Exchange-Split Adsorbate Bands: The Role of Substrate Hybridization

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Spin-split adsorbate-induced bands have been observed for $p(1\times1)$ oxygen and $c(2\times2)$ sulfur on Fe(001) by use of spin-polarized angle-resolved photoemission. For the p_z-symmetry orbitals, the exchange splitting is considerably larger at the Brillouin-zone center (1.3 eV for O, 0.5 eV for S) than at the zone edge (0.25 and 0.2 eV, respectively). This is attributed to enhanced hybridization with substrate d_{z^2} orbitals when the adsorbate p_z band overlaps the bulk continuum. Our observation of an exchange splitting provides evidence of a small magnetic moment on the adsorbate atoms. Our results also indicate that the adsorbate layer is ferromagnetically aligned with the substrate.

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The magnetic properties of thin films and surfaces are currently extremely active areas of research—thin films because their magnetic properties may differ markedly from their bulk counterparts,[1] and surfaces because of their modified magnetization due to the lower dimensionality.[2] Several experiments have investigated the influence of adsorbate atoms on surface magnetism. Oxygen and carbon-monoxide chemisorption has been studied with both spin-polarized inverse photoemission[3] and spin-polarized photoemission.[4,5] Discussion of the results ranged from possible adsorbate-induced "dead layers" through to the presence of a magnetic moment on the adsorbate atom. Spin-polarized adsorbate features have been predicted in theoretical calculations of the O $p(1\times1)$ Fe(001) adsorption system[6,7] and the S $c(2\times2)$ Fe(001) adsorption system.[8] These calculations suggest a magnetic moment of approximately $0.24\mu_B$ (Ref. 6) and less than $0.10\mu_B$ (Ref. 9) for the oxygen and sulfur, respectively. In this Letter we present spin-polarized photoemission studies of these adsorption systems and are able for the first time to compare directly experimentally observed exchange splittings with the calculated splittings. To our knowledge this also represents one of the first studies of the polarization of the adsorbate bands themselves as opposed to studies of the effect of adsorbates on the substrate bands. The observation of exchange-split adsorbate bands is direct evidence for the presence of a magnetic moment on the adsorbate atom.

Our studies show that at the center of the zone, $\bar{\Gamma}$, the exchange splitting of the p_z orbitals is 1.3 and 0.5 eV for oxygen and sulfur, respectively. These splittings are considerably larger than the exchange splittings of the p_x orbitals which are found to be approximately 0.35 and 0.2 eV, respectively. This we argue is a reflection of the increased hybridization of the adsorbate p_z orbitals with the substrate continuum. At the edge of the surface Brillouin zone, the exchange splitting of the p_z orbitals is reduced to approximately 0.25 eV for both oxygen and sulphur. This effect is not predicted by any thin-film calculation.

The spin-polarized photoemission experiments reported here were carried out on a new apparatus which will be described in detail elsewhere.[10] Briefly, spin detection is achieved with a compact low-energy spin detector[11] mounted on the modified exit lens of a commercial hemispherical analyzer.[12] The apparatus uses light provided by the U5 vacuum-ultraviolet undulator installed on the vacuum-ultraviolet ring at the National Synchrotron Light Source.[13] The overall energy resolution in the spectra presented here is approximately 0.30 eV. The time taken to acquire a spin-polarized spectrum ranges from 15 min for the Fe d bands to 2 h for the sulfur-induced adsorption features. In particular, each pair of spectra shown in Fig. 1 were acquired in only 30 min. The presence of the oxygen or sulfur overlayers rendered the surface relatively inert to contamination. The Fe(001) substrate was manufactured in the form of a picture frame with each leg along a $\langle 100\rangle$ direction.[14]

The sulfur $c(2\times2)$ structure was obtained by our segregating sulfur from the bulk. The oxygen $p(1\times1)$ structure was obtained by the exposure of the surface to approximately 6 L [1 L (langmuir) $=10^{-6}$ Torr sec] of oxygen and our annealing the surface to 550 °C to remove excess adsorbate. In all experiments, it was possible to examine only those bands whose symmetry was even with respect to reflection in the mirror plane defined by the incident light direction and the emitted electron direction.

In Fig. 1 we show spin-polarized photoemission spectra recorded from the Fe(001) surface following expo-

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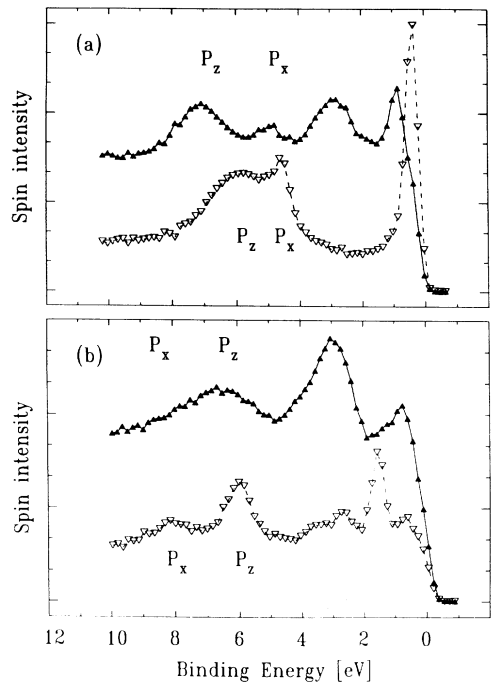

FIG. 1. Spin-resolved spectra from the O $p(1\times1)$ overlayer structure on Fe(001). The majority and minority components are indicated by a ▲ and ▽, respectively. The incident photon energy is 60 eV. (a) The light angle of incidence is 35° and the emission is along the surface normal and (b) the angle of incidence of 70° and emission corresponds to the $\bar{X}$ point in the surface Brillouin zone. In both sets of spectra the oxygen p_x and p_z orbitals are indicated.

sure to oxygen to form the $p(1\times1)$ overlayer. The sum of the two individual spin components in these spectra form spin-integrated spectra which are identical to those obtained in an earlier non-spin-polarized photoemission study of the same adsorption system.[15] In Fig. 1(a) the angle of incidence of the light was 35° with respect to the surface normal and electron emission is along the surface normal. At a photon energy of 60 eV the emission occurs near the Γ point in the bulk Brillouin zone and selection rules determine that for the Fe(001) surface the emission will show states of both Γ_{12} and Γ'_{25} symmetry.[16] It will be seen from Fig. 1(a) that following exposure to oxygen, the spectra are characterized by the appearance of the oxygen p_z orbitals exchange split by 1.3 eV and the p_x orbitals, identified by their sensitivity to the light polarization, exchange split by 0.36 eV. In Fig. 1(b) the angle of incidence of the light is now 70° and the emission angle corresponds to the $\bar{X}$ point in the surface Brillouin zone. The p_z orbitals are now found to exchange split by 0.25 eV and the p_x orbitals by 0.2 eV. We note that the more deeply bound adsorbate peaks show the same spin alignment as the majority components of the substrate. This we take as evidence of the ferromagnetic ordering, both within the overlayer and between adsorbate and substrate.

Changes are also observed in the d bands. The peak at a binding energy of 1.5 eV in the minority spectrum of Fig. 1(b), for example, is an adsorbate-induced feature at the zone boundary, $\bar{X}$. Further, the peak at a binding energy of 3.0 eV in the majority spectrum clearly has an adsorbate-induced component in addition to the bulk majority Γ'_{25} feature seen earlier[16] at 2.6 eV on clean Fe(001). This is evidenced both by the shift in the peak energy and its reduced sensitivity to the light polarization. These changes in the d bands will be discussed in more detail in a future publication.

In Fig. 2(a) we show the adsorbate-induced band structure derived from spin-resolved spectra recorded as a function of $k_\parallel$, again for the O $p(1\times1)$ structure. Within a given polarization, majority or minority, the bands at a binding energy greater than 4.0 eV show the dispersion to be expected for p orbitals on the basis of simple tight-binding models.[17] As a result of adsorbate-adsorbate interactions, the p_x orbitals show a larger dispersion than the p_z orbitals. Further, the presence of the substrate reduces the symmetry in the overlayer and allows hybridization between the p_z and p_x orbitals within a given spin. The exchange splitting of 0.25 eV is, we believe, a reflection of the size of the magnetic moment on the adsorbate atoms. Examination of Fig. 2(a) shows, however, that near the center of the zone the exchange splitting of the p_z bands increases from 0.25 to 1.3 eV. This we suggest is a reflection of increased hybridization with the substrate orbitals. This will be allowed at $\bar{\Gamma}$ for the p_z orbitals, which have the appropriate symmetry, but not for the p_x orbitals. We highlight this possibility in Fig. 2(b) where we show the measured exchange splitting of the p bands as a function of $k_\parallel$. The value of the enhanced splitting, 1.3 eV, falls midway between the measured exchange splitting of the substrate sp bands, 0.3 eV, and the typical substrate d splitting of 2.2 eV, and suggests hybridization with these d bands. This would reflect the bonding strength to the substrate. The variation of the exchange splitting across the zone will then depend on the relative weight of the substrate d component in the adsorbate bonding orbital as the zone is crossed.

Formation of the sulfur $c(2\times2)$ overlayer structure produces similar results but with an exchange splitting of the p_z orbital at the center of the zone of 0.5 eV, less than for oxygen. We suggest that this reflects the increased spacing of the sulfur from the Fe surface layer, 1.09 Å (Ref. 18) instead of 0.48 Å for oxygen.[19] The sulfur p_x orbitals are exchange split by 0.2 eV at the zone center.

In an earlier non-spin-polarized study of S $c(2\times2)$ on Fe(001), Didio, Plummer, and Graham,[20] following Liebsch,[17] suggested that the linewidths of the adsorbate-induced features reflected the same hybridization with the substrate. Examination of Fig. 1 shows that at the center of the zone the individual spin components of the p_z orbital are considerably broader than

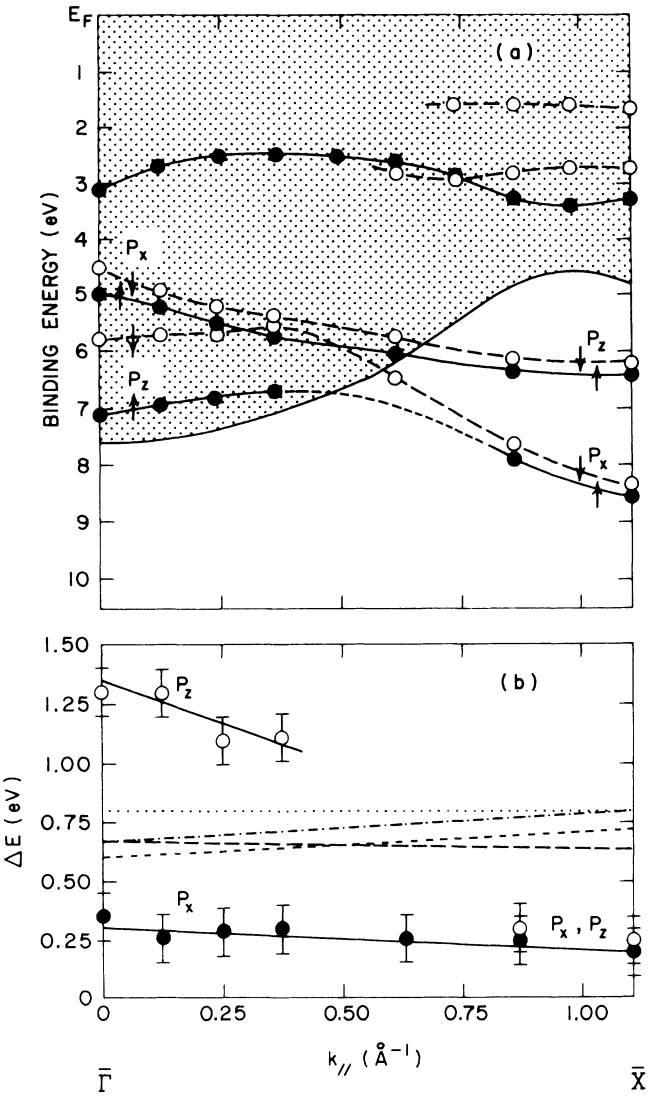

FIG. 2. (a) Spin-resolved oxygen-derived bands from ordered $p(1\times1)$ O on Fe. Bands at binding energies greater than 4.0 eV are derived from the oxygen p orbitals, while bands at smaller binding energies are oxygen-induced features in the Fe d bands. The majority and minority bands are denoted by ● and ○, the lines are given to guide the eye. The shaded region indicates the projection of the theoretical substrate continuum. (b) The measured exchange splittings ΔE (eV) of the p_z (○) and p_x (●) bands derived from the data points in (a). Also shown are the calculated exchange splittings of the p_z and p_x orbitals. ·-·- and --- are the p_z and p_x exchange splittings from Ref. 6. ··· and --- are the same from Ref. 7.

the p_x orbitals. The present study therefore supports the earlier study but now highlights the added complexity of an exchange splitting dependent on the level of hybridization with the substrate orbitals. Examination of the p_x orbitals in Fig. 1(a) and the p_z orbitals in Fig. 1(b) shows that the minority and majority components have a markedly different line shape. This we believe is a reflection of the lifetime of the different states, the minority photohole being longer lived than the majority photohole as a result of the lower density of minority electrons.

In thin-film calculations of these systems[6-8] the predicted exchange splittings of the p_x orbitals, shown in Fig. 2(b), are considerably larger than those observed experimentally. Furthermore, the hybridization-dependent exchange splitting for the p_z orbital at the center of the zone is also not predicted in these calculations. As noted earlier, the exchange splittings reflect the magnetic moment on the adsorbate atom; the calculated splittings will depend on the choice of exchange correlation potential, proportional to the spin-dependent density of states. It is therefore not possible to say whether the discrepancy between theory and experiment is due to an incorrect description of the adsorption itself or the use of an inadequate exchange-correlation potential.

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