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Electronic structure of a single layer of Na on Cu(111)

N. Fischer, S. Schuppler, R. Fischer, Th. Fauster, and W. Steinmann
Sektion Physik der Universität München, Schellingstrasse 4, W-8000 München 40, Germany

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High-resolution photoemission and two-photon photoemission have been used to investigate the electronic structure of a single layer of Na on Cu(111). In addition to an occupied Na-induced state 0.11 ± 0.03 eV below the Fermi energy, we resolved three unoccupied states with binding energies relative to the vacuum energy of 0.72 ± 0.03, 0.27 ± 0.03, and 0.13 ± 0.04 eV. These values are at variance to the predictions of a simple phase-analysis model. The effective mass of the lowest unoccupied state and the occupied Na-induced state were measured to be $m^*/m_e=1.3\pm0.1$. This is considerably larger than the expected free-electron value. More refined theoretical models accounting for the atomic structure of the adsorbate are necessary for a realistic description of the electronic structure of single alkali-metal layers on metal surfaces.

Adsorption of alkali metals on metal surfaces produces shifts of the surface states of the bare substrate[1-6] and induces adsorbate-derived states[1,2,4,6-11] as shown in a lot of photoemission and inverse-photoemission (IPE) experiments. The observed electronic structure of a single alkali-metal layer is commonly interpreted in two different ways. Either the results are compared to a self-consistent calculation of the band structure of an isolated monolayer[12] of the respective alkali metal[8-11] or they are related to the predictions of a phase-analysis model.[6,13-15] This model was originally introduced in order to describe the surface states of clean metal surfaces[16,17] formed in the potential well between the vacuum barrier and the crystal. Surface states occur at energies where the accumulated phase shift for one roundtrip in the potential well sums up to a multiple of 2π: $\Phi_C+\Phi_B=2\pi n$, $n=0,1,2,\ldots$ where Φ_C and Φ_B are the phase shifts upon reflection of an electron at the crystal and the image barrier, respectively. For the system Na/Cu(111), Lindgren and Wallden used this model to explain an extremely narrow peak close to the Fermi level E_F,[13,14] which they observed in photoemission.[1] In their modification of the above model, the sodium layer is accounted for by introducing a region of constant potential U_{Na} of thickness d between the crystal and the image barrier. For an electron with energy E, an additional phase shift $\Phi_D=d[2m/\hbar^2(E-U_{\text{Na}})]^{-1/2}$ has to be taken into account: $\Phi_C+\Phi_B+2\Phi_D=2\pi n$. As a consequence of the $1/r$ image potential, Φ_B diverges and a series of unoccupied states below the vacuum level is expected to be formed in the Na/Cu(111) system, similar to the image-potential states on clean metal surfaces.[16,17]

Measurements of the unoccupied-level structure of the alkali-metal-covered metal surfaces done so far were performed with IPE. Most of these investigations showed a single weak structure near the vacuum energy interpreted as an alkali-metal d-derived state[8,9,11] according to Wimmer.[12] No clear experimental evidence for the series of states predicted by the phase-accumulation model could be found so far. To clarify whether this is due to an inadequate description of the physical problem within the phase model or a result of insufficient resolution of IPE, we used two-photon photoemission (2PPE) to investigate a single layer of Na on Cu(111). 2PPE has proven to be an adequate tool for resolving image states of clean metal surfaces.[18-21]

In 2PPE, pulsed laser light is used to excite electrons from an occupied state below E_F into an unoccupied state below the vacuum level E_{vac}. Within the lifetime of this excited state, a second photon may be adsorbed and photoemission from the intermediate state can be observed. Details of the experimental setup have been published previously.[18] The experiments were performed under UHV conditions at a base pressure of $p\approx7\times10^{-11}$ Torr. A tunable dye laser pumped by an excimer laser is used as the light source for 2PPE. In all 2PPE measurements we used p-polarized light for both excitation steps. Ordinary one-photon photoemission (1PPE) is excited by the unpolarized monochromatized light of a mercury lamp. The photoelectrons are analyzed in a sectorial hemispherical analyzer with an energy resolution set to around 45 meV in the present experiments.

The upper part of Fig. 1 shows typical photoemission spectra of the clean Cu(111) surface recorded in normal emission. All data are referred to the Fermi energy E_F. The 1PPE spectrum at the left-hand side excited with a photon energy of 5.59 eV is dominated by the occupied surface state S existing in the $L_{2'}$-L_1 gap of the projected bulk band structure around $\bar{\Gamma}$. In agreement with recent publications,[22] we found a binding energy of -0.39 ± 0.02 eV at $\bar{\Gamma}$. For the work function Φ, determined by the low-energy cutoff of the photoemission spectra, we obtain 4.94 ± 0.02 eV which is in the range of previously reported values.[23] At the right-hand side of the upper part of Fig. 1 a 2PPE spectrum excited with a photon energy of 4.48 eV is shown. The sharp peak I at 4.11 eV above E_F results from emission out of the lowest image-potential state. In agreement with previous findings,[24,25] we get a binding energy relative to the vacuum energy of 0.83 ± 0.03 eV. As depicted in Fig. 1 at this photon energy very efficient resonant excitation[24,26] from the occupied state S into the image state I takes place.

Na is deposited onto the sample from a well-outgassed commercial getter source (SAES) mounted in a heated

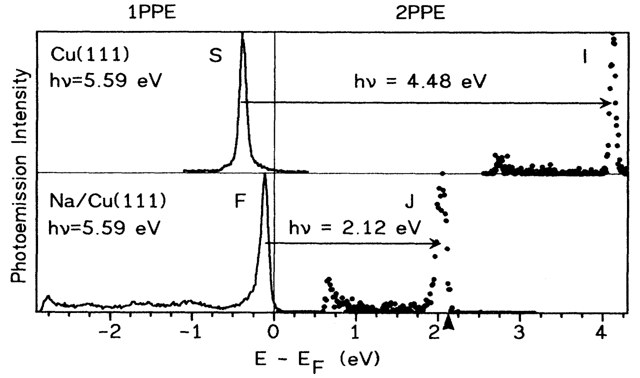

FIG. 1. Upper panel: 1PPE spectrum (left-hand side) and 2PPE spectrum (right-hand side) of the clean Cu(111) surface. The arrow depicts resonant excitation from the occupied surface state S into the lowest image-potential state I at a photon energy of 4.48 eV. Lower panel: Spectrum for a single layer of Na on Cu(111). Resonant excitation between the Na-induced states F (occupied) and J (unoccupied) occurs at $h\nu = 2.12$ eV. The position of the highest accessible state is marked on the energy scale.

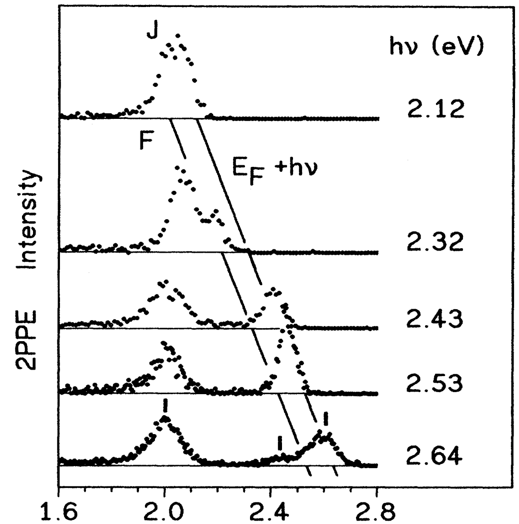

FIG. 2. Series of 2PPE spectra of a single-layer Na on Cu(111) recorded at different photon energies in normal emission. At $h\nu = 2.64$ eV, three unoccupied states (marked by bars) can be seen (see text).

collimating glass tube. The pressure during evaporation did not exceed 1.5×10^{-10} Torr. The adsorption of Na was monitored by low-energy electron diffraction (LEED), 1PPE, and 2PPE, including work-function measurements. In LEED and 1PPE we found the coverage dependence described by Lindgren and Wallden.[1] In accordance with their investigation we determined the completion of the first Na layer at the maximum intensity of the Na-induced peak F (Fig. 1) observed in photoemission at low photon energies.[1] This coincides with the weak maximum to the work function of $\Phi \approx 2.77$ eV which appears after passing through the work-function minimum typical for alkali-metal adsorption on metals.

In the lower panel of Fig. 1, 1PPE and 2PPE spectra of the Na-covered Cu(111) surface are shown. The 1PPE spectrum is wider than the one of the clean surface which is due to the reduced work function and exhibits the Na-induced peak F. F is found to have a binding energy of -0.11 ± 0.03 eV. It serves as the initial state in 2PPE for a resonant excitation with a photon energy of 2.12 eV into an unoccupied state J about 2 eV above E_F. The respective 2PPE spectrum and the excitation process are shown in the right-hand side of the figure. As the highest accessible unoccupied states populated with electrons from E_F have an energy of $E = E_F + h\nu$ (marked at the energy scale of the spectrum), one has to increase the photon energy to a value close to the work function in order to look for further states close to E_{vac}. This is demonstrated in Fig. 2 where a series of 2PPE spectra of a single layer Na on Cu(111) recorded at different photon energies can be seen. As in Fig. 1 the energy of the highest accessible unoccupied states ($E_F + h\nu$) at the corresponding photon energy is shown. The additional line F gives the energy where electrons excited from the state F would appear under absorption of two photons with energy $h\nu$. All spectra exhibit a peak J at about 2 eV binding energy which is due to emission out of the first unoccupied state. The peak intensity compared to the low-energy cutoff in the spectrum (not shown in the figure) decreases by a factor of about 20 when increasing the photon energy from 2.12 to 2.43 eV. This is a consequence of the fact that at the higher photon energy, J is populated with electrons from a region of low density of states, whereas at $h\nu = 2.12$ eV the efficient resonant transition from F into J takes place. At $h\nu = 2.32$ eV both the unoccupied state and F are seen in the spectrum, whereas no emission from F is detectable at $h\nu = 2.43$ eV. However, at this photon energy an additional peak appears at about 2.4 eV above the Fermi level and is seen in all spectra with $h\nu \gtrsim 2.43$ eV and is consequently a second unoccupied state. At $h\nu \approx 2.53$ eV this state is populated with electrons from the occupied state F. This resonance increases the photoemission intensity in this peak by a factor of 2 relative to J. After passing through this resonance, the peak intensity drops by a factor of 10 as can be seen in the spectrum recorded at $h\nu = 2.64$ eV. In this spectrum a third peak above the assumed position of F appears at $E - E_F \sim 2.6$ eV. As this state could not be excited with lower photon energies, it is also identified as a further unoccupied state near the vacuum level. Thus, three unoccupied states close to E_{vac} are identified and must be designated as the three lowest members of a Na-induced series of image-potential states.

We measured several series of spectra as shown in Fig. 2 and extrapolated data measured for coverages below one monolayer. In this way we find the following best values for the binding energies relative to E_{vac} of 0.72 ± 0.03, 0.27 ± 0.03, 0.13 ± 0.04 eV, and a work function $\Phi = 2.77 \pm 0.03$ eV for one layer Na on Cu(111).

The model calculation of Lindgren and Wallden using $d = 3.07$ Å and $U_{\text{Na}} - E_F = -3.2$ eV as the parameters for the Na potential describes well the occupied Na-induced state F as the $n = 1$ state, but yields a binding energy for the lowest image state ($n=2$) of $E-E_{\mathrm{vac}}=-0.5$ eV (Ref. 14) in disagreement with our experimental findings. To find out whether a variation of the parameters d and U_{Na} determining Φ_D would lead to a better agreement with the experiment, we made a calculation with the barrier shift Φ_B given by the McRae-Kane formula[27] which is a good approximation for states close to the vacuum level.[17] Φ_C was determined as described by Smith.[16] Agreement between the model and the experimental data within the error limits is achieved only for a certain range of d and the corresponding U_{Na}: $d=5$–9 Å and $U_{\mathrm{Na}}-E_F=0$–1.5 eV. Using this set of parameters no occupied Na-induced state would appear, as a consequence of the fact that U_{Na} lies above E_F. Thus, no set of parameters exists that describes the experimental binding energies of all four Na-induced states observed for a single layer Na on Cu(111), if the sodium layer is described by a simple square-well potential. This indicates that the atomic structure of sodium has to be taken into account for a realistic description of the electronic structure of a single layer of Na on Cu(111). Actually this conclusion holds even if the highest measured image state ($n=4$) was disregarded, since the above parameter range is determined by the lower two image states ($n=2,3$) only.

For a monolayer of Na on Cu(111) one might expect to find effective masses to be free-electron-like.[4] That holds especially for the image states of this system as they are located near the middle of the $L_{2'}-L_1$ gap. In that case, only slight deviations from the free-electron value are expected.[28] On the other hand, the effective mass of the partially occupied alkali-metal-induced states measured so far[4,7] were found to be larger than expected from self-consistent calculations for an isolated alkali-metal monolayer.[12] As pointed out in Ref. 4 enhanced self-energy corrections due to the two-dimensional nature of the adsorbate or hybridization of the alkali-metal band with the substrate bands might be responsible for this effect. We measured the effective mass for the occupied structure F and the lowest unoccupied image-potential-induced state. These measurements together with the binding energies at $\bar{\Gamma}$ for the higher imagelike states are shown in Fig. 3. Both states are found to disperse parabolically with the same effective mass of $m^*/m_e=1.3\pm0.1$. Therefore, in agreement with the above-mentioned experiments,[4,7] we find effective masses considerably larger than expected from a simple theory. Even for the image-potential state, which is expected to have an effective mass close to unity due to its location in the middle of the gap,[28] no free-electron behavior is found.

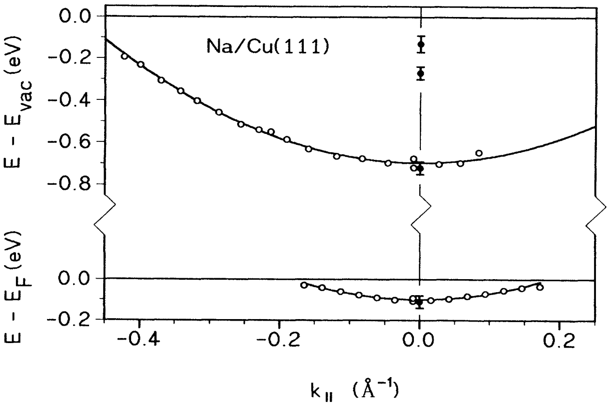

FIG. 3. Dispersion $E(k_\parallel)$ of the occupied and the lowest unoccupied Na-induced state measured along $\bar{\Gamma}\bar{M}$ (open circles). The best parabolic fits (lines) yield the effective masses of $m^*/m_e=1.3\pm0.1$ for both states. The solid circles mark the best values for the binding energies at $\bar{\Gamma}$ of the four measured Na-induced states (see text).

We conclude that the qualitative predictions of simple phase analysis concerning the existence of imagelike states on a single layer of sodium on Cu(111) are in agreement with our experimental findings. However, it is not possible to describe the measured binding energies and disperson quantitatively within this model. Investigations concerning the coverage dependence of surface-state energies upon alkali-metal adsorption are under progress.

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