics Department, New York University, 2 Washington Place, New York, NY 10003.

[1]*Polarized Electrons in Surface Physics,* edited by R. Feder (World Scientific, Singapore, 1985).

[2]J. Kirschner, *Polarized Electrons at Surfaces,* Springer Tracts in Modern Physics Vol. 106 (Springer-Verlag, Berlin, Heidelberg, 1985).

[3]E. Kisker, K. Schroder, W. Gudat, and M. Campagna, Phys. Rev. B **31**, 329 (1985).

[4]P. D. Johnson, A. Clarke, N. B. Brookes, S. L. Hulbert, B. Sinković, and N. V. Smith, Phys. Rev. Lett. **61**, 2257 (1988).

[5]C. R. Brundle, Surf. Sci. **66**, 581 (1977).

[6]Y. Sakisaka, T. Miyano, and M. Onchi, Phys. Rev. B **30**, 6849 (1984).

[7]R. Allenpach, M. Taborelli, and M. Landolt, Phys. Rev. Lett. **55**, 2599 (1985).

[8]P. D. Johnson, S. L. Hulbert, R. Klaffky, N. B. Brookes, A. Clarke, B. Sinković, and M. Kelly (to be published).

[9]J. Unguris, D. T. Pierce, and R. J. Cellota, Rev. Sci. Instrum. **57**, 1314 (1986).

[10]C. Carbone and E. Kisker, Solid State Commun. **65**, 1107 (1988).

[11]C. S. Fadley, D. A. Shirley, A. J. Freeman, P. S. Bagus, and J. V. Mallow, Phys. Rev. Lett. **23**, 1397 (1969).

[12]T. Yamaguchi, S. Shibuya, and S. Sugano, J. Phys. C **15**, 2625 (1982).

[13]G. M. Rothberg, J. Magn. Mater. **15–18**, 323 (1980).

[14]S. Doniach and M. Sunjić, J. Phys. C **3**, 285 (1970).

[15]N. S. McIntyre and D. G. Zetatuk, Anal. Chem. **49**, 1521 (1977).

[16]C. R. Brundle, T. J. Chuang, and K. Wandelt, Surf. Sci. **68**, 459 (1977).

[17]E.g., C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976).

[18]S. P. Kowalczyk, Ph.D. thesis, University of California, Berkely, Report No. LBL-4319, 1976 (unpublished).

[19]J. B. Goodenough, in *Progress in Solid State Chemistry,* edited by H. Reiss (Pergamon, New York, 1972).

[20]M. A. Lanyon and B. M. Trapnell, Proc. Roy. Soc. London A **277**, 3875 (1955).

[21]N. Cabrera and N. F. Mott, Rep. Prog. Phys. **12**, 163 (1948).