

Effect of adsorbates on the spin-polarized photoemission of itinerant ferromagnets

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The adsorbate systems $O(2 \times 1)/Ni(110)$, $Sc(2 \times 2)/Ni(110)$, and $Op(2 \times 2)/Fe(110)$ were investigated by means of spin-, angle-, and energy-resolved photoemission spectroscopy. For the Ni $3d$ bands with S_4 symmetry near the X point of the Brillouin zone we find no change of the exchange splitting due to adsorption of O and S. A majority-spin band with S_3 symmetry at the same k point shows a slight shift to lower binding energies under adsorption of O. For $Op(2 \times 2)/Fe(110)$ no changes in binding energy were observed for the Fe d bands with Σ_j and Σ_k symmetry. Depolarization effects of the photoelectrons caused by the adsorbates are interpreted in terms of exchange scattering processes. The same scattering process gives rise to very pronounced structures in the spin-resolved spectra of $Sc(2 \times 2)/Ni(110)$. Different scattering probabilities for majority and minority electrons indicate that O and S on Ni(110) are polarized parallel to the Ni bulk spin polarization.

I. INTRODUCTION

The influence of various adsorbates on the surface magnetism of $3d$ transition metals has been the subject of intense experimental and theoretical work in recent years. All the experimental results agree in one general point: that the surface magnetization is reduced under adsorption. Magnetometer investigations showed that the magnetization of small Ni particles decreases under adsorption.¹ By means of ferromagnetic spin resonance in thin Ni films it was found that H and CO quench the magnetic moments at the surface.² Besides these more integral methods some surface- and spin-sensitive experiments were carried out. Spin-resolved field emission³ and electron-capture spectroscopy⁴ of H on Ni surfaces showed a drastic reduction of the spin polarization. Recently, the intensity decrease of a Ni minority-spin peak in spin-polarized inverse photoemission upon adsorption of O and CO on Ni(110) was interpreted in terms of a filling up of the minority holes which should lead to a reduction of the magnetic moment.^{5,6}

While in the past magnetic effects were usually ignored in theoretical treatments of adsorption on transition metals, recent calculations include the magnetic moment at the surface. The result is that the magnetic moment of the layers in contact with the adsorbate should be more or less reduced compared to the bulk value.^{7,8} Only in very recent work about O on Fe(001) one finds no reduction of the magnetic moment at the Fe surface and a small moment of the oxygen adlayer.⁹ A magnetic moment for the adatom was also found in Ref. 8.

Spin-, angle-, and energy-resolved photoemission from the Ni(110) surface with $h\nu = 16.85$ eV offers the possibility of observing with high surface sensitivity (band-gap emission) a spin-split electronic state, i.e., the exchange splitting of Ni.¹⁰ This technique is therefore capable of giving detailed information about the influence of adsorbates on the magnetic behavior of the surface.

For Fe(110) the situation is less fortunate, because of a larger escape depth of the photoelectrons for $h\nu = 21.2$

eV due to real final states. But the surface sensitivity of the photoemission experiment is still sufficiently high to probe the surface magnetism.

II. EXPERIMENTAL PROCEDURE

The apparatus used for the present work is described in detail elsewhere.¹¹ Therefore in the present paper we restrict ourselves to a brief description.

The light source used was a gas-discharge lamp, operated with Ne and He gas in the case of Ni and Fe samples, respectively. For the investigation of Ni(110) a polarizer was attached to the lamp, providing a light polarization of about 90%.

Energy analysis of the photoelectrons was carried out with a 180° hemispherical analyzer with an energy and angle resolution of 100 meV and $\pm 3^\circ$, respectively. The spin analysis of the electrons was performed by means of a Mott detector.

To prevent magnetic stray fields the Ni single crystal was cut into a picture-frame shape with its sides parallel to $\langle 110 \rangle$ directions, as was also used for previous investigations.¹⁰ All measurements were carried out with permanently magnetized samples. The surface of the sample was cleaned in cycles of Ne^+ -ion bombardment using energies of 1200 eV and subsequent annealing at $600^\circ C$. After exposing the sample to 1 L ($= 1$ langmuir $= 10^{-6}$ Torr sec) O_2 the $O(2 \times 1)$ structure was obtained as evidenced by the appearance of sharp extra low-energy electron-diffraction (LEED) spots. The $Sc(2 \times 2)$ structure was obtained by heating the sample to about $150^\circ C$ and exposing it to H_2S until a sharp (2×2) LEED pattern was observed.

The iron sample was a 30-\AA -thick Fe(110) film which was grown epitaxially on W(110). The substrate was a W single-crystalline platelet of about 7 mm diameter. Single-domain remanent magnetization of the Fe film was achieved by magnetizing it in a separate coil by a field pulse of about 500 Oe. Stray fields were negligible because of the small thickness of the film. A detailed

description of the preparation of the Fe/W(110) films is given elsewhere¹² and is therefore omitted here.

A $p(2 \times 2)$ LEED pattern of O on Fe(110) was observed after exposing the Fe sample to 3–4 L O₂, which is a somewhat higher exposure than reported in the literature for Fe single crystals.^{13,14}

To obtain sufficient statistics in the spin-resolved photoemission intensities, measuring times of 5–30 h for one complete spectrum were necessary. These total times were achieved by adding several spectra with individual measuring times of up to 1 h for the clean surfaces and 1.5 h for the contaminated surfaces. Between consecutive runs the samples were freshly prepared in the manner described above.

III. EXPERIMENTAL RESULTS

A. O(2×1)/Ni(110)

The (2×1) superstructure of O on Ni(110) is due to a surface reconstruction. Recent investigations of the system O(2×1)/Ni(110) using various experimental methods come almost unanimously to the conclusion that this reconstruction can be described by a sawtooth model rather than the missing-row model.^{15–17} The sawtooth of Ni atoms builds up in the $[1\bar{1}0]$ direction and the oxygen atoms sit in long bridge positions along $[001]$. Scanning-tunneling-microscopy experiments showed that the reconstruction is not complete, i.e., one finds reconstructed domains which cover 35% of the surface.¹⁶

In the case of O on Ni(110) the normal-emission photoelectron spectra were measured using linearly polarized light with $\mathbf{A} \parallel [1\bar{1}0]$ or $\mathbf{A} \parallel [001]$ and $h\nu = 16.85$ eV. In a previous publication¹⁰ it was shown that under these conditions photoemission probes near the X point of the Brillouin zone the spin-split bands with S_4 symmetry for $\mathbf{A} \parallel [1\bar{1}0]$ and the occupied majority band with S_3 symmetry for $\mathbf{A} \parallel [001]$. In addition, for the given photon energy one finds band-gap photoemission, which should increase

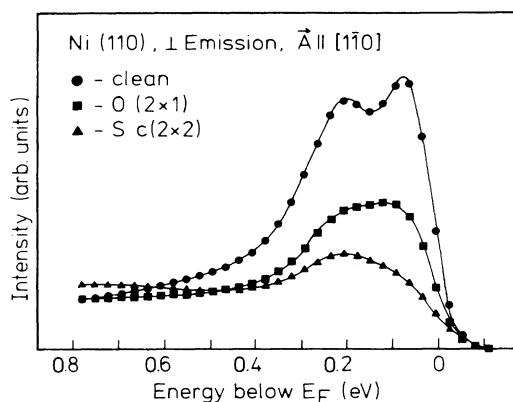


FIG. 1. Electron-distribution curves of clean and adsorbate-covered Ni(110) for emission from bands with S_4 symmetry. The intensities are normalized for the count rates.

the surface sensitivity of the experiment because of a very small escape depth of the electrons.¹⁰

After adsorption of oxygen there is a strong reduction of the intensity for emission from the Ni $3d$ bands with S_4 symmetry as shown in Fig. 1. The reduction is about 45% for the O(2×1) structure. The spin-resolved spectra for the S_4 bands are shown in Fig. 2. The uppermost panel shows the spectrum for the clean surface. Both the majority- and minority-spin spectra are dominated by a single distinct peak, which originates from the S_4^+ and S_4^- band, respectively. The exchange splitting can directly be determined to 180 meV.¹⁰

The corresponding spectrum after oxygen adsorption can be found in the middle panel of Fig. 2. It is obvious that the separation of the two peaks and therefore the exchange splitting has not changed. Besides a reduction in intensity the main difference of the spectrum of the contaminated surface with respect to that of the clean surface is an asymmetric broadening of the majority-spin peak to lower binding energies and of the minority-spin peak to higher binding energies.

Contrary to the results of the photoemission from the S_4 bands we do not find a significant decrease of the emission intensity of the S_3 band. The spin-resolved spectrum

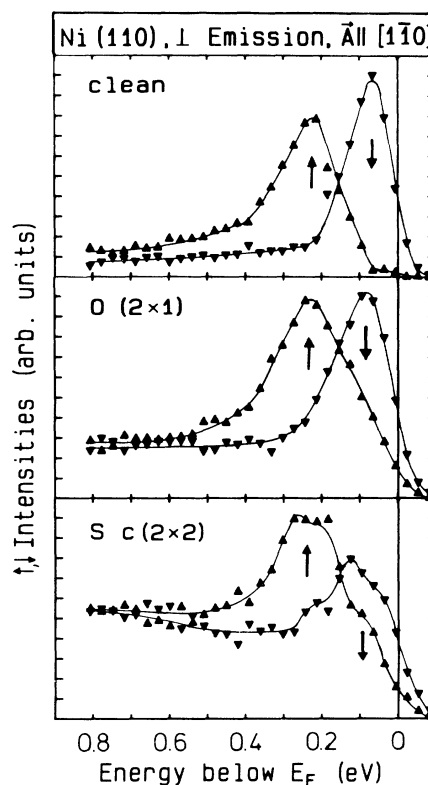


FIG. 2. Spin-resolved spectra for emission from Ni bands with S_4 symmetry for the clean, oxygen- and sulfur-covered (110) surfaces. \blacktriangle , majority-spin electrons; \blacktriangledown , minority-spin electrons. The error bars of the data points are in all cases smaller than the size of the symbols.

shows mainly one peak for the S_3^{\uparrow} band, since near the X point the S_3^{\uparrow} band lies above the Fermi energy and can therefore not be observed. As can be seen in Fig. 3 the S_3^{\uparrow} peak shifts by about 50 meV towards lower binding energies after adsorption of O_2 . For the minority-spin spectrum no significant change can be detected with respect to the statistical error.

B. $S c(2 \times 2)/Ni(110)$

Sulfur forms the $c(2 \times 2)$ structure with the S atoms in the hollow-site positions of the Ni(110) surface.¹⁸ Owing to the adsorbate the relaxation of the clean Ni surface is inverted, leading to a 10% larger interlayer distance between the surface and subsurface layer compared to the bulk value.¹⁹

For this system measurements were carried out only with light polarized parallel to $[1\bar{1}0]$, thus probing the S_4 bands, because the intensity of the S_3 band decreased strongly after S adsorption and became too small to make spin-resolved measurements feasible. This behavior is in contrast to the results obtained for the oxygen adsorption.

For the $S c(2 \times 2)$ structure (coverage $\Theta=0.5$) a 60% attenuation of the photoemission intensity is found for the S_4 bands as shown in Fig. 1. Although the energy-distribution curve becomes rather structureless after S adsorption, spin-resolved photoemission provides more detailed information. This can be seen in the bottom panel of Fig. 2, where new structures are observed.

In both the majority and minority spectra the peaks show a dip at the center of gravity of the maxima found for the clean surface. In addition, at the same energies the spectra of the opposite spin direction exhibit shoulders. The observed structures are reproducible and not due to

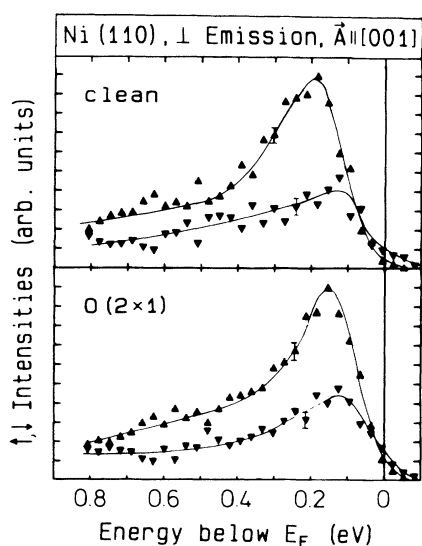


FIG. 3. Spin-resolved spectra of clean and oxygen-covered Ni(110) for emission from bands with S_3 symmetry. Symbols as in Fig. 2.

statistical errors. Like in the case of oxygen adsorption the center of gravity of the peaks does not shift compared to the peak positions for emission from the clean surface.

C. $O p(2 \times 2)/Fe(110)$

For the investigation of this system we chose unpolarized light with $h\nu=21.2$ eV and an angle of incidence of 60° . Under these conditions we have a large contribution of s -polarized light (perpendicular to the surface normal) with A parallel to the $[1\bar{1}0]$ direction, yielding emission from bands with Σ_4 symmetry. Another main contribution to the photoemission originates from bands with Σ_1 symmetry because of a considerable part of p -polarized light (parallel to the surface normal) due to the large angle of incidence. The magnetization of the sample was along $[1\bar{1}0]$, which is the easy-magnetization axis for Fe(110)/W(110) films with thicknesses below 60 \AA as discussed in Ref. 12 and references therein.

The spin-resolved spectrum for the clean Fe surface is shown in Fig. 4 (upper pane, solid lines). The minority-spin spectrum consists of one prominent peak at 0.4 eV binding energy which originates from a Σ_1^{\uparrow} band. The majority-spin spectrum exhibits a maximum at about 1.5 eV binding energy which is due to emission from a Σ_4^{\uparrow} band. Unresolved emission from a Σ_1^{\uparrow} band at higher binding energy leads to the strong asymmetry of the majority-spin spectrum at binding energies above 2 eV. The shoulder in the majority-spin spectrum near the Fermi energy could not be identified up to now.

Adsorption of O_2 on the Fe(110) surface has a less drastic effect compared to the case of Ni(110). The intensity reduction was only about 10% (Fig. 4, upper panel, dashed lines). A change of the peak positions was not observed. The most obvious influence of the O adsorption is an overall reduction of the spin polarization by 20–30 %

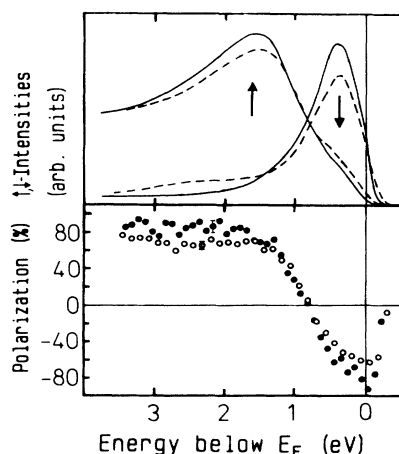


FIG. 4. Spin-resolved spectra and spin polarization for emission from clean Fe(110) (—, ●) and $O p(2 \times 2)/Fe(110)$ (---, ○).

(lower panel). As can be seen from the direct comparison of the two spectra in the upper panel of Fig. 4, this reduction in spin polarization is on one hand, due to the decrease in intensity. On the other hand, analogously to our results for the adsorption of O and S on Ni(110), we find an increase of the majority- (minority-) spin intensity at the maximum of the minority- (majority-) spin intensity.

IV. DISCUSSION

For all three investigated adsorbate systems we do not find a significant change in the peak positions of the spin-resolved intensities, except for the slight shift of the S_3^{\downarrow} band of Ni(110) under O adsorption. This is consistent with inverse-photoemission experiments,⁵ where the position of the unfilled Ni states with S_2 symmetry was also found to be unchanged under O adsorption. In particular, we find no hint of a decrease of the exchange splitting of the S_4 bands of Ni(110) under adsorption of O and S.

This last result is somewhat contrary to our conclusions from previous spin-resolved photoemission investigations of O/Ni(110) using unpolarized light.²⁰ The former interpretation came about because the contribution of the S_3^{\downarrow} band to the spectrum could not be separated from that of the S_4^{\downarrow} band. The practically unchanged intensity from the S_3^{\downarrow} band and the decrease of the emission from the S_4 bands under oxygen adsorption led to the observed shift of the peak of the majority-spin spectrum towards lower binding energy, which suggested a decrease of the exchange splitting.

Despite the unchanged exchange splitting, a formation of magnetic dead layers after adsorption of O cannot be excluded completely, because the overlap of the orbitals with S_4 symmetry is destroyed in the two topmost Ni layers due to the sawtooth reconstruction. Therefore we do not expect any contribution of these two layers to the photoemission from the S_4 bands. This is supported by the photoemission calculation in Ref. 21, where the exchange splitting was found to be independent of the magnetization of the first two Ni layers.

The slight shift of the S_3 peak towards lower binding energy may be an indication for a decrease of the magnetic moment at the surface. The orbitals with S_3 symmetry are oriented in the [001] direction, i.e., along the sawtooth ridges, and should therefore be less affected by the reconstruction, except for some hybridization with the $2p$ orbitals of oxygen in the long bridge positions along the ridges. Hence we expect photoemission from the S_3 bands in the surface layers. The oxygen itself does not seem to play an important role because in the calculation in Ref. 21 a shift of the peaks is found by taking into account the sawtooth reconstruction only, without putting oxygen on the surface. However, the lack of an increase of minority-spin intensity in the S_3 band spectrum after O adsorption indicates a negligible effect on the magnetic moment.

In the following we want to give a qualitative interpretation of the different effects of the adsorption of O and S on the spin-resolved intensities of Ni(110). In Fig. 5 we show the spin-resolved spectra of the S_4 bands on the same scale for both the O-covered (solid line) and the clean (dashed line) Ni(110) surface. For the O-covered

surface we find with respect to the clean surface an increase of majority- (minority-) spin intensity at the binding energy of the minority (majority) peak. One reason for such an effect could be a reduction of the magnetization due to a disturbed magnetic order as it is observed for iron at high temperatures.²² But such a disordering effect should equally affect both the spin-up and spin-down intensities. From Fig. 5, however, it is obvious that the intensity gain is larger in the majority-spin spectrum than in the minority-spin spectrum. The relative changes of the measured polarization at the peak position of the minority- (majority-) spin intensity is -57% (-34%). Even if one corrects the spin polarization for the intensity attenuation due to the adsorbate, there is an imbalance in the relative depolarization of the minority- and majority-spin intensities which amounts to 50% and 25%, respectively.

Thus we conclude that the observed behavior is due to "spin-flip" scattering at the O overlayer, which is twice as effective for minority electrons than for majority electrons. Such a spin-flip process due to exchange scattering was described by Helman and Siegmann for a "paramagnetic" surface layer²³ and was found experimentally in several cases.²⁴ In the calculation in Ref. 23 the spin-flip intensity is proportional to the degree of orientation of the spins in the surface layer with respect to the spin of the photoelectron. In our case the different strength of the process for the different spin components is an indication of a partial polarization of the oxygen atoms parallel to the majority-spin direction of bulk Ni. On the other hand, this indicates that the Ni layers in contact with the O atoms cannot be magnetically dead, because in this case there would be no coupling to the bulk.

A recent theoretical model calculation of oxygen on the Fe(001) surface⁹ shows that the surface magnetization is not destroyed by the adsorbate and that the oxygen atoms are spin polarized, carrying a magnetic moment of $0.24 \mu_B$. Of course, this system is different from O/Ni(110), but the result emphasizes the possibility of a magnetized adsorbate layer at the surface of an itinerant ferromagnet.

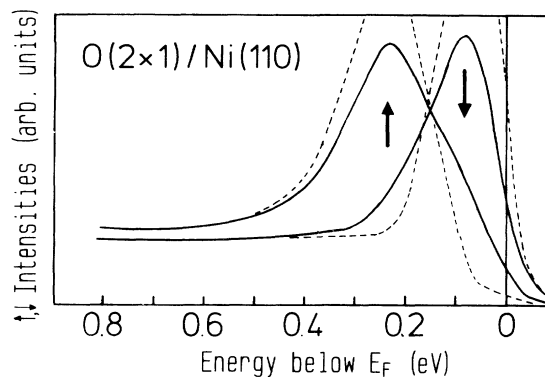


FIG. 5. For count rate normalized spin-resolved spectra for clean (---) and oxygen-covered (—) Ni(110) from Fig. 2. Intensity gains in the spectrum of the contaminated surface indicate spin-flip processes.

The changes in the spin-resolved spectra of $S c(2 \times 2)/Ni(110)$ and $O p(2 \times 2)/Fe(110)$ are due to the same spin-flip mechanism as for O on $Ni(110)$. In the case of the sulfur adsorption the depolarization is also stronger for the minority electrons than for majority electrons. This is, analogously to the case of $O/Ni(110)$, a hint to a partial polarization of the sulfur atoms parallel to the Ni bulk spin polarization. Differences in the behavior can be explained in terms of different spatial origins of the observed photoelectrons for the different systems. As can be seen in Fig. 2, the two spin-resolved S_4 peaks exhibit a rather peculiar shape after the contamination with sulfur. This shape, however, can easily be explained by the construction indicated in Fig. 6. First, the amount of intensity increase in the regions of the additional shoulders was roughly estimated by drawing the dashed curves, which were scaled down from those of the clean surface. This yielded the hatched areas labeled A. These additional intensities were then added to the peaks of the opposite spin direction, yielding the hatched areas labeled B. For this procedure it was assumed that the spin-flip scattering process at the partially polarized adsorbates is quasielastic, i.e., does not involve propagating magnon modes. Any inelastic excitation below 100 meV could not be resolved because of our experimental resolution. The important point is that we obtain nearly Lorentzian line shapes with maxima positioned at the same energies as for the clean surface, which are indicated by the two tic marks in Fig. 6. Thus we conclude that the pronounced shoulders and the dips in the maxima have the same origin. This modification of the peak shape is very selective in energy and can be described as an "energy-dependent spin-flip" scattering at the sulfur atoms with a scattering probability which is maximum near the peak positions of the spectra and has a full width at half maximum of about half the width of the photoemission peaks. This energy dependence clearly excludes the effect of magnetic disorder to be responsible for the spin depolarization in the case of S adsorption on $Ni(110)$.

The most plausible explanation for the energy depen-

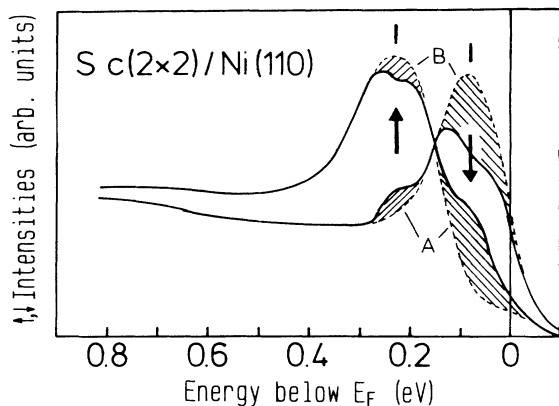


FIG. 6. Spin-resolved spectrum of $S c(2 \times 2)/Ni(110)$. For explanation of the hatched areas A and B see text.

dence of the scattering probability is the following. Since after S adsorption there is no surface reconstruction but rather a 10% expansion of the interlayer distance between the surface and the subsurface layers, the main contribution to the photoemission intensity comes from the first Ni layer (band-gap emission), which is in contact with the sulfur atoms. The sulfur atoms are actually located more or less within the first Ni layer. Therefore it is probable that the excitation of the photoelectron and the exchange scattering process take place in the same region and at the same time. This leads to the effect that spin-flip and lifetime broadening interfere, resulting in structures sharper than the broadened photoemission peaks. Another reason for this energy-selective effect could be a spatial dependence of the lifetime broadening. The latter may be smaller in the surface layer of Ni due to the reduced electron densities. For the case of oxygen we have a different situation. Here the electrons originate from a Ni layer which is well separated from the adsorbate layer, so that it is more likely that the excitation process can be separated from the scattering process. To get full insight into the phenomenon it is necessary to include spin-dependent scattering in one-step photoemission theories. This seems also to be desirable in the light of other experimental results which show that the exchange-scattering process is very effective compared to other interactions.^{24,25}

The above explanations of our data are rather speculative. The reason for that is the lack of a theory treating such exchange-scattering effects microscopically. Much more insight into the phenomena could be achieved if such a theory could be included into a photoemission calculation.

For the case of $O p(2 \times 2)/Fe(110)$ we find a similar spin-depolarization effect (see Fig. 4) as for $O(2 \times 1)/Ni(110)$, but less pronounced. This could be due to the dependence of the exchange scattering on kinetic energy. It is known that the strength of the scattering process decreases with increasing kinetic energy. This gives rise to a smaller effect in the spectra of Fe , where the photon energy was 21.2 eV compared to Ni , where the spectra were taken with $h\nu = 16.85$ eV. One also does not expect a sharp structure in the spectra as observed for S on Ni because the escape depth of the electrons in the case of Fe is larger due to real final states compared to the band-gap emission in the case of Ni . Thus an appreciable contribution to the photoemission originates from iron layers which are not in contact with the O atoms. From the present data it is not possible to decide whether the oxygen at the $Fe(110)$ surface is spin polarized or not, because the intensity changes cannot be determined accurately enough.

In conclusion, we find no strong effect on the surface magnetism of the investigated Ni and Fe surfaces due to adsorption. This is evidenced by the practically unchanged binding energies, i.e., exchange splitting of the observed d bands. Moreover, magnetic dead layers at the substrate surface can be ruled out because of the spin polarization of the adsorbate atoms with respect to the bulk magnetization of the substrate, giving rise to the imbalance in the spin-flip exchange scattering of spin-down and spin-up electrons.

Depolarization effects for the spin-polarized photoelectrons are ascribed in all three investigated adsorbate systems to spin-flip exchange-scattering processes at the partially spin-polarized adsorbate atoms and not due to a reduction of the surface magnetization. The system $S c(2 \times 2)/Ni(110)$ plays a special role, because the sulfur atoms sit in hollow-site positions in very close contact to the top Ni layer, which in combination with surface sensitive band-gap emission gives rise to an interference between the lifetime broadening and the exchange-scattering

process. This results for this particular case in sharp structures in the spin-resolved photoemission spectra.

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