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Discrete valence-electron states for Na overlayers on Cu(111)

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A narrow peak close to the Fermi edge in photoemission spectra recorded normally to Cu(111) at high monolayer coverages of Na is explained in terms of one of a series of discrete states formed in the potential well between the Na vacuum barrier and the Cu(111) surface, which acts as a barrier for electrons with energies and wave vectors within the Cu *s,p*-band gap at the *L* point of the Brillouin zone. The discrete overlayer states have tails on the substrate side of the Cu(111)/Na interface. Using a phase-shift analysis we account for the coverage dependence of the energy of the observed state and estimate energies for higher members of the series. The lifetime broadening of the higher states is discussed.

I. INTRODUCTION

In recent work we have reported and explained the appearance of discrete valence-electron states close below the Fermi level for full mono- and duolayers of Na and Ba adsorbed on Cu(111).[1] The states are formed in the potential well between the vacuum barrier and the Cu(111) surface, which is highly reflecting for electrons with energies within the Cu *s,p*-band gap producing the necks of the Cu Fermi surface. The energies of the states within this well may be obtained from the phase condition $\phi_B+\phi_C+2\phi_D=2\pi n$ where $n=0,1,2,\ldots,\phi_B$ is the phase change upon reflection by the vacuum barrier, ϕ_C the phase shift at the substrate-overlayer interface, and ϕ_D the phase change across the film. For surface states on a bare crystal the corresponding condition is $\phi_B+\phi_C=2\pi n$. The present overlayer states, like surface states, have wave functions with tails in the crystal. A characteristic of the overlayer states is that two different solids are involved in their formation. This composite nature is particularly evident when the overlayer is thin enough that a sizable fraction of the electronic charge associated with the state may reside in the tail.

Using a simplifying two-band model for the electronic structure to obtain a phase change at the crystal surface ϕ_C and using as ϕ_B the phase shift of an image-potential barrier, Smith[2] found that this phase condition predicts the surface and image-potential states of low-index Cu surfaces with good accuracy in the energy range above the Cu 3*d* band. Apart from providing surprisingly accurate energies the phase analysis has the additional advantage of making it easy to understand how the formation of the states and their energies will be affected by a change of quantities such as work function, position of the image plane, and band-gap width. Here this type of phase analysis will be applied to an overlayer system. Due to the lack of self-consistent first-principles electronic-structure calculations for overlayer systems there is for such systems an even greater need than for the clean metal surfaces to have access to reliable and simplifying models. The situation for the Cu(111)/Na system is fortunate. First, one knows that the Cu(111) surface electronic structure is well described by the simplified phase analysis. Secondly, first-principles calculations of the electronic structure of Na monolayers in vacuum[3] can be utilized to check that the parameters used to describe the overlayer have reasonable values.

A main purpose of the present work is to explain why, for monolayer coverages, the state observed close below the Fermi energy remains at nearly constant energy when the coverage is changed and why, for multilayer films, there are no discrete electron states close below the Fermi level. The measured spectra show a narrow emission peak close below the Fermi edge for coverages ranging between 60% of full monolayer coverage ($\Theta=0.6$) and full monolayer coverage ($\Theta=1$). Over this range the work function changes by around 0.4 eV and the electronic density by almost 70%. One would expect that such large changes of the surface conditions would affect the formation and the energy of a surface state. The observed coverage independence of the energy and the fact that the energy is close to the Fermi level, which means that the peaked shape of the emission spectrum could be due to the Fermi-Dirac distribution function cutoff, are two reasons why our Cu(111)/Na photoemission data have remained poorly understood. In a previous brief report[4] it was merely suggested that the peak is due to some kind of interface state and that its narrow width is associated with the fact that the state lies within the energy range of the Cu band gap.

Since the present phase analysis provides a rather detailed account of the experimental data we will also report the energies predicted for the states above the Fermi level. For each overlayer thickness chosen there is a characteristic spectrum of energies below the vacuum level. As the film thickness is increased the energy separation between the discrete levels becomes smaller until finally a quasicontinuous level structure typical of bulk solids is obtained. Close below the vacuum level there is a small level separation also for the thin overlayers discussed here. This is due to the image-potential tail of the vacuum barrier which produces a Rydberg-like series of states below the vacuum level. Of interest here is to find out whether these will survive as discrete states or will be difficult to observe as a result of lifetime broadening. For the metal overlayer systems lifetime-broadening effects pose a more severe threat in this respect than for the clean metal surfaces. The reason is that for the overlayer systems the absorptive part of the potential extends further away from the reflecting surface than for the clean crystal.

II. EXPERIMENTAL DATA

As Na is adsorbed on Cu(111), photoelectron energy spectra recorded in the normal direction show that the Cu(111) surface state 0.4 eV below E_F shifts to progressively lower energy as more alkali metal is adsorbed (peak *S* in Fig. 1). This occurs at relatively low monolayer coverages. When the coverage is somewhat less than half a full monolayer coverage the energy has shifted such that it coincides with its parent bulk band which has an energy of 0.85 eV below E_F at the *L* point of the Brillouin zone. The shift of this state due to adsorption of alkali metal and coadsorption of alkali metal and oxygen has been discussed previously.[2,4,8] The peak labeled *D* is due to the highest Cu 3*d* band.

Of main present interest is the peak *F* in Fig. 1, which appears at the Fermi edge for evaporation times longer than 3 min. Five minutes evaporation time is required for a full monolayer. The intensity of the peak increases rapidly as the monolayer coverage increases while its energy remains close to the Fermi edge as the coverage is changed. The peak is quite narrow. The width of the peak at the Fermi edge shown in Fig. 1 is mainly due to the limited experimental resolution. Taking the experimental resolution into account we find that the lifetime breadth is less than 0.1 eV. This means that the width is among the narrowest observed for solids.[9] The peak is not due to electrons which are excited in the Cu substrate and then scattered into the detection angle by the overlayer. This is excluded by the fact that the peak appears close to the Fermi edge and that it is strong for photon energies down to the threshold for photoemission. At these low photon energies there are no direct optical transitions in Cu involving initial states at the Fermi level.

The structure of Na layers on Cu(111) has been studied in previous work.[10] Above a certain monolayer coverage the low-energy electron-diffraction pattern indicates a $p(2\times2)$ overlayer which is gradually compressed as the monolayer coverage is increased. For the thickness range studied here multilayers consist of a stack of close-packed atomic planes.

If the evaporation is continued beyond the monolayer stage the peak at the Fermi edge decreases gradually in strength while another broad peak appears at lower initial energy (Fig. 2). Measurements at higher photon energies showed that the film thickness is quite inhomogeneous for films thicker than one monolayer if the substrate is kept at room temperature (RT) during the evaporation.[10] When the substrate is kept at liquid-N_2 temperature the film thickness is more homogeneous.[10] The peak at the Fermi edge shows the same coverage dependence for samples prepared at liquid-N_2 temperature as for samples prepared at RT. The broad peak, *G* in Fig. 2, does not appear in the spectra recorded for the sample prepared at liquid-N_2 temperature. We associate peak *G* with the thickness inhomogeneity and will not discuss this feature any further in the present paper.

III. PROCEDURES FOR OBTAINING ϕ_B, ϕ_C, AND ϕ_D

The potential in the surface region is shown schematically in Fig. 3. In the free-electron-like metal overlayer we regard the potential as constant over a distance z_1 between the ideal abrupt substrate-adsorbate interface and the surface barrier. As a surface barrier we use the image potential between the vacuum level and the plateau region. To describe the monolayer we assume that the thickness is independent of the coverage whereas the well

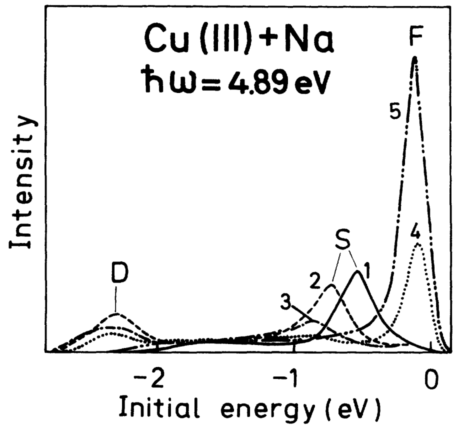

FIG. 1. Photoelectron energy spectra obtained in the normal direction from Cu(111) covered by different amounts of Na. The evaporation times in minutes are indicated in the diagram. 5 min evaporation time corresponds to one full monolayer.

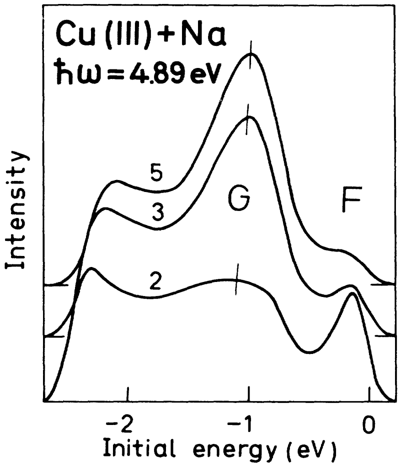

FIG. 2. Photoelectron energy spectra obtain in the normal direction from Cu(111) covered by the number of Na monolayers indicated in the diagram.

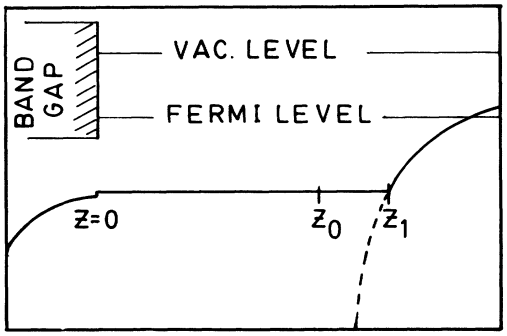

FIG. 3. Schematic drawing of the potential used to obtain electron energies for the Cu(111)/Na adsorption system in the energy range of the Cu band gap at the L point of the Brillouin zone. $z=0$ is placed half a Cu(111) interlayer separation outside the plane through the outermost Cu atoms. z_0 gives the position of the image plane.

depth is allowed to increase as more alkali-metal atoms fill the monolayer volume. The thickness is adjusted at full monolayer coverage such that the measured energy is reproduced.

To obtain the barrier phase shift when a full monolayer or more of Na has been adsorbed we calculate the wave function in the image barrier region. The work-function change saturates at around full monolayer coverage and the barrier is expected to be the same as for thick Na when a full monolayer or more is deposited. At less than full monolayer coverage it is convenient to use for the barrier phase change an approximate expression giving values for ϕ_B which only depend on the energy relative to the vacuum level.[11] This barrier phase change gives surface state energies in good agreement with experiment for low-index Cu surfaces.[2]

The Cu substrate has a 5-eV-wide band gap about the Fermi energy. We use a two-band model for the electronic structure to derive the phase shift at the substrate-overlayer interface.

Apart from the plateau energy and the height of the vacuum barrier the potential is similar to that used by Weinert *et al.*[12] for a discussion of how the surface state energies of Cu(111) are affected by a change in the position, z_0 of the image plane.

A. Phase change at the vacuum barrier, ϕ_B

For an image potential the phase shift close below the vacuum level is to a good approximation given by[11]

$$\phi_B/\pi=\left[\frac{3.4\text{ eV}}{E_v-E}\right]^{1/2}-1 .$$

For monolayer coverages we use this phase shift for energies between the vacuum level, E_v, and E_F. To obtain the barrier phase shift for energies a few tenths of an eV below E_F we make a linear extrapolation.

Recently the energy of image-potential states has been calculated for jellium barriers using a nonlocal density functional approximation which gives the correct asymptotic form of the image potential at large distances from the surface.[13] To allow surface states to be formed an infinite barrier was placed at the jellium edge. The results are that for $r_s=3$ the energy of the lowest state is the same as for a classical image barrier while for $r_s=4$, which is close to the value for Na, the binding energy is around 0.1 eV lower, 0.73 instead of 0.85 eV. The main reason for this difference is that the more realistic potential remains finite and is therefore less attractive than the classical image barrier. A counteracting effect is that the image plane shifts further away from the jellium edge as the r_s value decreases. This effect dominates for $r_s=2$ giving a binding energy of 1.13 eV for the lowest state. Since the correction is only around 0.1 eV at the Na density and since, for monolayer coverages, we are interested in energy shifts rather than absolute energies, no difficulties are foreseen with the use of the approximate expression for the barrier phase shift.

At full monolayer coverage and for Na films several atomic layers thick we obtain the barrier phase shift from a calculation of the logarithmic derivative, L_1, at $z=z_1$ of the wave function in the image-potential region, $z>z_1$. The wave function is here the Whittaker function $W_{k,1/2}(x)$ with

$$x=(z-z_0)(E_V-E)^{1/2}(2a_0\sqrt{0.85\text{ eV}})^{-1} ,$$

where $k^2=0.85\,(E_v-E)^{-1}$ eV and a_0 is the Bohr radius. With a work function of 2.75 eV and the plateau potential energy 3.2 eV below E_F one obtains $z_0=z_1-0.6$ Å. The barrier phase shift ϕ_B is obtained from $\phi_B=2\arctan\kappa^{-1}L_1$ where κ is given by $E=\hbar^2\kappa^2(2m)^{-1}$ if E is measured relative to the plateau. For the numerical evaluation of $W_{k,1/2}(x)$ in the energy range of present main interest, which corresponds to $k<1$, we use the integral representation of the Whittaker function[14]

$$W_{k,1/2}(x)=[\Gamma(1-k)]^{-1}xe^{-x/2}\int_0^\infty e^{-xt}t^{-k}(1+t)^k dt .$$

To get logarithmic derivatives for $k>1$ we use this integral representation combined with the relation[14]

$$W_{k+1,1/2}(x)=(\tfrac{1}{2}x-k)W_{k,1/2}(x)-xW'_{k,1/2}(x) .$$

B. Phase change across the overlayer, ϕ_D

1. *Full monolayer coverage*

To obtain the phase shift, $\phi_D=\kappa z_1$, across the constant potential region of the overlayer we need a value for the thickness parameter z_1 as well as the well depth.

In the present calculation we will use $z_1=3.07$ Å and assume that as for bulk Na the well bottom is 3.2 eV below E_F. As discussed below this choice of well depth and thickness parameter gives electron energies close to the measured values. We have chosen to use z_1 as an empirical parameter and to fix the well bottom. With our choice of well depth we get a better approximation the thicker the overlayer. To obtain the electron energies for multilayers we add an interlayer spacing for each atomic plane stacked on the substrate. For a stack of hexagonal-close-packed Na planes the interlayer separation is measured to be 3.06 Å.[10] With the Cu(111) crystal terminated half an interlayer spacing, 1.04 Å, outside the plane through the outermost Cu atoms and a value for z_1 of 3.07 Å, the image plane z_0 becomes located 3.5 Å outside the outermost plane of substrate atoms.

2. *Coverage less than a full monolayer*

For monolayer coverages greater than the coverage producing the work-function minimum typical of alkali-metal adsorption systems the overlayer is nearly neutral and the valence electrons form an electron gas. This gas has been studied using electron-energy-loss spectroscopy, which reveals plasmon excitations[15–20] and photoemission, which shows the characteristics of surface-barrier emission already at monolayer coverages.[21] The surface-barrier emission was studied for Na adsorbed on Cu(100). Since the Cu conduction-band gap at the X point of the Brillouin zone lies above the Fermi level there are no filled discrete overlayer states at the zone center with Cu(100) as substrate.

To obtain the depth of the potential well in the overlayer for this coverage range, which roughly are coverages greater than half of a full monolayer, we regard the thickness parameter z_0 as constant independent of coverage. This means that the monolayer defines a volume which is increasingly filled with electrons as more alkali metal is adsorbed. Assuming that the atoms are uniformly distributed on the surface and that the layer is free-electron-like one gets $(E_F)_\Theta = \Theta^{2/3}(E_F)_{\mathrm{Na}}$ as the Fermi energy of the free-electron bulk metal having the electron density of the adsorbed monolayer. Θ is the coverage in units such that $\Theta = 1$ is one full monolayer. As for the full Na monolayer we assume that the bottom of the well is $(E_F)_\Theta$ below the Fermi level.

C. Phase change of the substrate-adsorbate interface

To obtain ϕ_C we follow the procedure used by Smith[2] for low-index Cu surfaces. The Cu bands in the region of the band gap at L are approximated by a two-band model. We use the same band parameters as Smith, an energy at the middle of the gap E_g of 10.3 eV, and a Fourier component $V_{g_{111}}$ of 2.5 eV. The phase shift ϕ_C is then obtained from the relation $\kappa \tan(\phi_C/2) = (g_{111}/2) \times \tan(\pi/2+\delta) - q$. The quantities on the right-hand side characterize the wave function inside the substrate in the energy range of the gap $\Psi = e^{qz}\cos(pz+\delta)$. The phase shift δ is given by

$$\sin(2\delta) = -\frac{\hbar^2}{2m}\frac{g_{111}q}{V_{g_{111}}}$$

and the damping q by

$$\frac{\hbar^2}{2m}q^2 = (4EE_g + V_{g_{111}}^2)^{1/2} - (E+E_g) \; .$$

The value of the constant in the argument $(\pi/2+\delta)$ on the right-hand side of the expression for ϕ_C depends on how the crystal is terminated. The value $\pi/2$ used here and by Smith is obtained when the crystal potential is terminated half an interlayer spacing from the plane through the cores of the atoms in the outermost layer.

The difference between the present case and that of a bare Cu(111) surface enters via κ, which is the wave vector describing the wave function in the flat potential of the overlayer $\Psi = e^{-i\kappa z} + e^{i\phi_C}e^{i\kappa z}$. As discussed in a preceding section we assume that the flat bottom is at 3.2 eV below E_F for the full monolayer and that it shifts towards E_F when the electron density in the overlayer is reduced.

IV. RESULTS AND COMMENTS

A. Full monolayer coverage

The energy dependence of the total phase shift, $\phi_B + \phi_C + 2\phi_D$, for the full monolayer is shown in Fig. 4. For comparison we show also the total phase shift for the clean Cu(111) surface. For the full monolayer there is one filled state with an energy of around 0.1 eV below E_F. We associate this state with the narrow peak observed in photoemission spectra close below E_F. The energy corresponding to $\phi_B + \phi_C + 2\phi_D = 0$ is of no interest since this energy is in the Cu 3d-band region, which is not accounted for in the two-band model used here. For the clean Cu(111) the intersection at zero phase gives the energy, 0.4 eV below E_F, of the surface state in the Cu band gap at L. The main reason why a state is found at approximately the same energy for the clean Cu(111) surface and Cu(111) covered by a full Na monolayer is that the phase shift $2\phi_D$ for an electron making a round trip in the overlayer is close to 2π for energies near E_F. This is as expected. An electron at E_F is close to the nearest zone boundary in bulk alkali metal.

The separate components of the total phase shift are more clearly shown in Fig. 5. The energy of the state

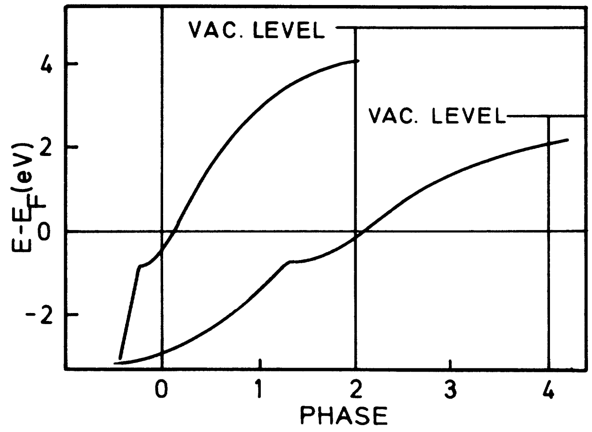

FIG. 4. The energy dependence of $\phi_B + \phi_C$ for Cu(111) and of $\phi_B + \phi_C + 2\phi_D$ for Cu(111) covered by a full monolayer of Na. The phase is given in units of π.

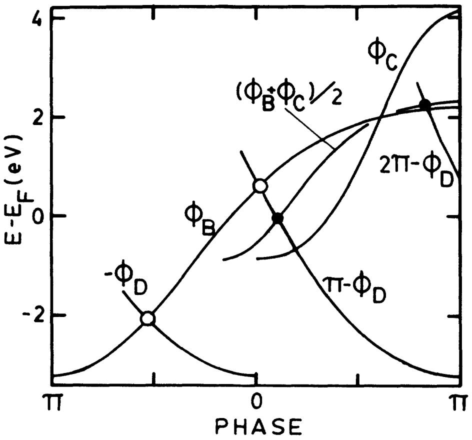

FIG. 5. Phase shifts of a Na vacuum barrier, ϕ_B, a Cu(111)/Na interface, ϕ_C, and across a Na monolayer ϕ_D. The intersections (solid circles) between the curves for $(\phi_B+\phi_C)/2$ and $\pi-\phi_D$, $2\pi-\phi_D, \ldots$ give the electron energies for a full Na monolayer on Cu(111). The intersections between the curve for ϕ_B and for $-\phi_D$ and $\pi-\phi_D$ (open circles) give the energies at the band edges of a Na monolayer in vacuum.

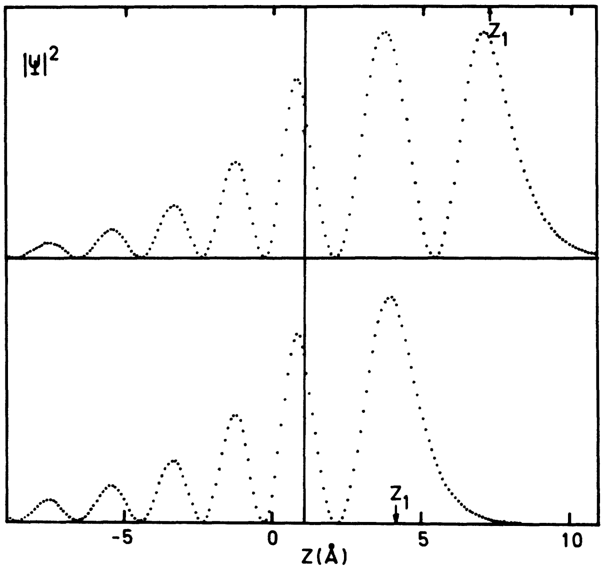

FIG. 6. $|\Psi|^2$ for the state close below E_F at full monolayer Na coverage on Cu(111) (lower panel) and for the state 0.2 eV above E_F for a two-atomic-layers-thick film on Cu(111). $z=0$ is placed at the plane through the outermost Cu atoms.

close below E_F is obtained from the intersection between the curves depicting $\pi-\phi_D$ and $(\phi_B+\phi_C)/2$ The energy of the lowest empty state (2.25 eV) is obtained from the intersection between the curves for $2\pi-\phi_D$ and $(\phi_B+\phi_C)/2$.

The diagram in Fig. 5 can also be used to obtain the energies at the low-energy edges of the electronic energy bands of a Na monolayer in vacuum described by a potential which has a flat region extending over 3.07 Å between image-potential barriers. These energies, given by the open circles in Fig. 5, are 2.1 eV below E_F for the lower band edge and 0.6 eV above E_F for the higher one. The values are quite close to the energies obtained by Wimmer[3] from a first-principles calculation of the electronic structure. His corresponding values are 2.1 eV below E_F, which is the value expected for a thin slab of electron gas with the density of Na, and 0.67 eV above E_F. Before making a direct comparison one should make a correction for the fact that according to Wimmer's calculation the work function of the Na film in vacuum is 3.1 eV. If we use this work-function value we get an energy of around 0.8 eV above E_F for the higher band edge. The lower edge is only marginally effected. The conclusion of this comparison is that the parameters used here for well depth and thickness are quite reasonable.

In Fig. 6 is shown a plot of $|\Psi|^2$ for the wave function of the state which at full monolayer coverage is close below E_F and a plot of $|\Psi|^2$ for the state 0.2 eV above E_F for a two-atomic-layers-thick Na overlayer. Inside the substrate the wave function is similar to that of the Cu(111) surface state 0.4 eV below E_F though with a somewhat stronger damping since the energy is further into the gap. The composite nature of the state is demonstrated by the fact that a large portion of the electronic charge, around 40% for the full monolayer, resides on the substrate side of the substrate-overlayer interface. The wave function has two characteristic periods, one for the substrate and one for the overlayer.

The discrete overlayer states for Na on Cu(111), for example those pictured in Fig. 6, are examples of metal-induced gap states. These are metal overlayer states with energies within the substrate band gap and with wave functions having tails on the substrate side of the interface. There is no fundamental difference between a metal substrate and a semiconductor substrate regarding how such states are formed. For practical reasons, in order to explain the rectifying properties of metal-semiconductor junctions, and though direct spectroscopic observations appear to be lacking, metal-induced gap states have been discussed extensively for metal-semiconductor interfaces.[22] According to one model the charge balance at the metal-semiconductor interface is established by the metal-induced gap states.[23,24]

It is interesting to compare the energies obtained for the Na monolayer on Cu(111) with the energies obtained for the Na monolayer bounded by vacuum on both sides. It is especially remarkable that the phase shift produced by the vacuum barrier and that due to the Cu band gap are similar enough that when the monolayer is taken from vacuum and placed on the Cu(111) substrate this leads to only the relatively small energy shift, from around 0.6 eV above E_F to close below E_F.

For the film in vacuum the electronic structure can be characterized by planes in k space parallel to the plane of the film. Each plane is defined by $2\phi_B+2\phi_D=2\pi n$, where $n=0,1,2,\ldots$. For wave vectors in the plane, the dispersion is free-electron-like. Electrons at E_F are found on the periphery of a circle given by $E_F-E_n=\hbar^2k_F^2/2m$, where E_n is the energy of the edge obtained from $2\phi_B + 2\phi_D = 2\pi n$. For the film in vacuum all the valence electrons are found in the plane corresponding to $n = 0$. When the film is placed on the Cu(111) substrate and the low-energy edge of the next lowest band is shifted below E_F this means that the plane in k space defined by $2\phi_D + 2\phi_D = 2\pi$ becomes populated in a small region around Γ.

In Fig. 7 are shown schematically the density of states for the Na monolayer in vacuum and on Cu(111). In two dimensions the density of states is constant for a free-electron gas. For the Na monolayer in vacuum the density of states is piecewise constant with steps at the energies of the band edges. As discussed above the lowest band edge is at an energy of around 1.1 eV above the bottom of the potential well in the overlayer. For the Na overlayer on Cu(111), electrons outside the range of energies and wave vectors of the Cu band gap are able to move across the Cu-Na interface. The density of states will then be three-dimensional-like for energies outside the Cu band gap. At low energies the density of states therefore is similar to that of bulk Na though with the low-energy edge smeared due to the fact that the wave functions of substrate valence electrons with energies below the edge have tails in the overlayer. For energies within the band gap the density of states has a two-dimensional component with sharp band edges. As discussed above the wave function of the step close below E_F places approximately 40% of the charge inside the substrate. Since we are interested in the density of states in the overlayer the step height for the Na overlayer is around 60% of the step height for the monolayer in vacuum. Between the energy at the lower edge of the Cu band gap $E_{L2'}$ and the step near E_F the density of states is reduced compared with the free-electron case since there are no states in this energy range for wave vectors within the band gap.

B. Coverage dependence for electron energies

As observed in the experiment the energy obtained here for the state close below E_F is remarkably constant considering the large variation in the electron density of the overlayer as the coverage is changed between $\Theta = 0.6$ and $\Theta = 1$, and the appreciable work-function increase of 0.4 eV in this coverage range. The individual changes of each of the phase shifts ϕ_B, ϕ_C, and $2\phi_D$ near E_F are significant whereas the net shift is small (Fig. 8). With the approximate expression for ϕ_B the energy at full monolayer coverage is reproduced by choosing $z_0 = 2.7$ Å.

For multilayers we use $z_1 = 3.07 + (m-1)3.06$ Å where m is the number of close-packed alkali-metal layers on the substrate. The shift with changing thickness of the energy of the various states can be obtained from phase diagrams similar to that shown in Fig. 9 for the state close to the Fermi level. For $m = 2$, 3, and 4 there are no states close below E_F in the energy range of the gap. This is in agreement with the experimental observation for Na overlayers that the peak at the Fermi edge gradually disappears when the evaporation is continued beyond the monolayer stage. For Ba overlayers, by contrast, a second narrow peak appears below the Fermi edge upon completion of the second atomic layer.[1]

The present work and the results obtained for Ba thus show that discrete overlayer states with thickness-dependent energies can be obtained for metal films on a metal substrate. The appearance of such states forms the basis for quantum size effects. So far there are few observations for metals. In previous work the quantized level structure has been observed for films which were much thicker (150–1000 Å) than in the present work and which were prepared on an insulating substrate.[25,26] At a thickness in the range mentioned the electronic structure is quite similar to that of the thick solid. The separation between the solutions in k space is, however, big enough that the corresponding differences in energy could be resolved via the I-V characteristic of a tunneling sandwich with the metal film as one electrode.

C. Level widths

In an indirect manner, via electron reflectivity measurements, several members of the Rydberg-like series of

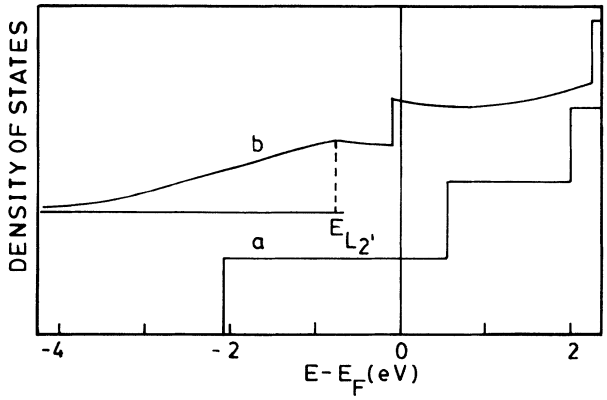

FIG. 7. Schematic density of states for a Na monolayer in vacuum (a) and on Cu(111) (b).

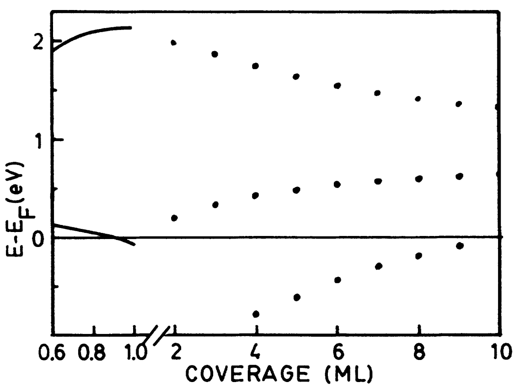

FIG. 8. Energy relative to E_F vs coverage in monolayers (ML) for the lowest discrete overlayer states for Na on Cu(111).

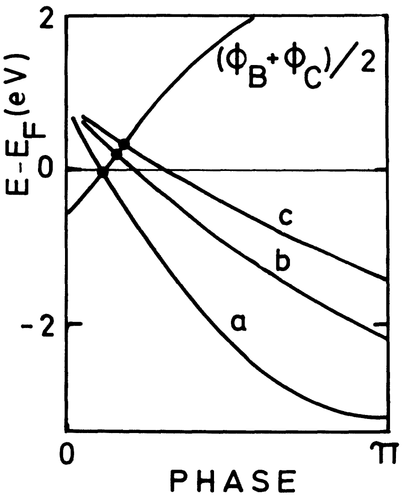

FIG. 9. Electron energies for states near the Fermi level for one, two, and three atomic layers of Na on Cu(111) obtained from the intersection between the curves for $(\phi_B+\phi_C)/2$ and $\pi-\phi_D$ for one (*a*), and two (*b*), and three (*c*) atomic layers.

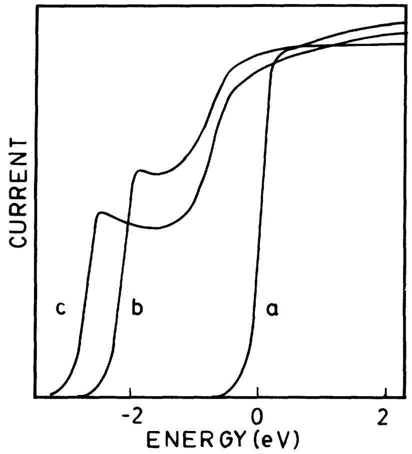

FIG. 10. Current to ground from a Cu(111)/Na sample vs the energy of electrons in a beam of normally incident electrons. The onset energy shifts with work-function change. The steplike character is due to the high electron reflectivity in the Cu(111) band gap at *L* which has its high-energy edge at around 4.2 eV above E_F. The Na coverages Θ are 0 (*a*), 0.5 (*c*), and 1.0 (*b*).

levels have been observed for clean metal surfaces[27,28] and explained using a realistic absorptive potential.[29]

For clean metal surfaces the absorptive potential is thus not strong enough and does not extend far enough into vacuum for the decay via electron-electron scattering to destroy the Rydberg-like series of states formed by the tail of the surface barrier. For an overlayer system the absorptive part of the potential extends further away from the reflecting substrate and the lifetime broadening will therefore be larger. It is then less obvious that the Rydberg states will be resolved. As for bare metal surfaces the whole series is expected to be resolved if the two first levels above E_F are resolved since the level separation and level broadening both scale as $1/n^3$.[30]

For Na monolayers on Cu(111) we suggest that there should be a good chance of observing the Rydberg series via inverse photoemission or two-photon photoemission. The suggestion is based on the experimental observation that the electron reflectivity in the energy range of the Cu*s*,*p*-band gap is still high, around 35%, when the Cu(111) crystal is covered by a full Na monolayer (Fig. 10). For the clean crystal the reflectivity cannot be measured due to the fact that the vacuum level falls above the gap. For Cu(100) the band gap at *X* gives a reflectivity of around 70% at the vacuum level. To get at least a very crude estimate of what these reflectivities mean in terms of the scattering rate Γ we assume that a value of 70% is appropriate also for reflectivity in the *L* gap of Cu(111) and use the expression

$$R=\frac{V_g^2}{(V_g+\Gamma)^2}$$

for the reflectivity in the middle of the gap.[31] One then finds that the Γ value is approximately 0.5 eV for $R=70\%$ and 1.5 eV for $R=40\%$, the value obtained when the measured reflectivity is extrapolated to the middle of the gap. The question is now whether the Rydberg series will survive this approximately factor-of-3 higher scattering rate. Most observations have been made using inverse photoemission with an experimental resolution which does not allow the lifetime to be measured. The two photon photoemission data reported for Ag(111) indicate a width for the lowest unoccupied state of less than 0.1 eV.[9] Even if the width is increased by a factor of 3 by the scattering in the overlayer the Rydberg series is therefore expected to be observable also for Cu(111) covered by monolayers of Na. The above estimates are for a full monolayer of Na. At less than full monolayer coverage the situation is more favorable. The electron gas is thinner and the electron reflectivity in the gap is higher (Fig. 10).

For films several atomic layers thick we obtain unfilled states rather close above E_F (Fig. 8). Electrons excited into these states spend a larger fraction of their time in the region where there is an absorptive potential. Since the energies for these states are so close to E_F the absorptive potential should however be small enough to allow these states to be observed.

V. CONCLUSION

The simple model used (a two-band approximation for the substrate band structure, a slab of jellium with fixed thickness, and an image barrier to describe the adsorbate over a range of monolayer coverages) produces a surprisingly accurate account of the energy at different coverages of the narrow valence state observed for Na-covered Cu(111). The model could therefore be useful for obtaining the energies of overlayer states for other cases where a substrate with a band gap is covered by simple metal adsorbates. First-principles calculations of the electronic structure for such systems are not available, and simplifying, reliable models are therefore needed.

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