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# Coverage-dependent shifts of *s* and *p* resonances of alkali metals chemisorbed on Al(111)

K.-H. Frank and H.-J. Sagner
*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-1000 Berlin 33, Germany*

D. Heskett
*University of Rhode Island, Kingston, Rhode Island 02881*
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The electronic structure of alkali-metal adatoms on Al(111) has been studied experimentally by inverse photoemission and ultraviolet photoemission spectroscopy. The unoccupied *np* resonances of Cs, K, and Na shift towards the Fermi level $E_F$ with increasing alkali coverage $\Theta$ from zero to monolayer coverage. Simultaneously, the *ns* resonances observed by inverse photoemission shift downwards and cross $E_F$. For K/Al(111) the 4*s* resonance emerges in the photoemission spectrum below the Fermi edge at $\Theta_K \approx 0.06$ monolayers (ML). Extrapolation of our results to the zero-coverage limit yields a position of the 4*p* level at $2.7\pm0.1$ eV above $E_F$ for a single K atom on Al(111) and the center of gravity of the 4*s* resonance (full width at half maximum equals 0.6 eV) at $0.7\pm0.2$ eV above $E_F$. Therefore, a single K adatom is mainly ionic. At $\Theta \geq 0.10$ ML the alkali-metal interaction induces the formation of two-dimensional bands and the overlayer becomes metallic. Our experimental results clearly corroborate the Gurney-type theoretical models of alkali-metal chemisorption.

Alkali-metal chemisorption has been an area of basic research as well as being important in technological applications for many years.[1] In the past decade the interest in alkali-metal adsorption has revived. The significant promoting action of alkali metals in heterogeneous catalysis[2] has stimulated a number of experimental and theoretical investigations of the coadsorption of alkali metals with atoms and molecules on surfaces.[3,4] In addition, an experimental and theoretical reinvestigation of the alkali-metal chemisorption problem itself can be observed in the literature of the past few years. One viewpoint of alkali-metal adsorption is based on a model presented by Gurney[5] in 1935 which has been refined by Lang and Williams[6] and Muscat and Newns.[7] According to this picture in the single-atom coverage limit the valence *ns* and *np* levels of the adsorbed alkali-metal atom are broadened into resonances due to the interaction with the substrate. The center of gravity of the *ns* resonance is located above the Fermi level, yet its tail is occupied, which is in agreement with recent measurements using metastable deexcitation spectroscopy.[8] Therefore, the alkali-metal atom is not completely ionized for the isolated adatom. The dipole moments of the partly ionized alkali-metal atoms and the corresponding image charge created at the metallic surface reduce the work function of the system. As the alkali-metal coverage increases the dipole moments give rise to an electrostatic field at the surface, which shifts the *ns* and *np* levels downwards to higher binding energies (depolarization effect). Consequently, the occupation of the *ns* resonance increases. The work function reaches a minimum and rises up again to a value typical for a full monolayer of alkali-metal atoms. This characteristic work function behavior has been found for all alkali metals independent of the metallic substrates.[9,10] The Gurney model or the transition from ioniclike bonding at low coverages to a metalliclike layer at the full alkali-metal monolayer has been supported by photoemission studies by Lindgren and Wallden[11] and Horn *et al.*[12] as well as inverse photoemission (IPE) measurements by Heskett *et al.*[13,14] and Jacob *et al.*[15] In these investigations the partial filling of the *ns* resonance[11,12] and the depolarization shift of the unoccupied *np* resonance[14,15] have been observed. Furthermore, two-dimensional band formation has been observed for K (Ref. 12) and Na (Ref. 13) overlayers on Al(111). Recently, a number of theoretical contributions has been published describing the characteristic work-function changes using more refined models.[16–21] While the Gurney picture is corroborated by the calculations of Muscat and Batra,[21] Serena *et al.*,[16] and Persson and Dubois,[20] Ishida and Terakura[19] claim that the alkali-metal adatom region is essentially neutral, even at low coverages. Based on their local-density-formalism pseudopotential calculation they propose a strong covalency of the alkali-metal–substrate bond independent of the alkali-metal coverage $\Theta$ with no change in the energy of occupied and unoccupied valence levels. This is in clear contradiction to the previously mentioned photoemission[11,12] and IPE results.[14,15] In order to corroborate these experimental findings we have performed IPE measurements on K/Al(111) and Cs/Al(111) as a function of alkali-metal coverage. This completes our investigation of the Na/Al(111) system, which has been published previously.[13,14] We have chosen aluminum as a substrate since this *sp* metal is most suited for comparison to jellium-model calculations, and avoids complications associated with occupied substrate *d* bands.

The following experiments have been performed in an ultrahigh-vacuum chamber with a base pressure of $1\times10^{-10}$ mbar. The system has been equipped with low-energy-electron diffraction (LEED), Auger-electron spectroscopy (AES), an ultraviolet photon source, and a hemispherical electron analyzer with an acceptance angle of about 10°. The angle-resolved inverse photoemission spectra have been taken in the isochromat mode, detecting 9.5-eV photons with a Geiger-Müller-type counter filled with iodine as a detecting gas and a $SrF_2$ entrance window. The electrostatically focused electron gun was mounted on a double-axis goniometer, allowing for a change in the electron incidence angle. The electron beam divergence angle was 3°. The overall energy resolution (electron source plus photon detector) is 350 meV.

The Al(111) crystal was cleaned by argon-ion sputtering at an elevated temperature of 200 °C. Cleanliness was checked by AES, IPE, and ultraviolet photoemission spectroscopy (UPS). The alkali-metals were evaporated from a commercial SAES getter source onto the crystal. The substrate was held at room temperature for the K evaporation and was cooled to liquid-nitrogen temperature for the Cs deposition. The alkali-metal coverages were determined by evaporation times, work-function measurements, and LEED. As for Na/Al(111) (Ref. 13) a number of different ordered overlayers exists.[9] For both K and Cs/Al(111) systems a $(\sqrt{3}\times\sqrt{3})R30°$ overlayer was found; in addition, Cs/Al(111) exhibits a $(2\times2)$ structure. The work-function change was measured by UPS and the diode method, namely, detecting the onset of electron current at the sample.

In the right panel of Fig. 1 IPE spectra of the K/Al(111) system are shown at various alkali-metal coverages. The spectra were taken at normal electron incidence. The spectrum of the clean Al(111) surface is depicted at the bottom. It is structureless except for the weak feature at 3.7 eV above $E_F$ (the complete spectrum has been published in Ref. 13). This peak has been assigned to the $n=1$ image potential surface state of the bare Al(111) substrate.[13] As expected from the well-known sensitivity to surface contamination, a potassium coverage of $\Theta_K=0.02$ monolayer (ML) quenches the image state almost completely (see Fig. 1). A shift of this state towards $E_F$ by 0.2 eV is also visible in the figure. In addition, we observe a new feature in the IPE spectrum appearing at 2.3 eV above $E_F$. As the coverage is increased, this K-induced peak decreases in energy. Finally, it reaches a minimum at 0.7 eV corresponding to a coverage of $\Theta_K=\frac{1}{3}$ ML, where we observed an ordered $(\sqrt{3}\times\sqrt{3})R30°$ K/Al(111) overlayer by LEED. Concomitant with the appearance of the ordered overlayer, a second feature emerges in the IPE spectra at 1.6 eV above $E_F$. The high-coverage spectra closely resemble the IPE spectra of $(\sqrt{3}\times\sqrt{3})R30°$ Na/Al(111) (Refs. 13 and 14) but with a relative shift of 0.4 eV towards $E_F$ for K/Al(111).

In the left panel of Fig. 1 complementary UPS spectra taken at 21.2 eV are shown. This coverage-dependent series exhibits behavior identical to measurements published recently by Horn *et al.*[12] A peak assigned to the 4*s*-derived resonance is clearly visible at the Fermi edge at $\Theta_K=0.16$ ML. At higher coverage the intensity of this peak increases rapidly. However, even at $\Theta_K=0.06$ and 0.09 ML the Fermi-edge region is modified, indicating an increase of emission due to the occupied tail of the K 4*s* resonance. It should be pointed out that at $\Theta_K\leq0.16$ ML a 4*s* signal has been found in the occupied region, while the unoccupied K derived feature at 1.1 eV is still well separated from the Fermi level. We therefore attribute this downward shifting peak in the IPE spectra discussed above to the empty 4*p* resonance of the potassium overlayer. The intensities of the 4*p* resonance cannot be taken too literally, as they may be influenced by small amounts of contamination. This is probably the reason for the relative decrease of the 4*p* signal in Fig. 1 at $\Theta_K=0.21$ ML. We have also found an extreme sensitivity to contamination of the features in the IPE spectrum of an ordered close-packed $(2\times2)$ Na monolayer on Al(111).[13] An exposure of 0.1 L oxygen caused a decrease in their intensities, but without affecting the energy positions. [1 langmuir (L) $\equiv10^{-6}$ Torr sec.] An exposure to 0.6 L oxygen quenched the Na-derived peaks completely. We expect that the more open alkali-metal structures at lower coverages would be even more reactive. After about 2 h measuring time the UPS spectra exhibited small traces of oxygen contamination at $E_B=6$ eV binding energy.[22] In any event, in the present paper we are mainly interested in the energies of the alkali resonances.

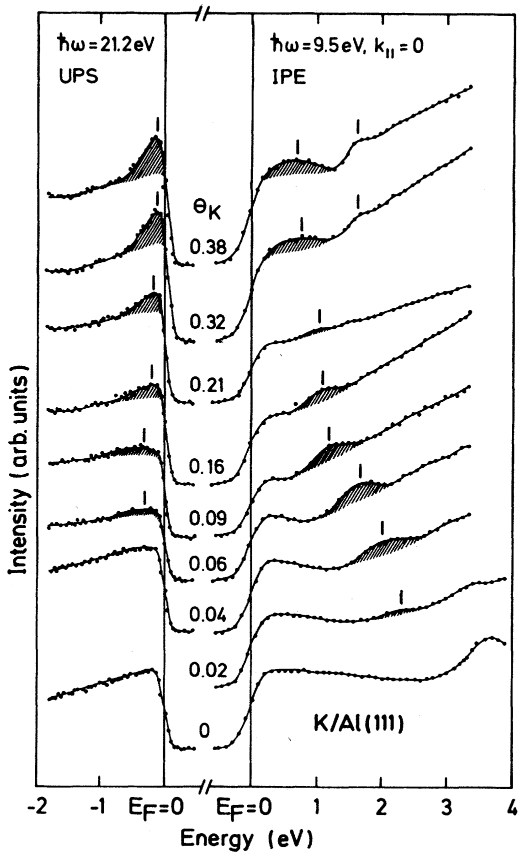

FIG. 1. Photoemission and inverse photoemission spectra of K on Al(111) at increasing K coverage. Hatched features indicate the unoccupied K 4*p*- and occupied 4*s*-derived states.

According to some of the calculations[6,7] mentioned above the center of gravity of the K 4*s* resonance should be located above $E_F$ in the zero-coverage limit. In fact, a careful inspection of the Fermi-edge region of the IPE spectra at low K coverages ($\Theta_K \leq 0.06$ ML) in Fig. 1 exhibits a very weak feature, which we attribute to the empty *s* resonance. To justify this assignment an enlarged plot of the Fermi-edge region for low K coverages is shown in Fig. 2. In this figure the weak K 4*s* contribution is compared to the IPE spectrum of the bare Al(111) substrate, which has been plotted underneath every alkali-metal spectrum. The K spectra have been normalized to the Al(111) spectrum at the onset of the 4*p*-derived feature. This region of the spectrum should not be significantly influenced by any alkali-metal feature. This point of normalization shifts towards $E_F$ due to the downward shifting K 4*p* resonance. Following this procedure, we have found a K-induced roman increase of spectral intensity at the Fermi level (see Fig. 2). At $\Theta_K = 0.02$ ML its center of gravity is located at about 0.6 eV above $E_F$, while the *p* resonance has been identified at 2.3 eV. The full width at half maximum (FWHM) of the Fermi-level feature can be estimated as 0.6 eV. Doubling of the K coverage increases its intensity. Simultaneously, the resonance shifts to about 0.4 eV. At $\Theta_K = 0.07$ ML the weak structure appears to cross the Fermi edge and at 9% of a full monolayer the crossing is almost completed and the peak has almost completely disappeared. Exactly in this coverage regime the occupied part of the *s* level is observed by UPS (Fig. 1). This comparison of UPS and IPE spectra confirms the Fermi-level crossing of the *s* resonance with increasing K coverage.

In Fig. 3 IPE isochromat spectra of Cs on Al(111) are shown for various alkali-metal coverages. At $\Theta_{Cs} = 0.06$ ML a feature appears at 1.7 eV above $E_F$, which shifts towards the Fermi level by increasing the Cs coverage to $\Theta_{Cs} = 0.13$ ML (not shown). We attribute this signal to the unoccupied Cs 6*p* resonance. At higher coverages corresponding to the ordered $(2\times2)$ and $(\sqrt{3}\times\sqrt{3})R30°$ Cs/Al(111) overlayers no Cs-derived feature could be observed in the IPE spectra. In Fig. 3 the normalized IPE spectrum of the clean Al(111) substrate is included for each Cs coverage. Similar to the case of K/Al(111), we identify the unoccupied part of the Cs 6*s* resonance at 0.4 eV above $E_F$ at $\Theta_{Cs} = 0.06$ ML, and crossing the Fermi level at about $\Theta_{Cs} = 0.10$ ML. The IPE spectra of the Na

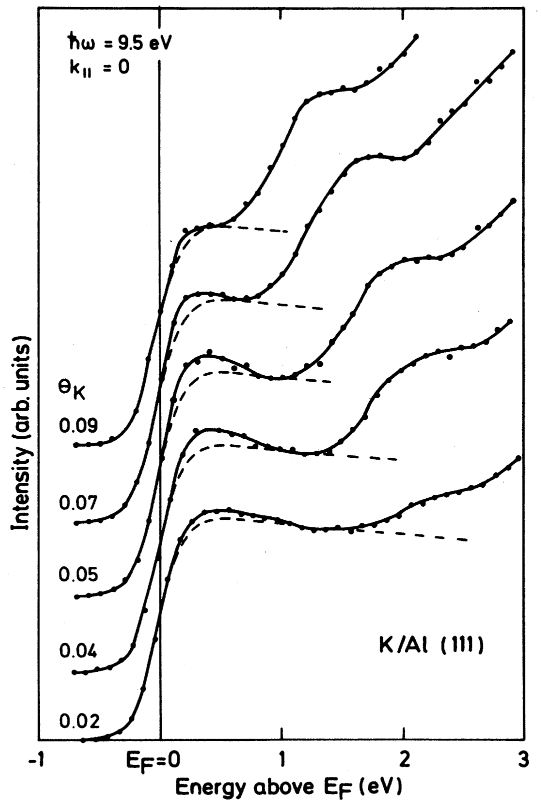

FIG. 2. Inverse photoemission spectra of K/Al(111) at various coverages, $\Theta_K$. For comparison, the IPE spectrum of the clean Al(111) substrate (dashed) is included under each spectrum. The difference in the $E_F$ regime is attributed to the empty part of the K 4*s* resonance crossing $E_F$ at increasing $\Theta_K$.

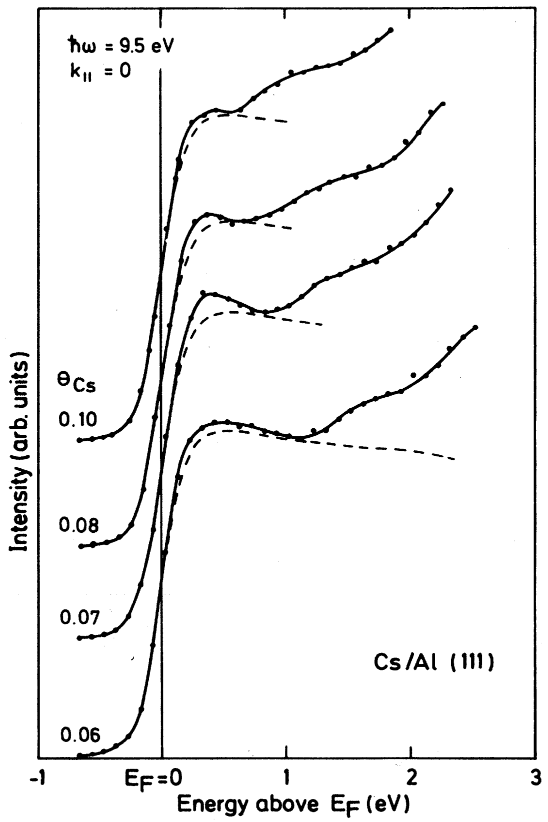

FIG. 3. Inverse photoemission spectra of Cs/Al(111) at various coverages, $\Theta_{Cs}$. For comparison the IPE spectrum of the clean Al(111) substrate (dashed) is included under each Cs spectrum. The difference in the Fermi-level regime is attributed to the empty part of the Cs 6*s* resonance crossing $E_F$ at increasing $\Theta_{Cs}$.

coverage dependence on Al(111) have been published in a previous paper.[14] The measurements are very similar to the results of K and Cs in Figs. 1–3. The unoccupied $3p$ resonance shifts towards $E_F$. Concomitant with the formation of an ordered $(\sqrt{3}\times\sqrt{3})R30^\circ$ Na/Al(111) structure, a second feature develops at about 1 eV above the $3p$ band. In the low-coverage regime we can also identify the unoccupied part of the $3s$ level at $\Theta_{\mathrm{Na}}=0.06$ ML as demonstrated in Fig. 4. The Fermi-level crossing has been completed at about $\Theta_{\mathrm{Na}}=0.10$ ML.

From our results it appears that 10% alkali-metal coverage on Al(111) is typical for an almost complete disappearance of the *ns* resonance in the IPE spectra. Assuming well-localized alkali-metal valence orbitals this would correspond to fully occupied alkali-metal *s* levels, which is physically improbable. Therefore, we attribute our observation to the onset of band-structure formation in this coverage regime. Since the IPE measurements have been taken in the angle-resolved mode at normal electron incidence, the spectra reflect direct transitions into unoccupied bands at the $\overline{\Gamma}$ point if a surface Brillouin zone has developed. Since the radial extension of the *s* valence orbitals of Na, K, and Cs is considerably different, we believe that the common onset of band-structure formation at about $\Theta=0.10$ ML is due to island formation of the adsorbates on Al(111). Furthermore, the LEED patterns start to develop at this coverage regime. It should also be noted that Woratschek *et al.*[8] have claimed to observe the metallization of K/Cu(110) at a coverage of 10% based on measurements using metastable deexcitation spectroscopy.

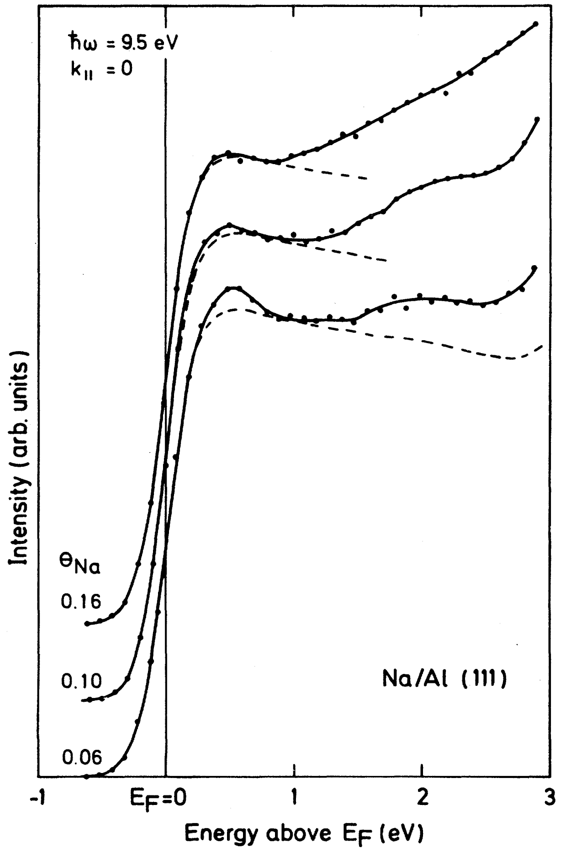

FIG. 4. Inverse photoemission spectra of Na/Al(111) at various coverages, $\Theta_{\mathrm{Na}}$. For comparison the IPE spectrum of the clean Al(111) substrate (dashed) is included under each Na spectrum. The difference in the $E_F$ regime is attributed to the empty part of the Na $3s$ resonance crossing $E_F$ at increasing $\Theta_{\mathrm{Na}}$.

In Fig. 5 the energies of the Cs, K, and Na (Ref. 14) *s* and *p* resonances have been summarized as found by our IPE and UPS measurements. The Na $3p$ and K $4p$ resonances exhibit a quite similar behavior versus coverage up to $\Theta=0.33$ ML. At low coverages the energies of the empty *p* resonances decrease almost linearly. Above 10% coverage they reach a saturation value at 1.1 and 0.75 eV for Na and K, respectively, corresponding to the formation of the ordered $(\sqrt{3}\times\sqrt{3})R30^\circ$ overlayer. Upon increasing the Na coverage further, the *p*-derived band shifts up again to 1.8 eV with the formation of a more dense-packed $(2\times2)$ overlayer. Below 10% coverage the unoccupied part of the alkali *s* resonances has been observed. At $\Theta_{\mathrm{K}}=0.06$ ML the K $4s$ resonance could be observed on both sides of the Fermi edge. Naturally, in this coverage regime the energy positions cannot be taken too literally, since the *s* level crosses $E_F$. In the series Na,

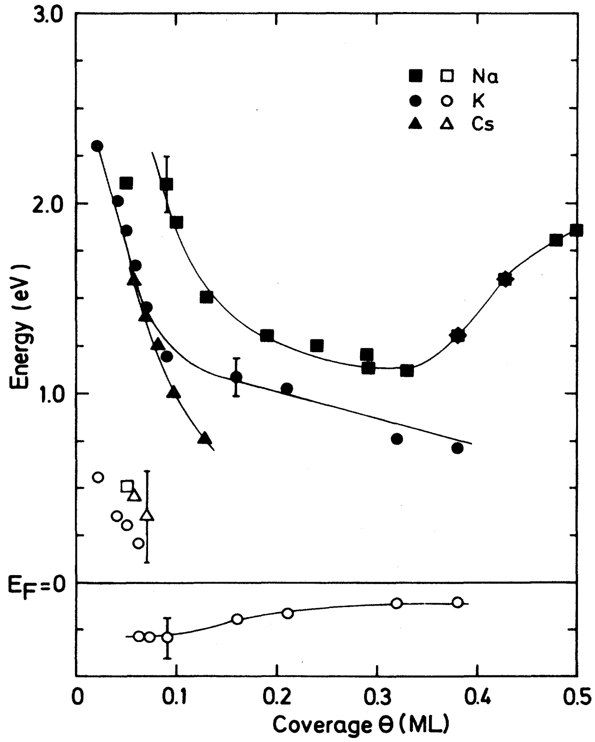

FIG. 5. Energetic positions of the *np* (solid symbols) and *ns*- (open symbols) derived states of Cs, Na, K, and Cs on Al(111) as a function of increasing alkali-metal coverage. (The solid lines are drawn to guide the eye). The $3p$ energies at $\Theta_{\mathrm{Na}}=0.38$ and 0.43 ML represent mean values of the superposition of the two ordered overlayer structures.

K, Cs there is a tendency for the *p* resonances to appear at a progressively lower energy. However, the *s* levels are very similar within the error limits, as is expected from theoretical models.[5–7] Below $\Theta=0.10$ ML the Na 3*p* level is almost 0.5 eV higher than the K 4*p* or Cs 6*p* resonance. These differences are consistent with the different separations of the valence *s* and *p* levels for the free alkali-metal atoms, as given in Ref. 7: $\Delta E_{sp}(\text{Na})=2.1$ eV, $\Delta E_{sp}(\text{K})=1.61$ eV, and $\Delta E_{sp}(\text{Cs})=1.44$ eV. The atomic values can be taken as a first approximation for the alkali adsorbates in the low-coverage regime. For example, from the IPE data we can extrapolate the energies of the K valence levels to the zero-coverage limit, with the result $E_{4p}(\Theta_{\text{K}}\rightarrow 0)=(2.7\pm 0.1)$ eV and $E_{4s}(\Theta_{\text{K}}\rightarrow 0)=(0.7\pm 0.2)$ eV. The experimental value $\Delta E_{sp}(\Theta_{\text{K}}=0)$ is then 0.4 eV larger than for the free atom. Therefore, a considerable *sp* hybridization[7] has to be excluded at low alkali-metal coverages. After band formation has occurred the *s* and *p* bands of the K overlayer might hybridize to some extent, since the bottom of the *p* band is close to $E_F$ with the bottom of the *s*-derived conduction band occurring right below $E_F$. For Na, *sp* interaction is less likely. An *s*-like dispersion has been demonstrated by Horn *et al.*[12] for the occupied K-derived feature. The unoccupied bands of the $(\sqrt{3}\times\sqrt{3})R30°$ K/Al(111) overlayer exhibit a very similar dispersion[23] to that found for Na.[13] Compared to the full-potential linear augmented-plane-wave calculation by Wimmer[24] of isolated alkali-metal monolayers, the lowest empty band has a $p_z$ character while the band 1.6 eV above $E_F$ is mainly *d* derived.

In conclusion, we have measured the energies of the unoccupied *np* resonances of Na, K, and Cs as a function of alkali-metal coverage on Al(111). The empty part of their *ns* resonances has also been identified in the IPE spectra at coverages below $\Theta\simeq 0.10$ ML. In agreement with some theoretical models of alkali-metal chemisorption,[5–7,20] the valence levels shift towards the Fermi level as a function of increasing coverage. In all cases studied, we observed the *ns* levels to cross $E_F$ below $\Theta\approx 0.10$ ML. Simultaneously, the occupation of the 4*s* level of potassium has been observed by UPS, confirming the recent results of Horn *et al.*[12] These findings disagree with the *ab initio* calculations by Ishida and Terakura,[20] who predict *no* downward shift of the adatom valence density of states. From the IPE measurements an extrapolation to zero coverage results in a 4*p* and 4*s* resonance position of $2.7\pm 0.1$ and $0.7\pm 0.2$ eV above $E_F$, respectively, for a single K atom on Al(111). Since we have found a FWHM of 0.6 eV for the *s* resonance at $\Theta_{\text{K}}=0.02$ ML, the tail of the *s* resonance has to be occupied. Therefore, a single K atom on Al(111) is not fully ionized. At $\Theta\geq 0.10$ ML the alkali-alkali interaction induces band formation and a metallization of the K overlayer is observed.

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