

4s Valence Level of Adsorbed K Atoms Probed by Metastable-He Deexcitation Spectroscopy

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Deexcitation of metastable He atoms has been used to probe the existence of a partially occupied 4s-derived level close to the Fermi level of K atoms adsorbed on a Cu(110) surface, even at very low coverages. The width of this level decreases from about 3 eV at low coverage to 2 eV at high coverage, reflecting the transition from the chemisorbed to the metallic state of the adsorbate.

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Adsorption of alkali-metal atoms on metal surfaces has been quite extensively studied in the past.¹ The simplest picture for the formation of the chemisorption bond was proposed by Langmuir² and assumes that the alkali-metal atom transfers its valence *s* electron completely to the metal substrate. With increasing coverage the resulting surface dipoles depolarize each other mutually, thus causing the characteristic variation of the work function. The more realistic, quantum mechanical model of Gurney³ assumes that the discrete *s* level of the free alkali-metal atom broadens and shifts down in energy when the atom approaches the surface. At the equilibrium separation the density of states of this resonance reaches partly down below the Fermi level E_F so that ionization is incomplete. This picture underlies a series of more recent theoretical treatments of this problem⁴ which predict partial occupancy of this *s*-level resonance even for a single adatom, i.e., in the limit of zero coverage. Any attempts to verify experimentally the existence of this level close to the Fermi level by ultraviolet photoelectron spectroscopy (UPS) have been so far rather unsuccessful because of overlap with the emission from valence states of the substrate and of the low excitation cross section of *s*-electronic states by photons.⁵ The only indication so far was reported for Cs adsorbed on Cu(111) *above half a monolayer* where the UPS data showed the emergence of a peak below E_F .⁶ Since, however, at higher coverages an alkali-metal overlayer is expected to become more metalliclike,⁴ this observation does not answer the question of whether *isolated* adsorbed alkali-metal atoms are completely ionized or not.

Electron spectroscopy by deexcitation of metastable noble-gas atoms (MDS), on the other hand, is an extremely surface-sensitive technique and probes only the valence electronic structure of the outermost atomic layer of a solid.⁷ Since, in addition, He* atoms exhibit a high cross section for excitation of *s* levels,

this technique provides unique possibilities for studying the outlined question. Recent studies with K/Ni(111)⁸ and K/Cu(110)⁹ already provided evidence for the existence of alkali-metal-derived states below E_F . The present work reports on a systematic study with the system K/Cu(110) over the whole range of coverages where, for the first time, the existence of a partially occupied alkali-metal *s* resonance even at very low coverages could be demonstrated.

The experimental system has been described previously.¹⁰ MDS was performed by 1S He* atoms with thermal kinetic energies. Since these undergo very efficient transformation into the triplet state at a K-covered surface prior to deexcitation,^{8,9} the presented spectra are actually due to deexcitation of 3S He* (excitation energy 19.8 eV). Potassium was evaporated from a SAES getter source onto a clean Cu(110) surface, and the K surface concentration was monitored by Auger spectroscopy via the peak-intensity ratio $\gamma = K(252 \text{ eV})/Cu(60 \text{ eV})$. The coverage θ is defined with respect to the density of Cu atoms in the topmost atomic layer ($1.09 \times 10^{15} \text{ cm}^{-2}$). A closed-packed layer of adsorbed K atoms (metallic radius 2.26 Å, yielding $5.65 \times 10^{14} \text{ atoms/cm}^2$) would thus correspond to $\theta = 0.52$. Since it was found—in agreement with Ref. 5a—that the Cu(110) surface undergoes reconstruction into a 1×2 phase by adsorption of small amounts of alkali metal, calibration of the *absolute* coverage by low-energy electron diffraction was not feasible. From the same arguments as Hayden *et al.*^{5a} (based on the theoretical work of Lang^{4a}) we assume that the work-function minimum occurs at about half of the first monolayer, i.e., around $\theta = 0.25$. The coverage scale is thus estimated to be uncertain to within about $\pm 20\%$, which will, however, be of only minor importance for the conclusions to be drawn.

The work function of the clean Cu(110) surface ($\phi = 4.4 \text{ eV}$) as well as its variation with K coverage were determined from the emission threshold in UPS.

The resulting data are displayed in Fig. 1 and exhibit the typical features of alkali-metal overlayer systems: Initially the work function decreases linearly (indicating constant dipole moments of the adsorbate complexes) up to $\Delta\phi \approx -2$ eV ($\theta \approx 0.06$) where the curve flattens and reaches a minimum ($\Delta\phi = -3.1$ eV) at $\theta = 0.25$. In the multilayer range finally the work function of bulk potassium ($\phi = 2.3$ eV,¹¹ corresponding to $\Delta\phi = -2.1$ eV) is approached.

A series of metastable deexcitation spectra for various potassium coverages is displayed in Fig. 2. The low-energy cutoff of electron emission was chosen as the zero of the energy scale E'_{kin} , which means that $E'_{kin} = E_{kin} + \phi + \text{const}$, where E_{kin} is the *true* kinetic energy and ϕ the *macroscopic* work function at the respective coverage. With a clean Cu surface deexcitation occurs through the resonance-ionization plus Auger-neutralization mechanism.¹² The smooth energy distribution is characterized by a shoulder at high kinetic energies due to emission from *s* surface states. In this case the maximum kinetic energy is determined by $E_{kin,max} = I_{eff} - \phi - \phi_{loc}$, where I_{eff} is the effective ionization potential of the (ground state) He atom in front of the surface and ϕ_{loc} is the *local* work function at the point of deexcitation. [One has to distinguish between ϕ_{loc} and ϕ because in the Auger-neutralization process the energy gain by the first electron undergoing a transition from E_F to the $1s$ hole is governed by ϕ_{loc} , while the second, outgoing electron is recorded far outside the surface dipole layer and therefore "feels" the macroscopic work function ϕ . In the case of a uniform surface, like the clean Cu(110) surface, of course ϕ_{loc} is equal to ϕ , which will, however, no longer be the case in the presence of an adlayer.] Absorption of K leads to the appearance of an additional spectral feature at even higher E'_{kin} . In

the vicinity of an adsorbed K atom ϕ_{loc} is considerably lower than at a bare-metal-substrate site, as was demonstrated by photoemission of adsorbed xenon¹³ as well as by MDS¹⁴ and is reflected by the overall decrease of the *total* work function ϕ . At the potassium sites, deexcitation now occurs via Auger deexcitation whose energy balance is similar to that of UPS.¹⁵ In this case the maximum kinetic energy is given by $E_{kin,max} = E^* - \phi$, where E^* is the effective excitation energy of the He* atom, and defines the position of the Fermi level E_F . $E_{kin,max}$ was found to be 1.5 eV smaller than that found with UPS ($h\nu = 21.2$ eV), which value is very close to the difference between $h\nu$ and E^* of $^3\text{He}^*$ (19.8 eV). The conversion of singlet into triplet He* prior to deexcitation was already mentioned above and had been studied previously.^{8,9}

The K-induced features originate from occupied states close to E_F and grow in intensity with increasing coverage until a pronounced peak emerges. However, up to $\theta \approx 0.10$ this spectral feature is still superim-

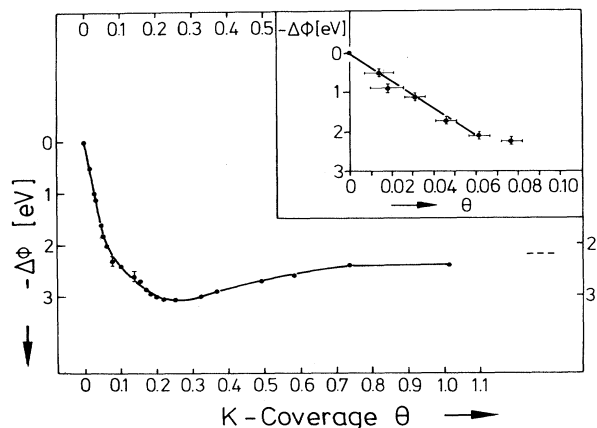


FIG. 1. Variation of the work function, $\Delta\phi$, of a Cu(110) surface as a function of the K coverage θ . The inset shows the data for low coverages with an enlarged abscissa.

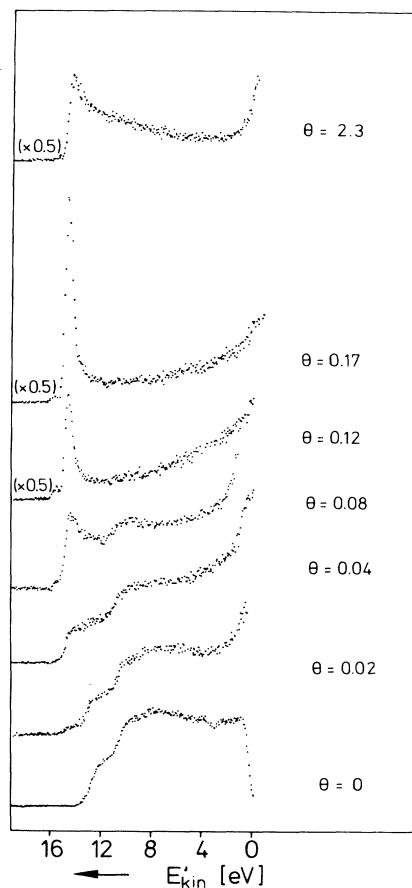


FIG. 2. He* metastable deexcitation spectra for various K coverages on Cu(110). (The weak structures at the highest kinetic energies arise from a small fraction of singlet He* atoms not converted into the triplet state; see Ref. 9.)

posed on structures arising from deexcitation at bare Cu sites which are unshifted on the E'_{kin} scale. This demonstrates that the He^* act as local probes distinguishing between K sites and bare Cu sites which are characterized by different deexcitation mechanisms (Auger detection and resonance ionization plus Auger neutralization, respectively). If one recalls that $E'_{\text{kin,max}} = I_{\text{eff}} - \phi_{\text{loc}} + \text{const}$ this result further means that the local work function ϕ_{loc} at bare Cu sites is still identical to that of the clean surface, although, e.g., at $\theta = 0.05$ the macroscopic work function ϕ has decreased by 2.3 eV. This conclusion is consistent with recent theoretical treatments of the variation of the local electrostatic potential in the vicinity of adsorbed alkali-metal atoms which demonstrated the short-range nature of these effects.¹⁶

Above $\theta \approx 0.10$, emission from the Cu substrate is no longer visible in the spectra while the K-induced peak grows further. If we assume a uniform distribution of the adsorbed K atoms, their mean mutual separation is about 7 Å at this coverage, and the rather big He^* atoms (radius ≈ 5 Å) are obviously completely deexcited by the protruding K atoms before they can reach the Cu surface. At $\theta \geq 0.20$ the peak intensity starts to decrease, probably because of the reduction of accessible impact parameters¹⁰ and to the increased energy loss and formation of secondary electrons. The latter effect becomes clearly evident in the spectra from multilayers, where the peak below E_F exhibits a pronounced tail extending to low kinetic energies.

Figure 3 shows a series of "difference spectra" which were obtained by subtracting the spectrum of the clean Cu surface from the spectra recorded at the

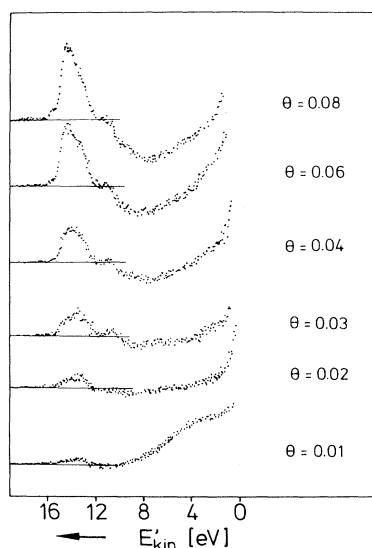


FIG. 3. Difference spectra for various K coverages showing the growth of the 4s-derived level.

respective K coverages. These data demonstrate clearly the growth of the intensity of the K 4s-derived level even from the lowest coverages. These difference spectra exhibit increasing negative intensities at $E'_{\text{kin}} \leq 12$ eV, since with the K-covered surfaces the emission from Cu sites is continuously suppressed, which effect should, however, be of no influence on the conclusions about the K 4s level at higher E'_{kin} . The integrated intensity of this peak is plotted in Fig. 4 as a function of the K coverage. This intensity increases practically linearly with θ up to about $\theta = 0.12$, where a break occurs and the further increase becomes even stronger.

Although the interpretation of intensities of spectral features in the metastable deexcitation spectra is not unambiguous, the following conclusions can be drawn from the data presented:

(1) The observation of emission from the K 4s-derived level at the lowest coverages indicates that even an isolated adsorbed potassium atom is not completely ionized. This is in agreement with the quoted quantum mechanical calculations⁴ on alkali-metal adsorption.

(2) The slope of the $\Delta\phi$ -vs- θ curve is constant up to $\theta \approx 0.06$ and then becomes smaller, indicating a continuous decrease of the average dipole moment. There is no indication for a similar effect in the data of MDS intensity versus θ which exhibit a constant slope up to $\theta \approx 0.12$. This might suggest that the initial decrease of the dipole moment is not associated with a

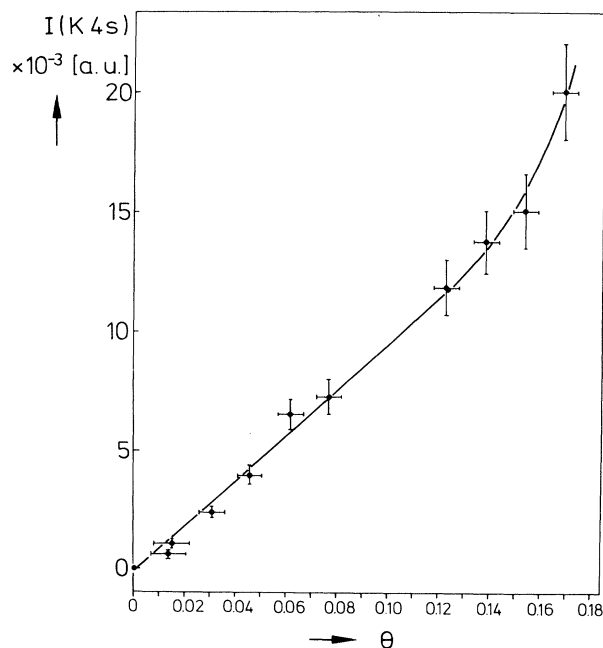


FIG. 4. Variation of the intensity of the 4s-derived level with coverage.

corresponding variation of the occupation and spatial extension of the 4s level (which is probed by MDS). In this connection it should be mentioned that the K-induced reconstruction of the Cu(110) surface was found to be completed at about $\theta=0.04$, but there is obviously no marked influence of this effect on the $\Delta\phi$ nor the MDS data.

(3) The pronounced increase of the MDS intensity above $\theta \approx 0.12$ has to be ascribed to the fact that the adsorbed K atoms become now more metallike. The calculations by Lang^{4a} revealed that at high coverages the negative charge distribution moves further outside from the substrate edge which accounts qualitatively for this observation. This transition is reflected also in the shape of the 4s peak which becomes considerably narrower above $\theta=0.10$: Its width is about 3 eV at low θ and is there determined by the chemisorption bond, while at high coverage it is only of the order of 2 eV in agreement with the width of the s band (2.1 eV) of bulk potassium.

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