

## Spin-resolved photoemission study of the clean and oxygen-covered Fe(110) surface

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The electronic structure of the Fe(110) surface is examined by means of spin- and angle-resolved photoelectron spectroscopy. A minority-spin surface state located at about 0.5 eV below  $E_F$  is identified midway along the  $\bar{\Gamma}-\bar{H}$  high-symmetry line of the surface Brillouin zone. The binding energy and dispersion of this state favorably compare with theoretical analysis of the Fe(110) surface electronic structure. Additionally the effects upon oxygen chemisorption are investigated. The hybridization with the Fe(110) substrate is found to induce a large exchange splitting (0.5 eV) on the O  $2p_x$  states.

Surfaces and thin films display a different magnetic behavior than bulk systems related at least partially to the modification of the electronic structure due to the lowered symmetry and coordination number at the surface. Indeed the study of the magnetic properties of surfaces is an area of great theoretical and experimental activity. The current capability of the modern *ab initio* numerical methods based on the local-spin-density-functional (LSD) theory permit one to predict in great detail the ground-state electronic structure of low-dimensional magnetic systems (i.e., surfaces and interfaces).<sup>1</sup> On the other side, the experiments are seldom able to examine exhaustively the electronic states localized at the surface. As a consequence, even macroscopic surface quantities, such as the resulting surface magnetization, are still essentially unknown. Furthermore, the information on the surface electronic structure and magnetism upon chemisorption is controversial, ranging from reported induced dead layers to magnetic order of the adatoms in the case of oxygen adsorption.

The aim of this work is to investigate the surface electronic structure in the case of an elemental ferromagnet and to follow its evolution upon chemisorption. To this purpose we have chosen the Fe(110) surface whose interaction with a low amount of oxygen is already known to proceed in a sequence of ordered overlayers and is therefore particularly convenient.<sup>2</sup>

The Fe(110) surface has already been investigated by means of angular-resolved photoemission.<sup>3,4</sup> Turner, Donoho, and Erskine<sup>4</sup> have shown that the photoemission spectra from Fe(110) could be interpreted in terms of bulk transitions, on the basis of single-particle ground-state electronic structure calculations. In contrast to the case of the Fe(100) surface, where prominent surface states have been observed,<sup>5</sup> up to now no surface-related features could be experimentally identified for the Fe(110) face.

In this paper we report on spin- and angle-resolved photoemission experiments. We are able to identify spin-polarized surface emission and its dispersion within

the two-dimensional Brillouin zone of the clean Fe(110) surface. The modification of these states for low oxygen exposures is also investigated. The magnetic ordering of oxygen adatoms can be directly probed with photoemission by measuring the O  $2p$  spin-resolved spectra. As will be shown below, the data for low oxygen exposure provide evidence for a strong magnetic interaction between oxygen adatoms and the Fe(110) surface.

The experimental setup consists of an ultrahigh-vacuum chamber (base pressure  $< 1 \times 10^{-10}$  mbar) equipped with the standard facilities for preparation and characterization of clean single-crystal surfaces, namely, a differentially pumped sputtering ion gun and a Low-Energy-Electron-Diffraction–Auger retarding field analyzer. The wiggler-undulator TGM5 beam line at the BESSY storage ring in Berlin provided the linearly polarized light used in these experiments. The spin- and angle-resolved photoemission spectra have been recorded by means of a  $90^\circ$  spherical energy analyzer coupled to a 100-kV Mott detector for the spin-polarization measurements. The geometry of the system is such that the (light) incidence and the (electron) emission direction always coincide. In normal emission the light polarization vector  $\mathbf{A}$  was oriented along the  $\langle 001 \rangle$  axis of the surface. The spin-resolved measurements have been performed in magnetic remanence after having applied a magnetic pulse along the in-plane  $\langle 1\bar{1}0 \rangle$  easy axis.

The clean Fe(110) surfaces were prepared *in situ* by means of *e*-beam evaporation on a W(110) substrate. After several hours of degassing, the Fe could be evaporated in a pressure below  $3 \times 10^{-10}$  mbar. The characterization of the growth mode of Fe/W(110) has already been reported in the literature by different groups.<sup>6</sup> The optimum degree of crystallographic order of the thick ( $> 20$  monolayers) epitaxial overlayers used in our experiments has been checked by means of low-energy electron diffraction (LEED). In agreement with previous studies we observed very sharp ( $1 \times 1$ ) LEED pattern. The surface cleanliness has been monitored by means of Auger spectroscopy and by valence-band photoemission. Oxy-

gen exposures were accomplished by admitting high-purity gas through a variable leak valve. Oxygen doses were determined from the ion-gauge reading without any additional correction for oxygen. Finally all the measurements have been performed at room temperature.

The interaction of oxygen with the Fe(110) surface has been the subject of a number of previous investigations.<sup>7</sup> It has been found that for low oxygen doses and at room temperature a series of well-ordered chemisorbed oxygen overlayers are formed: specifically a  $c(2 \times 2)$  LEED pattern is observed in the range 0.5–3 L and a more densely packed ordered overlayer [sometimes identified as a  $c(3 \times 1)$  or with a split  $c(3 \times 1)$ ] in the range 6–10 L. For higher exposures, corresponding to the onset of surface oxide formation, the LEED pattern becomes increasingly diffuse and eventually disappears for coverages higher than about 30 L. At a coverage of about 40 L a good (hexagonal) LEED pattern can be recovered after a flashing of the sample to  $T > 600^\circ\text{C}$  for a few seconds. The appearance of a hexagonal pattern together with the analysis of the Fe 3*p* core level shift suggested the formation of an FeO(111) thin overlayer at this stage.<sup>8</sup>

In Fig. 1, the development of the normal emission valence-band spectra ( $h\nu = 40$  eV) is shown during a sequence of oxygen exposures. Our data are in essential agreement with previous photoemission work on this system.<sup>9</sup> In our experimental conditions, the clean Fe spectrum is dominated by the 3*d* emission deriving from the

bulk  $\Sigma_3$  bands in the proximity of  $\Gamma$  through direct transitions into the bulk  $\Sigma_1$  states, which are allowed by the dipole selection rules, and from the high density-of-states region due to the majority-spin bulk band of  $\Sigma_4$  symmetry near the Fermi level (see also the spin-resolved spectra presented below). Accordingly, these features are only little affected by small oxygen doses and in the first oxygen steps shown in Fig. 1 the only significant change in the spectra is the appearance of an O 2*p* derived structure at about 6-eV binding energy. Only after about 3 L we observed some small modifications of the valence band and an oxygen-induced features appears at 2.5-eV binding energy. Finally, major effects are seen after about 10–15-L exposure. At this point the strong modification in the shape of the spectra reflects a profound rearrangement of the electronic structure, both of the Fe 3*d* and O 2*p* derived states, corresponding to the surface oxide formation. At about 40 L the heating of the sample results in the ordering of the surface layer oxide with only minor changes in the spectra.

In Fig. 2, we compare the spectra from the clean Fe(110) surface with those after 7.5-L O<sub>2</sub> exposure as a function of the emission angle. As already noticed, the valence-band features are practically unaffected in the normal emission spectra. On the contrary, some changes can be observed in the off-normal spectra. All the spectra have been normalized to the same height at about 8-eV binding energy. In this way, for the clean Fe(110) surface (left panel) a pronounced increase of the intensity of the

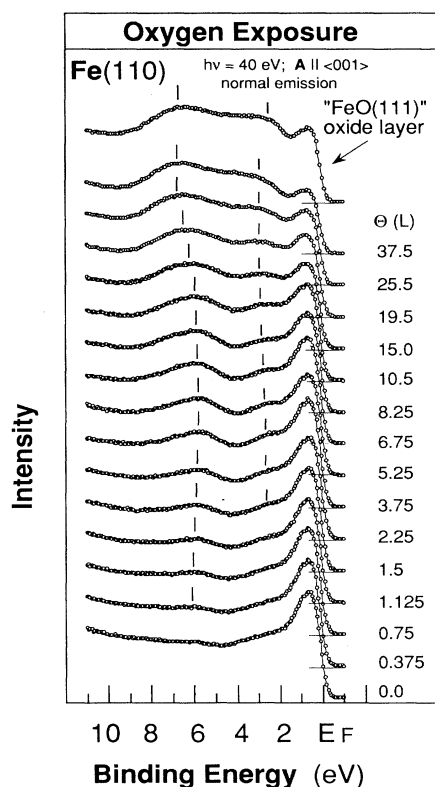


FIG. 1. Spin-integrated valence-band spectra of Fe(110) as a function of oxygen exposure ( $\Theta$  in L). The spectra have been taken in normal emission with 40-eV photon energy.

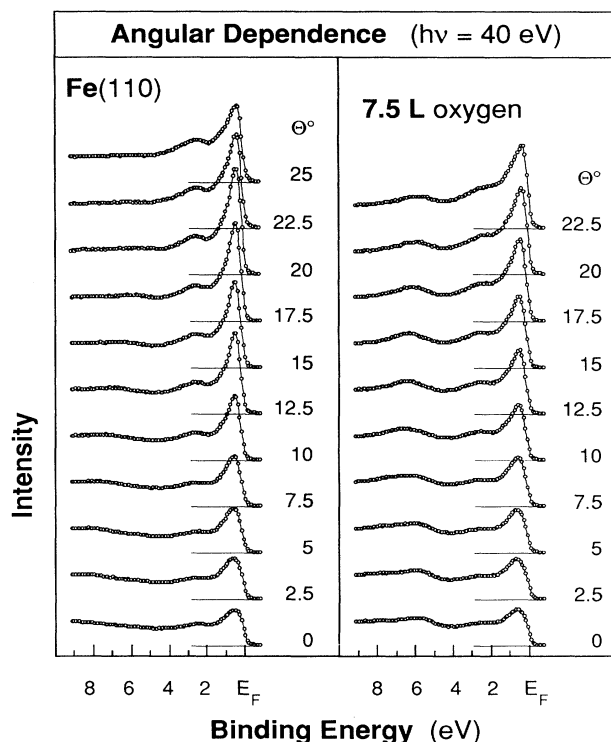


FIG. 2. Spin-integrated angle-resolved photoemission spectra for the clean Fe(110) surface and for 7.5-L O/Fe(110) as a function of the emission angle ( $\Theta$ ).  $h\nu = 40$  eV.

peak just below the Fermi level for emission angles between  $10^\circ$  and  $25^\circ$  is observed. After 7.5-L oxygen exposure (right panel) this effect is reduced. This behavior strongly suggests the surface origin of this emission.

An additional piece of information about these states can be deduced from the data reported in Fig. 3. Here we have collected a representative selection of spin-resolved photoemission spectra at three different emission angles (bottom row, normal emission; center row,  $15^\circ$ ; top row,  $20^\circ$ ) from the clean Fe(110) surface (left column), after 0.75-L  $O_2$  exposure (central column) and, after 7.5-L  $O_2$  (right column). The majority-spin energy distribution curves (EDC's) are indicated by open triangle symbols while the corresponding minority spins are marked with solid inverted triangle symbols.

Again at normal emission the effect of low oxygen exposure is very small and consequently the spectra reported in the bottom row are essentially identical. In the center and top rows the off-normal spectra at  $15^\circ$  and  $20^\circ$  are reported where the surface-sensitive emission near the Fermi level has already been identified from the spin-integrated measurements. The spin-resolved EDC's clearly show that this surface-sensitive emission is of minority-spin character. A very intense minority-spin feature is, in fact, observed at about 0.5-eV binding energy. The quite pronounced sensitivity of this feature to  $O_2$  exposure is then apparent in the comparison between the

spectra of the clean and oxygen-contaminated surfaces.

These results imply the existence of a minority-spin surface-related feature (surface state and/or surface resonance) along the  $\bar{\Gamma}$ - $\bar{H}$  high-symmetry line ( $\bar{\Sigma}$  line) of the surface Brillouin zone. The observed minority-spin states for  $10^\circ < \Theta < 20^\circ$  with 40-eV photon energy corresponds to  $0.52 < k_{\parallel} < 1.03 \text{ \AA}^{-1}$  ( $\bar{\Gamma}\bar{H} = 1.68 \text{ \AA}^{-1}$ ). Indeed, an old parametric tight-binding calculation for a 29-layer (110) ferromagnetic Fe thin film<sup>10</sup> consistently predicted a surface state in a minority-spin gap along the  $\bar{\Sigma}$  line at about 0.6-eV binding energy. The position and the quite flat dispersion of these states are well reproduced in our experimental results. From the experimental data we cannot, however, establish whether these states are actually located in the gap of the projected bulk bands (surface states) or whether they are partially degenerate with bulk states (surface resonances). This calculation also predicted the existence of the majority-spin exchange-split component at about 2-eV higher binding energy. In our spectra we have found no evidence for this majority-spin feature possibly as a consequence of the increased lifetime broadening at this higher binding energy.

Furthermore, a recent self-consistent LSDF electronic structure calculation using the full potential linearized-augmented-plane-wave (FLAPW) method for a seven-layer slab points out the importance of minority-spin surface states near the Fermi level for the Fe(110) surface.<sup>11</sup> As a result of the decreased symmetry at the surface, the valley between the bonding and the antibonding states becomes less pronounced in the surface-projected density of states. Indeed the valley, which is located right at the Fermi level for the minority-spin, is filled by surface states. The combined action of this effect together with the surface band narrowing, which appreciably reduces the weight of the majority surface density of states at  $E_F$ , determines a net minority-spin polarization near the Fermi level at the surface layer of Fe(110). The reversal of sign of the surface spin density at  $E_F$  (with respect to the energy integrated one) plays a key role in interpreting scanning tunneling spectroscopy (STM) and spin-polarized metastable atom deexcitation spectroscopy (SPMD) experiment.<sup>11</sup> These techniques are, in fact, extremely surface sensitive and in most cases are sampling electron states located in a narrow energy window around the Fermi level. Clearly the minority-spin surface emission observed in our spectra contributes to the predicted negative surface polarization near  $E_F$ .

In Fig. 4, we have reported the spectra for the  $O 2p$  derived states at two different oxygen exposures corresponding to the formation of the  $c(2 \times 2)$  (0.7 L) and to the more densely packed ordered overlayer (7.5 L). In our experimental conditions we are sampling the in-plane  $O 2p_x$  states at  $\bar{\Gamma}$  for which we observe an experimental exchange splitting ( $\Delta_{ex}$ ) of 0.5 eV, which is induced by spin-dependent substrate-atom hybridization. An exchange splitting ( $0.7 \pm 0.2$  eV) for the  $O 2p$  states on Fe(110) has been reported by Getzlaff *et al.*<sup>12</sup> However, these authors used unpolarized light (He I:  $h\nu = 21.22$  eV) which makes it impossible to discriminate between  $O 2p_x$ ,  $2p_y$ , and  $2p_z$  states. In addition, the structure of the  $O$  overlayer is not specified and renders the determina-

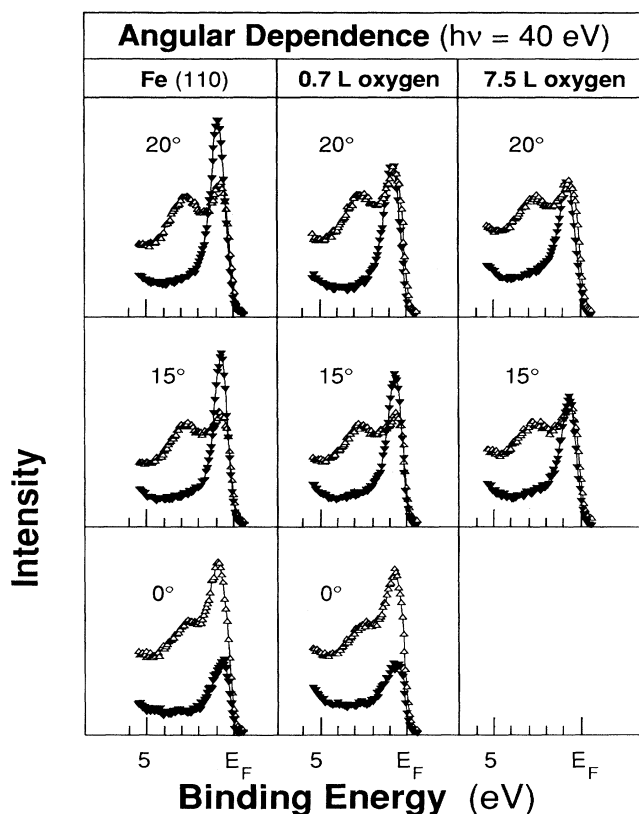


FIG. 3. Spin- and angle-resolved energy distribution curves from clean Fe(110), 0.7-L O/Fe(110), and 7.5 L O/Fe(110) for selected emission angles ( $0^\circ$ ,  $15^\circ$ ,  $20^\circ$ ).

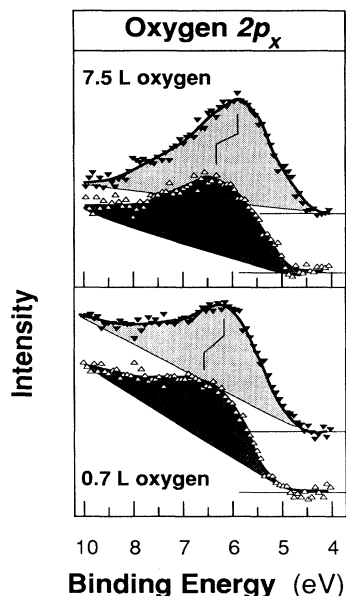


FIG. 4. Spin-resolved photoemission spectra of the oxygen  $2p_x$  states taken at oxygen coverages corresponding to the  $c(2 \times 2)$  ordered overlayer (0.7 L) and to a more dense ordered oxygen packing (7.5 L).

tion of  $\Delta_{ex}$  ambiguous.

For the in-plane  $2p_x$  states the exchange splitting we have observed is unusually large. Indeed, previous studies have shown that at  $\bar{\Gamma}$  the exchange splitting of the  $2p_x$  orbitals is considerably smaller than that of the  $2p_z$  states. It has been suggested that this reflects the weaker hybridization of the in-plane  $2p_x$  orbitals with the substrate. Values for the  $2p_x$   $\Delta_{ex}$  of 0.35 and 0.1 eV have been reported for the  $p(1 \times 1)\text{O}/\text{Fe}(100)$  (Ref. 13) and for  $p(1 \times 1)\text{O}/\text{Fe}/\text{W}(100)$  (Ref. 14) systems, respectively. Rather surprisingly,  $\Delta_{ex}$  is found to be the same, within experimental uncertainties, for the two different

oxygen overlayers. In fact, distinctive differences in the character of the O  $2p$  bands have been reported in an angular-resolved photoemission investigation for  $c(2 \times 2)\text{O}/\text{Fe}(110)$  and  $c(3 \times 1)\text{O}/\text{Fe}(110)$ .<sup>9</sup> It has been shown that, while in the  $c(2 \times 2)$  configuration, the dispersion of the oxygen  $2p$  derived states is negligible, in  $c(3 \times 1)$  the in-plane overlapping  $2p_x$  states form a rather wide band (more than 1.0 eV).

Wu and Freeman<sup>11</sup> have calculated the electronic structure for the system  $p(1 \times 1)\text{O}/\text{Fe}(110)$ . They found an expectedly large ( $0.7\mu_B$ ) induced oxygen magnetic moment. Unfortunately, the  $p(1 \times 1)$  oxygen overlayer does not form at room temperature on Fe(110). Nevertheless, our data suggest a quite effective (magnetic) interaction between the O adatoms and the Fe(110) substrate and support thus, in principle, their theoretical conclusions. Obviously a large exchange splitting is a prerequisite for the formation of a large magnetic moment on the oxygen sites. The presence of a large induced exchange splitting on the oxygen sites also proves that the Fe(110) surface remains "magnetically alive" after small oxygen adsorption. This is also consistent with the highly spin-polarized  $3d$  spectral features observed after oxygen exposure (see Fig. 3).

In summary, we have used spin- and angle-resolved photoemission to study the clean and oxygen covered Fe(110) surface. The theoretical prediction<sup>10</sup> of the existence of a majority-spin surface state on the clean Fe(110), located 0.5 eV below  $E_F$  midway along the high-symmetry  $\bar{\Sigma}$  line of the surface Brillouin zone, has been experimentally confirmed. The importance of these minority-spin surface states in creating a negative value of the surface spin density at the Fermi level has been recently discussed.<sup>11</sup> Furthermore, we have investigated the effect upon oxygen chemisorption. We found that in the low coverage regime the Fe surface magnetism is not quenched. The data for low oxygen exposure provide evidence for a strong magnetic interaction between the adatoms and the Fe(110) surface, resulting in a large induced exchange splitting of the oxygen states.

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