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# Oxygen-induced enhancement of the spin-dependent effects in electron spectroscopies of Fe(001)

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Oxygen adsorption in an ordered $p(1\times1)$ fashion on the Fe(001) surface has been studied by empty states spectroscopies using a spin-polarized electron beam. The low-energy electron absorption and reflection display a much larger spin dependence in Fe(001)-$p(1\times1)$O than in Fe(001). Peak values of the spin asymmetries of the absorbed (reflected) current larger than 13% (45%) at around 9–11 eV above the Fermi level are found. Spin-resolved inverse photoemission reveals that in the same energy range the exchange splitting between majority- and minority-spin states in Fe(001)-$p(1\times1)$O is $\sim$50% larger than in the clean surface. [S0163-1829(99)09905-1]

## I. INTRODUCTION

Adsorption of foreign atoms on a solid surface is in general accompanied by structural relaxation and rearrangement of the electronic density. These modifications affect the surface magnetic properties that are extremely sensitive to contamination by chemisorbed atoms or atoms segregated from the bulk. Magnetic phenomena connected with chemisorption on well-characterized single-crystal surfaces have been extensively investigated, also taking advantage of the development of spin-polarized techniques.[1,2] In general it is found that adsorption considerably reduces the substrate magnetic moment,[2] while a nonvanishing magnetic moment can be induced in the adatoms. The latter finding was also predicted by theory, at least for O and S chemisorbed on Fe(001).[3–5] However, conforming to theoretical expectations,[6] the picture arising as a whole from the research reported so far, indicates that the overall surface magnetism is reduced by chemisorption.

We present here electron spectroscopy results showing an enhancement of the spin-dependent effects induced by adatoms adsorption on a clean ferromagnetic surface, at variance with the expectations based on the above general behavior. The chemisorption system showing this unusual property is oxygen adsorbed on Fe(001) in a well-ordered fashion, displaying a primitive $1\times1$ $[p(1\times1)]$ low-energy electron-diffraction (LEED) pattern. O adsorption on Fe(001) has been studied by many groups,[7–10] also with spin-resolved methods.[11–14] We have investigated the Fe(001)-$p(1\times1)$O surface by different spin-resolved techniques, namely, target absorbed and reflected current (AC and RC, respectively) and inverse photoemisson (IPE) spectroscopy, probing the empty electron states with the use of a polarized electron beam. For all spectroscopies we find a huge dependence of the spectral features on the beam polarization. A direct comparison with measurements on Fe(001) shows that the spin-dependent effects, present also in the clean surface, are strongly amplified in the oxidized surface. In particular spin-resolved IPE shows that, upon O adsorption, the exchange splitting between empty majority- and minority-spin levels increases. These results point towards an O-induced enhancement of the magnetic moment of the Fe(001) surface. An unambiguous statement is however prevented by the complexity of the relationship connecting electron spectroscopy data to the surface magnetic moment.[1,15]

## II. EXPERIMENT

Our experiments are inverse photoemission, target electron current absorption, and reflection spectroscopies, all performed in the spin-resolved mode in an ultrahigh vacuum system (base pressure $\leqslant 5\times10^{-11}$ Torr) equipped with standard surface characterization techniques.[16] The starting Fe(001) surface is obtained by growing a thick Fe film ($\geqslant$300 nm) on a MgO(001) substrate in ultrahigh vacuum conditions. After annealing at 850 K, a clean and ordered Fe(001) surface is obtained, as evidenced by XPS (x-ray photoelectron spectroscopy) and LEED analysis.[17] The clean surface is then exposed to 30 L of $O_2(1L=10^{-6}\ \text{Torr}\times\text{s})$ at 450 K and then flash-heated at 900 K for few seconds.[18] This procedure yields a perfectly ordered structure, as evidenced by the very sharp $p(1\times1)$ LEED pattern. XPS analysis for coverage determination is also found in perfect agreement with previous data for the Fe(001)-$p(1\times1)$O surface.[10]

Samples are magnetized in plane along the [100] direction of the Fe lattice, then spectra taken in magnetic remanence, as usual in electron spectroscopies. The collimated and transversely polarized electron beam impinging on the sample is produced by a spin-resolved electron gun, based on a negative electron affinity GaAs photocathode.[16] Absolute calibration of the beam polarization was performed in a separate experiment by Mott scattering,[19] yielding a value $P_0=(25\pm2)\%$. The IPE spectra are taken in the isochromat mode by collecting photons at a fixed photon energy of $h\nu=(9.4\pm0.3)$ eV while varying the incident beam energy.[16] The AC spectra are recorded by measuring the target electron current running to ground, while the RC spectra are collected in the specular geometry by means of a Faraday-cup collector, without any energy filtering. All spectra are normalized to the current impinging on the sample. Data are taken at room temperature and at normal incidence, thus probing states along the $\Gamma H$ direction of the bcc Brillouin zone (BZ), except for the case of reflection spectroscopy, for which the incident (and take-off) angle is $15°$ off normal, the minimum angle compatible with our experimental setup. In order to evidence only true magnetic effects, series of spectra have

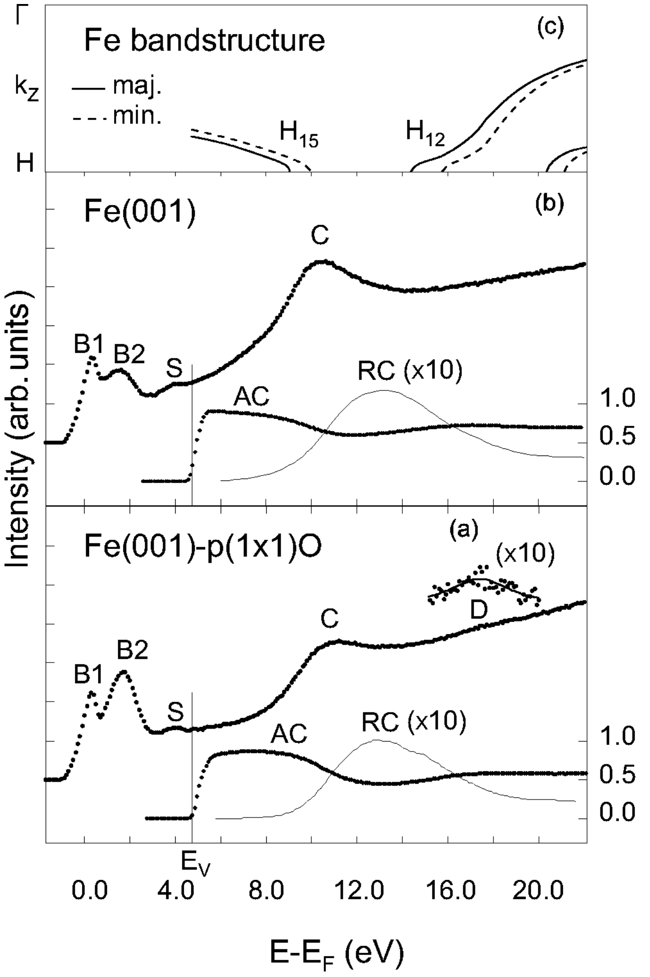

FIG. 1. (a) Inverse-photoemission, adsorbed-current, and reflected-current spectra from Fe(001)-$p(1\times1)$O. The spectra are normalized to the current impinging on the sample. The energy scale is referred to the Fermi level, while the right-hand scale applies to the AC and RC spectra. The position of the vacuum level is indicated by the solid vertical line. (b) As in (a) for a clean Fe(001) surface. (c) Electron band structure for bulk Fe along the normal to the (001) plane, after Ref. 27.

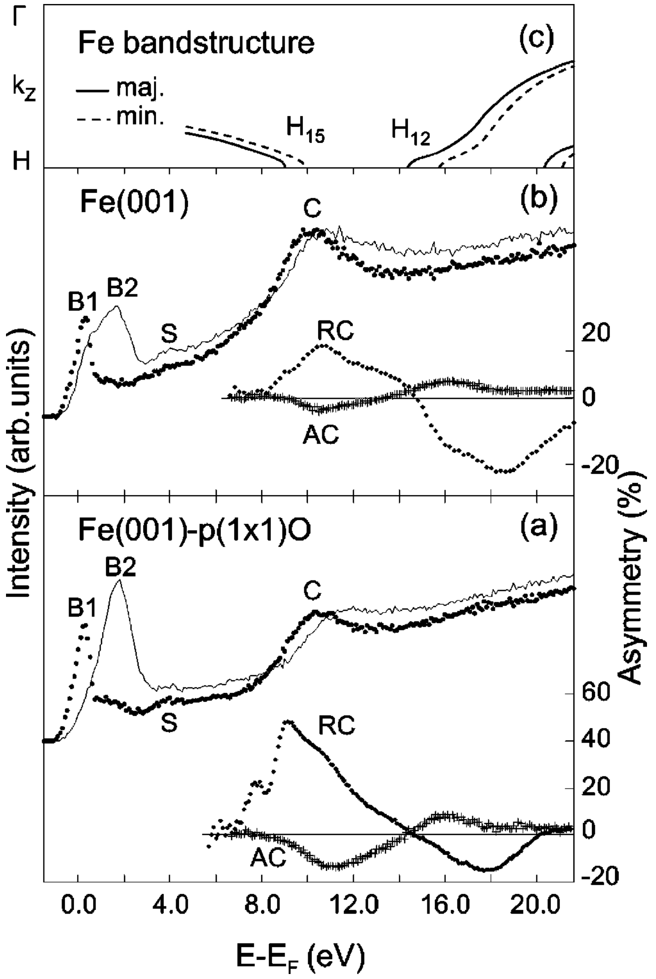

FIG. 2. Spin-resolved spectra for the Fe(001)-$p(1\times1)$O and Fe(001) surfaces. The data are normalized to a hypothetical 100% incident beam polarization through a standard procedure (Ref. 2).

been recorded for each of the four possible relative vector orientations of sample magnetization (**M**) and beam polarization. Spurious effects, due for instance to the presence of stray fields, are however found to be negligible.

## III. RESULTS AND DISCUSSION

Figure 1 shows spin-integrated IPE, AC, and RC spectra from the Fe(001)-$p(1\times1)$O and Fe(001) surfaces. They are presented using a common natural energy scale referred to the Fermi level $E_F$. For the AC and RC cases, this corresponds to the energy of the incoming beam, while for IPE to the energy of the final state of the radiative transition involved in the process. The spin-resolved results are collected in Fig. 2, showing the IPE spectra for majority- and minority-spin electrons along with the AC and RC spin asymmetry $A$, defined as

$$A=\frac{1}{P_0}\frac{I_\uparrow-I_\downarrow}{I_\uparrow+I_\downarrow}, \qquad (1)$$

where $I_\uparrow$ and $I_\downarrow$ represent the AC (RC) intensities for primary electrons with magnetic moment parallel and antiparallel to **M**.

The energy range below the vacuum level ($E_V$) is accessible only to IPE spectroscopy, since at these energies electrons do not enter the solid. Spin-resolved IPE data from Fe(001) and Fe(001)-$p(1\times1)$O in this region have been already published,[20,21,14] and are reported here for the sake of completeness. Three features are seen in the spectra, labeled as $B_1$,$B_2$, and $S$. In Fe(001) $B_1$ and $B_2$ correspond to bulk transitions towards majority- and minority-spin empty states near the $H$ point of the bcc BZ ($H'_{25}$ levels).[22,20] The feature $S$ originates from transitions into the image state resonance, which in Fe(001) presents an unusual inversion of the majority- and minority-spin levels.[21] In Fe(001)-$p(1\times1)$O the bulk-derived structures are attenuated, while a new and completely polarized O-induced peak, overlapping $B_2$, appears.[14] An image state peak is also visible at the same energy as in the clean surface. The energy of such a state is indeed bound to $E_V$, which does not change upon oxidation (see below).

Above $E_V$ all three spectroscopies can be applied. The data can be interpreted in terms of the electron band structure, as has actually been done for Fe(001) (Refs. 23–25) and Fe(110).[26] Unfortunately, theoretical calculations for the

Fe(001)-$p(1\times1)$O in this energy range are not yet available. We note, however, that the overall line shapes for the clean and the oxidized surface are very similar for all spectroscopies. This indicates that in this energy range O adsorption causes only slight modifications to the system band structure. Thus, at a very qualitative level, we use the results for the clean surface for discussing the data of both surfaces. For this reason, a sketch of the Fe(001) spin-resolved band structure, as calculated by Tamura and Feder,[27] is also shown in Figs. 1 and 2. Only the totally symmetric $\Delta_1$ states are considered, which are those available for coupling to free-electron states describing the incoming beam outside the crystal.

Considering first the AC and RC signals, we note that they are strictly connected, being AC $= 1 - (\mathrm{RC} + \mathrm{DC})$, where DC is the fraction of the primary current diffused out from the specular direction.[23] In fact (see Fig. 1), when crossing the vacuum level, the AC signals reach a value close to unity, corresponding to a complete electron absorption, while the RC intensities are nearly zero. The step increase of the AC curves at $E_V$ can be used to determine the sample work function. We get a value of 4.65 eV for both surfaces, with no variation upon oxidation within the experimental accuracy of $\pm 0.05$ eV, in good agreement with previous studies.[7,9] At around 12 eV the AC curves present a broad minimum (more pronounced in the oxidized surface) and in correspondence we find a maximum in the RC curves. Finally above 18 eV, electrons are again strongly absorbed corresponding to small values of the reflectivity. These modulations are directly explained in terms of the band structure: between 10 and 14 eV the electron energy falls in a band gap so that the incoming electrons cannot couple with states inside the crystal and thus are strongly reflected. The spin dependence of the AC and RC signals can be interpreted along the same lines. The presence of different energy gaps for minority- and majority-spin electrons causes spin asymmetries in the spectra.[24] For instance (see Fig. 2) at 10–12 eV, i.e., for incoming beam energies between the majority and minority $H_{15}$ levels, minority-spin electrons can enter the crystal while the majority-spin ones are strongly reflected. This gives rise to a negative (positive) spin asymmetry in the AC (RC) intensity. The opposite situation occurs above 15 eV, i.e., when crossing the $H_{12}$ levels, and the asymmetries changes sign. For the clean surface, we find maximum values of the spin asymmetry as large as 4% and $-25\%$ at 16 and 18.5 eV for the AC and RC signals, respectively, in fair agreement[28] with published data for Fe(001).[24,25] The spectra from the Fe(001)-$p(1\times1)$O surface resemble very much those observed in Fe(001), apart from a very relevant quantitative difference. All the spin-dependent features are strongly amplified in this case. The AC asymmetry spectrum presents an oscillating behavior, in close analogy with the data from the clean surface, but the amplitude is quite different, with a peak value of $-13.5\%$ at 11 eV. The same considerations apply to the RC asymmetry spectrum, for which the peak value is 48% at 9 eV. An analysis of the spectral fine structure, going beyond this qualitative discussion, would require a detailed theoretical study of the Fe(001)-$p(1\times1)$O surface. The observed enhancement of the spin-dependent effects would suggest an increase of the magnetic moment at the oxidized surface. However, the relationship between spin-dependent scattering asymmetries and surface moments is in general quite complex, so as to prevent an unambiguous and accurate determination of the last quantity from spectroscopic data. In particular, previous spin-polarized LEED studies of Fe surfaces, comparing experimental data and theoretical calculations, have shown that in many cases the exchange asymmetry is only modestely affected by changes in the surface moment.[15]

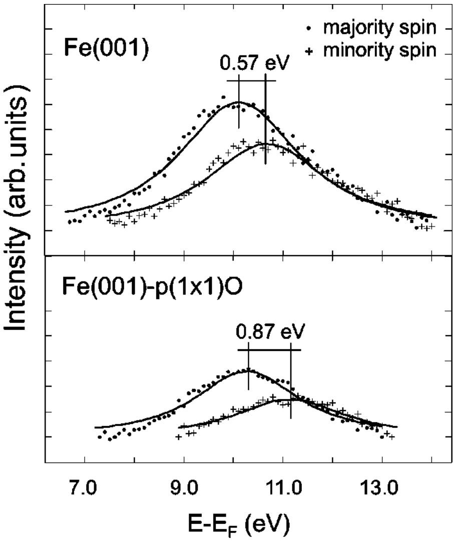

FIG. 3. Spin-resolved IPE spectra in the region of feature $C$ of Fig. 2 after a linear background subtraction. Points: majority spin. Crosses: minority spin. The Lorentzians best fitting the data are also shown along with the resulting value of the exchange splittings.

Coming to the IPE measurements, above $E_V$ the spectra are dominated by the structure $C$ (see Fig. 1), present on both surfaces at $\sim 10$ eV. The spin-resolved data (see Fig. 2) show that such a structure is actually composed by an exchange split doublet, which was not resolved in previous spin-integrated measurements.[22] By comparison with the band structure, it is seen that the doublet corresponds to transitions into the majority and minority $H_{15}$ critical points. A similar exchange split feature is expected at around 15–16 eV in correspondence to the $H_{12}$ critical point. This correspond to the wide structure $D$, barely emerging from the background in Fe(001)-$p(1\times1)$O at 16–19 eV, and not unambiguously detected for the clean surface. A closer examination of Fig. 2 reveals that the exchange splitting of the feature $C$ is larger in Fe(001)-$p(1\times1)$O than in Fe(001). In order to determine this variation in a quantitative way, we have performed a least-squares fit with a Lorentzian representing transitions to the $H_{15}$ critical points superimposed to a linear background. The resulting curves, broadened with a Gaussian 0.7 eV wide (full width at half maximum) representing the experimental response function, are shown in Fig. 3 as lines through the data points. We have repeated the fitting procedure using various different background shapes and the energy separation between spin-up and spin-down peaks was found to change within 50 meV. The splittings are determined as 570 and 870 meV for the Fe(001) and Fe(001)-$p(1\times1)$O surfaces, respectively, corresponding to an increase of more than 50%. The larger splitting provides a direct explanation in terms of the electron band structure of the increased asymmetries measured in the AC and RC spectra from the oxidized surface. On the basis of the experimentally established relationship between the exchange spittings and the local magnetic moments,[29] this result provides a further qualitative indication for the enhancement of the surface moment induced by O adsorption. An increase of the magnetic moment of the surface Fe atoms in Fe(001)-$p(1\times1)$O was actually predicted by theory.[5] The present data give experimental support to those calculations. The surface magnetism enhancement can be qualitatively interpreted in terms of the giant adsorption-induced relaxation occurring at the oxidized surface[4]. In fact, this gives rise to a Fe-Fe bond length at a surface larger than in the bulk, with an increase of the magnetic moment towards the value of isolated Fe atoms. Note that this applies only to the first two Fe atomic layers and the magnetic moment of the third-layer atoms is practically as in the bulk. The large spin-dependent variations of the spectra imply that the penetration depth of the low-energy electron used in our study is quite small (of the order of a few atomic layers), in agreement with recent findings in transition metals.[30]

## IV. SUMMARY

In conclusion, we have presented a set of spin-resolved data providing experimental evidence for the enhancement of the spin-dependent effects at the Fe(001) surface upon O adsorption in a $p(1\times1)$ ordered fashion. The spin asymmetries of the absorbed and reflected target current are strongly amplified with respect to the clean surface. Inverse photoemission spectroscopy shows that in the oxidized surface the majority-to-minority exchange splitting in the empty-state region is increased too. The data have been discussed in terms the Fe band structure, with O-induced modifications possibly leading to an enhancement of the surface magnetic moment. This can be ascribed to the increased Fe-Fe distance at the surface caused by a large structural relaxation accompanying the formation of the $p(1\times1)$O layer.

## ACKNOWLEDGMENTS

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