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Unoccupied electronic band structure of an ordered potassium layer on copper: Cu(111)-(2×2)K

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The unoccupied electronic structure of potassium on Cu(111) is determined by angle-resolved inverse photoemission. The observed spectral features are assigned to unoccupied $4p$ and $3d$ states of potassium. For a complete monolayer an ordered (2×2) overlayer structure is formed. The dispersion of the K-induced states is determined and compared to a recent band-structure calculation for an isolated K monolayer.

I. INTRODUCTION

The adsorption of alkali-metal atoms on metal surfaces has been studied quite extensively.[1] The promoting action of alkali-metal atoms in heterogeneous catalysis and their drastic effect on the work function of various substrates has stimulated a number of experimental and theoretical investigations of adsorption of alkali-metal atoms on surfaces.[2-4] The generally accepted model describing the adsorption of alkali-metal atoms on metal surfaces was presented by Gurney[5] and has been refined by Lang and Williams[6] and by Muscat and Newns.[7] For an isolated alkali-metal adatom the valence states are broadened into resonances due to the interaction with the substrate surface. While the center of gravity of the *ns* resonance for a single adatom lies above the Fermi level, a tail of this valence state becomes occupied. Thus an alkali-metal adatom is not completely ionized. Experimentally the occupied part of the potassium 4*s* resonance adsorbed on a Cu(110) surface has been observed by Woratschek *et al.*[8] using Penning spectroscopy even for very low coverages. Frank *et al.*[9] observed unoccupied states of adsorbed alkali-metal atoms on Al(111) by inverse photoemission. Since these states shift below the Fermi level with increasing coverage before completion of a monolayer, they have been attributed to the *ns* resonances of the alkali-metal adatoms. With increasing alkali coverage the resulting increasing electrostatic field at the surface is expected to shift the *ns* and *np* levels downwards to higher binding energies (depolarization effect). Consequently, the occupation of the *s* levels increases, which lowers the surface dipole moment, yielding a minimum in the work function. Actually in photoemission experiments alkali-metal *s* states have been observed near the Fermi level for K and Na on Al(111) (Ref. 10) and Cs and Na on Cu(111) (Ref. 11) for completed monolayers. Using an Anderson-model calculation, Muscat and Batra[4] predicted that the progressive neutralization of the alkali-metal adatoms is accompanied by a surface-atom distance relaxation. For adsorbed Cs on Ag(111) a coverage-induced increase in bond length was recently observed using surface extended x-ray-absorption fine-structure (SEXAFS) spectroscopy.[12] In the present study we have determined the unoccupied electron band structure of a complete monolayer of potassium on Cu(111) by angle-resolved inverse photoemission in the isochromat mode. While recent inverse and direct photoemission studies have attempted to approximate a jelliumlike substrate by using Al(111),[9,10] we investigate the potassium metal *d*-band interaction by using a close-packed copper substrate.

II. EXPERIMENT

The experiments were performed in a two-chamber UHV system.[13] The base pressure in the measuring and preparation chamber was in the 10^{-11}-mbar range. The system is equipped for inverse photoemission (IPS) and direct (ultraviolet) photoemission (UPS), Auger-electron spectroscopy (AES), and low-energy electron diffraction (LEED). The IPS measurements were carried out in the isochromat mode, detecting 9.5-eV photons with a Geiger-Müller-type tube with a SrF_2 window. An electrostatically focused electron gun with a BaO cathode and the photon detector were fixed relative to one another at an angle of 30°. The angle of incidence of the electrons θ was varied by rotating the sample. The electron beam divergence was determined[14] to be better than 4° resulting in an uncertainty of the wave vector $k_{\parallel}$ of about $\Delta k_{\parallel}=0.08$ Å^{-1}. The overall energy resolution was 0.35 eV.

The Cu(111) crystal was cleaned by Ne-ion sputtering and annealing. Cleanliness was checked by Auger, UPS, and IPS measurements. K was evaporated from a commercial SAES Getters, Italy, getter source onto the sample at room temperature. During preparation the total pressure stayed below 10^{-10} mbar. The K surface concentration was calibrated by AES via the peak intensity ratio $y=I(\text{K (252 eV)})/I(\text{Cu (60 eV)})$. The resulting work-function change of the sample was determined by the diode method, namely detecting the onset of electron current at the sample. For the preparation conditions used in this study the work-function values and Auger ratios are given in Fig. 1. The minimum of the work-function curve corresponds to an Auger peak-intensity ratio of $y=0.3$. Concomitant with the small increase in the work function at higher coverage, a (2×2) overlayer is formed. We attribute the completion of a (2×2) overlayer structure to a coverage of $\theta=0.25$ monolayers (ML), with an Auger ratio of $y=0.5$. The (2×2) struc-

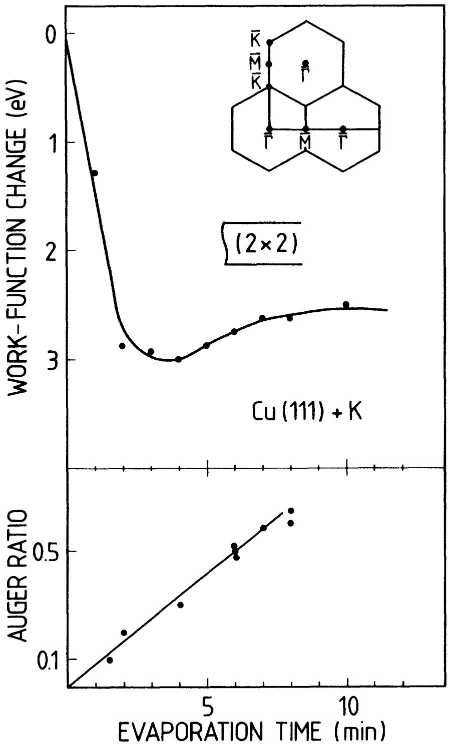

FIG. 1. Work-function change and Auger peak-intensity ratio $y = I(\mathrm{K}\ (252\ \mathrm{eV}))/I(\mathrm{Cu}\ (60\ \mathrm{eV}))$ as a function of potassium evaporation time. The inset shows the surface Brillouin zone of the (2×2) potassium overlayer.

ture is observable between $y = 0.4$ and 0.6. In this coverage regime the intensity of K-derived structures in IPS depends on the amount of evaporated K but no energy shifts of the K features were observed for coverages between 0.2 and 0.3 ML.

III. RESULTS AND DISCUSSION

The IPS spectrum of the clean Cu(111) surface is shown at the bottom of Fig. 2. The Fermi edge is determined by the onset of detected photons. At 4.2 eV above the Fermi edge (i.e., 0.8 eV below the vacuum level) the sharp emission of an image-potential surface state is observed.[13] From angle-resolved photoemission,[15] a Shockley-type surface state is known to lie 0.39 eV below the Fermi edge at the center $\overline{\Gamma}$ of the surface Brillouin zone ($k_{\parallel}=0$). Using UPS, we have observed this state on the clean copper surface. After deposition of K for 45 sec the surface state is shifted by 150 meV to higher binding energy. This surface state is completely quenched at further K adsorption. Lindgren and Wallden have studied in detail a similar effect of the influence of Cs adsorption on this occupied surface state.[16] This Shockley-type surface state is not observed in angle-resolved IPS for normal incident electrons ($\theta=0$) but is known as an upward dispersing feature starting at $k_{\parallel}=0.2$ Å^{-1} in IPS.[17] The deposition of 0.25 ML of K at room temperature results in a (2×2) K overlayer structure. The development of commensurate and incommensurate structures of K on a Ni(111) surface over a wide temperature and coverage range has recently been studied by Chandavarkar *et al.*[18] In this study a (2×2) commensurate overlayer structure has been observed at room temperature. On the Cu(111) surface studied here a (2×2) overlayer of K is formed under the same preparation conditions as reported for Ni(111).

For the (2×2) K overlayer two structures are observed in IPS. The two surface states of the clean Cu(111) surface at -0.39 and 4.2 eV relative to E_F are completely quenched. The first unoccupied K state is located 0.69 eV above the Fermi level. A second weaker structure is observed at 1.8 eV. A very similar two-peak structure was reported by Frank *et al.*,[9] who investigated K on Al(111) for coverages above 0.3 ML located at 0.75 and 1.7 eV. In an IPS study by Jacob *et al.*[19] for K on Ag(110), two states were observed 1.0 and 2.7 eV above E_F for coverages above 0.3 ML. In both recent studies the two empty K states have been attributed to the K 4*p* and 3*d* levels, respectively. By comparison to the band-structure calculations of Wimmer[20] for a free hexagonal layer of K we arrive at the same assignment for the K states.

Varying $k_{\parallel}$ of the incident electrons in well-defined azimuth directions of the surface Brillouin zone we have determined the two-dimensional band structure of the (2×2) K overlayer on Cu(111). The IPS spectra as a function of the electron incidence angle along the $\overline{\Gamma}-\overline{K}$ azimuth are shown in Fig. 2. The weaker structure at 1.8 eV can only be followed to a polar angle of 10° before it disappears. No energy shift is observed for this state in the limited momentum range.

The lower-lying 4*p*-derived emission disperses upwards until it reaches the zone boundary at point $\overline{K}$ at an energy of 2.65 eV. Starting at about 27° a new peak is observed at 0.95 eV having a weak upward dispersion with increasing $k_{\parallel}$. For angles above 15° a broadening of the upward dispersing state is observed. This greatly reduces the intensity of this emission. The state at about 2 eV at angles above 27° also shows very weak spectral intensity. The energetic position of these states is therefore determined only within ±0.2 eV. The corresponding $E(k_{\parallel})$ points are collected in Fig. 4 in comparison with the band-structure calculation by Wimmer.[20] The spectra showing the angular variations in $\overline{\Gamma}-\overline{M}$ direction are given in Fig. 3.

It is obvious from Fig. 4 that the calculations by Wimmer reproduce the experimentally determined binding energy of the 4*p* band at point $\overline{\Gamma}$ and the bandwidth of 2 eV in the $\overline{\Gamma}-\overline{K}$ azimuth. For the band-structure calculations Wimmer used a value of 4.53 Å for the nearest-neighbor spacing of the K atoms. The (2×2) overlayer studied here shows a distance of 5.11 Å between the K atoms. Additionally, Wimmer assumed a hexagonal close-packed K layer not interacting with a substrate surface. For the higher-lying *d*-*s*-hybridized band, Wimmer expects an upward dispersion that is not verified experimentally. Actually a smaller bandwidth can be expected for more localized 3*d* states as compared to the more extended 4*p* levels in an ordered K layer. The broadening of the upward dispersing *p* state occurs in the momentum range where the calculations predict the crossing of a downward dispersing band. Possibly a hybridization between these bands is responsible for the observed intensity reduction. In an angle-resolved IPS study of ordered Na overlayers on Al(111),[21] a similar broadening of a low-lying *p* band was observed and attributed to hybridization with a downward dispersing band. The occurrence of a new peak at angles $\geq 27°$ is again consistent with Wimmer's calculations in Fig. 4. From these calculations two closely lying bands of *s* and *p* character are expected in the $\bar{K}-\bar{M}$ direction at somewhat higher binding energies than experimentally observed. While Wimmer expects a downward dispersion for these states, we found this

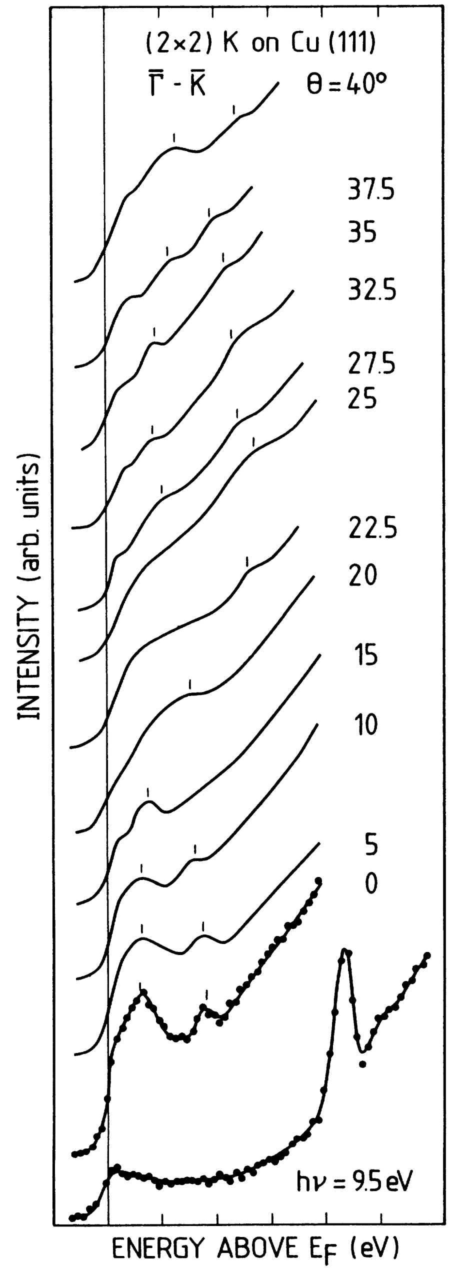

FIG. 2. Inverse photoemission spectra of a (2×2) overlayer K on Cu(111) at different electron incidence angles θ in the $\bar{\Gamma}-\bar{K}-\bar{M}$ direction.

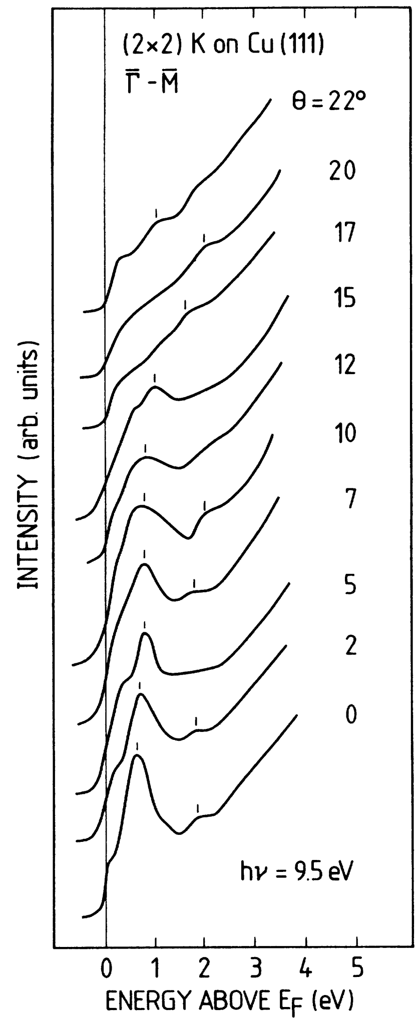

FIG. 3. Inverse photoemission spectra of a (2×2) overlayer K on Cu(111) at different electron incidence angles θ in the $\bar{\Gamma}-\bar{M}$ direction.

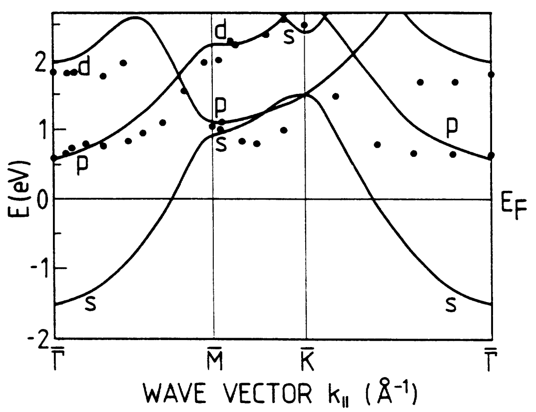

FIG. 4. Experimentally determined dispersion of potassium states in a (2×2) overlayer on Cu(111). The solid lines give the calculated dispersion of an isolated K monolayer as published by Wimmer (Ref. 20). The $\bar{K}$ point of the overlayer corresponds to a value of $k_{\parallel} = 0.615$ Å^{-1}.

feature dispersing weakly upward. The weak structures at higher angles about 2 eV above E_F in Fig. 2 coincide in Wimmer's $E(k_{\parallel})$ diagram with a d-derived potassium band. Since the states are very difficult to observe in IPS, the experimentally determined dispersion is of the same order of magnitude as we estimate the error bars of the binding energy for this emission.

Again in the $\overline{\Gamma}-\overline{M}$ direction, good agreement between experiment and calculation is obtained for the K $4p$ band. Yet very small or no dispersion is found for the $3d$-derived state up to $\frac{1}{2}\overline{\Gamma}-\overline{M}$. A state at 1 eV above E_F is observed near point $\overline{M}$. No indication for the unoccupied part of the $4s$ band is found in this IPS study. Using angle-resolved photoemission, Horn *et al.*[10] recently observed the crossing of the Fermi level for the $4s$ band of a $(\sqrt{3}\times\sqrt{3})R30°$ overlayer K on Al(111). Using IPS, Frank *et al.*[9] have identified a $4s$-derived state of K on Al(111) at very low coverages below 0.09 ML. This state exhibited a very low cross section in IPS and was identified using difference spectra. We attribute it to the very low cross section of the $4s$ state that this band was not observed in our study.

In summary we have determined the unoccupied electron band structure of an ordered (2×2) overlayer of K on Cu(111). The measured bands originate from the empty atomic $4p$ and $3d$ orbitals. The energetic positions and the bandwidth of the features in IPS are similar to a band-structure calculation by Wimmer, although this calculation assumes a 12% smaller nearest-neighbor spacing and does not consider any interaction with an underlying substrate. From this we conclude that some of the properties of the two-dimensional band structure of a completed monolayer of K on Cu(111) can be described even without consideration of alkali-substrate interaction. An influence of hybridization of alkali states with copper d bands could not be demonstrated experimentally. For the monolayer coverage regime investigated here the inverse photoemission spectrum for normal incident electrons is identical to that observed for potassium on Al(111). We hope that this study will stimulate new theoretical calculations of alkali overlayers on jelliumlike and real surfaces in order to develop a more detailed description of the properties of alkali-metal overlayers on metal surfaces.

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