Spin-polarized surface states of Fe(100)

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Spin- and angle-resolved photoemission has been used to reinvestigate the origin of some prominent surface-related features of the Fe(100) spectra. In agreement with earlier studies the spin-integrated spectra show intense surface emission near the Fermi level from states at the center of the surface Brillouin zone. The spin-polarization measurements show that this surface emission is of majority-spin character, in contrast with the previous interpretations. By exposing the clean surface to 0.1–0.4 langmuir O_2 the intensity of the majority-spin surface-related feature is strongly reduced, whereas an oxygen-induced minority-spin state develops with increasing exposures at a binding energy of 1.4 eV.

The modification of the electronic structure at the surface is of primary importance for surface magnetism. For this reason the study of surface electronic states is of both experimental and theoretical interest. Self-consistent and spin-polarized calculations are now able to provide a detailed description of the charge and spin surface densities and of the surface-state band dispersion.[1] In the ferromagnetic 3d metals the calculated surface density of states presents a band narrowing due to the reduced atomic coordination. Remarkably this effect causes an enhancement of the Fe(100) surface magnetic moment by more than 30% with respect to the bulk value.[1]

Angle-resolved photoemission is a well-established method to experimentally investigate the electronic structure of surfaces[2] and thin films. A direct identification of the spin character can be obtained by adding to the conventional measurements the photoelectron spin polarization analysis.[3] Indeed spin- and angle-resolved photoemission has been applied to map the electronic bulk band structure of Fe(100).[4] Moreover a recent experiment by Brookes et al.[5] could identify a minority-spin state resonance (2.4 eV binding energy at $\bar{\Gamma}$) and a minority-spin surface state (2.25 eV binding energy at $\bar{X}$) of the ferromagnetic Fe(100) surface. The majority counterpart of the minority surface resonance could not be observed.

Turner and co-workers[6] have previously performed extensive studies of the Fe(100) surface electronic structure by angle-resolved photoemission but without spin analysis. Those results have given experimental evidence of intense surface-related spectral features, whose overall energy dispersion appears to be in good agreement with the theoretical predictions.[7,8] The surface emission is particularly intense at relatively low photon energy (12–17 eV) and normal electron emission. In these conditions Turner and co-workers[6] show that most of the valence-band photoemission intensity is actually due to surface states near the $\bar{\Gamma}$ point, the center of the surface

Brillouin zone. The most prominent feature is observed near the Fermi level. This structure, which is extremely sensitive to oxygen adsorption, is assigned to a minority-spin Shockley-type surface state,[6] by comparison with the theoretical results.[6,7] It is pointed out that these minority-spin states can play a major role in determining surface magnetic properties as well as their importance for near-threshold spin-polarized photoemission.

By spin- and angle-resolved photoemission we have reinvestigated the origin of these surface states of Fe(100). In this paper we show that the intense surface emission is of majority-spin character, in contrast with the previous interpretations. In addition the effect of low oxygen exposures on the surface states has been studied, leading to a reinterpretation of another previously observed spectral feature.

The experiment has been performed on the TGM-1 beamline[9] at the BESSY storage ring in Berlin. We used monochromatic s-polarized light incident normal to the sample ($A\|\langle 010 \rangle$). The angle-resolved photoemission spectra have been measured with a 90° spherical energy analyzer coupled to a Mott detector for the spin polarization measurement. The measurements were performed in magnetic remanence at room temperature. The clean Fe surfaces were produced *in situ* by e-beam evaporation on Pd(100). Thick epitaxial overlayers (>20 monolayers) were found to produce photoemission spectra indistinguishable from the bulk Fe(100) samples.[10,11] The details of the system characterization, including the dependence of the electronic structure on the overlayer thickness at lower coverages, will be presented elsewhere.[11] The low-energy electron diffraction pattern of the clean Fe surface showed sharp spots on a very low background. With oxygen exposures between 0.3 and 2 langmuir (1 L = 10^{-6} Torr s) the diffraction spots became broader with a very weak $c(2\times2)$ reconstruction on an increasingly diffuse background. The base pressure in the UHV system was 1×10^{-10} mbar. It could be kept below 3×10^{-10} mbar

during Fe evaporation. As will be shown in the following, very low amounts of surface impurities can profoundly affect the Fe(100) spectral features. Changes in the photoemission spectra due to the residual gas contamination could be detected about 1 h after the surface preparation. The spin-resolved spectra of the clean Fe surface presented here were thus collected in less than 1 h time.

In Fig. 1 we show the spin-resolved and spin-integrated spectra of Fe(100) measured at 16 eV photon energy for normal electron emission. The spin-integrated spectrum is very similar to those reported by Turner and co-workers.[6] The most intense peak is observed near the Fermi level at 0.3 eV binding energy. A second structure is found at 2.7 eV binding energy. *The spin-resolved spectra show that all these main features have a majority-spin character.* In the majority-spin spectrum we indeed observe a strong peak at 0.3 eV binding energy and a less pronounced structure with a maximum at 2.7 eV binding energy. The minority-spin spectrum shows a much weaker intensity and a lack of any pronounced features.

We have also investigated the surface sensitivity of the spectra upon oxygen exposures, in order to identify the surface emission. The spin-integrated photoemission results for the initial stage of oxidation (0.08–3 L) are presented in Fig. 2. In agreement with the previous results,[6] we observe already at very low exposure (0.08–0.4 L) a strong decrease of the emission near the Fermi level. This is of course a clear indication that this feature is actually related to surface electronic states. Further evidence has been provided by Turner and co-workers.[6] who have reported its lack of dispersion by varying photon energy. In Fig. 2 from the sequence of spectra for increasing oxygen exposures other trends can be observed. A new feature at 1.4 eV binding energy is seen in the exposure range 0.3–2 L. This structure also appears in the photoemission spectra by Turner and co-workers[6] of the Fe(100) surface exposed to 0.3-L oxygen. The relative intensity of this surface (Fig. 2) with respect to the other spectral features is a function of the exposure reaching a
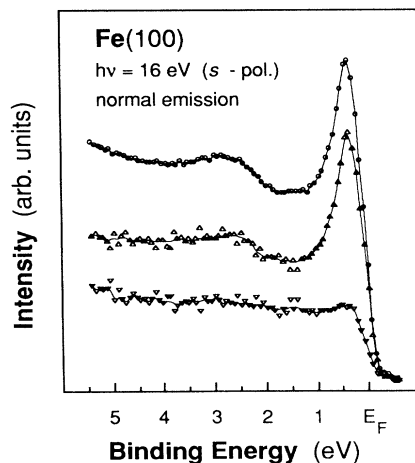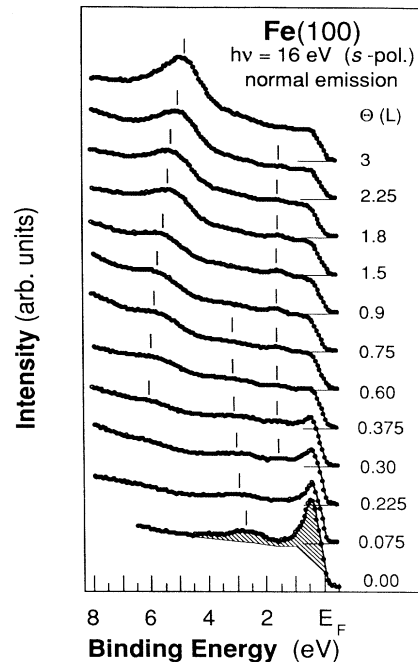

FIG. 2. Collection of spin-integrated photoemission spectra from Fe(100) film as a function of oxygen exposure (in langmuir). The spectra are taken in normal emission with s-polarized light ($h\nu = 16$ eV).

maximum at about 1 L followed by a decrease for higher exposures. In the 2–4-eV binding energy range we observe relatively weak changes in the low exposure regime. Finally, at higher binding energy, 5–7 eV, the oxygen-derived $2p$ emission intensity grows with increasing exposure and shifts toward lower binding energy for exposures above 0.7 L.

The corresponding spin-resolved spectra measured for selected exposures are presented in Fig. 3. These data help to clarify the origin and spin character of the various spectral features discussed above. The spectrum of the clean substrate has already been presented in Fig. 1. It is now convenient to discuss the changes upon oxygen exposures in the two spin channels separately. In the majority-spin spectrum the oxygen adsorption produces a strong reduction of the 0.3-eV binding energy peak already in the low exposure range (0.1–0.4 L). This indeed corresponds to the strong changes observed near the Fermi level in the spin-integrated spectra, indicating the surface-related origin of this structure. It is thus clear that *the surface emission quenched by oxygen adsorption has majority-spin character.* The higher binding energy (2–4 eV) majority-spin features are only weakly affected by oxygen exposure. A small shift of the peak position to higher binding energy (from 2.7 to 3.0 eV) with oxygen exposure supports the interpretation[6] of the clean Fe feature as partially due to majority-spin surface emission. In the minority-spin spectra a new feature at 1.4 eV binding energy develops with oxygen exposure. Similar to the corresponding structure in the spin-integrated spectra, this feature reaches maximum intensity at about 1-L ex-

FIG. 1. Spin-resolved photoemission spectra from Fe(100) film taken in normal emission with s-polarized light ($h\nu = 16$ eV).

posure.

The results presented above give evidence that the very prominent photoemission peak near the Fermi level, previously identified as a minority-spin surface structure, is instead of majority-spin character. This is surprising since theoretical results reported in the literature do in fact predict a minority-spin Shockley-type surface state near E_F at $\overline{\Gamma}$.[7,8] Furthermore, no majority-spin surface state or surface resonance is expected at this binding energy. The occupied majority-spin state with the lowest binding energy, predicted by Ohnishi, Freeman, and Weinert, is 0.88 eV below E_F. The calculated majority-spin band structure does not have a gap of the projected bulk states near E_F which could support the localization of states at the surface. It may be worthwhile to observe however that the upper edge of the projected bulk majority-spin states on $\overline{\Gamma}$ is just above the Fermi level. It is therefore conceivable that the experimentally observed majority-spin feature is derived from a surface resonance or a surface state located near the upper energy edge of the majority-spin projected bulk bands, possibly in a symmetry gap. In this connection it is interesting to note that a theoretical investigation by Feder et al.[12] on the bases of spin-resolved photoemission data of Fe(100) (Ref. 4) predicted the existence of a majority-spin surface resonance located just below the Fermi level. The surface-related origin of the feature observed at 0.3 eV below E_F appears to us experimentally well documented by the results of Turner and co-workers[6] and by the present work. The explanation of this prominent feature could therefore be a test case for a more detailed theoretical analysis of the surface and subsurface layer electronic structure.

It is also worthwhile to point out that the present results demand a reinterpretation of the 1.4-eV feature. Turner and co-workers[6,13] interpreted this peak observed with 0.3-L oxygen as a majority-spin state of bulk character, underlying the intense surface emission in the clean spectrum. Our data show that this state has minority-spin character and its intensity depends on the oxygen exposure. Most noticeably no such feature can be observed in the spin-resolved spectra of clean Fe. We therefore conclude that the 1.4-eV minority-spin feature is oxygen induced, rather than an intrinsic bulk Fe feature. This interpretation is also consistent with its lack of dispersion by varying photon energy.[11] Its origin may be closely related to the one reported at the same energy for the (1×1) O/Fe(100) and the $c\,(2 \times 2)$ S/Fe(100) systems.[14]
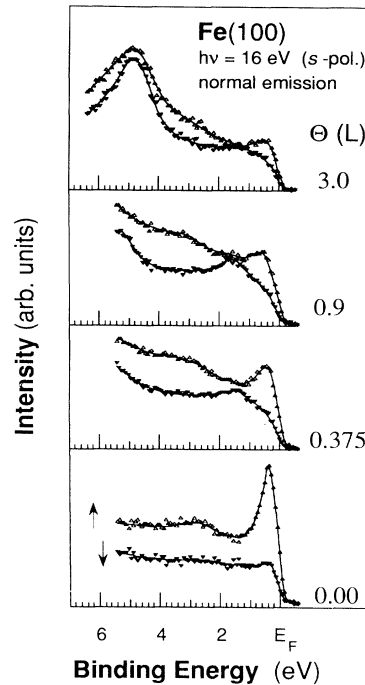

FIG. 3. Collection of spin-resolved spectra from Fe(100) thick film as a function of oxygen exposure (Θ in langmuir). The spectra are taken in normal emission with s-polarized light ($h\nu = 16$ eV).

In conclusion, the origin of some prominent surface features of Fe(100) has been investigated by spin- and angle-resolved photoemission. The results show that the normal emission spectra at low photon energy are dominated by surface-related polarized emission of majority-spin character. This observation cannot be simply explained by a comparison with the available surface band-structure calculations. By exposing the clean surface to O_2 the intensity of this majority-spin surface-related feature is strongly reduced, whereas an oxygen-induced minority-spin state develops at 1.4 eV binding energy.

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