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Electronic structure of $c(2\times 2)$ oxygen chemisorbed on Ni(001)

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A detailed theoretical study of the electronic structure of an ordered $c(2\times 2)$ oxygen overlayer adsorbed on a Ni(001) surface is performed using the layer-Korringa-Kohn-Rostoker multiple-scattering method. Effects on the local density of states due to the extended nature of the substrate as well as adsorbate-adsorbate interactions are discussed. Emphasis is placed upon the different role of Ni 4*s* and 3*d* states in forming bonds with the oxygen 2*p* levels. The interaction with the 3*d* bands leads to a splitting of the *p* levels into bonding states below and unfilled antibonding states above the *d* bands. These states extend approximately two layers deep into the substrate although in specific regions of the surface Brillouin zone related to the bulk band structure, they may become considerably longer ranged. Interference with the Ni *s*-*p* band broadens the oxygen-induced states up to 0.5 eV, the width depending on orbital symmetry and on $\vec{k}_{\parallel}$. Both bonding and antibonding states are split apart due to the anisotropy of the crystal potential at the surface. Their absolute as well as relative energies are shown to vary with $\vec{k}_{\parallel}$. The results are in qualitative agreement with several spectroscopic observations.

I. INTRODUCTION

One of the main goals of studying surfaces by means of angle-resolved photoemission is to obtain information on chemical bonds of adsorbed species.[1] Although measured spectra are not related to the electronic structure of adsorption systems in any direct manner, the understanding of the ground-state electronic properties provides, nevertheless, a useful basis for a theoretical interpretation of spectral features. To achieve a reasonably accurate description of adsorbate-induced electron states, several methods are currently employed.[2] In the so-called surface-molecule[3] approach, the system is replaced by a relatively small cluster of atoms containing the adatom and several substrate atoms. By their very nature, these models focus on the local aspects of the bonding, thereby underestimating possible effects due to the extended character of the substrate wave functions which participate in the bond. In addition, measurements are usually performed in the high-coverage region where ordered overlayer structures are formed. The close spacing between adsorbed atoms can also have observable effects[4] on the surface electronic structure which are not contained in a cluster approach. Two obvious consequences of the extended nature of the system are the finite width[5] of adsorbate-induced states and the variation of their energies with $\vec{k}_{\parallel}$.[6] To include these types of long-range effects, various alternatives to the cluster scheme have been developed which consider either a single adatom or an entire adlayer on a finite or semi-infinite slab of substrate layers.[2] Self-consistency generally represents a crucial aspect of these studies, in particular for quantities such as binding energy or charge transfer. In the case of chemisorption on transition metals, only one such calculation, for N on Cu(001), has been performed to date.[7]

In the present paper, we discuss results obtained for the local density of states of a $c(2\times 2)$ oxygen layer on the (001) face of a semi-infinite nickel substrate. Since the density is not determined self-consistently, we make no attempt to calculate the potential energy surface. Instead, the aim of this work is to illustrate, for a reasonable choice of the one-electron potential and a known adsorption geometry, the character of the adsorbate-induced states throughout the surface Brillouin zone (SBZ). Both local and extended aspects of the surface electronic structure are pointed out. Also, the different roles of Ni 4*s* and 3*d* bands in the bonding of the O 2*p* states are discussed. We show that the essential behavior of the local density can be understood in relatively simple physical terms. Although improvements due to self-consistency will alter the detailed features of our results, they should not affect the general conclusions of this paper. The following picture emerges from our calculations:

(i) The presence of the oxygen layer leads to the formation of two groups of levels, bonding states below and unoccupied antibonding states above the Ni *d* bands.[8] This splitting is caused by the O 2*p*–Ni 3*d* interaction. Both types of states are predominantly of *p* character within the overlayer and of *d* character in the first two or three substrate planes. In certain parts of the SBZ related to the Ni band structure, these states may, however, become rather long ranged. At energies within the *d* band, the adatom density has only very small featureless spectral weight.

(ii) The bonding, as well as antibonding, states are split, partly due to the direct coupling between oxygen levels and partly due to their interference with the Ni conduction bands. The splitting differs at various points of the SBZ, i.e., the energy of the $2p$ resonances shows a dispersion with $\vec{k}_{\parallel}$.

(iii) In contrast to the O $2p$–Ni $3d$ interaction, the hybridization with the Ni s-p band broadens the p levels up to about 0.5 eV. The peak width depends strongly on $\vec{k}_{\parallel}$ and on the orbital symmetry.

These results are qualitatively consistent with several experimental observations. Angle-integrated ultraviolet photoemission spectra[9] (UPS) and ion-neutralization spectra[4] (INS) for oxygen on Ni(001) show an approximately 2-eV-wide adsorbate-induced peak at about 5.5 eV below E_F. The calculations described in this paper suggest that broadening, splitting, and dispersion of the $2p$ levels are important contributions to the observed width. Furthermore, recent angle-resolved photoemission measurements[10] for $c(2\times 2)$ O on Ni(001) indicate a splitting and dispersion of the oxygen levels, in qualitative agreement with our results. In this experiment, the individual $2p$ components are identified by varying the polarization of the incident radiation. If unpolarized light is used instead,[11] at least two of the p components are excited simultaneously at any given emission angle. Since the p levels are energetically not resolvable due to their large intrinsic width, the resulting 2-eV broad peak shows very little dispersion with $\vec{k}_{\parallel}$.[11] We also note that recent appearance-potential spectra (APS) for oxygen on Ni indicate[12] the existence of adsorbate-induced valence states just above the Fermi energy similar to those found in our calculations. This observation is consistent with electron-energy-loss spectra (EELS). These suggest[12] that, upon oxygen adsorption, electronic excitations corresponding to transitions between occupied and unfilled oxygen-induced states take place. A quantitative comparison of our results with the available spectroscopic data cannot be made, of course, as this would require consideration of the various excitation processes.

Two analogous calculations of the electronic structure of $c(2\times 2)$ O on a thin Ni(001) slab have been performed by Kasowski[13] and by Bullett and Cohen.[14] Our results are comparable to these studies only to a limited extent since they are not aimed at the $\vec{k}_{\parallel}$ dependence of the local density of states. In Sec. III we discuss some of these calculations and also make contact to other related chemisorption studies.

II. FORMAL PROCEDURE

We assume that the oxygen atoms are adsorbed in the fourfold centered positions with a Ni–O bond length of 1.98 Å as found in low-electron-energy-diffraction (LEED) studies.[15] The geometry is illustrated in Fig. 1. The self-consistent Wakoh potential[16] is used for the Ni substrate up to the surface plane. Since the Ni–O bond is likely to be relatively covalent, a neutral-atom $X\alpha$ potential ($\alpha = 0.744$) is used for the oxygen overlayer. The muffin-tin model is adopted with a constant of −1.0 Ry in the interstitial region throughout substrate and adsorbate. Using the same constant in overlayer and bulk appears to be justified in view of the small size of the oxygen atoms and the short distance to the first Ni plane (see Fig. 1). In the exterior, the potential is assumed to depend only on the coordinate z normal to the surface.

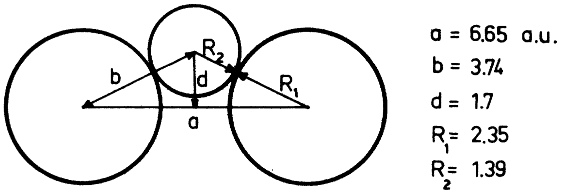
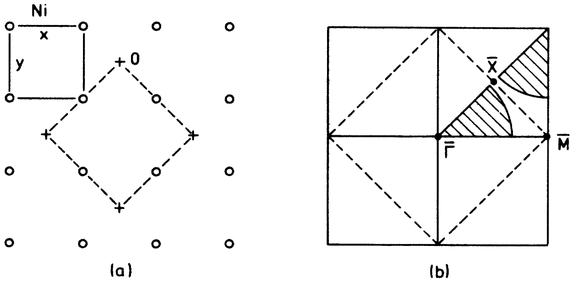


FIG. 1. Adsorption geometry for $c(2\times 2)$ overlayer structure. The two Ni atoms are along the (100) axis.

Figure 2 shows the (a) two-dimensional unit cells and (b) Brillouin zones of the clean Ni(001) surface (solid lines) and of the oxygen overlayer (dashed lines). The coordinates system is chosen such that the x axis coincides with the crystallographic (110) direction. Because of the larger adsorbate unit cell, $\vec{k}_{\parallel}$ points that differ by an overlayer reciprocal-lattice vector are equivalent although in the substrate SBZ they are not.

The technique of evaluating the bound states of this system is based on the so-called complex band-structure method[17] and has been employed previously to determine photoemission spectra



(a) (b)

FIG. 2. Surface unit cells (a) and Brillouin zones (b) for clean substrate (solid lines) and $c(2\times 2)$ overlayer (dashed lines). The shaded area indicates those $\vec{k}_{\parallel}$ values at which the oxygen levels can hybridize with the Ni s-p band. In the remaining parts of the SBZ, they form split-off states.

for a (1×1) oxygen layer on a Ni surface.[18] It is equivalent to a scheme recently used by Kar and Soven for the calculation of the field-emitted current from an adsorbate covered substrate.[19] Formally, three types of bound states of the metal-adsorbate system may be distinguished. At energies and $\vec{k}_{\parallel}$ points within the range of the substrate conduction bands, the adsorbate levels are able to hybridize with them unless the interaction is forbidden on symmetry grounds. In the first case, the bound states form, asymptotically, a standing wave whose amplitude is strongly peaked near the overlayer if the energy approaches the adatom resonance. The second case is that of a sharp adsorbate resonance whose wave function falls off exponentially toward the interior. Finally, below the conduction band or within band gaps, there may exist split-off states that are also like the sharp resonances, localized in the vicinity of the surface. A state that hybridizes with the metal bands is expressed inside the semi-infinite solid as a superposition of a propagating Bloch wave incident on the surface and a series of reflected waves that propagate or decay toward the interior.[20] All waves are characterized by the same $\vec{k}_{\parallel}$ within the overlayer SBZ. The incident wave is normalized such that it carries unit-normal current.[19] The scattering properties of the adsorbate are conveniently formulated in terms of a transfer matrix which relates the two-dimensional Fourier coefficients of a wave function and of its normal derivative on one side of the plane to those on the other. In the vacuum region, the bound state is expressed as a superposition of solutions to the z-dependent potential. In the case of sharp resonances or split-off states, the state in the interior consists only of evanescent waves. The wave functions of these levels are normalized to unity over the surface unit cell.[19]

According to the UPS[9] and INS[4] data, the oxygen levels lie roughly in the range of the Ni s-p band below the d bands. Thus at $\bar{\Gamma}$, the conduction band minimum lies below the $2p$ states. Going toward $\bar{X}$ or $\bar{M}$, however, the edge shifts rapidly to higher energies until it lies above them. The shaded area in Fig. 2(b) indicates approximately those $\vec{k}_{\parallel}$ points at which it is energetically possible for the p levels to hybridize with the Ni bands. In the remaining parts of the SBZ, they can exist only as split-off states.

III. RESULTS AND DISCUSSION

A. $\vec{k}_{\parallel}=0$

Figure 3 shows several partial wave projections of the local density of states (integrated over the muffin-tin sphere volume) at $\vec{k}_{\parallel}=0$ as function of energy, (a) at an oxygen site, (b)-(d) in the first Ni plane, and (e) in the second. For clarity, only two of the Ni d components are shown. The Ni s-p band extends approximately from -12.5 to -8.5 eV, the $3d$ bands from -8 to about -4 eV. The Fermi energy of paramagnetic Ni lies just below the top of the d bands. The presence of the overlayer induces five main features:

(i) The oxygen levels are split by about 7 eV into two groups of states: a pair of bonding levels below the Ni d band and a pair of unoccupied antibonding levels, above the d band. At energies within the range of the d band, the oxygen density of states exhibits a rather weak spread-out weight.

(ii) Because of the anisotropy near the surface, the bonding as well as antibonding levels are split into a p_z-derived state and doubly degenerate p_x, p_y-derived states. As in the case of the (1×1) adsorbate structure,[18] the p_z-bonding level lies at $\bar{\Gamma}$ *below* the p_x, p_y states.

(iii) The Ni d_{z^2} and d_{xy} components are strongly enhanced at energies near the p_z levels, with the d_{z^2} component having appreciable weight also in the second Ni layer. At energies near the p_x, p_y resonances, the Ni density has mainly d_{xz}, d_{yz} character (not shown here). While the bonding p_x, p_y states extend about two layers into the substrate, the antibonding p_x, p_y states decay more slowly into the solid (to $1/e$ in the third layer) because of their small separation from the Ni d_{xz}, d_{yz} bands. For the clean surface, the d density at the energies near the oxygen levels is negligible (dashed curves). This pronounced enhancement indicates that a metal-adsorbate surface molecule[3,8] is formed with occupied valence states well below E_F and unfilled states just above E_F. Both states have essentially p character on the oxygen sites and d character within the Ni planes near the surface. Oxygen-induced molecular orbitals of similar character are also obtained in calculations performed for oxygen-nickel clusters.[21] This picture is qualitatively consistent with O $1s$ appearance potential spectra for oxygen chemisorbed on Ni which show[12] relatively narrow unfilled states involving the oxygen atoms at about 2 eV above E_F. Furthermore, EELS[12,22] for the same system indicate that a transition of about 7 eV exists from occupied to unoccupied nickel-oxygen valence states. These spectra are shown in Figs. 4(c) and 4(d), respectively, together with (a) angle-integrated UPS[9] and (b) INS[4] data. The APS data are of particular interest here since they can clearly attribute the rather narrow feature above the Ni d bands to chemisorbed oxygen in agreement with our results. In contrast, the surface oxide phase exhibits[12] a much wider spectrum of

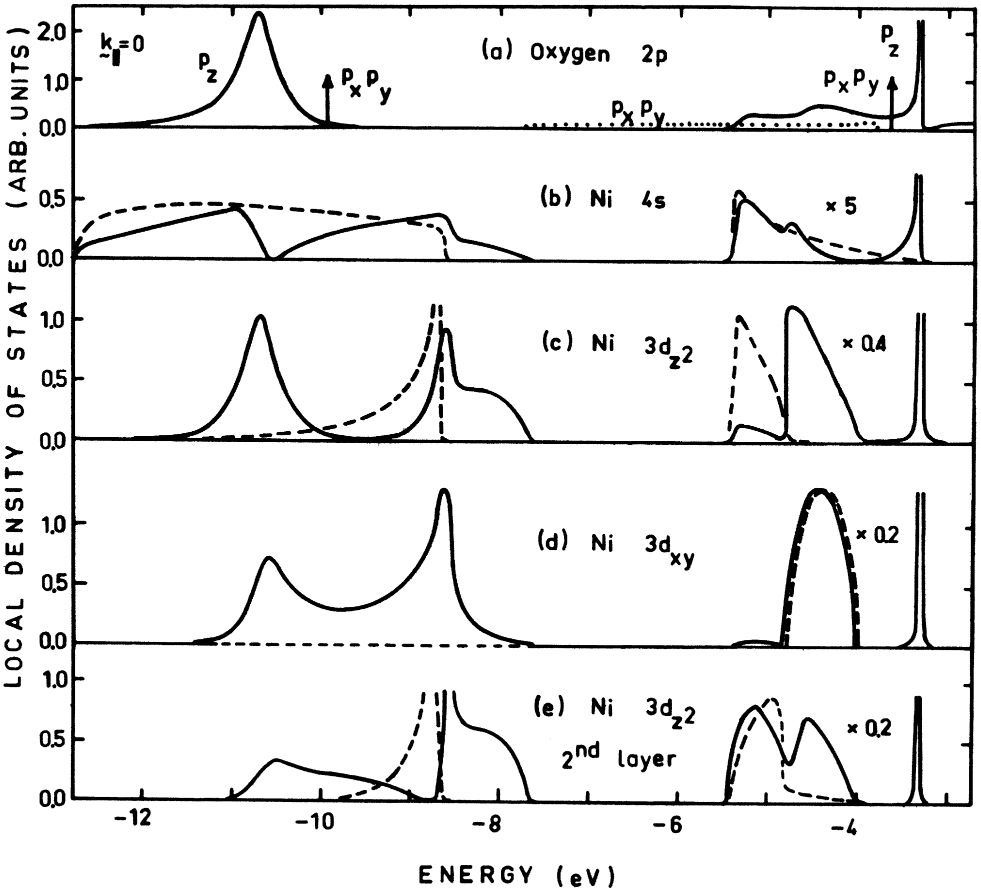


FIG. 3. Various partial-wave projections of the local density of states at $\bar{\Gamma}$, (a) at an overlayer site, (b)–(d) in the first substrate plane, and (e) in the second layer. Energies are relative to the vacuum. In (b)–(e), the dashed lines are for the clean surface, the solid lines for the adsorbate covered surface. Note the different scales.

empty states with considerable fine structure. In connection to these observations, we also note that recent photoemission data for $c(2\times2)$ O on Cu(001) show[23] a small adatom-induced peak between the top of the Cu d bands and E_F. These results indicate that metal-oxygen antibonding levels exist similar to those for O on Ni, but that they are partially filled as a result of the lower-lying Cu d bands.

(iv) The p_z-bonding level exhibits a width of about 0.5 eV due to its hybridization with the Ni s-p band. The O $2p$–Ni $3d$ interaction does not contribute to this broadening as the oxygen induced levels lie outside the range of the d bands. The p_z antibonding level is considerably narrower as a result of the smaller Ni s-p density at the higher energies. At the $\bar{\Gamma}$ point, the p_x, p_y states remain sharp since their hybridization with the s-p band is forbidden on symmetry grounds.

(v) Near the p_z bonding level, the Ni 4s density exhibits a pronounced resonance behavior. This can be understood as follows. The clean-surface s-p states may be represented essentially as standing waves with a node near the solid-vacuum interface. The effect of an overlayer potential on these states is to modify their amplitude in the vicinity of the surface and to introduce an energy-dependent phase shift. This is illustrated in Fig. 5(a) which shows the s-wave density of states as function of layer index at two energies, just below and above the p_z resonance. At the lower energy, the density has a maximum in the nickel-oxygen bond region while at the upper energy, a strong depletion occurs indicating the antibonding character of the states. This interpretation agrees with what one expects from the interaction of a single level with a continuum of states each of which leads to a small splitting. The result is a broadened peak in which the bonding states accumulate in lower part and the antibonding states in the upper part. Figure 5(b) shows the oxygen induced phase shift η_s of the Ni 4s states as a

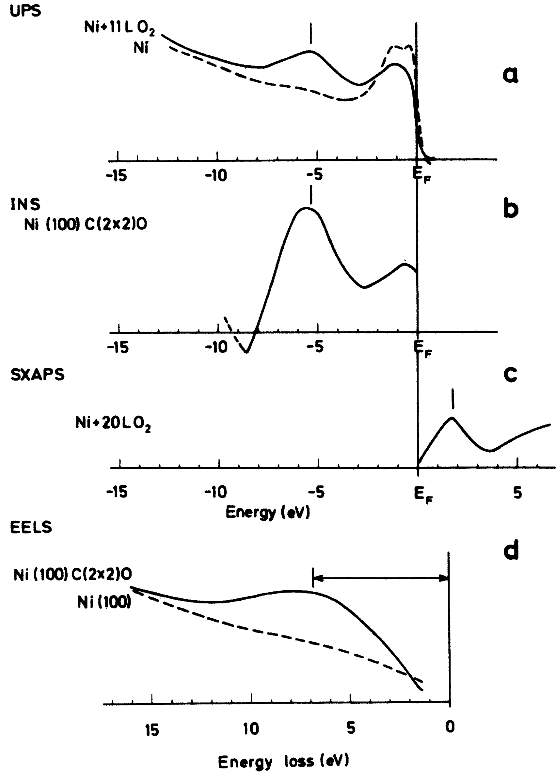


FIG. 4. (a) UPS data from a clean Ni film (dashed line) and with oxygen adsorbed on it (solid line). (b) INS transition state density from Ni(001) $c(2\times2)$ O. (c) O 1s APS data from oxygen adsorbed on a Ni film (smooth background subtracted). (d) EELS from clean Ni(001) (dashed) and Ni(001) $c(2\times2)$ O (solid), primary energy 27 eV (Ref. 12).

function of energy. The width of the p_z level in Fig. 3(a) is directly proportional to the slope of η_s at the resonance energy [vertical dashed line in Fig. 5(b)]. Remarkably similar behavior has recently been found by Gunnarsson *et al.*[24] and Muscat and Newns[25] in the case of hydrogen adsorption on jellium. As the adatom approaches the surface, the resonance level gradually loses its atomic character and is increasingly lowered as well as broadened. On moving the atom into the substrate, the level becomes again sharper until a bound state is split off below the bottom of the conduction band. The comparison with Figs. 3(a) and 5(b) suggests that the oxygen p_z level at $\vec{k}_\parallel = 0$ forms, with respect to the Ni s-p band, mainly an atomiclike resonance[25] with some bonding character. More strongly bound states can occur, however, in the interior of the SBZ as will be discussed further below.

Several additional points should be made regarding Fig. 3. The Ni 4s component (b) in the surface layer is reduced near the p_z bonding resonance, whereas at the antibonding resonance it is enhanced. Similar behavior is obtained at finite $\vec{k}_\parallel$ indicating a small overall shift of s weight toward higher energies above the 3d bands. The d states are not shifted upwards, however, as the d_{z^2} components above −8.7 and −4.8 eV might suggest. These peaks arise simply due to the coupling to other substrate states via overlayer reciprocal-lattice vectors. [The −8.7-eV peak is related to k_z at X in the bulk Brillouin zone (BZ).] At general $\vec{k}_\parallel$ points, the oxygen-induced changes in the d density tend to be very complicated with range and magnitude of the perturbation depending sensitively on energy as well as band symmetry. Over the entire SBZ, a reduction of d weight in the band region takes place near the first substrate layer since some d states participate in the oxygen bonding and antibonding levels. In the present paper, we do not discuss these modifications within the Ni d band any further and focus instead, in Sec. III B, on the behavior of the occupied oxygen-induced states throughout the SBZ.

B. Finite $\vec{k}_\parallel$

The variation of the energies of the 2p levels with $\vec{k}_\parallel$ may arise from two sources, the metal-adsorbate coupling and the interaction between adatoms. In order to analyze the relative significance of these two contributions, it is useful to determine first the effects of the direct interaction between adatoms in the absence of the substrate. This is illustrated in Fig. 6(a) which shows the two-dimensional bands that result from the overlap of the atomic p functions for an isolated monolayer.[26] The oxygen atoms are arranged on a square lattice with a unit cell corresponding to

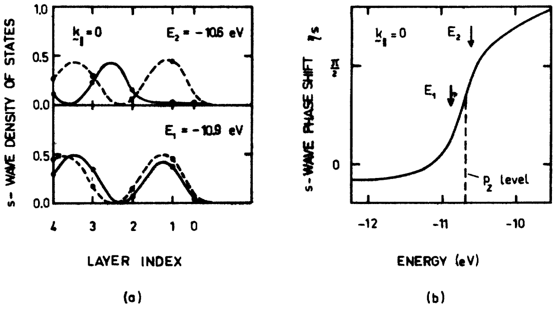


FIG. 5. (a) s-wave projection of local density of states for clean surface (dashed lines) and overlayer covered surface (solid lines). The dots represent calculated values, the lines are schematic. (b) Oxygen-induced s-wave phase shift near bonding p_z resonance.

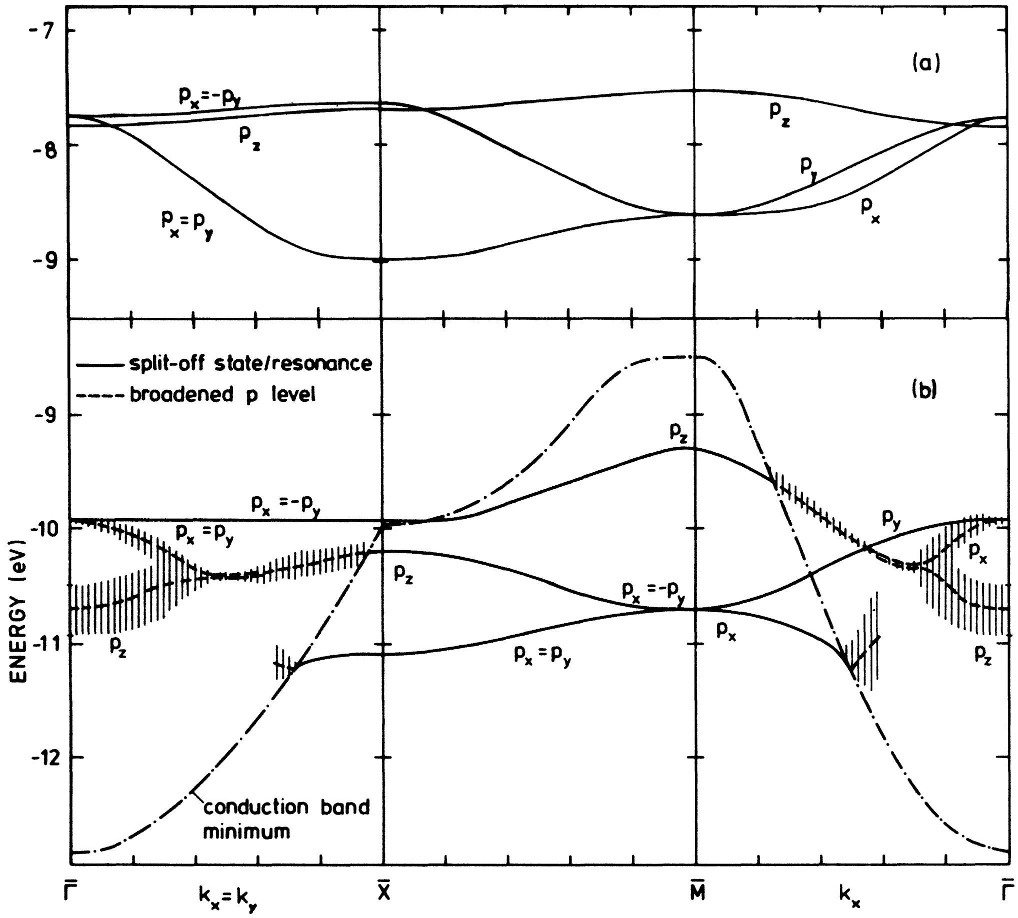


FIG. 6. (a) Two-dimensional energy bands of a free oxygen monolayer. The lattice constant corresponds to the $c(2\times 2)$ geometry. (b) Dispersion for chemisorbed overlayer. The shaded area denotes the approximate halfwidth of the hybridized levels.

the $c(2\times 2)$ structure. The overall behavior is similar to that of the (1×1) structure.[18] The band width, however, is greatly reduced because of the larger interatomic spacing. The qualitative behavior of the dispersion of the three p bands can easily be understood in terms of a simple tight-binding model.

Figure 6(b) shows the energy of the p states along the same symmetry directions after adsorption of the monolayer onto the semi-infinite substrate. The dashed line represents those levels that are broadened due to the interference with the s-p band. Plotted are the energies at which the local density of states at an oxygen site reaches a maximum. The shaded area indicates the approximate halfwidth. The solid lines denote the adsorbate levels that remain sharp, either as split-off states below or as resonances above the conduction band edge (dot-dashed line). Examples of the latter type are the p_y level along $\overline{\Gamma M}$ and the $p_x=p_y$ state along $\overline{\Gamma X}$, respectively. Figure 7 illustrates in greater detail the dispersion and broadening of the p levels for a series of $\vec{k}_\parallel$ points along $\overline{\Gamma M}$. Indicated are the three p-wave projections of the local density at an oxygen site. The arrows denote sharp resonances or split-off states. The dot-dashed line represents again the conduction-band minimum.

The dispersion of the p levels after adsorption follows closely that of the isolated monolayer. Several characteristic modifications, however, can be noted:

(i) The levels are shifted downwards by about 2 to 3 eV depending on their symmetry and on $\vec{k}_\parallel$. The lowering has, in principle, two sources, (a) the interaction with the Ni d electrons as indicated by the formation of bonding and antibonding states, and (b) the interaction with the s-p electrons

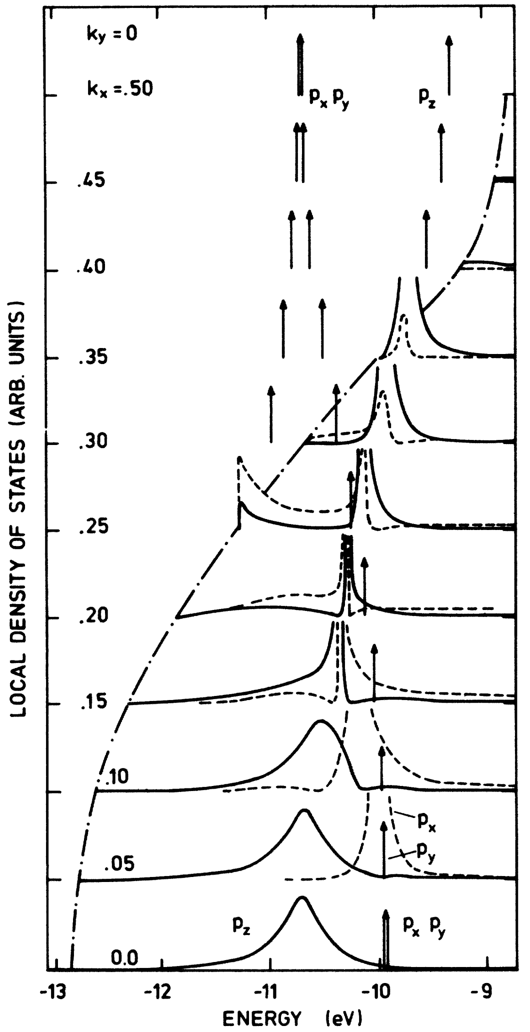


FIG. 7. p-wave projections of the local density of states at an oxygen site for $\vec{k}_{\parallel}$ along $\overline{\Gamma M}$. The arrows indicate sharp adsorbate resonances above or split-off states below the conduction-band minimum (dot-dashed line).

which may be viewed as corresponding to an overall lowering of the potential near the oxygen atoms in comparison to the free monolayer.

(ii) The comparison of Figs. 6(a) and 6(b) demonstrates that the level broadening is entirely caused by the adsorbate-substrate coupling. The *direct* interaction between adatoms only leads to the formation of discrete, two-dimensional bands. The *indirect* interaction between oxygen atoms via the Ni-substrate, on the other hand, influences the broadening rather strongly. This is discussed in more detail further below. Figure 6(b) shows that the width differs greatly for the three levels and depends sensitively on $\vec{k}_{\parallel}$. The largest broadening, about 0.5 eV, is obtained for the p_z-derived level at the $\overline{\Gamma}$ point.

(iii) In the case of the monolayer, the p_z band does not hybridize with the p_x, p_y bands. Due to the lower symmetry of the metal-adsorbate system, however, mixing of these states is allowed which may cause deviations from the free monolayer dispersion. Along the $\overline{XM}$ direction, for example, this leads to a hybridization gap of about 0.25 eV between the p_z and $p_x = -p_y$ bands. Along $\overline{\Gamma M}$ and $\overline{\Gamma X}$, strong mixing occurs between the p_z, p_x and $p_z, p_x = p_y$, respectively. A gap, on the other hand, does not arise since these states are broadened by the s-p band.

(iv) A striking departure from the monolayer dispersion takes place as the states that are predominantly of p_x and $p_x = -p_y$ character cross the conduction-band minimum. Both states are strongly bent downwards below the edge, whereas above the edge their weight is rapidly spread out and shifted toward the p_z resonance as clearly seen in Fig. 7. In contrast, the other states enter the s-p band without undergoing any such distortion. As in the case of the above hybridization effect, this behavior indicates that the dispersion is not entirely due to the intraoverlayer interaction, but that it is also related to the substrate band structure.

To verify the basic correctness of this last feature, we have performed an elementary tight-binding calculation for a simple cubic substrate containing a single s band and a (1×1) overlayer adsorbed in the centered position. As unperturbed adsorbate states we take, at first, individual p bands like those in Fig. 6(a). As Green's function of the semi-infinite substrate, we use the expression derived by Kalkstein and Soven.[27] We include only nearest-neighbor interactions between adatoms and substrate atoms. We find indeed that the perturbation of the p_x and $p_x = p_y$ bands differs qualitatively from that of the remaining bands. Because of their symmetry, the latter retain their cosine form regardless of the strength of the adsorbate-substrate coupling. The former exhibit below the band edge a characteristic lowering similar to that in Fig. 6(b). Above the edge, they are considerably broadened and also lowered except for strong overlayer-substrate interactions which lead to an upward bending. (Apparently, this latter case approaches that of an effective two-layer system.) If all three levels are considered simultaneously, their dispersion above the edge is dominated by their mutual hybridization. The lowering of the p_x and $p_x = p_y$ levels corresponds evidently to the formation of a bondinglike resonance close to the conduction-band minimum. The behavior of the Ni s density in the surface region

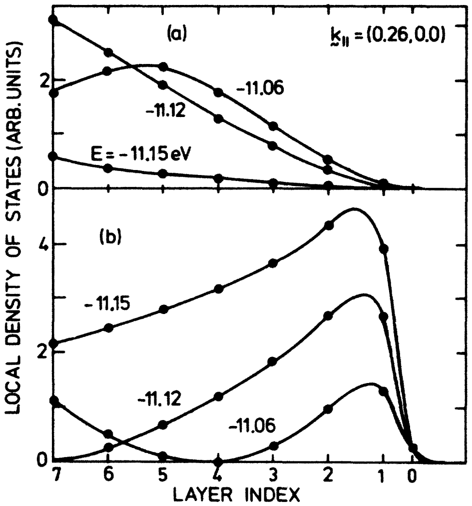


FIG. 8. s-wave projection of local density of states near crossing of p_x and conduction band edge (a) for clean surface and (b) for adsorbate-covered surface. The dots represent calculated values; the lines are schematic.

supports this interpretation as illustrated in Fig. 8. The s-wave projection at $\vec{k}_\parallel = (0.26, 0.0)$ ($\overline{\Gamma}\overline{M}$ direction) is shown as function of layer index. The p_x resonance still lies within the band at this point and the three energies are slightly above the band minimum. For the clean surface (a), one obtains standing waves whose wavelength becomes very large near the edge. The presence of overlayer (b) modifies these states in such a way that the charge density reaches a maximum in the region close to the overlayer. Approaching the edge, these states take on a long-ranged exponential-like character indicating the smooth transition from essentially oscillating waves within the band to decaying states outside the conduction band. Thus, as the adsorbate-induced state is pushed below the band minimum, its penetration depth within the substrate becomes infinite. For larger k_x values, the degree of localization near the surface increases rapidly and is proportional to the inverse square root of the gap between the split-off state and the band minimum. Near the crossing point of p_x resonance and band edge, the phase shift of the Ni 4s states due to the adsorbate is of the order of $\frac{1}{2}\pi$, i.e., the resonance is incomplete.[2] Within the Newns-Anderson model,[8] this behavior is characteristic of a bondinglike resonance[25] in contrast to the results obtained for the p_z level at $\vec{k}_\parallel = 0$, where the total shift is of the order π [see Fig. 5(b)]. Thus, we are able to identify those regions of the SBZ in which weakly bound, nearly atomiclike adatom resonances are formed and those where the oxygen atoms interact more strongly with the Ni s-p states. Because of the nearly-free-electron shape of the s-p band, the bondinglike resonances exist approximately along a ring $|\vec{k}_\parallel| \approx \text{const}$ around $\overline{\Gamma}$.

Comparing the results shown in Figs. 6 and 7 with those for the (1×1) overlayer structure,[18] one notes that, apart from the smaller overall splitting, the substrate-induced broadening of the p levels is also diminished. At $\overline{\Gamma}$, for example, the p_z level has a halfwidth of about 0.5 eV. For the (1×1) geometry, the corresponding value is 0.9 eV, even though the Ni-O bond length as well as the potentials are the same in both cases. This difference is an indication of the substrate-mediated *indirect* interaction between oxygen sites. The presence of a chemisorbed atom modifies the electronic structure at the substrate atoms nearby. These changes, in turn, influence the width of levels at other adsorbate sites. Analogous differences, though on a smaller scale, can be expected between the valence-electron distributions of the $c(2 \times 2)$ and $p(2 \times 2)$ structures. Such effects due to the indirect adatom interaction might be related to the observation that EELS show rather distinct vibrational frequencies for these two geometries, namely, 40 and 53 meV, respectively.[28] LEED data, on the other hand, being mainly sensitive to the ion core potentials, do not reveal any noticeable change.[29] A smaller broadening for the oxygen levels for the $p(2 \times 2)$ structure than for $c(2 \times 2)$ would imply a less effective overlap between adatom and metal states, i.e., an increased potential barrier for vibrations against the Ni surface. This, in turn, enhances the force constant for the $p(2 \times 2)$ geometry and, accordingly, the vibrational frequency, in qualitative agreement with the observed spectra.[28]

It should be emphasized that the absolute energies of the p levels as well as their relative positions are sensitive to the choice of the one-electron potential. The use of the same muffin-tin constant -1.0 Ry within overlayer and bulk, as well as the rather small oxygen muffin-tin radius (see Fig. 1), tend to overestimate the dispersion of the 2p resonances. In the case of the free monolayer, reasonable adjustments of these parameters were found to produce a *decrease* in the overall width of the oxygen bands by roughly a factor of 2. Choosing an exchange parameter greater than $\alpha = 0.744$ also decreases the bandwidth.[30] On the basis of our results, therefore, a dispersion of the order of 0.5 eV would appear to be realistic. Finally, there is some uncertainty in the surface barrier potential which influences the relative position of the p_z and p_x, p_y states. A self-consistent treatment is clearly required for a more quantitative determination of the various absolute as well as relative level energies. The dispersion of the $2p$ levels in Fig. 6(b) suggests that the ordering of the oxygen resonances does not remain the same throughout the SBZ. At $\overline{\Gamma}$, the p_z level lies *below* the doubly degenerate p_x, p_y states while at $\overline{M}$, it lies *above* the doublet. It is not certain at present whether this feature will be reproduced by an improved potential. We have not investigated this point further since the primary aim of this work is to obtain a qualitative understanding of the nature of the Ni–O bonds.

Recently, Lapeyre *et al.*[10] have performed angle-resolved photoemission measurements for $c(2\times 2)$ O on Ni(001). Using polarized light at $\hbar\omega = 26$ eV, they were able to resolve two components of the broad oxygen peak that is seen in angle integrated spectra. At normal emission ($\vec{k}_{\parallel} = 0$), a mixture of s-and p-polarized light shows a peak near -6.0 eV below E_F while pure s polarization gives a peak at about -5.5 eV. Since normal emission from the p_z-like level with s-polarized light is forbidden as a consequence of selection rules, the data imply that at $\overline{\Gamma}$ the energy of the p_z state lies *below* the p_x, p_y levels. At emission angles corresponding to $\vec{k}_{\parallel}$ close to the $\overline{M}$ point in the SBZ, a peak near -5.5 eV is observed for s-polarized light if the polarization vector lies within the emission plane. The spectrum shows a feature at roughly -6.5 eV below E_F if the polarization vector is perpendicular to the emission plane. Since a transition from the p_z-like state is not allowed for the latter configuration, the p_z level has to lie *above* the p_x, p_y doublet at $\overline{M}$. These experimental results indicate that a dispersion of the oxygen peaks with $\vec{k}_{\parallel}$ of the order of 0.5–1.0 eV does in fact exist. Furthermore, the ordering of the p levels at $\overline{\Gamma}$ is opposite to that at the $\overline{M}$ point as is also found in our calculations. While this qualitative consistency between experimental and theoretical results is encouraging, it should be treated with some caution. The semilocalized nature of the adsorbate-induced states suggests that aspects not included in the present calculation may be important factors in the correct interpretation of observed spectral features.[31] Experimental evidence for the existence of such effects is the fact that despite the high angular resolution (±2°), the individual p levels show a width of nearly 2 eV.[10] This is much greater than what can be expected from our results as a consequence of O $2p$–Ni $4s$ hybridization. In fact, the oxygen levels exhibit this rather large width even at those symmetry points at which the induced density becomes δ-function-like (e.g., p_x, p_y at $\overline{\Gamma}$, see Fig. 7). Evidently, lifetime, and/or phonon broadening of these levels play an important role. It remains to be investigated to what extent the dispersion relation derived in the present work will be modified if such phenomena are taken into consideration.

Using a localized-orbital scheme, Bullett and Cohen[14] have recently determined the $\vec{k}_{\parallel}$-integrated local density of states for a $c(2\times 2)$ oxygen monolayer on a slab of three Ni layers. They obtain an approximately 1.5 eV wide adsorbate peak, with the p_z and p_x, p_y projections occuring at about the same energy. Since the quoted width is presumably the result of contributions from different parts of the SBZ, these calculations would imply that position and ordering of the p resonances vary with $\vec{k}_{\parallel}$. Also, antibonding states are found above the Ni d bands in agreement with the results described in the present paper. Kasowski[13] has used the muffin-tin orbital method[32] to calculate the bound states of a (1×1) oxygen layer on a five-layer Ni film at the $\overline{\Gamma}$ point. He obtains, below the d bands, two oxygen derived levels which are separated by 2 eV and whose ordering is the same as that in our case (p_z below p_x, p_y). On the other hand, the energy of these states apparently does not vary significantly with $\vec{k}_{\parallel}$. This would imply that the p_z and p_x, p_y projections of the $\vec{k}_{\parallel}$-integrated density lie at rather different energies in contrast to the results described in this paper and those of Ref. 14. We have at the moment no explanation for this discrepancy. Paulson and Rhodin[33] have estimated the substrate-induced broadening of the energy levels of a NiO molecule. Within a tight-binding approximation of the indented solid, they obtain, to second order in the molecule-substrate hopping integral, a width of about 0.001 Ry. This value appears to be rather small in view of our results. A quantitative comparison, however, between the $c(2\times 2)$ structure and the single adatom limit is difficult since the broadening depends on the adsorbate coverage, as we have pointed out above.

In summary, we have presented a detailed analysis of the electronic structure of $c(2\times 2)$ O on Ni(001). Several effects on the local density of states due to the extended nature of the substrate and due to adsorbate-adsorbate interactions have been discussed. These include the finite width of the oxygen-induced levels and the variation of their energies with $\vec{k}_{\parallel}$. We have shown that the qualitative behavior of the local density can be interpreted using relatively simple physical arguments and that its main features are consistent with available spectroscopic observations. These calculations should be improved by taking into account self-consistency requirements. Also, for a quantitative comparison with angle-resolved-photoemission spectra, some consideration of the excitation process appears necessary.

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