Magnetic Surface State Becomes Nonmagnetic by Oxygen Adsorption

F. Passek and M. Donath

Max-Planck-Institut für Plasmaphysik, EURATOM Association, W-8046 Garching bei München, Germany

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The influence of oxygen adsorption on a partly occupied spin-split surface state at Ni(111) has been studied by spin-resolved inverse photoemission. With increasing oxygen exposure the surface state shifts to higher energy, thereby becoming totally unoccupied and no longer contributing to the surface magnetic moment. Moreover, its exchange splitting of about 100 meV on the clean surface is reduced to less than 25 meV for the ordered $p(2\times2)$ oxygen overlayer, whereas the splitting of an *sp* bulk band transition remains unaffected. The data demonstrate on a microscopic level the oxygen-induced reduction of the magnetic moment at the surface of Ni(111).

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Adsorbate-induced changes of surface magnetic properties have attracted considerable interest in recent years. Two groups of investigations can be distinguished focusing on different aspects of this issue. The first was concerned with "macroscopic" quantities: surface magnetization and magnetic moment. A reduction of the surface magnetic moment was found by various techniques for H, O, and CO adsorption on nickel and iron surfaces [1] in agreement with theoretical work [2]. The second group of experiments dealt with the spin-dependent electronic structure trying to give a "microscopic" picture of the physics involved. Studies concentrating on *d* states observed adsorbate-induced modifications of the spin-dependent emission intensities. They were interpreted as being caused by a reduced surface magnetization and/or by spin-flip scattering in the adsorbate layer [3]. On the other hand, the spin analysis of Auger electrons provided evidence for nonvanishing magnetic moments even at the adsorbate atoms induced by hybridization of the electronic states of the adatoms with the spin-split bands of the ferromagnetic substrate [4]. Intensive studies on the exchange splitting of adsorbate-induced states were performed by spin- and **k**-resolved inverse [5] as well as ordinary photoemission [6]. The bands which were investigated are either totally empty or occupied. Therefore they do not contribute directly to the magnetic moment. The observed spin splittings were interpreted as indications of magnetic moments at the adatoms transferred from the ferromagnetic substrate to the adsorbate in agreement with theoretical calculations [7]. All in all, there are two kinds of conclusions which seem to be at variance: strong reduction of the surface magnetic moment or even magnetically dead layers from magnetization measurements on one side and induced magnetic moments at the adsorbate atoms from electronic-structural studies on the other side. The experimental results presented in this Letter give an example of how the reduction of the surface magnetic moment is reflected in the spin-dependent surface electronic structure.

Adsorption of adatoms different from the surface atoms certainly changes the surface electronic structure. The modifications depend on the bonding mechanism and, in general, are not easy to interpret. Adsorbate-induced changes appear in photoemission and inverse photoemission spectra as energetic shifts and/or (dis)-appearance of spectral features whose spin dependence reflects modifications of surface magnetic properties. In general, primarily surface state emissions but also bulk state emissions of the clean surface are quenched by adsorption. An exception is image-potential surface states, which are shifted according to the work function change, because they are pinned to the vacuum level. Their intensity depends strongly on the crystal reflectivity, which may be reduced or enhanced by adsorption [8]. In many adsorption systems additional spectral features appear. They can be due to bulk band transitions via surface umklapp effects, provided the adsorbate forms an ordered overlayer. In this case, they give no additional information on the adsorbate apart from the overlayer geometry. The additional emission can, however, also stem from (anti)bonding states, containing essential contributions from adsorbate electronic states. The spin dependence of these states is of particular interest in the study of surface magnetism [4–6].

The first determination of an empty adsorbate band dispersion $E(\mathbf{k}_\parallel)$ was reported for the $p(2\times2)$ oxygen overlayer on Ni(111) [9]. For the same adsorption system, a decrease of about four Ni moments per oxygen atom was deduced from torsion oscillation magnetometry data [10]. This is equivalent to about one magnetically dead nickel surface layer induced by an oxygen coverage of 0.25. Recently, on the clean Ni(111) surface a spin-split partly occupied surface state has been detected, which directly contributes to the surface magnetic moment [11]. All these findings describe the adsorption system Ni(111)+O as a perfect candidate for studying the influence of an adsorbate on the spin-dependent surface electronic structure.

Our experimental setup for spin-resolved inverse photoemission (IPE) and details about the measurement are described in the literature [12]. Low-energy spin-polarized electrons from a GaAs photocathode impinge on the (111) surface of a hexagonal picture-frame single crystal of nickel. Single-domain magnetization in rema-

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nence, monitored by Kerr microscopy, was achieved by applying a current pulse through a magnetization coil wound around one leg of the crystal. The angle of electron incidence Θ was varied in the $\bar{\Gamma}\bar{K}$ direction of the surface Brillouin zone. Spectra measured for positive and negative Θ are equivalent in this azimuth with respect to the incoming electron beam. The photon emission intensities, however, may be different due to the nonequivalent photon detection geometry. The surface was prepared by sputtering with 1.2 keV argon ions and subsequent annealing at 950 K. Oxygen was exposed to the sample at room temperature. Low-energy electron diffraction (LEED) and Auger electron spectroscopy were used to characterize the sample. Photons emitted from the sample were detected in the isochromat mode at a detection energy of 9.4 eV. All IPE spectra presented here were recorded at room temperature.

Figure 1 displays spin-averaged and spin-resolved IPE spectra for normal electron incidence on Ni(111) as a function of oxygen exposure. A sharp $p(2\times2)$ superstructure in LEED was observed for an exposure of 6 L ($1\text{ L}=1.33\times10^{-4}$ Pa s), which is a factor of 2 to 3 more than previously reported values [9,13]. This indicates a high-quality surface with low step density. The data for the clean surface exhibit two distinct features SS and IS. SS is mainly due to a partly occupied crystal-induced surface state of Λ_1 symmetry, which is exchange split by about 100 meV [11]. IS stems from transitions into the $n=1$ image-potential-induced surface state with an exchange splitting of 18 meV [14]. The exchange splitting of both surface states prove the Ni(111) surface to be magnetically alive. With increasing oxygen exposure, IS loses intensity and shifts upwards in energy according to the oxygen-induced work function increase of about 0.9 eV for the $p(2\times2)$-O overlayer [9,13]. The intensity loss is caused by a reduced surface reflectivity, which has been detected in target current spectra. In a fashion similar to IS, feature SS shifts continuously to higher energy as a function of increasing oxygen exposure. It is found 1.1 eV above E_F for the $p(2\times2)$ overlayer, now being completely empty and no longer contributing to the surface magnetic moment. Spectra taken at different photon takeoff angles show low intensity emitted normal to the surface and high intensity for large angles, indicating that SS keeps its Λ_1 symmetry. Remarkably, the development from partly occupied to totally empty is

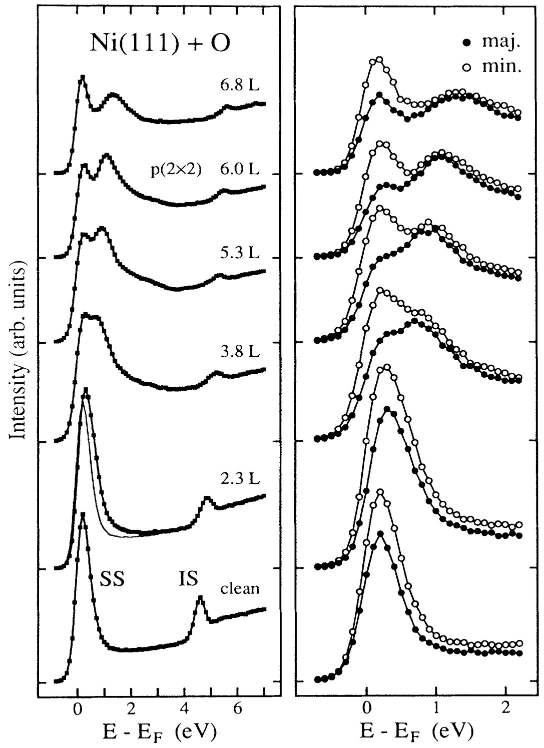

FIG. 1. Spin-averaged (left panel) and spin-resolved (right panel) inverse photoemission spectra for normal electron incidence on Ni(111) as a function of oxygen exposure. SS and IS denote emission features originating from crystal-induced and image-potential surface states, respectively. For reasons of comparison, the spectrum of the clean surface is included in the spectrum for 2.3 L in the vicinity of E_F as a solid line without data points.

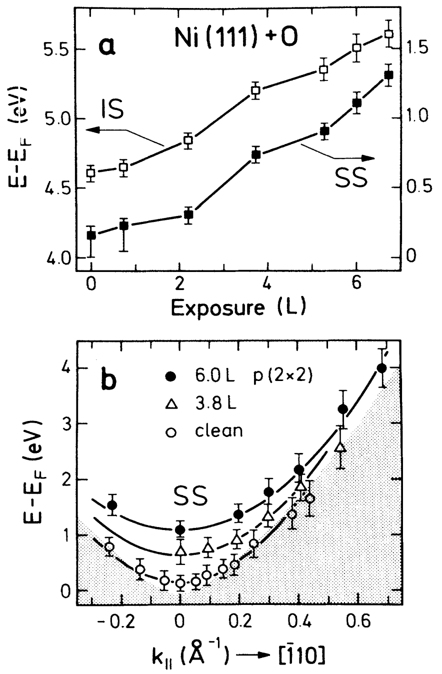

FIG. 2. (a) Energy above the Fermi level E_F of SS and IS for normal electron incidence on Ni(111) as a function of oxygen exposure. (b) $E(\mathbf{k}_\parallel)$ diagram of SS in the $\bar{\Gamma}\bar{K}$ direction of the surface Brillouin zone. The solid lines through the data points for 0, 3.8, and 6.0 L of oxygen exposure are parabolas describing free-electron-like dispersions with effective masses $m^*/m=0.4$, 0.5, and 0.6, respectively. The white area denotes a gap of the projected bulk band structure (spin-averaged).

reflected in an intensity increase for small oxygen exposures, which can be seen by comparing the data for 2.3 L with the data of the clean surface (solid line in Fig. 1). In addition, the spin-resolved data show the Fermi level onset of spin-up and spin-down spectra slightly more separated for 2.3 L than for the clean surface. With SS shifted away from E_F, a feature of mainly minority character remains close to E_F, which is attributed to indirect transitions into minority d states. For oxygen exposures larger than 6 L, the LEED pattern becomes less sharp and the spin-dependent electronic structure exhibits further changes (see spectra for 6.8 L), which will not be discussed here.

The continuous energy shifts of both IS and SS as a function of oxygen exposure are plotted in Fig. 2(a). The results of angle-resolved measurements in the $\bar{\Gamma}\bar{K}$ azimuth for the clean surface as well as for 3.8 and 6 L of oxygen, the latter corresponding to $p(2\times2)$-O, are summarized in Fig. 2(b) as the $E(\mathbf{k}_\parallel)$ diagram. The dispersions roughly follow the gap boundary of the projected bulk band structure. The effective mass m^*/m increases from 0.4 for the clean surface to about 0.6 for the $p(2\times2)$-oxygen overlayer, the more the state moves away from the bottom of the gap. An additional experimental result has been obtained by IPE measurements with variable photon energy, which prove SS to be independent of $\mathbf{k}_\perp$, showing its two-dimensional character [15].

The surface state SS shifts continuously to higher energy with increasing oxygen exposure, exhibits free-electron-like $E(\mathbf{k}_\parallel)$ dispersion, and shows no dependence on $\mathbf{k}_\perp$: All these findings lead us to the conclusion that the adsorbate-induced feature at 1.1 eV above E_F in the system Ni(111)-$p(2\times2)$-O represents a surface state, modified by the oxygen adsorbate, rather than an adsorbate band, characteristic of the oxygen-oxygen interaction. Direct oxygen-oxygen interaction can be excluded anyhow if one considers the distance of about 5 Å between the oxygen atoms. In addition, for an adsorbate band, characteristic of the ordered $p(2\times2)$-oxygen overlayer, one would expect the appearance of a new feature at a fixed energy with increasing oxygen exposure; i.e., more islands of the ordered overlayer are formed. SS, however, is apparently not sensitive to the local bonding of the adsorbate; it rather reflects long-range electronic effects. It develops continuously from the p-like crystal-induced surface state of the clean surface. This conclusion goes beyond the earlier interpretation of SS as adsorbate band [9]. We are aware of the fact that the distinction between the surface band and adsorbate band is somewhat artificial, because both are localized at the very surface. By calling it a surface state we just want to indicate its origin. Future theoretical work in a more chemical picture will have to evaluate to what extent SS has antibonding character and where its wave function is located. Nevertheless, it represents an electronic state located at a ferromagnetic surface, capable of telling us about any adsorbate-induced magnetic changes.

Measurements of the magnetic exchange splitting ΔE_{ex} of SS are shown in Fig. 3. Since on the clean surface SS is partly occupied at $\bar{\Gamma}$, a quantitative determination of ΔE_{ex} is only possible for off-normal electron incidence, where SS becomes completely empty. For $\Theta = -12°$ (lower part of Fig. 3), the surface state emission has been separated from transitions into empty d states by exposing the surface to 0.9 L CO, which quenches SS almost completely. From the difference spectra ΔE_{ex} has been deduced to 106 ± 22 meV [11]. Spectra for the $p(2\times2)$-O overlayer recorded for a similar angle of incidence $\Theta = 10°$ are shown in the upper part of Fig. 3. They reveal a ΔE_{ex} of only 22 ± 10 meV, 5 times smaller than on the clean surface. Similar values for ΔE_{ex} ranging from 15 to 25 meV have been found in spectra for a number of different Θ (see for example the $\Theta = 0$ spectra in Fig. 1).

To get an impression about the oxygen-induced changes of the bulk electronic structure of Ni(111), we have studied a transition between sp bulk bands. Figure 4 shows spin-resolved IPE data of an sp bulk band transition B observed at about 1.5 eV above E_F for $\Theta = 40°$ in the $\bar{\Gamma}\bar{K}$ azimuth. Comparing the data for B of the clean surface with those of the $p(2\times2)$-O overlayer reveals an

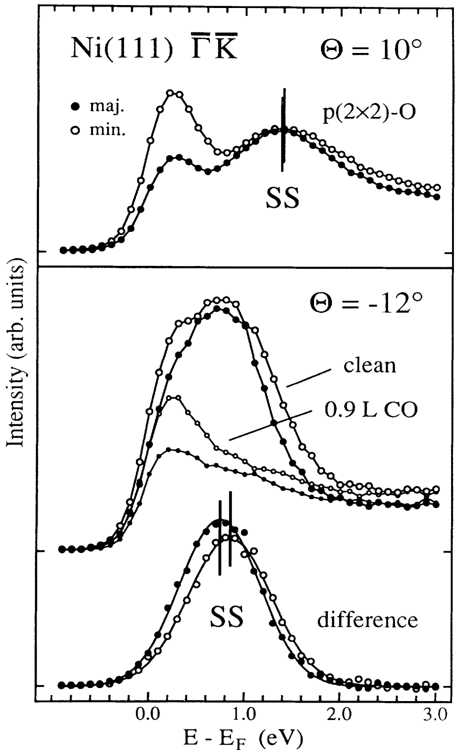

FIG. 3. Spin-resolved IPE spectra of Ni(111) for $\Theta = -12°$ (lower part) and of Ni(111)-$p(2\times2)$-O for $\Theta = 10°$ (upper part). The surface state (SS) emission of the clean surface has been separated from transitions into d states by exposing the surface to 0.9 L of CO. The exchange splitting of SS is reduced from about 100 meV at the clean surface to less than 25 meV for the $p(2\times2)$ oxygen overlayer.

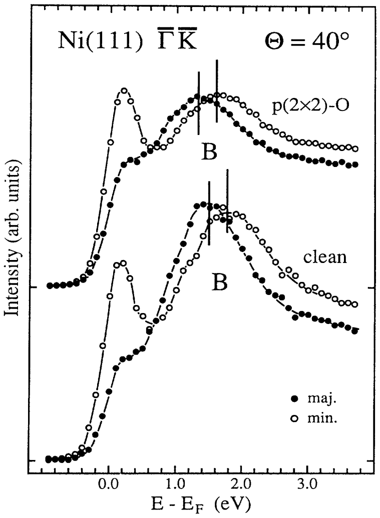

FIG. 4. Spin-resolved IPE spectra of an *sp* bulk band transition (B) observed on Ni(111) for $\Theta = 40°$ in the $\overline{\Gamma K}$ direction. The spin splitting of B on the clean surface remains unaffected by the $p(2\times2)$ oxygen overlayer.

oxygen-induced attenuation of the intensity, but no change of the spin splitting ΔE_{ex} of about 280 meV. This result shows that the spin-dependent bulk electronic structure of Ni(111) is not affected by the oxygen overlayer. The slight shift to the lower final energy of B accounts for the work function change, leading to a different $\mathbf{k}_{\parallel}$ for spectra recorded at the same Θ.

In conclusion, spin-resolved inverse photoemission data of Ni(111) as a function of oxygen exposure exhibit a truly magnetic surface state on the clean surface that becomes nonmagnetic by oxygen adsorption. With increasing oxygen exposure the partly occupied state becomes completely empty and no longer contributes to the surface magnetic moment. Moreover, its exchange splitting is lowered by a factor of 5. Certainly, a quantitative determination of the reduced magnetic moment is not possible from **k**-resolved electronic-structural data. However, the data show the adsorbate-induced reduction of the surface magnetic moment reflected in the surface electronic structure. The unchanged spin splitting of an *sp* bulk band transition shows that the magnetic influence of the oxygen is limited to the very surface. The result is not contradictory to experiments on other adsorption systems, which revealed exchange-split adsorbate-induced bands. The appearance of adsorbate-induced states in electronic-structural data does not show directly where their wave functions are concentrated and what degree of localization they have. In addition, hybridization with electronic states of the substrate has to be taken into account. In general, the spin splitting of adsorbate-induced states cannot be translated directly into numbers for magnetic moments. Nevertheless, in case the origin of adsorbate-induced spectral features is known, they provide detailed information about the bonding mechanism between substrate and adsorbate and about changes of the surface magnetic properties. Consequently, results on reduced surface magnetization as well as spin-split adsorbate-induced bands complement each other, an example of which has been given in this Letter. Studying both aspects helps to develop a detailed picture about the influence of adsorbates on surface magnetic properties.

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