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Spin-resolved photoemission investigation of the $c(2\times2)$ and $c(3\times1)$ oxygen overlayers on the Fe(110) surface

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The oxygen adsorption on the Fe(110) surface has been studied by spin- and angular-resolved photoemission and low-energy electron diffraction techniques. At very low coverage, oxygen adsorbs in a sequence of well-defined ordered structures: a $c(2\times2)$ followed by a $c(3\times1)$. For the $c(2\times2)$ overlayer the oxygen bands show hardly any dispersion along the $[1\overline{1}0]$ direction of the surface Brillouin zone. A slightly larger dispersion is instead detected for the $c(3\times1)$ overlayer. In both cases, the two-dimensional models for the oxygen $2p$-derived bands do not seem to be appropriate. The spin-resolved data suggest a considerable interaction with the Fe substrate. A relatively large exchange splitting ($\Delta_{\mathrm{ex}}=0.3$ eV) is induced on the oxygen $2p$ bands, indicating a local magnetic moment on the oxygen sites. The considerably different line shape of the O $2p$ emission in the two spin channels is also an indication of strong interaction of the oxygen adatoms with the spin-dependent electronic structure of the ferromagnetic substrate. [S0163-1829(98)05444-7]

I. INTRODUCTION

The study of adsorbed atoms on solid surfaces has been one of the traditional applications of angle-resolved photoemission.[1] These studies have been particularly focused on single crystalline surfaces onto which the adsorbed species form well-defined, ordered (super)structures. From the fundamental point of view, these cases are interesting because they are good candidates to analyze the electronic structure of two-dimensional (2D) systems. Furthermore, these studies provide valuable information on the surface chemical bonds, which in turn are the starting point for important subjects such as catalysis and corrosion.

Particularly interesting is to analyze these ordered overlayers when the adsorption of the atomic species takes place on a ferromagnetic surface. In all those cases the situation is complicated because the spin-split electronic structure of the substrate introduces spin-polarized boundary conditions for the interaction. One can then address issues such as the magnetic coupling between the adsorbed atoms and the substrate, the quenching of the surface magnetization on the substrate or, quite the opposite, the induced magnetization on the adsorbed nonmagnetic species.

Here we briefly report on an investigation of oxygen adsorbed on the Fe(110) surface. This system seems to be particularly appropriate for various reasons. It has been previously reported that, at low coverage, oxygen adsorbs in a series of well-defined ordered overlayers on the Fe(110) surface: first a $c(2\times2)$ at 0.25 ML followed by a $c(3\times1)$ at 0.33 ML.[2] Additionally, there exist already a few spin-resolved studies of oxygen adsorbed on various Fe surfaces[3,4] with which to compare photoemission data.

Our results show that for both oxygen overlayers—$c(2\times2)$ and $c(3\times1)$—the Fe-O interaction is dominant with respect to the O-O one. As a consequence, the 2D picture normally used for the electronic structure of these overlayers[2] is not appropriate. The picture of the electronic structure of these overlayers has to be replaced with a more complex model, which takes into account the strong spin-dependent hybridization with the polarized bands of the Fe substrate.

II. EXPERIMENT

The experiments have been performed at the U5UA undulator beamline at the National Synchrotron Light Source located at the Brookhaven National Laboratory.[5] The 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+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. The deposition of thick Fe films (>50 Å) have been performed via e-beam evaporation on the W(110) substrate kept at room temperature. The total pressure increased to about 2×10^{-10} torr during film depositions. After a short postannealing of 1 min to about 500 °C, the Fe films exhibit a sharp (1×1) low-energy electron diffraction (LEED) pattern. The spin-resolved measurements have been done in magnetic remanence with the sample magnetized along the [001] axes, which correspond to the easy axes for these thick Fe films.[6] The oxygen exposures have been performed with the sample kept at room temperature and without additional postannealing, in order to avoid oxide formation.

III. DISCUSSION

The photoemission spectra (left column) for the clean Fe surface (bottom) and for the two oxygen overlayers [$c(2\times2)$, middle; $c(3\times1)$, top] are reported in Fig. 1. The corresponding LEED patterns are shown on the right side. In the case of the $c(3\times1)$ overlayer, the superstructure spots are considerably broader than in the $c(2\times2)$ case. Furthermore, they sometimes appear to be split, possibly indicating microscopic faceting.[7]

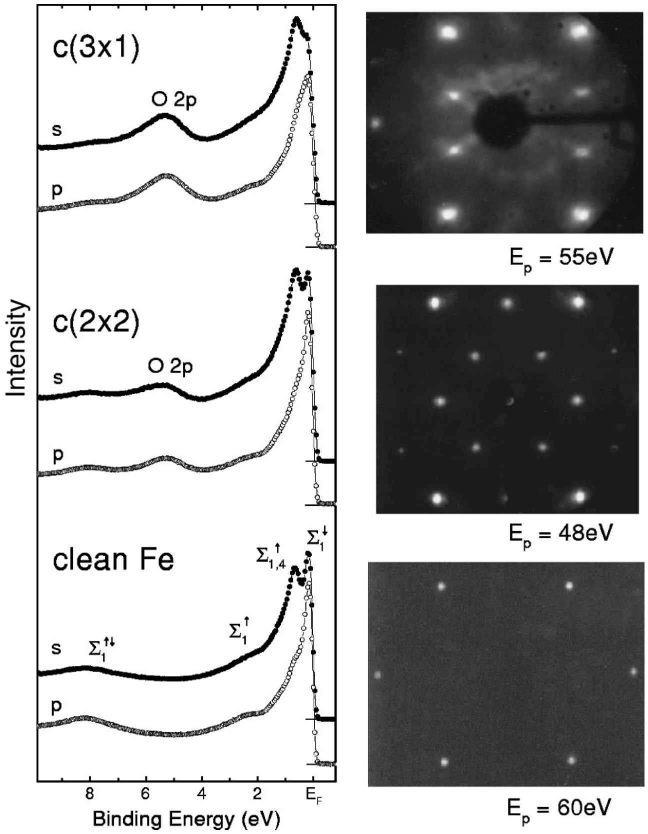

FIG. 1. Left column, comparison of the valence-band photoemission spectra taken in normal emission at 40 eV photon energy with p light ($\theta_i = 56°$) and with s light ($\theta_i = 35°$). Bottom panel, clean Fe(110) surface; middle panel, O $c(2\times2)$ overlayer, 3 L oxygen exposure; top panel, O $c(3\times1)$ overlayer, 6 L oxygen exposure. Right column, LEED patterns corresponding to the photoemission spectra shown on the left side.

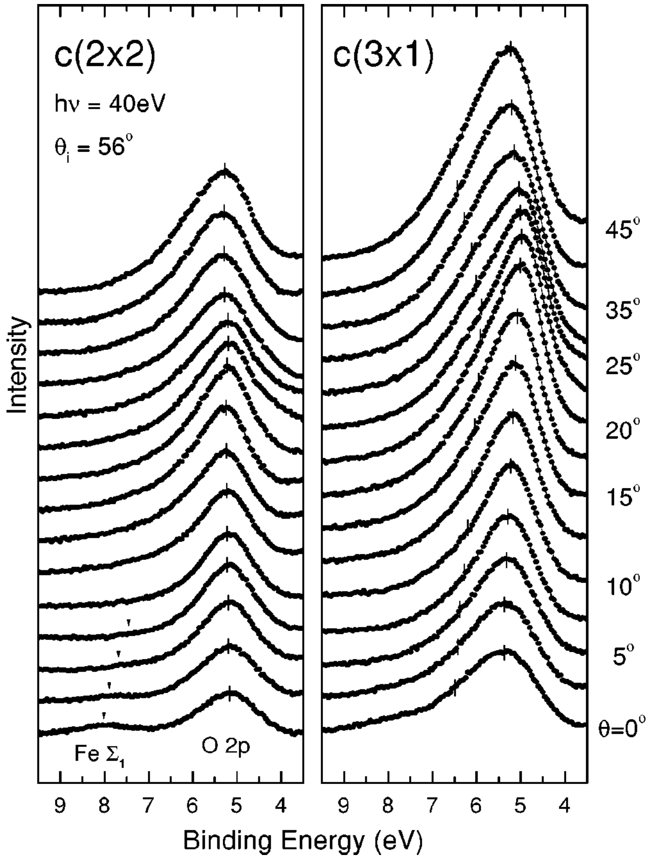

FIG. 2. Comparison of the angular dependence of the oxygen $2p$ peak along the $[1\bar{1}0]$ direction for the two oxygen overlayer on the Fe(110) surface: $c(2\times2)$, left ($\bar{N}' = 16°$); $c(3\times1)$, right ($\bar{H}'' = 20.5°$). The photon energy is 40 eV.

The photoemission spectra in Fig. 1 are taken at 40 eV photon energy in normal emission. In these conditions, the emission originates from states close to the Γ point of the Fe Brillouin zone. In all three cases, a comparison is shown between spectra taken with p light ($\theta_i = 56°$) and with s light ($\theta_i = 35°$). For the clean Fe surface, with perfectly s-polarized light ($\mathbf{A}\|[1\bar{1}0]$), the allowed initial states are of Σ_4 symmetry; with perfectly p-polarized light ($\mathbf{A}\|[110]$), the allowed initial states are instead of Σ_1 symmetry.

A comparison with the Fe bulk band structure leads to the following interpretation of the Fe spectra (bottom panel). The peak at 0.15 eV binding energy—enhanced with p-polarized light—corresponds to the minority Σ_1 in proximity of the $\Gamma_{2,5}'^{\downarrow}$ point. The peak at 0.8 eV binding energy contains majority states of both Σ_1 and Σ_4 symmetry close to the $\Gamma_{1,2}^{\uparrow}$ point. The shoulder at about 2.5 eV instead represents the exchange-split majority counterpart of the peak close to E_F ($\Sigma_1, \Gamma_{2,5}'^{\uparrow}$). Finally, at about 8 eV the broad feature originates from the Σ_1 band at $\Gamma_1^{\uparrow\downarrow}$. The spin character of these Fe features has also been directly verified by spin-resolved photoemission.

Upon oxygen adsorption at room temperature (RT) two main changes occur in the spectra. First, the intensity of the peak near the Fermi level decreases, suggesting the presence in this emission of some surface-related feature, besides the bulk Σ_1 band already mentioned. Second, the oxygen $2p$ emission develops, with its typical feature located at about 6 eV binding energy. However, apart from the minor changes connected with the surface emission, the $3d$ bands of the Fe substrate do not change. This suggests that at these small oxygen exposures (<10 L) and at RT, the surface really consists of an oxygen overlayer adsorbed rather than an oxide surface layer.

It is worth noting that contrary to the Fe states, the oxygen $2p$ states do not show any appreciable dependence with the light polarization. Indeed, at all coverages, the oxygen $2p$ peaks are practically identical with the two different s- and p-light polarizations. This fact is important because it already suggests that the dominant interaction in this case is the Fe-O rather than the O-O one. In the presence of a dominant O-O bond (a good 2D overlayer), one would expect a strong polarization dependence of the oxygen states. The in-plane $2p_y$ states being enhanced with s light ($\mathbf{A}$ oscillating in the surface plane) and the out-of-plane $2p_z$ enhanced with p-polarized light ($\mathbf{A}$ oscillating perpendicular to the surface plane).

In Fig. 2, the angular dependence of the oxygen $2p$ bands is shown along the $\bar{\Gamma}$-$\bar{N}'$ and the $\bar{\Gamma}$-$\bar{H}''$ for the $c(2\times2)$ and $c(3\times1)$ overlayer, respectively. In the case of the $c(2\times2)$ overlayer, the oxygen $2p$ emission is a relatively broad peak

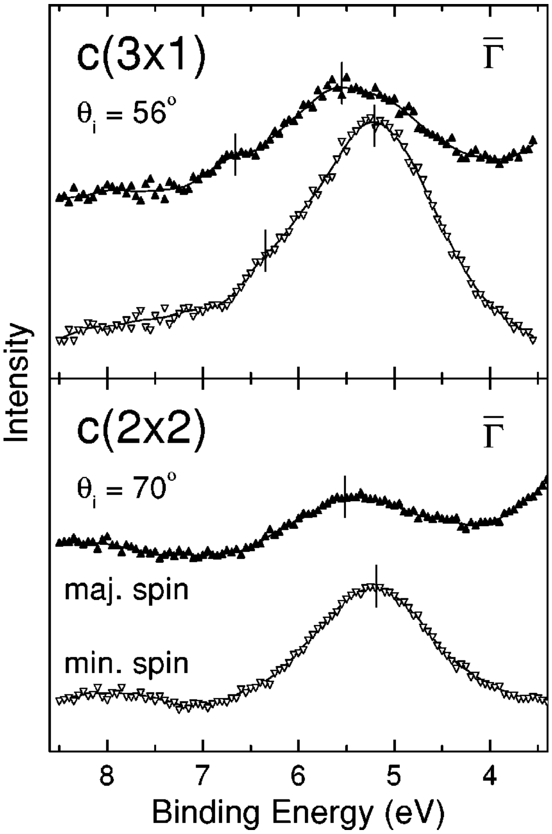

FIG. 3. Spin-resolved photoemission spectra of the oxygen $2p$ states at $\bar{\Gamma}$ for the two oxygen reconstructions on the Fe(110) surface: $c(2\times2)$, bottom; $c(3\times1)$, top. The photon energy is 40 eV. Notice that the high polarization results from the secondary background of the Fe substrate.

centered at about 5.3 eV binding energy and slightly asymmetric towards the high-binding energy side. This feature does not show any appreciable dispersion with the emission angle. Upon further oxygen adsorption, the O $2p$ emission grows in intensity. In the $c(3\times1)$ overlayer, a small angular dispersion is detectable. Furthermore, the O $2p$ peak is now considerably broader, suggesting the presence of more than one component, which, however, cannot be clearly resolved because of the large overlap. Indeed, two peaks separated by approximately 1 eV at $\bar{\Gamma}$ move closer and eventually reach a minimum separation at the $\bar{H}''$ zone boundary (see tick marks in Fig. 2).

The very weak angular dispersion of the oxygen $2p$ bands is well understood when one considers the large O-O nearest distance in both overlayers: 5.1 Å in the $c(2\times2)$ and 4.1 Å in the $c(3\times1)$. These distances are too large compared to the oxygen covalent diameter (1.5 Å) to allow any direct overlap. For this reason the small dispersion seen on the $c(3\times1)$ has to be attributed to indirect oxygen interaction via the Fe substrate.

More insight in the O $2p$ states is gained with the spin-resolved measurements. The normal-emission spin-resolved spectra in the region of the oxygen $2p$ states are shown in Fig. 3 for both the $c(2\times2)$ and the $c(3\times1)$ overlayers (filled up triangles, majority; empty down triangles, minority). In the case of the $c(2\times2)$ overlayer the spin analysis reveals that the broad oxygen $2p$ peak in the spin-summed spectra is actually the composition of the two spin components, exchange split by about 0.3 eV. Notice that the origin of the asymmetric line shape of the O $2p$ emission in the $c(2\times2)$ spectra of Fig. 2 is the difference in intensity in the two spin channels and not the existence of more than one component under this feature. In the case of the $c(3\times1)$ superstructure the situation is more complex. The asymmetric shape remains also in the spin-resolved spectra. Indeed the data at $\bar{\Gamma}$ suggest the presence of two peaks—both exchange split ($\Delta_{\mathrm{ex}}=0.3$ eV)—separated by about 1.2 eV. The widening of the emission indicates that the formation of the O $2p$ bands starts at this stage.

An interesting feature in these spin-resolved spectra is the different line shape for majority and minority states: the minority peak is much more pronounced than the corresponding majority. This is an additional proof of the strong O-Fe interaction. Indeed, we interpret this different line shape as a direct result of the spin-polarized interaction with the ferromagnetic substrate. The precise mechanism of this interaction cannot be deduced in the absence of theoretical calculation. However, the proximity of the O $2p$ bands with the high *sp* partial density of states corresponding to the upper extreme of the Fe majority Σ_1 band (5 eV binding energy, at N point in the Fe-bulk band structure), suggests a stronger interaction of the majority O $2p$ with the Fe states. As a consequence, the O $2p$ majority states will tend to be more distributed in energy and possibly also further inside the film layer, while their minority counterpart will remain more sharp and closely localized on the surface layer. This mechanism would indeed result in sharper and more intense minority peaks compared to its majority counterparts.

As already mentioned, there exist a few previous studies of oxygen adsorption on the Fe surface. All these studies interpret the experimental data using the electronic structure calculation for a 2D oxygen overlayer as a starting point. The experimental foundation of this approach lies in the distinction, via light polarization, of the $p_{x,y}$ and the p_z states. This approach has also been applied to the O/Fe(110) system,[2] where a good agreement with a 2D model has been claimed for the $c(3\times1)$ oxygen overlayer. Our data do not support this view. On one side we do not find the light-polarization dependence—which is the crucial test to identify the experimental peaks with the $p_{x,y}$ and p_z states of the 2D oxygen overlayer—even though we clearly distinguish the symmetry of the Fe states. Furthermore, in the $c(2\times2)$ overlayer our data clearly show that the emission of the oxygen $2p$ states originate from a single band, although exchange split by the interaction with the substrate. And even in the $c(3\times1)$ the width of the oxygen $2p$ emission (about 1 eV at $\bar{\Gamma}$) is considerably smaller than previously reported (about 1.6 eV at $\bar{\Gamma}$).[8] Our spin-resolved data show that a careful mapping of the overlayer bands on a ferromagnetic substrate must consider the exchange splitting induced on the overlayer substrate.

The role of the hybridization with the ferromagnetic substrate bands has indeed been considered in spin-resolved measurements of adsorbate on ferromagnetic surfaces.[3,4,9–12] Particularly, there are detailed studies for the case of oxygen adsorbed on the Fe(100) surface.[10,11] In the case of the Fe(100) surface the oxygen adsorbs in a $p(1\times1)$ geometry and the O-O distance (2.8 Å) is then small enough to make it more favorable to the formation of direct oxygen bonds. In this case, experimentally one can indeed detect a clear dispersion of the oxygen $2p$ bands (about 1 eV for the p_x and about 2 eV for the p_y) and furthermore, it is possible to distinguish the symmetry of the various p bands. On this basis, the data have been interpreted in terms of the 2D model of the oxygen overlayer. In this case, however, one has to notice that the photoemission spectra of the valence band do show profound modification of the Fe $3d$ states, which would rather indicate the formation of some oxide on the surface more than the simple adsorption of an oxygen overlayer on it. This could well be the case when the Fe(100) substrate has been annealed to 550 °C after oxygen exposure.[3] Furthermore, this could also explain the anomalously high exchange splitting found for the p_z states (more than 1 eV at $\bar{\Gamma}$).

IV. CONCLUSION

In conclusion, we have studied the oxygen adsorption on the ferromagnetic Fe(110) surface. Increasing the gas exposures, two well-defined ordered oxygen overlayers form on the Fe(110) surface: a $c(2\times2)$ at about 3 L, followed by a $c(3\times1)$ at about 6 L. In both cases, the Fe-O interaction dominates with respect to the O-O one. Furthermore, no justification is provided by the data to interpret the results in terms of the 2D model of the oxygen overlayer. Quite the opposite, the spin-resolved data reveal a considerably more complex situation arising from the interaction of the O $2p$ states with the spin-polarized electronic structure of the ferromagnetic substrate.

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[1] E. W. Plummer and W. Eberhardt, in *Angle Resolved Photoemission as a Tool for the Study of Surfaces*, edited by I. Prigogine (Wiley, New York, 1982).

[2] Y. Sakisaka, T. Komeda, T. Miyano, M. Onchi, S. Masuda, Y. Harada, K. Yagi, and H. Kato, Surf. Sci. **164**, 220 (1985).

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

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

[5] E. Vescovo, G. Nintzel, D. Carlson, and S. L. Hulbert, Report No. BNL-52517 (unpublished).

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

[7] A. J. Pignocco and G. E. Pellisier, Surf. Sci. **7**, 261 (1967).

[8] A possible explanation of the difference between the new data and the old one of Ref. 2 is that their p_z emission can be due, at least partially, to the emission from the close Fe Σ_1 band.

[9] W. Schmitt, K.-P. Kaemper, and G. Guentherodt, Phys. Rev. B **36**, 3763 (1987).

[10] A. Clarke, N. B. Brookes, P. D. Johnson, M. Wienert, B. Sinkovic, and N. V. Smith, Phys. Rev. B **41**, 9659 (1990).

[11] R. L. Fink, G. A. Mulhollan, A. B. Andrews, J. L. Erskine, and G. K. Walters, Phys. Rev. B **45**, 9824 (1992).

[12] W. Clemens, E. Vescovo, C. Carbone, W. Eberhardt, O. Rader, and W. Gudat, Phys. Rev. B **46**, 4198 (1992).