Coverage-dependent electronic structure of Na on Cu(111)

N. Fischer, S. Schuppler, Th. Fauster *, W. Steinmann
Sektion Physik, Universität München, Schellingstr. 4, 80799 München, Germany
(Received 4 January 1994; accepted for publication 14 March 1994)

Abstract

The electronic states of Na on Cu(111) have been studied by high-resolution two-photon photoemission. Image states which are well separated from alkali states are observed at all coverages. An abrupt change of the occupancy of the alkali state is observed at coverages between 0.40 and 0.45 ML. We interpret this as the transition from a more ionic bonding of alkali atoms on the surface to the metallic bond in alkali islands. Other alkali metals on close-packed surfaces show a very similar electronic structure as a function of alkali coverage.

1. Introduction

The adsorption of alkali metal atoms on metal surfaces has been studied extensively for a long time (for a review see Ref. [1]). Despite these efforts there is still an ongoing debate whether at small coverages the bonding is more ionic or more covalent. An ionic bond implies a charge transfer from the alkali atom to the metal which would come predominantly out of the outermost s orbital. In a covalent bond the occupancy of the electronic levels would remain unchanged, i.e., the s orbital would be occupied. For a clarification of this question careful studies of the electronic structure of adsorbed alkali atoms are needed. An experimental investigation of these questions requires a technique with high energy resolution, low background, and high surface sensitivity in order to unambiguously identify the alkali states. Two-photon photoelectron spectroscopy [2] fulfils these requirements and has the unique advantage of making a study of occupied and unoccupied states with the same resolution possible.

In previous work [3,4] we have reported our results for full monolayer coverages of Na and K on Cu(111), Co(0001), and Fe(110). The main conclusion was that two-photon photoemission can be applied to alkali-covered surfaces and that the observed electronic states and the proper work function depend on the alkali metal but not on the substrate [4]. In this paper we will present our results for the whole coverage range.

Two-photon photoemission is particularly well suited to investigate image states. These bound states exist in the attractive potential well created in front of a metal surface by the Coulomb potential acting between the electron and its image inside the metal [5]. The image states can give valuable information about the potential near the surface [2,4] and the growth and morphology of thin metal films [6,7]. With respect to the adsorption of alkali metal atoms the following questions

* Corresponding author.

0039-6028/94/$07.00 © 1994 Elsevier Science B.V. All rights reserved
SSDI 0039-6028(94)00152-Y
arise: At which coverages do image states exist? Are there alkali states observable? There have been several inverse photoemission studies [8–15] which observed unoccupied states but were – due to their limited energy resolution – unable to distinguish unambiguously between image states and alkali states. A coverage-dependent two-photon photoemission study for K on Ag(100) reported an “alkali s resonance” but no image states [16].

2. Experiment

In two-photon photoelectron spectroscopy [2] pulsed laser light with a photon energy below the work function $\Phi$ of the sample is used to excite electrons from occupied states into unoccupied states below the vacuum level $E_{\text{vac}}$. A second photon may lift these excited electrons above $E_{\text{vac}}$ enabling them to leave the sample. Energy analysis and detection of the electrons can proceed by standard techniques and it is possible to transfer the good energy and momentum resolution of photoelectron spectroscopy to the spectroscopy of unoccupied states. The experimental setup used in the present study is the same as in Refs. [3,4]. The analyzer resolution was set to about 45 meV, and electrons emitted normal to the surface (i.e., with parallel momentum $k_z = 0$) were collected. The photons came from a tunable dye laser pumped by an excimer laser and were p polarized. The distinction between unoccupied and occupied states can be made by the photon-energy dependence of their peak position [2,3].

Regular photoemission spectra of the occupied states were taken either with the unpolarized monochromatized light of a mercury lamp ($h\nu = 5.59$ eV) or with the photon energy of the dye laser tuned above $\Phi$. The light of either source was focused onto the sample from outside the ultrahigh vacuum chamber through fused-silica windows.

The experiments were performed at room temperature and at a base pressure of around $5 \times 10^{-11}$ Torr. The clean Cu(111) surface was prepared by sputtering and annealing. Alkali metals were deposited from well-outgassed commercial getter sources (SAES) mounted in a heated collimating glass tube. The pressure during evaporation did not exceed $1.5 \times 10^{-10}$ Torr. The adsorption was monitored by low-energy electron diffraction (LEED) and photoemission experiments, including work-function measurements.

We calibrate the Na coverages on Cu(111) through the work function determined by the sharp low-energy cutoff of the photoelectron spectra [2,4]. Fig. 1 shows the work function as a function of the Na coverage assumed to be proportional to the evaporation time. After the sharp initial decrease a broad minimum is observed followed by a small maximum which defines the completed monolayer (ML). This behavior is typical for alkali adsorption and agrees well with other measurements for Na on Cu(111) [17,18]. The work function changes from 4.93 eV for the clean Cu(111) surface to the minimum value of 2.18 eV at $\sim 0.4$ ML Na coverage. This change of 2.75 eV is close to the value of 2.7 eV given by Lindgren et al. [18], but significantly larger than the value of 2.3 eV reported by Dudde et al. [11]. Tang et al. [17] obtained 2.4 eV, but state that a
different analysis of their data would yield a value of 2.6 eV for the work-function change.

The maximum in the photoemission intensity of the occupied Na-induced state F near the Fermi energy $E_F$ [3,4] coincides within 10% with the monolayer coverage (see Fig. 1). The data were taken using the mercury lamp and are normalized to the background at lower kinetic energies. We also observe the best-developed ($\frac{\sqrt{3}}{2} \times \frac{\sqrt{3}}{2}$) structure in LEED around 1 ML. The first indication of an ordering in the alkali layer appears at a coverage around 0.5 ML with the development of a ring structure, which changes between 0.7 and 0.9 ML into the hexagonal ($\frac{\sqrt{3}}{2} \times \frac{\sqrt{3}}{2}$) pattern as indicated by the arrow in Fig. 1. The radius of the ring is independent of coverage at the position of the $\frac{\sqrt{3}}{2}$ spots and corresponds to the nearest-neighbor distance of a close-packed Na layer. Our LEED observations for Na/Cu(ll1) are in accordance with other reports [17,19]. From the coincidence of all these observations we conclude that the monolayer coverage is well defined and that coverages can be determined with an accuracy of 10%. Note, that our coverage calibration defines the monolayer as the close-packed alkali structure. In terms of alkali atoms per substrate atoms this would correspond to a coverage of 0.44 [17].

3. Results

Two-photon photoemission spectra for coverages up to 1 ML of Na on Cu(ll1) are shown in Fig. 2. The data are plotted relative to $E_F$ for the unoccupied intermediate states. All spectra show a structure L at low energies. The cut-off corresponds to electrons leaving the sample with zero kinetic energy. The low-energy structure L is dominated for most spectra by one-photon photoemission of thermally-excited electrons above $E_F$ [20]. The distance between the low-energy cut-off and $E_{\text{vac}}$ (tic marks in Fig. 2) is just the photon energy $h\nu$. For the two spectra at the top of Fig. 2 bichromatic two-photon photoemission [20] has been employed.

The further presentation of the experimental data will be divided according to the character of the various states which can be distinguished unambiguously: alkali-derived states, copper surface state, and image states.

3.1. Alkali states

For coverages smaller than $\sim 0.4$ ML a broad peak A is seen in Fig. 2 which is not observed on the clean surface (see also Figs. 5 and 7 of Ref. [22]). It is already visible at the smallest Na coverage of 0.03 ML and its energy shifts roughly as the work function. This state must be related to the Na atoms on the surface. The photon energy dependence reveals that it is unoccupied. The full width at half maximum of the peaks A is $410 \pm 30$ meV independent of coverage which is significantly larger than the experimental resolution ($45$ meV) and considerably larger than the intrinsic linewidth of image states [23]. We note that the lineshape of the peaks A cannot be fitted by a Lorentzian convoluted with a Gaussian rep-
Fig. 3. Energies of the observed states for Na on Cu(111) as a function of coverage. The vacuum level is indicated by the solid line. The inset shows the region of small coverages on an enlarged coverage scale. The energy of the state \( J_2 \) for the clean surface is taken from Ref. [21] (see also Ref. [2]).

representing the experimental resolution. This indicates that the peak width is not due to the finite lifetime of a single electronic state. Above 0.40 ML the states \( A \) are no longer visible. From 0.45 ML on an occupied alkali-induced state \( F \) appears below \( E_F \) which has its highest intensity around the full monolayer coverage (see Fig. 1 and for spectra Refs. [3,4]). There is no continuous transition from the unoccupied (peaks \( A \)) to the occupied (peaks \( F \)) alkali-induced state. The occupied state has a much narrower width (100 meV, see Ref. [4]) and the transition is abrupt as can be seen from the observed energies of the states plotted as a function of coverage in Fig. 3 (large open circles and squares). The experimental data in Fig. 3 for the unoccupied state \( A \) show an almost constant energy of \( \sim 0.6 \text{ eV} \) for coverages between 0.28 and 0.40 ML. We mention here, that in two-photon photoemission the identification of a peak becomes difficult for energies closer to \( E_F \) than \( \sim 0.3 \text{ eV} \). Since photon energies close to the work function are then necessary, the low-energy background increases, making the distinction between peak and background difficult. A very careful examination of many spectra taken at various photon energies gave no indication for a continuous shift of the peak \( A \) through the Fermi energy.

The energy of the occupied alkali-induced state \( F \) for coverages above 0.45 ML lies within 0.11 eV below \( E_F \) [4]. We mention here that we observe with two-photon photoemission an occupied alkali-induced state \( B \) in the same energy range for coverages between \( \sim 0.003 \) and 0.05 ML (shaded rectangle in Fig. 3, spectra not shown). There is no indication that the state \( B \) exists for higher coverages. It is not seen with one-photon photoemission which makes it unlikely that it can be related to the occupied state \( F \) seen at higher coverages. A similar state has been seen at low coverages on other surfaces with metastable He deexcitation spectroscopy [24].

### 3.2. Copper surface state

On the clean Cu(111) a surface state \( S \) exists 0.39 eV below \( E_F \) which is well known from regular photoemission experiments [23,25–27]. This surface state \( S \) shifts down in energy after the adsorption of alkali atoms (see small open squares in Fig. 3, spectra not shown). Above a coverage of 0.16 ML the state \( S \) is no longer visible. Around 0.15 ML its energy is 0.8 eV below \( E_F \) which is close to the \( L_2' \) point in the copper band structure (0.9 eV) [27,28]. This point is the lower edge of the \( L_2' - L_1 \) band gap which is responsible for the existence of the surface state and the image states. If the downward shift would continue at higher coverages the state \( S \) would be degenerate with the bulk bands of copper. It could continue to exist as a surface resonance, but it is no longer observed by our photoemission experiments.

### 3.3. Image states

As can be seen from a careful inspection of Fig. 2 there exists always a state close to the
In Fig. 4 the region close to the $E_{\text{vac}}$ is shown in more detail. The assignment of the states J as image states is demonstrated by the existence of a series of states converging towards the vacuum level. Most spectra in Fig. 4 show the second state $J_2$. The observation of the higher image states depends on the availability of occupied initial states [2,3] and, therefore, on the photon energy. The spectra in Fig. 2 were recorded with lower photon energies (compared to Fig. 4) to reduce the background at low kinetic energies. For 1.0 ML the third state $J_3$ at $-0.13$ eV appears in Fig. 4 stronger than the second state $J_2$ at $-0.27$ eV due to a resonant excitation from the occupied alkali state F close to $E_F$ [3,4]. The compilation of all data for the image states is presented in Fig. 3. The vacuum energy is plotted as a solid line since the experimental data exhibit a scatter not much larger than the width of the line (compare to Fig. 1). Figs. 3 and 4 show that a series of image states exists at all coverages and that the image states are independent of the alkali states A which are located at an energy of more than 0.9 eV below the image states $J_1$. The binding energy of the image states $J_1$ relative to $E_{\text{vac}}$ changes continuously with coverage. Around 0.2 ML a minimum of $\sim$ 0.3 eV is reached. This value is quite low compared to the clean surface (0.83 eV) or the monolayer (0.72 eV) and is the lowest value reported so far for any surface [2]. The width of the image states stays quite narrow at all coverages, but is for the Na-covered surfaces about a factor of two larger than for the clean surface. This is not too surprising if one recalls that the image state on Cu(111) has the smallest linewidth for all surfaces studied to date [2,23]. This puts the linewidth observed on the alkali-covered surfaces in the regime known for other systems.

The energies of the image states (relative to $E_F$) stay almost constant for coverages below 0.025 ML (see inset in Fig. 3). This behavior contradicts the usual picture of image states pinned to the vacuum level. The work function changes by 0.58 eV, whereas the energy of $J_1$ changes only by 0.15 eV. This implies a shift of the binding energy by 0.43 eV, a reduction by a factor of two. The obvious interpretation is that we observe the image-state electrons located on the open patches of the copper substrate. For 0.01 ML the average distance between two adsorbate atoms corresponds to $\sim$ 15 copper atoms. The corresponding area of $\sim$ 1300 Å² is sufficiently large to accommodate an image state [7]. The work function is measured as the vacuum level far away from the surface and averages, therefore, over the whole surface including all the alkali atoms. This is compatible with a linear decrease of the work function with coverage. It is interesting to note that the state $J_2$ starts to decrease in energy before the state $J_1$ (see inset in Fig. 3). Electrons in the state $J_2$ are found with maximum probability $\sim$ 10 Å outside the surface and average over larger areas than the electrons in the state $J_1 \approx 4$ Å away from the surface [6]. Therefore, the state $J_2$ is influenced by the Na atoms at lower coverages than the state $J_1$.
For coverages between 0.025 and ~0.5 ML the energy of the image state \( J_1 \) follows approximately the decrease of the work function accompanied by a continuous change of the binding energy relative to \( E_{\text{vac}} \) (see Fig. 4). This picture is consistent with the widely accepted view that the alkali atoms in an ionic bonding configuration tend to stay away from each other due to the dipole repulsion [1]. If the alkali atoms were clustering, states from the Na islands and the free Cu terraces should be observed. The intensity of these states should be changing with coverage but not the energies [6] in contrast to the observations.

For coverages above ~0.45 ML the measured work function shows a continuous increase. The energy of the image state \( J_1 \) increases also but reaches the value characteristic for the completed monolayer [4] already at a coverage of 0.8 ML (see Fig. 3). These observations are most easily explained by aggregation of Na atoms into islands. The observed image states then correspond to electrons located on these islands. Above 0.8 ML the islands have reached the density characteristic for the closed monolayer [4] and must have lateral dimensions of at least 100 Å [7]. The latter statement is in agreement with the observation of an ordered LEED pattern. We cannot decide whether the area between the islands consists of free copper areas or is covered with some Na atoms, since the observation of the corresponding image states would require photon energies above the work function.

4. Discussion

The high resolution, the sensitivity, and the low background of two-photon photoemission enabled us to identify the unoccupied alkali state \( A \) even at very low coverages. We could also clearly prove that the image states \( J \) exist independently of the alkali state \( A \) and are located more than 0.9 eV higher in energy. The alkali state undergoes an abrupt transition from unoccupied to occupied at a coverage between 0.40 and 0.45 ML which is slightly above the coverage of 0.38 ML at which the work function goes through a minimum. It is tempting to correlate this transition with the transition between an ionic and metallic state of the alkali atoms on the surface. There are no discontinuities in the work function (Figs. 1 and 3) or core-level binding energies in this coverage range [19,29]. The transition can be inferred from the Na2p core-level energy losses which change from an atomic-like value of 1.8 eV to a plasmon loss of 4.4 eV [19]. The transition is seen also in the observation of a ring structure by LEED. This indication of ordering of the alkali layer is followed above 0.8 ML by the development of a \((\frac{5}{2} \times \frac{2}{3})\) structure accompanied by a saturation in the image-state energy. These latter observations point towards a structural change of the alkali layer, i.e., the formation of islands.

Table 1

<table>
<thead>
<tr>
<th>System</th>
<th>( \Phi_0 )</th>
<th>( E_0^A )</th>
<th>( \Phi_{\text{min}} )</th>
<th>( E_{\text{min}}^A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>K/Fe(110)</td>
<td>5.12</td>
<td>2.5–3.0</td>
<td>1.8</td>
<td>1.0</td>
</tr>
<tr>
<td>K/Cu(111)</td>
<td>4.93</td>
<td>2.8</td>
<td>1.69</td>
<td>0.67</td>
</tr>
<tr>
<td>Na/Fe(110)</td>
<td>5.12</td>
<td>2.5–3.0</td>
<td>2.25</td>
<td>0.8</td>
</tr>
<tr>
<td>Na/Co(0001)</td>
<td>5.20</td>
<td>2.5–3.0</td>
<td>1.90</td>
<td>0.9</td>
</tr>
<tr>
<td>Na/Cu(111)</td>
<td>4.93</td>
<td>2.86</td>
<td>2.18</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Besides Na on Cu(111), we have studied with two-photon photoemission other alkali adsorption systems: Na on Co(0001), Na on Fe(110), K on Cu(111), and K on Fe(110). The results for all systems are very similar as reported before for the monolayer coverages [4]. Instead of reproducing the graphs corresponding to Figs. 1–4 for each system, we summarize the results in Table 1. The type of adsorbate (Na or K) determines the minimum value of the work function \( \Phi_{\text{min}} \) and the work function at the full monolayer coverage (see Ref. [4]). There is no characteristic dependence of any alkali-related values on the substrate. The minimum of the work function always occurs between 0.38 and ~0.5 ML.

Particularly surprising is the fact that the energy of the unoccupied alkali state \( A \) extrapolated to zero coverage, \( E_0^A \), and at the highest coverage, \( E_{\text{min}}^A \), where it can be observed (which is near the minimum of the work function) do not depend on the alkali species within the experi-
mental uncertainty (see Table 1). The value of 2.8 eV above $E_F$ agrees with studies for K on Ag(100) (2.4 eV) [16], for K on Ag(110) (3.0 eV) [8], for Na on Ag(110) (2.7 eV) [14], K on Al(111) (2.7 eV) [10], Na on Cu(110) (3.0 eV) [15]. For Na on Ni(111) a considerably higher value of 3.7 eV has been reported [31]. The calculations for Na and K on jellium of Lang [32] predict a $p_z$ resonance $\sim 2$ eV below the vacuum level. Similar results were obtained by other authors [33,34]. Though the theoretical values for the $p_z$ resonance agree well with our results (Table 1), we do not observe, however, the predicted $s$ resonance at 1 eV lower energy. This state has been observed by Frank et al. [10] on Al(111). We cannot decide whether this is an effect of the substrate or the experimental methods employed. It should be pointed out that the decomposition into $s$ and $p_z$ is somewhat ambiguous [32]. The width of our alkali-derived state A of 0.4 eV is considerably smaller than the calculated values of the order of 2 eV [32,35]. Other experimental studies gave only estimates for the width of $\sim 0.7$ eV independent of coverage [16].

Our results show clearly a sharp transition in the occupancy of the alkali-induced electronic states near the work-function minimum. At higher coverages the alkali atoms aggregate in islands and are in a metallic configuration. The traditional picture of the alkali adsorption [36] assumed that the adsorbate atoms would stay separated due to the Coulomb repulsion between the dipole moments of the adsorbed alkali atoms. This view gives a continuously decreasing adatom separation with coverage. Calculations for Na on Al(111) predicted recently [37] that island formation in a metallic bonding configuration is energetically more favorable above a certain coverage. Our study confirms that the island formation is related to the metallic state as reflected by the alkali-induced electronic states. The larger alkali separation at lower coverages results in a small dispersion of the alkali state. Indeed do we observe at lower coverages a considerably smaller dispersion of the unoccupied alkali-induced state A compared to the states at the monolayer coverage [3]. This observation is in agreement with the results of Jacob et al. [8].

In model calculations the alkali layer is often represented by a square potential [13,38,39]. A variation of the width [13] or the depth [38] of the potential well is used to describe the coverage dependence. Such calculations predict a continuous transition from the image state $J_1$ of the clean surface to the occupied state F just below $E_F$ at the full monolayer coverage [40]. Our observation of well separated alkali-induced states and image states at low coverages disproves this picture and makes the use of such simple model calculations questionable. A proper description of the alkali-derived states at low coverages has to take the atomic orbitals of the alkali atoms into account which cannot be replaced by a square well.

Acknowledgement

Support by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

References