

Electronic structure of atomic oxygen adsorbed on Ni(100) and Cu(100) studied by soft-x-ray emission and photoelectron spectroscopies

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The electronic structure of $c(2 \times 2)$ -O/Ni(100) and $p(2\sqrt{2} \times \sqrt{2})R45^\circ$ -O/Cu(100) has been studied by soft-x-ray emission spectroscopy (SXES), ultraviolet, and x-ray photoemission spectroscopies (UPS and XPS). For O/Ni(100), the $2p$ -derived states are centered at 6 eV below the Fermi level. There is intensity from these states all the way up to the Fermi level, due to the $2p$ - $3d$ hybridization. The sharp edge of the SXES intensity at the Fermi edge indicates that the antibonding $2p$ - $3d$ states are partly occupied. This is also manifested in the asymmetric line shape of the O $1s$ XPS peak. In O/Cu(100), on the other hand, these states are close to fully occupied, and observed around 1–2 eV binding energy in the UP and SXE spectra. The higher energies of the excitations from the filled $2p$ - $3d$ states result in a discrete satellite about 3 eV from the O $1s$ main line in the O/Cu(100) XPS spectrum. The main SXES intensity is positioned at about 4–5 eV, i.e., in the region of the Cu d band, indicating a larger O-Cu hybridization in this energy region than previously reported.

I. INTRODUCTION

Atomic oxygen adsorbed on metal surfaces has been the subject of a large number of investigations. In particular, the interaction between oxygen and transition metals¹ has attracted interest, partly due to important technical implications. Oxygen chemisorbed on Ni(100) and Cu(100) are examples of well-characterized systems, as far as the geometrical structures are concerned (e.g., Refs. 1–7). In both cases, oxygen forms ordered overlayers of strongly chemisorbed atoms at a coverage of half a monolayer.^{2,3,6,8} On Ni, a $c(2 \times 2)$ structure is formed, where the O atoms occupy fourfold hollow adsorption sites^{2,3} about 0.8 Å above the surface Ni layer.⁴ The O/Cu(100) surface is reconstructed, forming a $p(2\sqrt{2} \times \sqrt{2})R45^\circ$ structure.^{5,6,8} This overlayer corresponds to a $c(2 \times 2)$ phase of oxygen atoms, where every other row of Cu surface atoms is missing⁵ and the oxygen atoms adsorb close to in the plane of the Cu surface layer.⁷

The electronic structure of O/Ni(100) and O/Cu(100) has been studied using various theoretical methods (e.g., Refs. 9–18). It has also been studied experimentally, by e.g., (angle-resolved) ultraviolet photoelectron spectroscopy (ARUPS or UPS),^{19–24} and inverse photoemission (IPE).²⁵ Some major conclusions have been agreed upon from experimental and theoretical results. Hybrid orbitals are formed between the O $2p$ and the metal $4sp$ and $3d$ states, and the hybridization with the $4sp$ states is the strongest. Liebsch used a (layer-Korringa-Kohn-Rostocker) multiple-scattering method in order to calculate the electronic structure of O/Ni(100).¹⁰ He found that the hybridization splits the O $2p$ level into bonding states below and unoccupied antibonding states close to the Fermi level. The bonding states appear around 6 eV below the Fermi level, according to *ab initio* band calculations performed by Wang and Freeman¹¹ and linearized augmented-plane-wave calculations by Godby *et al.*¹² Using the localized-orbital pseudopotential method, Bul-

lett found similar states at about 4 eV.⁹ The theoretical results are in agreement with UPS measurements of the $c(2 \times 2)$ phase of O/Ni(100), where an oxygen-induced feature was observed at about 6 eV binding energy.^{19,20} An oxygen $2p$ -derived state has also been found in UP spectra from O/Cu(100) at about 6 eV below the Fermi level.^{21–24} Furthermore, states related to the adsorbate have been observed in the UP spectra above the Cu d band.^{21–24}

The role of the $3d$ band in the formation of the chemical bond has been a subject for discussion through the years. It is therefore interesting to compare the adsorption of oxygen on Ni and Cu, since the substrates have different d -band properties. In Ni it is positioned near the Fermi level, and there are empty d states above the Fermi level. In Cu, the d band is almost completely filled and positioned about 3 eV below the Fermi edge.

A drawback of the experimental methods previously used for the studies of these aspects of the electronic structure is the strong substrate-induced features overlapping weaker contribution from the adsorbates. In the case of Ni and Cu, the d band will be the dominant feature in a UV excited valence spectrum, because of the large photoionization cross section. In this paper, soft-x-ray emission spectroscopy (SXES) is used, a method which provides complementary information about the valence states. SXES is well established for gas phase and bulk studies,²⁶ but is new for surface studies. It is not inherently surface sensitive when photons are used for excitation. Only recently has it been used for studying adsorbate systems.^{27,28} The surface sensitivity was enhanced by using synchrotron radiation for excitation in grazing incidence.

The final state in SXES is the same as for UPS, i.e., it involves a valence hole. However, the initial state of SXES is different, since a core hole is present on one atom. The probability for a particular valence state to be involved in the decay of the core hole, and thus contribute to the intensity in the fluorescence spectrum, is given

by the dipole matrix element between this state and the initial core hole. If the core hole is located at the adsorbate, the decay will mainly involve the adsorbate valence states, whereas the substrate features contribute little to the spectrum. Since dipole selection rules apply, it is possible to determine the atomic character and bonding symmetry of the states observed in the SXE spectra. An initial O 1s core hole, for example, implies that the spectral intensity is mainly due to decay from the O 2*p*-derived states in the adsorbate-substrate valence levels. The local symmetry properties of the valence states can be probed by performing angular resolved SXE measurements. SXES and UPS are thus complementary methods when studying the hybridization between adsorbate and metal states upon chemisorption.

In the present paper, the electronic structure of O/Ni(100) and O/Cu(100) is studied using SXES, UPS, and x-ray photoelectron spectroscopy (XPS). We show spectra recorded from the $c(2 \times 2)$ phase of O/Ni(100) and the $p(\sqrt{2} \times \sqrt{2})R45^\circ$ phase of O/Cu(100), both corresponding to $\theta_0 = 0.5$ in surface units when fully developed.^{2,3,6,8} It is of particular interest to compare the valence regions from these adsorbate systems, since the *d*-band positions are different for Ni and Cu. The difference in electronic structure of O on Ni(100) and Cu(100) is also manifested in the O 1s XPS shake-up spectra, since the satellite structures are related to valence excitations upon oxygen core ionization.

II. EXPERIMENT

The SXES experiments were performed at MAX, the national synchrotron radiation facility in Lund, Sweden. White light from a bending magnet was used for excitation, using only a thin Al foil (130 mg/cm²) as a filter in order to reduce the UV background and the sample damage. Radiation in a fan of about 25 mrad was collected by an ellipsoidal mirror and focused onto the sample at 2–5 deg grazing angle. This angle was chosen in order to enhance the surface sensitivity. The fluorescence was detected at normal emission, using a multigrating grazing incidence spectrometer, described in detail elsewhere.^{26,29} Spectra were recorded in first order of diffraction using a 5-m-radius spherical grating with 1200 lines/mm. This provides an instrumental resolution of 0.3 eV. The O *K* emission energy scale was calibrated by recording in second order of diffraction, the emission due to the 3*d*-2*p*_{1/2,3/2} transitions in Ni. The energies of these transitions are well known³⁰ and we estimate the uncertainties in the energy scales to be less than ± 0.3 eV.

The experimental equipment for photoemission, located in Uppsala, is provided with both high-resolution and high-intensity Al *K* α excitation, as well as monochromatized He II α radiation. The system, described in detail elsewhere,³¹ consists of two interconnected vacuum chambers, one preparation chamber which is placed on top of the spectrometer chamber. The x-ray source consists of a rotating, water-cooled anode and a crystal monochromator, mounted in a Rowland circle arrangement. The UV photons are provided by a gas-discharge lamp. A toroidal grating is used to obtain pure He II α ra-

diation. The analyzer is hemispherical and electrostatic with a mean radius of 36 cm, and it employs a multichannel detection system.

The samples were cleaned by conventional methods, i.e., repeated cycles of Ar⁺ sputtering and annealing. The Ni(100) crystal was heated in oxygen in order to remove carbon impurities diffusing from the bulk, before annealing to above 1100 K. The Cu(100) crystal was annealed to 950 K in vacuum. The atomic O overlayers were prepared by decomposing O₂ at elevated temperatures. On Ni(100), great care was taken in order to avoid the formation of NiO islands when preparing the $c(2 \times 2)$ phase. The overlayers were monitored by low-energy electron diffraction and, in the photoemission work, also with XPS. Although the photon flux was in the order of 10¹⁴ s⁻¹ in the SXE experiments, the atomic overlayers were stable during the measurements, and no time effects could be observed. The sample temperature was kept at 500 K during the measurements in order to avoid contamination. The XPS and UPS spectra were recorded at 80 K.

III. RESULTS

Figure 1 shows the *K* emission from atomic oxygen adsorbed in the $c(2 \times 2)$ phase on Ni(100) (upper) and the $p(\sqrt{2} \times \sqrt{2})R45^\circ$ phase on Cu(100) (lower). The spectra were recorded normal to the surface. The normal emission implies that the spectral intensity is dominated by the decay from the *p* orbitals parallel to the surface, i.e., *p*_{*x*} and *p*_{*y*}. The details in the spectra from the two substrates are quite different. In the case of Ni(100), a broad peak [full width at half maximum (FWHM) ≈ 2.6 eV] is centered at 524 eV. There is a plateau of intensity towards higher emission energy, which ends with a sharp edge at about 530 eV. For O/Cu(100), the spectrum is dominated by a broader structure (FWHM ≈ 4.2 eV) with

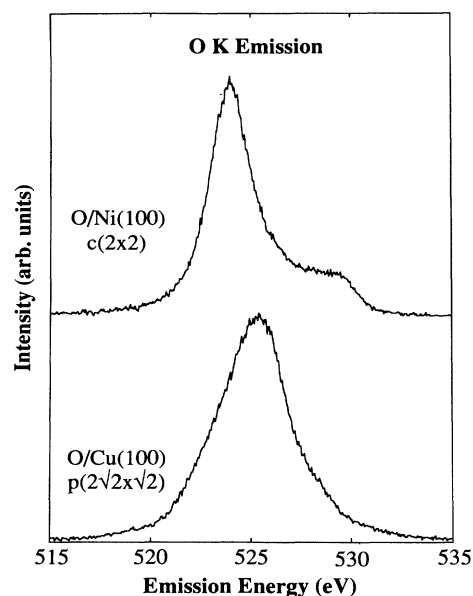


FIG. 1. The O *K* emission spectra from $c(2 \times 2)$ -O/Ni(100) (upper) and $p(\sqrt{2} \times \sqrt{2})R45^\circ$ -O/Cu(100) (lower).

a maximum at 525.4 eV. No high-energy plateau or sharp edge is seen in the spectrum.

The XPS core-level spectra from the same systems are shown in Fig. 2. The spectra were recorded at 80 K. The binding energy for $c(2 \times 2)$ -O/Ni(100) is 530.2 eV. The FWHM is 1.07 eV, which is narrower than the previously reported value for this system.³² The change is due to better resolution and lower temperature in the present measurement, but possibly also to detector saturation effects in the previous recording. For the $p(2\sqrt{2} \times \sqrt{2})R45^\circ$ structure of O/Cu(100), the peak appears at 530.1 eV and the FWHM is 0.78 eV. There are clear differences both in linewidths and line profiles between the two oxygen core levels. The peak from O/Ni(100) is substantially broader than the O/Cu peak and is also strongly asymmetric. For O/Cu, the line is more symmetric. In this case a weak but distinct shake-up structure can be observed about 3 eV from the main line.

The main line in core-level photoemission spectra of a chemisorbed species generally corresponds to a completely screened final state. The screening charge is taken from the Fermi level, and the ionization process can thus be viewed as a core excitation to the Fermi level. The final state in XPS corresponds to the initial state in SXES. The XPS main line binding energy is therefore used to determine the Fermi level for the SXE spectra.

The SXE and UP spectra provide information about the occupied states in the valence region, although the intensity is governed by different processes, as discussed in Sec. I. It is therefore of interest to compare how the valence regions are mapped by the two methods. This is done in Figs. 3 and 4, for O/Ni(100) and Cu(100), respectively. The SXE spectra are shown in the upper parts, and the UP spectra from the adsorbate systems as well as

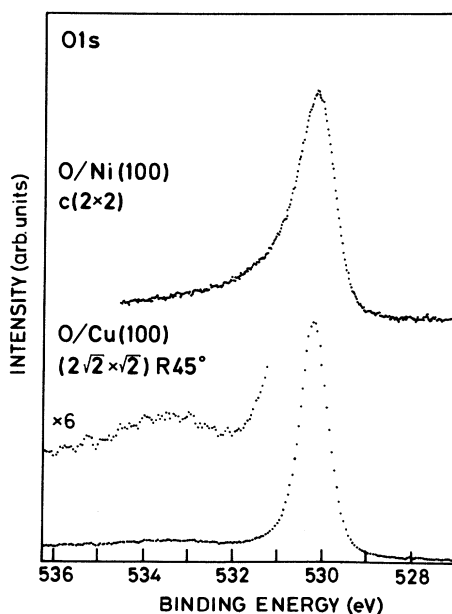


FIG. 2. XPS spectra of the O 1s level in the $c(2 \times 2)$ and $p(\sqrt{2} \times 2\sqrt{2})R45^\circ$ phases from O on Ni(100) and Cu(100), respectively.

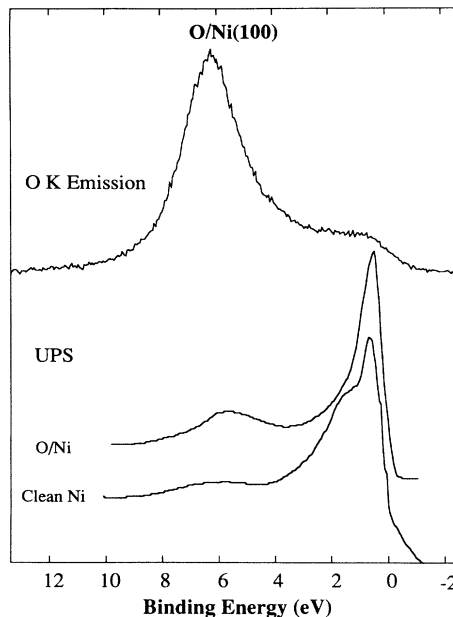


FIG. 3. Comparison between the SXE and UP spectra from the $c(2 \times 2)$ phase of O/Ni(100). The UP spectrum from the clean substrate is shown in the lower part of the figure. The UP spectra are taken from Ref. 20. The spectra are aligned to the Fermi level. The SXES Fermi level is obtained from the XPS main line binding energy (see text).

from the clean substrates in the lower part. The spectra are aligned according to the Fermi levels. For the SXE spectra, the position of the Fermi levels are given by the respective XPS binding energies, as discussed above. The O/Ni(100) and clean Ni(100) UP spectra are from Ref. 20.

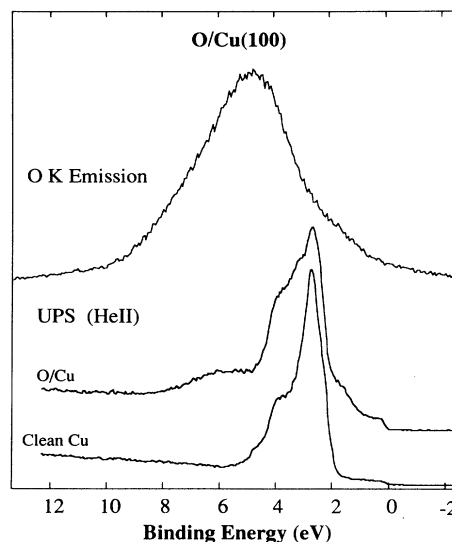


FIG. 4. Comparison between the SXE and He II excited UP spectra from the $p(\sqrt{2} \times 2\sqrt{2})R45^\circ$ phase of O/Cu(100). The UP spectrum from the clean substrate is shown in the lower part of the figure. The spectra are lined up so that the Fermi levels coincide. The SXES Fermi level is obtained from the XPS main line binding energy (see text).

In a simple picture, the SXE spectra probe the occupied part of the $2p$ derived partial density of states (DOS). Two reservations should be made, though. First, the intensity can be somewhat modified by dynamical effects. According to model calculations for free-electron systems,³³ these effects tend to build up a singular response at the Fermi level and thereby enhance the intensity at threshold. The adsorbate systems are more complicated, and it is not obvious how the dynamical response will affect the intensity distribution in the SXE spectra. Second, the spectral intensity is modified by the decay from core-hole shake-up states (nondiagram transitions). This results in a broadening of the complete spectrum towards higher emission energy (lower binding energy).

IV. DISCUSSION

A. Background

Before discussing the SXES and UPS spectra in more detail, let us consider a model for the chemisorption bond between O and Ni or Cu, based on previous studies. Since the O/Ni(100) system is more extensively studied than O/Cu(100), this part of the discussion will mainly concern the former. A schematic picture, illustrating the hybridization between O and Ni in a simple way, is shown in Fig. 5. The O $2p$ states mix with the metal $4sp$ band and form occupied bonding states, called $(2p4sp)_b$ in the figure. The underline indicates that these states have mainly $2p$ character, which has been suggested by calculations.¹⁰⁻¹² Godby *et al.* calculated the bond order, which clearly indicates that they are bonding states,¹² in agreement with previous theoretical predictions.⁹⁻¹¹ The states are centered around 5–6-eV binding energy in O/Ni(100) (Refs. 11, 12, 19, and 20) and around 6–8 eV in O/Cu(100).²¹⁻²⁴

There are corresponding antibonding states, called $(2p4sp)_a$. These are harder to see in the calculations, but Godby *et al.* mentioned states which are largely Ni sp -like well above the Fermi level in their paper on O/Ni(100).¹² $2p$ -derived states have been observed in x-ray-absorption spectroscopy (XAS) from O/Ni(100) around 10 eV above threshold.³⁴ Furthermore, the existence of these states is indicated in XA spectra from transition-metal oxides.³⁵ The large splitting between the bonding and antibonding $2p$ - $4sp$ states indicates a strong interaction between the O $2p$ and metal $4sp$ levels.¹²

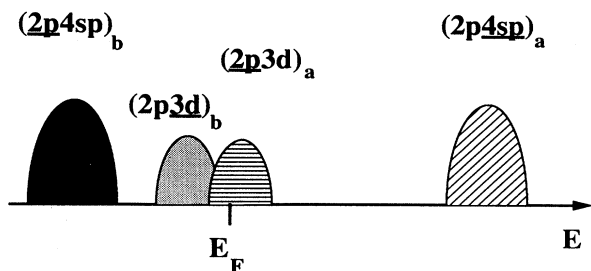


FIG. 5. Schematic picture illustrating a simple model for the hybridization between the O $2p$ and Ni $4sp$ and $3d$ states.

The interaction between the O $2p$ and the $3d$ electrons of the metal results in bonding and antibonding $2p$ - $3d$ states closer to the Fermi level, $(2p3d)_b$ and $(2p3d)_a$ (see Fig. 5). Since the interaction between the $2p$ and $3d$ states is weaker, the splitting between the bonding and antibonding states is smaller.¹² The bonding $2p$ - $3d$ states have main $3d$ character. Their position is manifested in a broadening of the calculated Ni d partial DOS towards lower binding energy,^{9,11,12} centered at about 2–3 eV. In this energy region, the O $2p$ partial DOS is very low.⁹⁻¹²

The $(2p3d)_a$ states are partly filled. The existence of adsorbate-induced states with $2p$ character close to (above and under) the Fermi level is supported by calculations.^{9-12,36} The occupied part has been difficult to observe experimentally for O/Ni(100), because of the overlapping d band in the UP spectrum. The unoccupied part, however, has been studied by Scheidt, Glöbl, and Dose who observed a substantial amount of unoccupied oxygen-derived states close to the Fermi level for O/Ni(100) in their IPE experiments.²⁵

In Cu, the d band is lower in energy, compared to Ni. This affects the energies of the $2p$ - $3d$ hybrid orbitals in a way that can be modeled by shifting the $(2p3d)_b$ and $(2p3d)_a$ states in Fig. 5 to the left. The states will come closer in energy to the bonding $2p4sp$ states, which implies that a distinction between states is more difficult in the case of O/Cu(100). The $(2p3d)_b$ states, with the large d character, appear in the energy region of the Cu d band, 3–4 eV below the Fermi level. Furthermore, the antibonding $(2p3d)_a$ states will be more occupied in Cu than in Ni. This is supported by experimental results. For O/Cu, oxygen-induced states have been observed at 1–2 eV binding energy,^{22-24,37-39} attributed to the antibonding states, whereas no unoccupied states have been observed close to the Fermi level.^{39,40} The large population of the $(2p3d)_a$ states for O/Cu is suggested to be the driving force for the reconstruction of this surface.^{15,16}

B. New results

The dominating feature in the SXE spectrum from O/Ni(100) appears at about 6 eV binding energy (see Fig. 3). It matches the adsorbate-induced spectral feature observed in the UP spectra, and agrees well with the predicted position of the $(2p4sp)_b$ states. The large SXE intensity confirms the prediction that these states have mainly $2p$ character.

The SXE feature is about 2.6 eV broad. The width is mainly governed by the bandwidth of the $2p$ derived states, but also by the energy distribution of the initial core-hole state. According to the calculations, the $(2p4sp)_b$ states have a bandwidth of nearly 2 eV.¹⁰⁻¹² Kilcoyne *et al.* obtained a similar result from their ARUPS measurements.²⁰ The FWHM of the core-hole state is about 1 eV, extracted from the XPS main line. Nondiagram transitions might give rise to an extra broadening of the SXE spectrum. In a previous publication,²⁷ it was argued that since the XPS satellite intensity from atomic adsorbates are relatively low, compared to, e.g., CO adsorbed on Ni and Cu, the contribution from these transitions would be of minor importance. Howev-

er, recent resonant Auger studies of O/Ni(100) indicate an effect of shake-up states also for this atomic adsorbate.⁴¹

The O *K* emission intensity is finite up to zero binding energy. As Godby *et al.* pointed out, the $(2p4sp)_b$ states are completely filled¹² and will not contribute to the intensity close to threshold. The extension of the $2p$ -derived states is, however, expected because of the hybridization with the Ni $3d$ states,¹² i.e., the SXE intensity close to the Fermi level originates from the $(2p3d)_a$ states. The sharp edge at the Fermi level indicates that the $(2p3d)_a$ states are partly filled, which is in agreement with the observed empty states from O/Ni(100) above the Fermi level from IPE.²⁵ It is also supported by XAS results from O/Ni(100).³⁴ The bonding $(2p3d)_b$ states have mainly $3d$ character. We expect some of the intensity about 2–3 eV below the Fermi level to be due to the $2p$ -derived part of these states.^{9,11,12}

The $2p$ orbitals are split into two groups with different symmetry characteristics when the atom is coordinated to the surface. If we define the x and y components to be parallel to the surface, they form the doubly degenerate p_x, p_y -derived states on the Ni(100) surface. The p_z orbital is oriented along the surface normal. The band calculations by Wang and Freeman suggest that $2p_x, p_y$ interact mainly with the $4sp$ states, and the $2p_z$ with the d states, since the p_z states lie slightly higher in energy, and thus closer to the d band.¹¹ This result is supported by ARUP spectra.⁴² The result can also be checked by utilizing the polarization dependence of states with different symmetry in XAS. The $(2p4sp)_a$ states, positioned about 10 eV above threshold, are only observed in XAS at normal incidence of the exciting radiation, i.e., when the $2p_{xy}$ states are probed.³⁴ As mentioned in the previous paragraph, the $(2p3d)_a$ states were observed close to the Fermi level in the XA spectra. However, they show more intensity at grazing incidence, that is, they are of dominating p_z symmetry. The XAS results thereby support the theoretical results regarding the hybridization.

The SXE spectra were recorded at normal emission. The spectral intensity is therefore mainly a mapping of the $2p_{xy}$ -derived states. The SXE intensity close to the Fermi level indicates that the $2p_{xy}$ states are involved also in the $(2p3d)_a$ states. This being the case has been shown in the calculations by Wang and Freeman.¹¹ In their orbital DOS plot of $p_{xy}(e)$ and $p_z(a_1)$, there are contributions from both orbitals at 5–6 eV and around the Fermi level, although the relative intensity at the Fermi level is larger for p_z . In the case of O/Cu(100), the broader SXE feature is centered at a slightly lower binding (higher emission) energy as compared to Ni, at about 5 eV. Adsorbate-induced features are observed in our UP spectra below (6 eV) and above (1–2 eV) the Cu d band, in agreement with previous results.^{21–24} The states at 6 eV have been assigned to the bonding $2p4sp$ states^{21–24} and have mainly p_{xy} character.^{23,24} These states are manifested in the strong x-ray emission intensity in this energy region. The bonding and antibonding $2p$ - $3d$ states [$(2p3d)_b$ and $(2p3d)_a$] have been suggested to appear below and above the d band, respectively.^{23,24} This is

supported by angular-resolved photoemission spectra from O/Cu(110) by Courths *et al.*³⁷ The antibonding states are dominated by p_z , but have also a small amount of p_x contribution on Cu(110).³⁷ We suggest that the SXE intensity around 2 eV binding energy is due to the p_{xy} contribution to the $(2p3d)_a$ states on Cu(100). The low intensity at the Fermi level indicates that the $(2p3d)_a$ states are more filled than for O/Ni(100), as discussed in Sec. IV A.

The main intensity in the SXE spectrum from O/Cu(100) is positioned around 4 eV, i.e., in the Cu d -band region. A comparison between the clean and O covered Cu UP spectra reveals changes in the d band at about 3 eV (Fig. 4 and Ref. 22). The SXES results do not compare well with the $2p$ partial density of states calculated by Jacobsen and Nørskov.¹⁵ According to their results, the bonding and antibonding $2p$ -derived states [i.e., $(2p4sp)_b$ and $(2p3d)_a$] are clearly separated, positioned about 7 eV below and 1 eV above the Fermi level, and the partial DOS in the intermediate region is low.

There has been some debate in the literature about the role of the $3d$ states in the bonding of oxygen. In cluster calculations modeling O on both Ni and Cu,^{13,14,18} the covalent bond between the $2p$ and $3d$ states was found to be truly minor, i.e., the $3d$ electrons should not contribute directly to the chemisorption bond. However, the calculations on the all-electron level showed a large effect of the $3d$ relaxation.^{13,14,18} On the other hand, more recent cluster calculations on Cu₂O indicated an important contribution of the Cu $3d$ electrons in the covalent bond.¹⁷ Our experimental data clearly indicate $2p$ - $3d$ interaction since the SXE intensity in the regions of the d band is large. In the O/Ni(100) SXE spectrum, the hybridization with the Ni d band leads to a substantial amount of $2p$ -derived states close to the Fermi level, i.e., in the energy region of the Ni d band. On Cu, the O $2p$ and Cu $3d$ states are closer in energy, and we expect at least the same amount of hybridization with the d band in O/Cu(100). However, a more detailed interpretation is difficult from our result.

We now turn to discuss the differences in the O $1s$ line profiles between O/Ni(100) and O/Cu(100), clearly seen in the XP spectra shown in Fig. 2. The line profiles are dominated by vibrational and electronic excitations in the photoionization process. The halfwidth of the low-energy side of the core lines is dominated by the vibrational broadening, which originates in a vibrationally excited final state, due to differences in the initial- and final-state potential-energy curves. The vibrational broadening can be temperature dependent, because of the thermal excitation of low-energy vibrational modes.^{32,43} The electronic excitations, i.e., shake-up excitations, give rise to spectral intensity at the low-energy side of the main line. The difference in the O $1s$ shake-up spectra probe the differences in the electronic structure between O/Ni(100) and O/Cu(100), since they are related to the local valence excitations in the core-ionized oxygen-metal system.

Børve and Siegbahn have performed cluster calculations in order to interpret the differences in the O $1s$ line

profiles.⁴⁴ They suggest that the main line in both cases corresponds to a final state screened by the $4sp$ band, and that the shake-up state is due to screening from the $3d$ band. A close-lying shake-up component would then explain the broadening of the O/Ni peak, since the d band is at the Fermi level in Ni. In Cu, where the d band is positioned about 2–3 eV below the Fermi level, the excitation would give rise to a discrete shake-up state. The cluster model does not take into account the bandlike electronic structure of the substrate, which results in continuous shake-up states rather than discrete states. An example is the asymmetric Donjac-Sunjic line profile of metal core levels, due to low-energy excitations across the Fermi level. The asymmetric line shape of O/Ni(100) indicates that there are low-lying excitations for this system, i.e., transitions between filled and empty states around the Fermi level in core-ionized O/Ni(100). As discussed above, O adsorbed on Ni(100) has $2p$ -derived states below and above the Fermi level, namely the $(2p3d)_a$ states. The effect of the core hole will be a larger occupancy of these states. However, they are not completely filled. In recent XAS measurements, some unoccupied states are observed close to threshold in core-ionized O/Ni(100).³⁴ This enables the low-energy shake-up excitations which give rise to the asymmetric core line.

For O/Cu(100), $(2p3d)_a$ states are expected to be more filled than for O/Ni(100). For O/Cu(100) the emission intensity close to the Fermi level is very weak (as far as the p_{xy} emission is concerned), and we expect even fewer states at the Fermi level in the presence of the core hole. The shake-up transitions consequently have to be from the filled $(2p3d)_a$, centered about 2 eV below the Fermi level, where the SXES intensity is strong. This would result in a discrete shake-up feature, which is observed in the O/Cu(100) XP spectra.

V. CONCLUSIONS

The interaction between atomic oxygen and the Ni(100) and Cu(100) surfaces, respectively, has been studied by soft-x-ray emission, UV and x-ray photoemission. The O $2p$ states are observed to hybridize mainly with the metal sp states, but the substantial amount of $2p$ -derived states observed in the region of the d band for both O/Ni(100) and O/Cu(100) indicate that also the $2p$ - $3d$ hybridization is of importance for the chemisorption bond. On Ni(100), the antibonding $2p$ - $3d$ states are centered at the Fermi level, resulting in a sharp drop of the SXE intensity at zero binding energy and a strongly asymmetric O $1s$ core line in the XPS spectrum. For O/Cu(100) the $2p$ - $3d$ states are almost completely filled. This is manifested in the low SXE intensity close to the Fermi level and a discrete shake-up structure about 3 eV from the O $1s$ XPS main line.

Note added in proof. The O/Ni(100) and O/Cu(100) x-ray emission experiments have recently been performed using selective excitation. For O/Ni(100), the differences between the spectra excited by threshold and higher energies are small. For O/Cu(100), the spectrum recorded at threshold excitation energy shows a clear dip in the intensity at about 526 eV emission energy. This indicates that the strong SXE intensity about 4 eV below the Fermi level in the presented O/Cu(100) spectrum (Figs. 1 and 4) is due to multielectron excitations.

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