Electron-Energy-Band Determination by Photoemission from Overlayer States

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Discrete valence electron states are formed in adsorbed multilayers of Cs atoms on Cu(111) at energies within the Cu conduction-band gap at the L point of the Brillouin zone. We measure the energies of these states by photoemission and obtain the wave vectors from the phase conditions satisfied by the states, and thereby determine the dispersion $E(k)$ in the perpendicular direction for part of the filled Cs valence band.

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By photoemission we observed quantum-size-type standing-wave states for multilayers of Cs atoms on a Cu(111) substrate and use the results to obtain the valence-band dispersion of Cs metal over part of the filled band. We are aware of no previous similar measurement of band energies, but the potential advantages of using thin-film samples for photoemission studies of band structure have been discussed by Loly and Pendry[1] and are evident also from the tunneling experiments by Jaklevic and Lambe.[2] The latter authors found periodic structure due to standing-wave states in $I(V)$ spectra of tunneling junctions, one electrode of which was the film to be studied. The results were used to determine energy bands for a number of metals.

There will be discrete valence electron states in an overlayer if the substrate has a band gap. The states appear at energies in the gap for which the phase condition $\Phi_B+\Phi_C+2\Phi_D=2\pi m$ is satisfied. Φ_B, Φ_C, and $\Phi_D=Nka$ are the phase shifts at the vacuum barrier, at the substrate-adsorbate interface, and across the film, respectively. N is the number of atomic layers in the film, a is the separation between the layers, and k is the wave-vector perpendicular to the film. Previously, overlayer states have been observed by photoemission for Na and Ba adsorbed on Cu(111) but only for monolayers and duolayers.[3,4] As for Na and Ba the overlayer states found for Cs are formed by electrons which are reflected back and forth between the vacuum barrier and the Cu(111) surface. This surface has a high reflectivity for normally incident electrons with energies in the Cu conduction-band gap ranging between 0.8 eV below the Fermi level and 4.2 eV above it. From the phase condition it is evident that states with a well defined energy are formed only if the overlayer thickness is homogeneous. Secondly, the crystalline order should be good, allowing the electrons to complete many round trips in the overlayer before being scattered.

The main advantage of the use of thin-film samples in photoemission is the information available about the perpendicular wave vector of the initial state. The conservation rules for the photoemission process do not include this quantity. Therefore the band structure along the normal to the sample cannot mapped with use of the results of a photoemission experiment on a bulk sample. The common procedure is to compare the measured spectra with spectra expected for assumed or calculated energy bands, which are then adjusted to agree with the experiment. For a film, if it is thick enough that surface effects can be ignored or if the influence of the surfaces can be accounted for, k is known directly from the phase condition provided the thickness is known and the correct quantum numbers, m, can be assigned to the observed states. In the tunneling experiments[2] the films were 150–1000 Å thick and the authors ignored the phase shifts at the interfaces. The present observations are for Cs overlayers, which are between 4 and 65 Å thick. At such small thicknesses it is necessary to make corrections for the boundary phase shifts, although we find that in the present case these corrections are small for all but the thinnest layers. Another advantage of the use of thin-film samples is that the emission peaks are broadened only as a result of the finite hole lifetime, which therefore can be determined. For a thick sample the breadth of an emission peak due to bulk bands depends on both hole and final electron state lifetimes as well as on the dispersion of each of the two bands involved in the optical transition.

Photoelectron energy spectra recorded in the normal direction from Cu(111) covered by different amounts of Cs are shown in Fig. 1. We obtain the coverage values from the evaporation times, using as a reference the time needed to form one atomic layer. The first atomic layer is regarded as complete when the intensity maximum is reached for the emission peak due to the overlayer state characteristic of the monolayer. Cs is evaporated onto the sample from a heated glass ampoule broken in the experimental chamber. The evaporation rates are varied between around 3 and 8 min per atomic layer. The sample is kept at a temperature of around 100 K during the experiment. At room temperature, because of the high vapor pressure of Cs, no more than slightly less than one full atomic layer remains on the substrate. The LEED pattern indicates that a Cs overlayer is a stack of close-packed Cs planes.

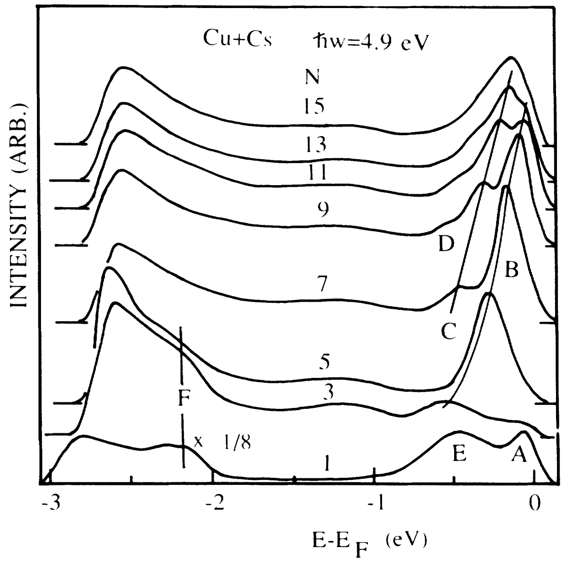

FIG. 1. Photoelectron energy spectra recorded along the surface normal at a photon energy of 4.9 eV from Cu(111) covered by the number of atomic Cs layers indicated in the diagram. A, B, C, and D are emission features due to discrete overlayer states, while E and F are due to the substrate.

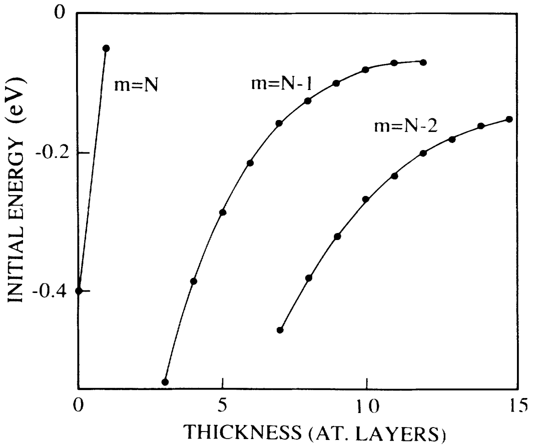

FIG. 2. The energy relative to E_F of observed overlayer states for Cs on Cu(111) plotted against the coverage in units of atomic layers, N. Indicated in the diagram are also the quantum numbers m assigned to the states.

The full Cs monolayer produces a very narrow emission peak quite close to the Fermi edge (peak A in Fig. 1). As the deposition is continued this peak remains at constant energy but loses intensity. After an evaporation time corresponding to around two atomic layers the peak has disappeared. No new peak appears which is characteristic of a two-atomic-layer thick Cs overlayer. As the third layer is forming there rises an emission peak at an initial energy of around 0.55 eV below the Fermi level. When additional layers are deposited the energy of the observed overlayer state increases (peaks labeled B in Fig. 1). From a plot of the intensity of this peak versus the coverage we conclude that the initial state passes the Fermi level as the thickness is increased from eleven to twelve atomic layers. A second emission peak (C in Fig. 1), which also shifts progressively towards the Fermi edge, is observed for films consisting of seven or more atomic layers. The weak shoulder D is observed for films which are between nine and thirteen layers thick. At first glance the shift towards higher initial energy may appear to be in conflict with the fact that as a potential well widens the energy decreases for a state with a given quantum number. The quantum number is not the same, however, for the peaks given a certain label in Fig. 1. This is clarified in Fig. 2. Here the measured initial-state energies are plotted against the number N of atomic Cs layers. In this diagram are also indicated the quantum numbers m assigned to the observed states. This assignment follows trivially from the assignments made for the Cu(111) surface state 0.4 eV below E_F, $N=m=0$,[5] and for the Na monolayer state, $N=m=1$.[3] Thus $m=N$ for A, $m=N-1$ for B, and $m=N-2$ for the peaks labeled C.

To obtain the wave vector from the phase-shift condition it now remains to determine $\Phi_B+\Phi_C$. By repeated use of the phase condition this sum can be obtained from experiment if measurements have been made for a sufficiently large number of different thicknesses such that overlayer states having the same or nearly the same energy are observed for more than one thickness. If there are overlayer states with the same energy for the two thicknesses N_1a and N_2a and the quantum numbers are $m_1=N_1-1$ and $m_2=N_2-2$, respectively, then $\Phi_B+\Phi_C=2\pi(2N_1-N_2)/(N_2-N_1)$ at that energy. With N_2-N_1 obtained from the distance between the two curves drawn through the points in Fig. 2 we get the barrier phase-shift sum shown in Fig. 3. The procedure can be used in the energy range between 0.45 and 0.20 eV where overlayer states are observed at more than one thickness. Outside this energy range we use extrapolated values for the phase-shift sum. We note that this sum is small over the energy range where overlayer states are observed.

Having thus obtained the wave vectors we now plot in Fig. 3 the measured energies against $(ka/\pi)^2$. The points removed by more than around 0.1 eV from the Fermi edge fall along a straight line. If the line is continued to zero wave vector one obtains a filled-band width for Cs of 1.3 eV, which should be compared with the value of 1.58 eV calculated from the free-electron model on the assumption that the density is the same for the present close-packed Cs overlayers as for bcc Cs. We note that filled-band widths appreciably smaller than predicted by the free-electron model have been obtained also for other simple metals.[6] We also note that the present band narrowing of around 0.3 eV agrees well with the self-energy correction recently calculated by

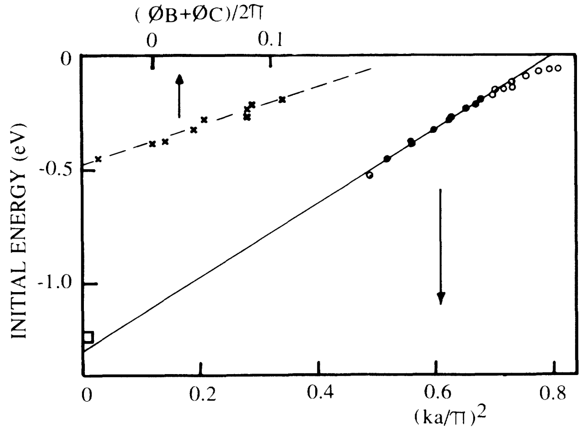

FIG. 3. The energy relative to E_F of observed overlayer states for Cs on Cu(111) plotted (as crosses) against $\Phi_B+\Phi_C$ (upper scale). The dashed line is used to obtain values for $\Phi_B+\Phi_C$ outside the measured energy range. Along the lower scale the energy relative to E_F is plotted (as circles) against $(ka/\pi)^2$, where k is the perpendicular wave vector and a the Cs interlayer distance. Empty circles are used when $\Phi_B+\Phi_C$ has been obtained by extrapolation. The square on the vertical axis indicates the band bottom as calculated in Ref. 6.

Lyo and Plummer[6] for an electron gas with the density of that for Cs. For energies close to E_F the wave vectors are close to the Brillouin-zone boundary and therefore one expects a deviation from free-electron dispersion similar to that observed here (Fig. 3). In the present case the deviation from a straight line in Fig. 3 can, however, also be explained by the limited experimental resolution (0.12 eV) combined with a somewhat inhomogeneous film thickness. Compared with the experimental resolution, the energy of an overlayer state close to E_F changes by only a small amount when the thickness is increased by the addition of one more atomic layer. If part of the film has a thickness smaller than the dominant one then there will remain filled overlayer states in this part of the film when the corresponding states are empty in the rest of the film. The thickness inhomogeneity can explain the constant energy of peak B when it is close to the Fermi edge and its gradual intensity decrease on continued Cs deposition (Fig. 1).

Next we comment on the hole lifetimes obtained from the present peak widths. The peaks observed close below the Fermi edge have a width which we cannot measure because of the limited experimental resolution. The peak at 0.54 eV below the Fermi edge observed for $N=3$ has a width corresponding to a hole lifetime of 0.22 eV. The wave function calculated for this state has a substantial tail on the substrate side of the adsorbate/substrate interface (Fig. 4). The wave function shown in Fig. 4 is calculated by use of the two-band model to describe the Cu electronic structure in the band-gap region and the assumption that the potential is constant in the alkali overlayer out to the vacuum barrier, which is approximated by an image potential. The plane waves in the overlayer are matched to the Whittaker functions, which are the solutions to the wave equation for an image barrier. Similar calculations are found to account well for the surface electronic structure of low-index Cu surfaces[5] and for the Na overlayer state observed for a Na monolayer adsorbed on Cu(111).[4] Because of the tail in the substrate the state is not purely a Cs state. The lifetime at this energy for Cs metal can therefore be expected to differ slightly from the value measured for the overlayer state.

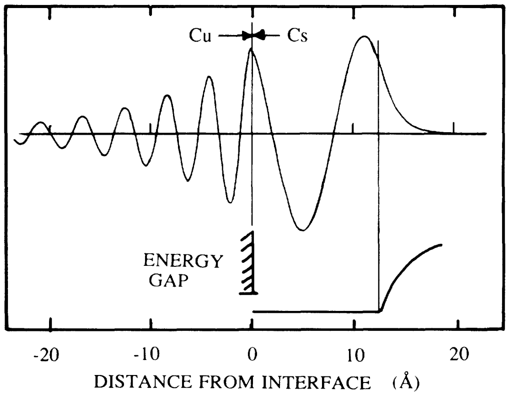

FIG. 4. Schematic diagram of the potential in the overlayer and the wave function for the discrete overlayer state in a three-atomic-layer thick Cs film on Cu(111).

Finally, we discuss the rather strong intensity variations of the overlayer-state emission with changing film thickness and initial-state energy (Fig. 1). When the overlayer is a nearly-free-electron metal with only weak optical absorption the tails of the wave function become important for the intensity. At monolayer coverages the emission intensity at the present low photon energies is similar to that produced by the well-known Cu(111) surface state 0.4 eV below E_F which has a similar tail. As the overlayer thickness increases the excitations associated with the tail on the substrate side become gradually less important on account of electron scattering in the overlayer. For the thicker of the present films the emission intensity is primarily due to the tail on the vacuum side of the overlayer. It is this tail which supplies the electrons ejected by the surface photoelectric effect. If the detector is turned away from the surface normal such that emission is measured for the wave-vector region outside the Cu band gap at L then the spectrum shows the triangular-shaped emission peak with maximum at E_F characteristic of the surface photoelectric effect for free-electron-like metals.[7,8] For Cs the peak has a width at the base of around 0.6 eV and is quite similar to that observed here for $N=15$ (Fig. 1) in the direction normal to the sample. The triangular-shaped emission spectrum of a thick sample can be regarded as the envelope to the spectra recorded for the thin films. This explains why the emission intensity increases as the energy of the overlayer state comes closer to the Fermi level.

The intensity also depends on the film thickness. In the present case when the emission is mainly due to the surface photoelectric effect the intensity is expected to be proportional to that part of the charge associated with the overlayer state which is located in the vacuum barrier. This part decreases when the film becomes thicker and the overlayer state is more spread out in space. From this normalization of the wave function one expects the intensity to be inversely proportional to the thickness if an exception is made for the thinnest films. For these a considerable fraction of the charge can reside in the tails of the overlayer state. The thickness dependence of the intensity discussed here explains why the peak at 0.2-eV initial energy observed for $N=12$ is smaller than the peak observed for $N=6$ at nearly the same initial energy. The intensity is reduced by a factor of around 2.5 instead of the factor of 2 expected from the thickness increase.

In conclusion, we have determined the dispersion $E(k)$ for valence electrons by photoemission in a novel manner by using thin overlayer samples in which there are standing-wave states.

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