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Image states and the proper work function for a single layer of Na and K on Cu(111), Co(0001), and Fe(110)

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High-resolution photoemission and two-photon photoemission spectroscopy have been used for a comparative study of the electronic structure of a single layer of Na and K on Cu(111), Co(0001), and Fe(110). All systems under investigation exhibit an occupied alkali-induced state near the Fermi energy as well as a series of unoccupied states converging toward the vacuum energy, which are identified as image-potential states. For Na (K) on any of the substrates we find the lowest image state to be located at an energy of 2.04±0.03 eV (1.62±0.03 eV) above the Fermi level. From this and from the convergence behavior of the image-state series we conclude that the work function for the perfect single alkali layer is independent of the substrates investigated, and is characteristic for the alkali metal. This is in contrast to results of conventional work-function measurements, but in accordance with the theoretical expectation.

I. INTRODUCTION

The electronic structure of one monolayer (ML) of an alkali metal adsorbed on metal surfaces has been investigated intensively during the last years.[1] Direct information on the occupied electronic states comes from ordinary, single-photon photoemission (1PPE) experiments,[2-6] whereas the unoccupied states are studied with inverse photoemission (IPE) (Refs. 5 and 7–13) and two-photon photoemission (2PPE).[14] For a single layer of an alkali metal adsorbed on a metal surface, in most cases an alkali-induced occupied state is seen near the Fermi energy E_F.[2-6,14] IPE measurements of the unoccupied states for these systems generally show a structure near the vacuum energy E_{vac}.[7-9,11-13]

In the literature, the observed level structure is compared to theory using two different approaches:

(i) In Refs. 11 and 15–18, the experimental results are compared to the eigenvalues of Schrödinger's equation for a simple one-dimensional potential well. This model is—apart from an additional square-well potential describing the alkali-metal layer—identical to that originally proposed by Smith[19] for the description of surface states on clean metal surfaces. Lindgren and Walldén, who did the first calculations within this one-dimensional model for one monolayer Na on Cu(111), showed that, in addition to an occupied alkali-induced state near E_F, a series of unoccupied states converging toward E_{vac} should exist.[15-17] These states are similar to the image states on clean metal surfaces,[19,20] which have their origin in the long-range $1/z$ image potential. A fundamental characteristic of these states is that they are energetically "pinned" to the vacuum level,[19-21] a fact which turns out to be very important for the message of this paper.

(ii) Alternatively, as in Refs. 5 and 7–9, a self-consistent calculation of the band structure of an isolated monolayer[22] of an alkali metal is related to the experimental results. The authors interpret the structure near E_{vac} observed in IPE to be an alkali-*d*-derived state.[5,7-9] Recently the band structure of a hexagonal alkali-metal layer on jellium was calculated,[23] but failed to describe the experimentally observed unoccupied state for $(\sqrt{3}\times\sqrt{3})R\,30°$ Na (K)/Al(111) (Refs. 4 and 8) (see Ref. 24). Both these self-consistent calculations go beyond the simplified one-dimensional model mentioned above in that they account for the atomic structure of the adsorbates. However, they are performed within the local-density approximation (LDA) and therefore cannot describe the image potential.[25] Consequently, no (infinite) series of unoccupied states can appear in this type of calculation, in contrast to the 2PPE results for Na/Cu(111).[14] The new calculation for Na and K on jellium in Ref. 23 shows clearly that the interpretation of the unoccupied structure near E_{vac} as an alkali-*d*-derived state[8] is not correct: This feature does not appear in the calculations, whereas an occupied alkali-induced state seen in 1PPE (Ref. 4) can be reproduced. In a further theoretical attempt to describe 1-ML Na (and Cs) on Al(111), the existence of an imagelike series of states near E_{vac} is shown.[18] The authors use a jellium description of both the semi-infinite substrate and the alkali-metal overlayer. In front of the surface, the otherwise self-consistent potential is modified to yield the image potential. This modification gives rise to a series of (image) states converging toward E_{vac}, in contrast to the calculations of Ref. 23.

The scope of the paper is the following: Recently we obtained in 2PPE experiments[21] direct proof that there is indeed a series of unoccupied states for 1-ML Na/Cu(111).[14] Due to the high resolution of 2PPE we were able to resolve three members of this image-state series. We could show that no quantitative description of the measured binding energies within the model proposed in Ref. 16 was possible. In the present work, we use 2PPE for studying 1-ML Na and K on different substrates in order to reveal the systematics of this class of systems. In particular, it seems important to test if the

TABLE I. Energies of band edges in eV relative to E_F at $k_{\|}=0$ [from Refs. 27 (Cu) and 28 (Co, Fe)]. They are important for the linewidths of the adsorbate-induced states. For the ferromagnetic materials Co and Fe, the values are given for each spin orientation.

	Cu(111)	Co(0001)		Fe(110)	
		↑	↓	↑	↓
p band	−0.85	−1.26	−1.04	0.40	0.56
s band	4.10	6.03	6.77	7.25	8.51
d band	−2.25	−0.35	0.80	0.38	2.52

deviations from the ordinary image-series behavior observed for Na/Cu(111) (Ref. 14) also show up in other alkali-metal adsorption systems. The results should help to understand these deviations and stimulate further theoretical attempts.

Na and K were chosen since theoretical calculations predict significant influence of the d states of K whereas no such effects are expected for Na.[23] Up to now no experimental confirmation for this prediction has been found.[10] For the substrates we chose Cu(111), Co(0001), and Fe(110), which all are close-packed surfaces. Thus there is hope that the adsorbed alkali metal will form a close-packed layer as well.[26] Furthermore, the geometry of these surfaces is relatively similar. However, since their band structure is quite different, we expect information about its influence on the electronic structure of the adsorbate system: There are differences in the location of the sp gap relative to E_F and even much stronger differences in the location of the substrate d bands, as can be seen from Table I. In contrast to copper, where the highest d bands are located around 2 eV below E_F, on cobalt and iron one finds unoccupied d bands which may influence the level structure of the adsorption system.

II. EXPERIMENT

Two-photon photoemission (2PPE) spectroscopy is the method with the best energy resolution available to date for the investigation of unoccupied states.[21,29,30] Pulsed laser light with a photon energy below the work function Φ of the sample is used to excite electrons from occupied states into unoccupied states below E_{vac}. By absorbing a second photon, these excited electrons may be lifted above E_{vac}, and can then be analyzed like ordinary photoelectrons. In this way it is possible to transfer the good energy and momentum resolution of (single-photon) photoemission (1PPE) to the spectroscopy of unoccupied states. The experimental setup used in the present study is the same as in Ref. 14. The analyzer resolution was set to about 45 meV, and only electrons emitted with zero momentum parallel to the surface (i.e., $k_{\|}=0$) were collected. A tunable dye laser pumped by an excimer laser is used as the light source for 2PPE. In 2PPE we used p-polarized light for both excitation steps. 1PPE was produced either with the unpolarized monochromatized light of a mercury lamp or, alternatively, with the frequency-doubled output of the dye laser tuned to $2h\nu > \Phi$. The light of both sources was focused onto the sample from outside the UHV chamber through a fused-silica window. The experiments were performed at room temperature and at a base pressure of around 5×10^{-11} Torr. K and Na were deposited onto the sample from well-outgassed commercial getter sources mounted in a heated collimating glass tube.[31] The pressure during evaporation did not exceed 1.5×10^{-10} Torr. The adsorption was monitored by low-energy electron diffraction (LEED), 1PPE, and 2PPE, including work-function measurements.

The work function Φ was determined by the sharp low-energy cutoff of the 1PPE and 2PPE spectra.[30,32] In this way it is possible to determine the binding energies of the electronic states and Φ simultaneously. The previous 2PPE investigations of image states on clean metal surfaces performed in our group[21,29,30] have shown that Φ obtained in this way gives reliable values to within ±0.03 eV or better. It is important for the systems of this study, however, that the work function experienced by the image states can be determined in yet another way, which is independent of the low-energy cutoff in photoemission: The energetic position of the third image state relative to E_F must obviously form a strict lower limit of the work function. Since the binding energy of the third image state in the simple one-dimensional theory[19] varies only between 0.07 and 0.10 eV, one can estimate the work function in this way to within 0.05 eV. On clean metal surfaces, we have never found a discrepancy to the value obtained from the low-energy cutoff in 1PPE and 2PPE. However, this is no longer true for the adsorbate systems studied in this work, as we will show below. Therefore, it should be understood that the values for Φ given in this work are obtained by the energy-cutoff method, if not stated otherwise.

For Na, the completion of the first monolayers on all substrates is defined at the coverage where the work function vs coverage curve exhibits its weak maximum after passing through the well-pronounced minimum typical for alkali-metal adsorption.[1] The respective work function Φ for a single Na layer on the three substrates as observed in our experiments are listed in Table II. Additional experimental observations are used to confirm the determination of the monolayer coverage:

(i) The Na coverage as estimated from the evaporation time that is necessary to produce the maximum in Φ coincides to within 10% with that of the highest 1PPE intensity of the occupied Na-induced state near E_F. This state, which will be discussed in more detail below, was observed for all systems investigated and is shown in Fig. 1.

(ii) In addition, we observed for Na/Cu(111) and Na/Co(0001) the best-developed $(\frac{3}{2}\times\frac{3}{2})$ structure in LEED around 1-ML coverage.

From the coincidence of all these observations, we conclude that the monolayer coverage is reproducible and can be determined to within 10%.

Our LEED observations for Na/Cu(111) are in accordance with recent experiments,[33,34] but also a 2×2 structure is reported.[12,16] As the nearest-neighbor distance for the atoms in the close-packed surfaces of Cu(111) and Co(0001) is almost identical (2.56 vs 2.51 Å) and also about equal to $\frac{2}{3}$ of the nearest-neighbor spacing for bulk

TABLE II. Work function Φ, 2PPE energies of image states J_1, J_2, and J_3, and the full width at half maximum of J_1 measured for one monolayer alkali metal on metal substrates (in eV). The limits of error for the energies on Co(0001) are ± 0.04 eV, and ± 0.03 eV otherwise. The error limit for the widths is ± 0.02 eV. Note the constant value for the energetic positions relative to E_F for Na or K on any substrate, in spite of the different values of Φ. This indicates that the image-state series is fixed to a vacuum energy defined by a different, "proper" work function Φ_{ML}, which is independent of the substrate. An estimate for Φ_{ML}, obtained by fitting a simple quantum defect model to the image states (see text), is given in the last column. The calculated energy positions from the best fit are also included for both adsorbates.

Adsorbate	Substrate	Φ	$E-E_F$ J_1	 J_2	 J_3	FWHM J_1	$\Longrightarrow \Phi_{\mathrm{ML}}$
K	Fe(110)	2.32	1.62	2.05	2.18	0.28	
	Cu(111)	2.26	1.62	2.07	2.21	0.14	2.27
	(calc.)	2.27	1.62	2.08	2.18		
Na	Cu(111)	2.77	2.05	2.50	2.64	0.14	
	Co(0001)	2.58	2.02	2.47	2.57	0.15	2.69
	Fe(110)	2.69	2.05	2.47		0.17	
	(calc.)	2.69	2.04	2.50	2.60		

Na (3.66 Å), the ($\frac{3}{2}\times\frac{3}{2}$) LEED structure is consistent with a close-packed hexagonal Na overlayer at 1-ML coverage on Cu(111) and Co(0001). The result for Ni(111) with a nearest-neighbor distance between Co and Cu, where the Na layer also produces a ($\frac{3}{2}\times\frac{3}{2}$) structure,[35] provides further support.

For K, the situation is slightly different, since at room temperature the adsorption of K saturates at around 1-ML coverage. As a result, we observed a saturation of the work function for K on Cu(111) and Fe(110). In a way similar to Na we defined the completion of the first K layer to be at the coverage where the maximum 1PPE intensity of the occupied K-induced state near E_F (see Fig. 1) is observed. This maximum occurred close to the saturation coverage, and the respective value for Φ is also given in Table II. For K/Cu(111), we observed a (2×2) LEED pattern at 1-ML coverage in agreement with a recent publication.[9]

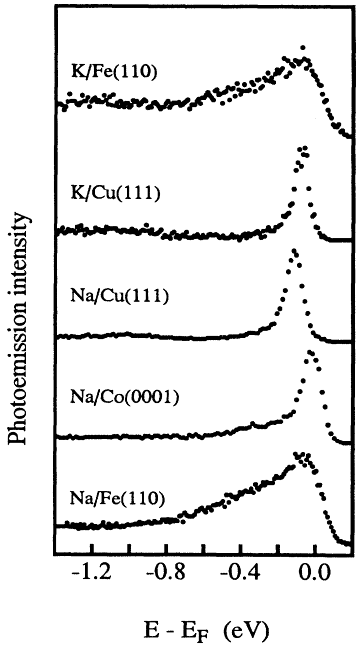

FIG. 1. 1PPE spectra in normal emission for a single layer of Na and K on different substrates, taken with photon energies between 4.2 and 5.6 eV. On each system an occupied alkali-induced state close to E_F is found.

III. RESULTS

Typical 1PPE spectra recorded at low photon energies are shown in Fig. 1. For all systems, we observed an occupied alkali-induced state near E_F with maximum intensity at 1-ML coverage (see Sec. II). For a discussion of possible interpretations of this state, we refer to Refs. 3 and 15–17. It must be emphasized that we chose low photon energies (between 4.2 and 5.6 eV in Fig. 1) because the photoexcitation cross section of the alkali-induced state increases strongly with decreasing $h\nu$. For instance, we found the signal for the K-induced state on Cu(111), which is the dominant feature in spectra like those of Fig. 1, to be down to the detection limit when using $h\nu = 16.85$ eV (Ne I). A similar effect was found for the surface states on clean metal surfaces.[36] This photon-energy dependence may also explain why a 1PPE investigation of K on Fe(110) with $h\nu \geq 16.85$ eV (Ref. 26) did not observe an alkali-induced feature at E_F.

For K or Na on Cu(111), and for Na on Co(0001), the alkali-induced state in Fig. 1 is quite narrow, exhibiting a full width at half maximum (FWHM) of about 0.1 eV. For K or Na on Fe(110), however, it is significantly broader (FWHM≈0.4 eV). This can be easily explained by the band structure of the substrate: For Co(0001) and Cu(111) the occupied alkali-induced state is located in the *sp* gap at $k_{\parallel}=0$, whereas on Fe(110) it is degenerate with *p* bands of the substrate (Table I) and thus broadened to a surface resonance. Since the state for Na/Co(0001) remains narrow, the *d* bands do not seem to contribute much to the width. Binding energies E_b will be given only for states whose width is smaller than E_b. We find $E_b \approx 0.11$ eV (relative to E_F) and ≈ 0.06 eV for Na and K on Cu(111), and an even smaller value for Na on Co(0001).

Figure 2 shows 2PPE spectra of the unoccupied states for 1-ML coverage of K on Fe(110) and Cu(111) and for Na on Cu(111), Co(0001), and Fe(110). The energy scale is referred to E_F. The solid lines through the data points are best fits of a model function to these data. The model function is a sum of up to three Lorentzians, one for each image state, which are convoluted with a Gaussian approximating the analyzer function. This fitting procedure has been used for the determination of the intrinsic linewidth of image-potential states on clean metal surfaces[29,30,37] and is described there. The spectra show three unoccupied states $J_1, \ldots, J_3$, apart from Na/Fe(110), where emission out of two unoccupied states can be seen. These states must be assigned to the lowest members of the alkali-induced image-state series.[14] For the upper three spectra in Fig. 2, the photon energy was chosen to be approximately the energy difference between the occupied alkali-induced state and the third image state. Thus the very efficient resonant excitation between these states gives rise to the strong 2PPE signal of the third state. For Na/Cu(111), this resonance is described in detail in Ref. 14. The photon energy used for Na/Co(0001) was chosen to be just below the resonance—and therefore the third states does not appear stronger than the second. For Na/Fe(110), $h\nu$ was set even lower,[38] and is only sufficient to excite the second state. Under these conditions, the higher states cannot be populated with electrons and do not appear in the spectrum.

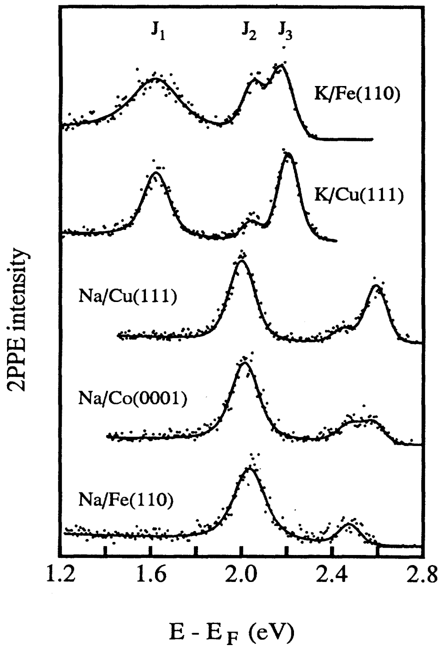

FIG. 2. 2PPE spectra in normal emission for a single layer of Na and K on different substrates. On each system a series of unoccupied states $J_1, \ldots, J_3$ can be seen. The photon energies for the different spectra are $h\nu = 2.214$ eV for K/Fe(110), 2.275 eV for K/Cu(111), 2.640 eV for Na/Cu(111), 2.583 eV for Na/Co(0001), and 2.480 eV for Na/Fe(110). For most systems, $h\nu$ was chosen for resonant and therefore efficient excitation of the third state. For Na/Co(0001), $h\nu$ is below that resonance, and for Na/Fe(110) it is only sufficient to excite the second state.

Apart from these differences, which are only an effect of the different excitation energies, the spectra for the adsorbate Na look almost identical. Since there are many more similarities to be seen by comparing all the spectra, we summarize the important information about the unoccupied states at 1-ML alkali coverage as follows:

(i) The *energetic positions* of the image states for the same adsorbate are almost equal if referred to E_F. This is obvious from Fig. 2, and the numerical values can be found in Table II. For 1-ML Na (K) on any substrate, the first image state J_1 is located at $E_1 - E_F = 2.04 \pm 0.03$ eV (1.62 ± 0.03 eV). In contrast to 1-ML K on Fe(110) and Cu(111), where the two work functions agree within the error limits, the work functions in the case of 1-ML Na differ by almost 0.2 eV for the different substrates (see Table II). This leads to significant variations in the binding energies relative to E_{vac}. Thus we find that the energies appear to be fixed to E_F rather than fixed to E_{vac}, a result which at first sight is completely incompatible with the nature of image states.

(ii) By comparing spectra for different adsorbates on the same substrate, we note that K and Na on Cu(111) lead to almost identical series of states which are only *shifted in energy.* To a first approximation this energy difference (0.43 eV) equals the difference in Φ (0.51 eV). The same shift can also be seen for Na and K on Fe(110), where the difference in Φ is 0.37 eV. This is more like the behavior expected for image states, which was not found when comparing systems with the same adsorbate on different substrates [see (i)]. We would also like to point out that although some theoretical work expects an effect of the potassium *d* bands[22,23]—which should not be present for sodium—no indications for this appear in the spectra.

(iii) The *energy separations* between consecutive image states are found to be equal for all adsorption systems investigated, regardless of substrate or adsorbate: The energy separation between J_1 and J_2 is 0.44 ± 0.02 eV, the one between J_2 and J_3 is 0.13 ± 0.02 eV. Note that the limits of error are relatively small since the energy difference does not contain the uncertainty in the determination of E_F.

(iv) The *widths* of the image states are also very similar. The values for J_1 are listed in Table II. The only value deviating significantly from the generic value 0.15 eV (FWHM) is the width of the lowest state for K/Fe(110), which is about twice as large as that of all other states.

IV. DISCUSSION

First we are going to discuss the widths of the image states. Then the longer discussion of the various aspects of the binding energies will follow.

As was mentioned above in (iv) of Sec. III, the only striking difference between the spectra—apart from the energy shift (ii)—concerns the width of the lowest image state (see Table II). The significantly larger width for

K/Fe(110) cannot be just an effect of the adsorbate, as can be seen for K on Cu(111). On the other hand, the width for Na/Fe(110) is also slightly increased, thus indicating an effect of the substrate. As we have shown previously,[29,30,37] the density of unoccupied states determines the intrinsic widths of image potential states. So the reason for the extra broadening for Na and K on Fe(110) may be the empty p bands near E_F on Fe(110) which provide decay channels for the electrons in the image states, and which are not present on Cu(111) and Co(0001). In addition, the occupied alkali-induced states should also give rise to a further broadening: Since they lie close to E_F, they are partially unfilled at room temperature even at $k_{\parallel}=0$. This effect should be more pronounced for Na or K on Fe(110) and Na on Co(0001), as the binding energy of the occupied state for these systems is particularly small (see Fig. 1). The fact that the lowest state for K and Na on Fe(110) is energetically degenerate with the empty d bands of Fe, which extend up to around 2.5 eV above E_F (Table I), may cause a further contribution. We point out, however, that all these effects should affect the width for K/Fe(110) similarly to that for Na/Fe(110), so that there is apparently no simple explanation for (iv).

The energetic positions of the image states, as observed in our experiments and as summarized in (i)–(iii) of the preceding section, give rise to several problems. In short, a behavior like this seems to contradict the nature of image states, which must be fixed energetically to $E_{\rm vac}$. A particularly illuminating example is the binding energy for J_3 on Na/Co(0001), which would be 0.01 eV relative to $E_{\rm vac}$ (see Table II and also Fig. 3). Keeping in mind paragraph (iii), which says that the states $J_1, \ldots, J_3$ for Na/Co(0001) exhibit the same convergence behavior as for the other adsorbate systems, it seems indeed very unlikely that just for this system the whole rest of the series should then be crammed into the small energy interval of 0.01 eV.

In the following, we propose an explanation for the unusual behavior of the adsorbate-induced image series, and discuss its various implications. The basic idea is that all these problems could be resolved if the image states converge to a vacuum energy that is *not* defined by Φ measured at the low-energy cutoff in 1PPE and 2PPE, but is defined by a different, *"proper" work function*, which is characteristic for the perfect monolayer, and which we will be calling $\Phi_{\rm ML}$. This explanation retains the imagelike character of the series of states observed in 2PPE. Apart from its appealing simplicity it is also consistent with the theoretical results quoted in Sec. I, which rule out an interpretation in terms of alkali d bands. On the other hand, the proposed explanation rests on two important assumptions which will be discussed now:

(i) First of all, the preparation of the "monolayer" coverage as outlined in Sec. II may in general *not* result in a surface covered homogeneously with 1 ML of the alkali metal. Instead, we assume that even though the alkali metals exhibit a layer-by-layer growth mode the formation of the second layer may start on small areas before the first is fully completed. For Na/Cu(111), this has recently indeed be confirmed experimentally.[33] Small amounts of contaminants during evaporation may also contribute to defects which keep the adsorption system from forming a perfect monolayer. The fact that the linewidths observed for the alkali-covered surfaces (Table II) are all larger than for the clean surfaces[37,41] may also indicate the existence of a certain amount of imperfection[37] on the adsorbate-covered surfaces. Thus the experiment is performed on an imperfect surface that may be close to a homogeneous one, but will contain inhomogeneous patches in a way that is difficult to control experimentally. This has consequences for the work function: Φ measured in the "usual" way at the low-energy cutoff in 1PPE and 2PPE is then an average over different areas of the surface and will therefore in general differ from the work function of the perfect monolayer, $\Phi_{\rm ML}$.

(ii) Moreover, the explanation requires the assumption that the observed image states exist only in the homogeneous regions of the surface with the well-defined proper work function of the perfect monolayer, $\Phi_{\rm ML}$. For this assumption we have support from recent 2PPE experiments.

(a) By quantitatively investigating the additional broadening of image states upon disordered adsorption of oxygen ($\ll 1$ ML), we were led to assume that the adsorbed oxygen atoms act as scattering centers which confine the image state laterally.[30,37] This means that the image states exist predominantly on the relatively undis-

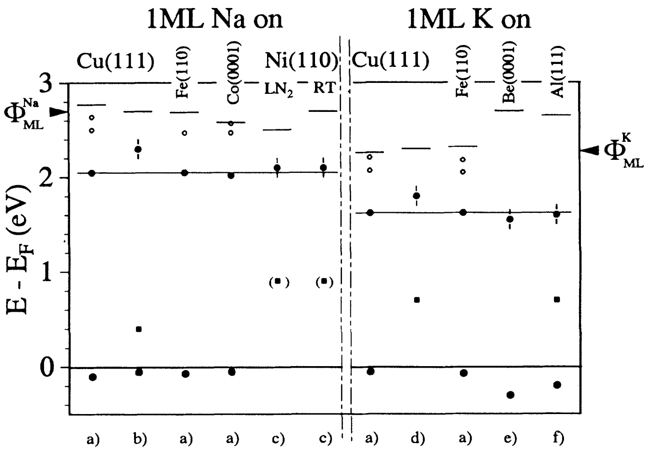

FIG. 3. Compilation of alkali-induced electronic states as found in 2PPE (a), IPE [(b)–(f)], and 1PPE for a single layer of Na (left-hand side) and K (right-hand side) on different substrates. Energies are referred to E_F. The short bar in every column denotes the "usual" work function. The lowest members of the alkali-induced image-state series (small full circles) for any substrate can be well described by the binding energy found in 2PPE of 2.04 eV for Na and 1.62 eV for K indicated by the respective line (see text). The proper work functions $\Phi_{\rm ML}$ for 1-ML alkali metal as derived from the convergence of the image-state series (see Table II) are marked by arrows. (a) This work and Ref. 14; (b) Ref. 12, see also Ref. 39; (c) Ref. 11. LN$_2$, liquid-nitrogen temperature; RT, room temperature; the states in parentheses vanish at coverages close below the completion of the first layer. (d) Reference 9, see also Ref. 39; (e) Ref. 13; (f) Refs. 5 and 40.

turbed areas of the surface.

(b) The same conclusion can be drawn more directly from measurements of the binding energy of image states on Cu(111) under adsorption of K and Na at very low coverages.[42] In this case the image-state series of the clean Cu(111) surface remains almost fixed in energy relative to E_F when adsorbing low coverages of an alkali metal, even though the adsorbate-induced work function decrease in this coverage regime amounts to more than 0.5 eV.

(c) For the adsorption system Ag on Pd(111) at coverages below 1 ML,[43] *two* series of image states can be detected simultaneously: The upper one converges to $E_{\text{vac}}^{\text{Pd}}$, the other one to an E_{vac} which is about 0.7 eV lower and corresponds to the work function of Ag islands of thickness 1 ML. (This work function is termed the "local" work function[44] in the context of Ref. 43, but has the same characteristics as the "proper" work function brought up in the present work.) All the experimental results can most easily be understood by assuming that our experiment detects only image states on areas that are either clean and still unaffected by the adsorption, or covered homogeneously by the adsorbate metal.

(d) Similar support comes from our measurements for the system Na on Cu(111) in the coverage range 0.8 ML to slightly above one nominal ML. Within this range the image-state series is located at constant energies relative to E_F, whereas Φ is still varying by about 0.3 eV. This indicates that from 0.8 ML on, sufficiently large areas of 1-ML Na exist which define the reference level $\Phi_{\text{ML}}^{\text{Na}}$ for the image states independently of what happens on the other areas.

Within this explanation scheme the problems (i) and (ii) of Sec. III can easily be resolved: The energy which the image-state series converges to is nothing but the proper work function Φ_{ML} of the perfect alkali-metal monolayer. In other words, investigating the image-state series of alkali-metal adsorption systems close to 1-ML coverage is a means of indirectly measuring Φ_{ML} of the respective alkali metal. The constant energy of J_1 referred to E_F that seemed to contradict the nature of image states as being fixed to E_{vac} now just means that Φ_{ML} is specific for the adsorbate and independent of the substrate—and no contradiction remains. [For this conclusion we also made use of result (iii) of Sec. III, stating the material-independent convergence behavior of the image-state series.]

We now try to determine from our data the specific proper work functions for 1-ML K and Na on any substrate investigated. In Sec. II we already pointed out that the work function experienced by the image states can be estimated through the binding energy of the third image state. Here we want to quantify this somewhat by evaluating the convergence of the image-state series. If we assume a simple convergence behavior of the series by introducing a "quantum defect" a (Refs. 45, 19, and 30) in the hydrogeniclike formula for image-state binding energies (referred to the proper E_{vac}), we have

$$E_b(n)=\frac{0.85\text{ eV}}{(n+a)^2};\quad n=1,2,\ldots\,. \tag{1}$$

From the constant energy difference between the first two states, one could derive the binding energy of the first state, and combining this with the energetic position of the first state relative to E_F would yield an estimate for Φ_{ML}. We note, however, that the simple quantum-defect scheme, which works very well for clean surfaces, is not as good on these alkali-covered surfaces, since it results in an energy difference of 0.10 eV between the second and third state instead of the experimental value 0.13 eV. In order to include this experimental information without bias, we performed a weighted least-squares fit of a function like Eq. (1) to all the energetic positions of image states from Table II. Result (iii) from Sec. III is taken into account by assuming that a single quantum defect a describes all image-state series measured. In this way we arrive at the values for Φ_{ML} given in Table II. Among others, the problem of the extremely low binding energy relative to the "usual" E_{vac} of 0.01 eV for J_3 on Na/Co(0001) is obviously removed now.

Comparing our data to IPE results for 1-ML Na or K reveals a very interesting connection. Figure 3 shows a collection of experimental results for 1-ML Na (left-hand side) and K (right-hand side) on different substrates. Occupied states from 1PPE experiments—where reported—as well as unoccupied states from 2PPE and IPE are included. The energy scale is referred to E_F and the "usual" work function Φ is marked by a horizontal bar in each column. All systems where 1PPE measurements were performed showed an alkali-induced occupied state near E_F. An additional unoccupied state close to E_F is observed in IPE for K/Al(111) (Ref. 5) and K and Na on Cu(111),[9,12] and is denoted by a small square. This state was observed in our measurements only for coverages below half a monolayer. It is not of importance for the following, and we will discuss its behavior in a subsequent paper.[42]

The unoccupied states found in 2PPE can be assigned to the alkali-induced image-state series. Their lowest members are denoted in Fig. 3 by full circles. The corresponding unoccupied states found in IPE are also marked by full circles, since in analogy to the 2PPE results, and with the theoretical remarks from Sec. I in mind, they are also interpreted as the first member of the respective alkali-induced image-state series. [IPE work on K/Cu(111) assigned the respective state to a mainly alkali-*d*-derived state,[9] but this is not confirmed in the present work and Ref. 12.] The error bars for these states in the 2PPE experiment are only slightly larger than the diameter of the symbol. For the IPE measurements no error limits were explicitly given, and we assume a value of ±0.10 eV. The higher image states, which can be resolved in 2PPE only, are shown as open circles. From the convergence behavior we estimated the adsorbate-specific Φ_{ML} for Na and K, which are marked in Fig. 3 by arrows. The important point now is that for both alkali metals the energetic positions found in IPE for the lowest image state are well described by the value 2.04 eV (Na) and 1.62 eV (K) from 2PPE (see Ref. 39). These values are marked by the respective long horizontal lines. Thus the IPE data support the 2PPE result that the energy of J_1 is fixed relative to E_F by the respective alkali metal and is independent of both substrate and Φ.

From this we are led to the conjecture that also the whole series J_n would show the same convergence behavior and thus the same Φ_{ML} as found in 2PPE. Of course, this is not a compelling conclusion as in the case of our 2PPE data, since the $n=2$ state could not be detected in the IPE investigations. We also note that for 1-ML alkali metal adsorbed on Be(0001), Al(111), and Ni(110), the image states may have a slightly different binding energy relative to the proper E_{vac}, since they do not fall inside a band gap of the substrate—unlike the situation for the systems of this work. But even bearing these restrictions in mind, the fact that the IPE results are compatible with the constant position of J_1 found in our work is most easily understood by assuming a constant work function Φ_{ML} independent of the substrate. Thus the result that 1-ML alkali metal yields a work function independent of the substrate, which is deduced from our 2PPE data, seems also plausible for the systems investigated by IPE.

Though this result appears very surprising at first sight, theoretical work by Lang[46] showed 20 years ago that this should indeed be the case (for jellium), as long as the interatomic distance of the alkali layer, determining its effective electron density, is kept constant. This seems to be a good approximation at least for the systems of this work, where the alkali metals tend to form a close-packed structure with a nearest-neighbor distance almost equal to that of the bulk alkali metal.[26] Moreover, even though the absolute values for the work functions in Ref. 46 are not quite correct, these calculations predict a work-function decrease of about 0.4 eV when going from the adsorbate Na to K. A more recent calculation for free monolayers of Na and K (Ref. 47) yields a difference in the work function of 0.49 eV. In our work we found the corresponding difference of the two proper work functions to be 0.42 eV. An additional result of Ref. 46 is that 1-ML alkali metal adsorbed on a metal should exhibit the same work function as the respective bulk alkali metal. The experimental reference values from Ref. 48 are 2.75 eV for Na and 2.30 eV for K, and compare very favorably to our determination of $\Phi_{\mathrm{ML}}^{\mathrm{Na}}$ and $\Phi_{\mathrm{ML}}^{\mathrm{K}}$ (see Table II). Without being in the position to offer an explanation, we note also that the values of Φ given in the IPE papers for the adsorbate systems of Fig. 3 in general show a larger variation *inter se* and about Φ_{ML} than the values obtained in the present work.

V. CONCLUSION AND OUTLOOK

What we have not yet explained is that the binding energy of J_1 is 0.65 eV for all systems, and that, therefore, the series of image states are all characterized by the same energy separations of consecutive states. There is clearly the need for more refined theoretical calculations. In order to find an indication where this similarity might come from, we nevertheless treated the adsorption systems within a one-dimensional model similar to those used in Refs. 15 and 11. We used the same model successfully for describing the adsorption system Ag/Pd(111).[43] The substrates are dealt with in the two-band model,[19] utilizing the band-gap parameters from Table I, and a WKB-type phase shift for the image potential[45] is used for the wave-function matching at the metal-vacuum interface. The idea was to detect systematic deviations between this simple model and the experimental results. For the $n=1$ image state on clean Fe(110) and Co(0001), we obtain in both cases an experimental binding energy of 0.73 eV,[41] whereas our model calculations yield 0.57 and 0.64 eV. The experimental value 0.83 eV for clean Cu(111), however, is exactly reproduced by our calculation. Thus we performed the same type of calculation for Na and K on Cu(111) first, using a square-well potential to model the alkali-metal layer, and adjusted the depth and width of the potential well in order to obtain the correct binding energies of the occupied alkali-induced state and the first image state for both systems. The proper work functions of Table II were used. By transferring these potential-well parameters—which are for Na roughly equal to those obtained in Ref. 16 and appropriately scaled for K—to the other adsorbate systems, we obtained binding energies for the $n=1$ state of 0.54 and 0.61 eV for Na on Fe(110) and Co(0001); the respective values for K are larger by 0.01 eV. The variation in binding energy is mainly due to the fact that the image states occur at different energies relative to the *sp* band gap of the substrate. To remove the discrepancies to the experimental values would require an unrealistically large adjustment of the parameters of the potential well or of the work function. We find that the deviation from the experimental value 0.65 eV is about 0.1 eV for Fe(110) and thus again larger than on Co(0001) by about 0.04 eV. This is the same trend as for the clean surfaces. We note that the discrepancies between the simple theory and the experimental binding energies are smaller for the alkali-covered surfaces than for the clean surfaces, which coincides with the fact that the image states for the former systems are substantially closer to E_F than those for the latter. These observations indicate that the discrepancies observed for the *d*-band metals have a common origin for both clean and alkali-covered metal surfaces.

In summary, the main subject of this paper was to investigate the unoccupied electronic structure of a single layer of K and Na on Cu(111), Co(0001), and Fe(110). The high resolution of 2PPE allowed us to observe a wealth of fine structure. The extreme similarity of the image-stage series for all substrates and adsorbates under investigation, regardless of the measured work function, led us to the conclusion that it is not the "usual" vacuum energy defined by Φ to which the image states converge. Instead, the image states converge to an energy defined by a proper work function Φ_{ML}, which for the perfect single alkali layer is independent of the substrate and characteristic of the alkali metal only. This concept quite naturally explains the otherwise striking discrepancies from the ordinary image-state behavior. On the other hand, it is itself supported by 2PPE experiments on other adsorbate systems as well as being consistent with jellium calculations. It is also able to describe the more coarse IPE results on additional alkali-adsorption systems. In our previous paper on 1-ML Na/Cu(111),[14] the observed deviations from the behavior expected of a simple one-dimensional model raised the conjecture that a proper description of occupied and unoccupied states for an alkali-metal monolayer on a metal must include the atomic structure of the adsorbate. By comparing all the systems in this study, however, it has now become clear that introducing the concept of a proper work function defining the reference level for image states is the more appropriate way of understanding these deviations.

Obviously it would be very rewarding also to investigate the coverage dependence of the spectral features discussed in this work. We will discuss our results on this topic in a forthcoming paper.[42]

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