Identification of the s-derived Valence-Electron Level in Photoemission from Alkali-Metal Adlayers on Aluminum

K. Horn, A. Hohlfeld, J. Somers, Th. Lindner, P. Hollins, and A. M. Bradshaw

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6,
D-1000 Berlin 33, Federal Republic of Germany

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Photoemission spectra from potassium adsorbed on an Al{111} surface show a K 4s-derived state just below the Fermi level, E_F, which is first observed just prior to the onset of ordering in the overlayer. The feature disperses upwards with increasing $\mathbf{k}_\parallel$ and crosses E_F before reaching the Brillouin-zone boundary. Its coverage dependence is indicative of a transition from strongly ionic to metallic bonding.

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The generally accepted model describing alkali-metal adsorption on metallic surfaces is based on a description originally given by Gurney[1] and subsequently put on a more quantitative basis by Lang[2] and by Muscat and Newns.[3] The s-electron valence level of the isolated adatom lies energetically near the Fermi level, E_F, and is broadened as a result of the interaction with substrate states. The fractional occupation of this broadened level, which of course depends on its exact position relative to E_F, determines the dipole moment and thus the decrease in work function. At finite coverage the mutual interaction between adatoms will push the broadened level down ("depolarization"); thus increasing its fractional occupation. This progressive neutralization decreases in turn the dipole moment per adatom, normally leading to a minimum in the work-function versus coverage curve.[4] By probing the surface electronic density of states with a suitable technique, it should be possible in principle to follow the fractional occupation of the adsorbate-induced level at E_F in what should be a simple model chemisorption system. Unfortunately, uv photoemission (probably *the* most direct probe available) has so far signally failed to give much useful information on the electronic structure of alkali-metal-atom adlayers. Thus Hayden *et al.* were unable to detect alkali-derived states near E_F on Ag(110) even though a wide range of photon energies was used.[5] Similarly, Hesket *et al.* remark upon the frequent observation of alkali-metal-induced features below the substrate d band but not at E_F.[6] This lack of observation of the s-derived level may be due to the low cross section at the photon energies used in some of these studies. In fact, Lindgren and Wallden, in the only successful photoemission observations so far, show that for Cu{111}-Na and Cu{111}-Cs a feature can indeed be observed at E_F for $h\nu < 5$ eV.[7,8] Electron spectroscopy by deexcitation of metastable rare-gas atoms (Penning spectroscopy), on the other hand, exhibits a high cross section for the excitation of s levels; Woratschek *et al.* have thus recently been able to detect the s-derived feature at E_F in the system Cu{110}, even at very low K coverages ($\sim$0.01).[9] For this reason we decided to reinvestigate the problem of alkali-metal chemisorption with photoemission by taking an aluminum surface which is a good approximation to the jellium substrate used in the self-consistent calculations of Lang and Williams.[2] In addition, aluminum exhibits a relatively structureless, low valence-band emission suitable for the observation of weak adsorbate-derived features.

The photoemission data were taken by use of a VG ADES 400 angle-resolving spectrometer on the 1-m Seya beam line at the Berlin electron storage ring BESSY. The aluminum crystal had been oriented and cut by spark erosion to within 0.5° of the ⟨111⟩ direction; it was subsequently electropolished. *In situ* cleaning consisted of argon-ion bombardment and annealing cycles until no further oxygen contamination was seen in photoemission at $h\nu=25$ eV. The potassium was evaporated from a SAES getter source which required considerable outgassing in order to obtain oxygen-free layers. (The peak at E_F reported below proved very sensitive to contamination.) The relative potassium coverage was determined by the intensity of the K 3p photoemission feature. The spectrum taken just before the emergence of a second 3p feature at 0.5-eV higher binding energy due to multilayer formation was taken as indicative of monolayer completion ($\theta=0.33$). This point corresponds to the small maximum in the work-function versus coverage curve which occurs after the pronounced minimum (see inset to Fig. 1). Most important in the present work is also the occurrence of a K-induced $(\sqrt{3}\times\sqrt{3})R30°$ surface structure which is first observed near the minimum in the work-function curve.[10] The adsorbate-induced fractional-order LEED features show maximum intensity at the monolayer point as defined above. Based on the reasonable assumption that the new surface periodicity is due to an overlayer with one atom (or ion) per unit cell, the monolayer is a hexagonal close-packed structure with a density of 4.7×10^{14} atoms cm^{-2}.

Figure 1 shows a series of photoemission spectra taken at increasing potassium coverage with $h\nu=25$ eV and at normal emission. The lowest spectrum corresponds to the clean surface. The inset shows the corresponding

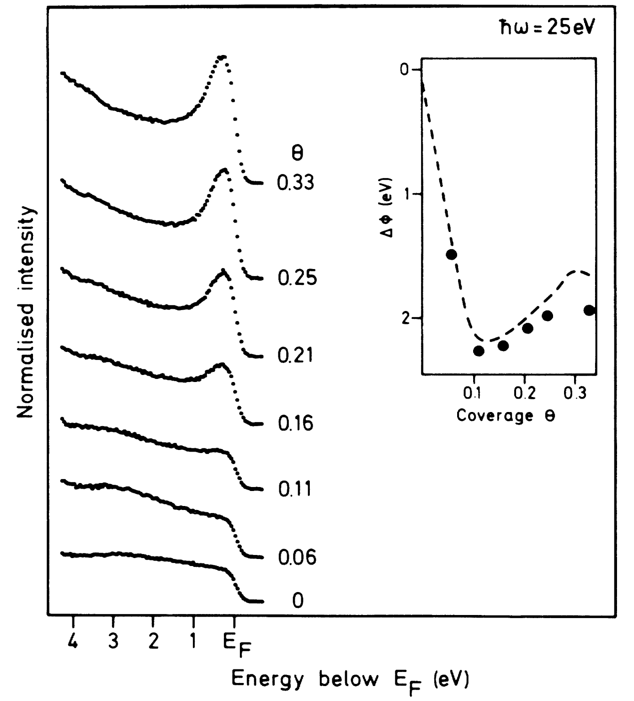

FIG. 1. A sequence of photoemission spectra at increasing K coverage on Al{111}. $h\nu = 25$ eV, normal emission, 100 K. Inset: Work-function change as a function of increasing coverage. The dashed line is the result of a separate experiment with a vibrating capacitor (Ref. 10). The points are values determined from the (full) width of the energy distribution curves shown in the figure.

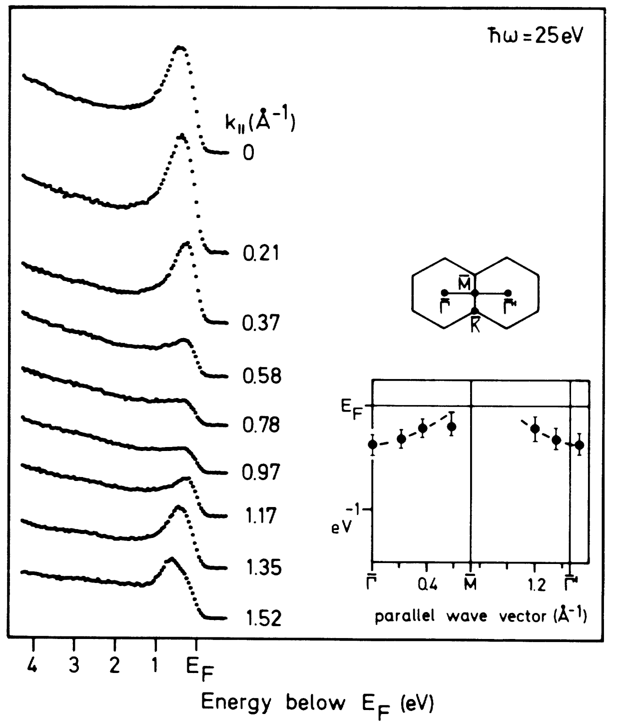

FIG. 2. Photoemission spectra at $h\nu = 25$ eV taken for the Al{111} $(\sqrt{3}\times\sqrt{3})R30°$-K structure at various values of $\mathbf{k}_{\parallel}$ along the $\bar{\Gamma}$-$\bar{M}$-$\bar{\Gamma}'$ line of the adsorbate SBZ. Inset: Dispersion curve derived from the photoemission spectra in the figure.

work-function change as measured in separate experiments with a vibrating capacitor (dashed line).[10] The work-function changes measured from the width of each spectrum in Fig. 1 are also indicated. It is immediately obvious that the adsorbate-induced feature at 0.4 eV below E_F does not appear until a coverage of roughly half a monolayer has been reached, corresponding to the minimum in the work-function curve. Its intensity then increases rapidly, concomitant with the observation of the extra diffraction features associated with the $(\sqrt{3}\times\sqrt{3})R30°$ overlayer. In fact, a plot of the intensity of the K-derived feature at E_F against coverage shows a stronger than linear increase after the onset. The photon energy dependence of the feature is not that which might have been expected from an extrapolation of the results obtained by Lindgren and Wallden for Cu{111}-Na (Ref. 7) and Cu{111}-Cs (Ref. 8) at lower photon energies. In the present results, the K-induced feature is visible over the photon energy range 17–35 eV with a rather broad maximum at 25 eV. This agrees reasonably well with the cross-section calculations of Yeh and Lindau[11] (actually for Ca) and rules out any strong influence of the surface photoelectric effect which would give an enhancement below the bulk plasmon energy at 15 eV.[12] Having ruled out trivial explanations such as contamination or surface umklapp, we assign the observed feature to a K 4*s*-derived state. It is tempting to draw the preliminary conclusion that the K atom is indeed completely ionized at low coverages and that only after the onset of depolarization does a partial refilling of the broadened 4*s* resonance occur. Before discussing this point in more detail, however, it is important to investigate the dispersion, $\epsilon(\mathbf{k}_{\parallel})$, of the K-induced feature.

As is now well known, angle-resolved photoemission can be used to plot directly surface band structures, since the binding energy ϵ is given directly by the electron energy analysis and the parallel component of momentum $\mathbf{k}_{\parallel}$ is, if we assume its conservation in the photoemission process, simply related to the polar angle of emission. Figure 2 shows the effect of changing the polar angle from 0° to 45° in the ⟨110⟩ azimuth, which corresponds to the sampling of $\mathbf{k}_{\parallel}$ along the line $\bar{\Gamma}$-$\bar{M}$-$\bar{\Gamma}'$, where $\bar{\Gamma}'$ designates the center of the second (adsorbate) surface Brillouin zone (SBZ). The K-derived feature disperses upwards, disappears above E_F before reaching the zone edge, and then reappears in the second SBZ. If spectra are measured along the $\bar{\Gamma}\bar{K}\bar{M}\bar{K}$ direction, the K-induced peak does not reappear at $\mathbf{k}_{\parallel} > 1.1$ Å^{-1}. The dispersion plot is shown in the inset of Fig. 2. The spectrum taken at $\bar{\Gamma}'$ ($\mathbf{k}_{\parallel} = 1.52$ Å^{-1}) in Fig. 2 is complicated by a substrate feature which Kevan, Stoffel, and Smith have shown to be due to a surface state located in a bulk band

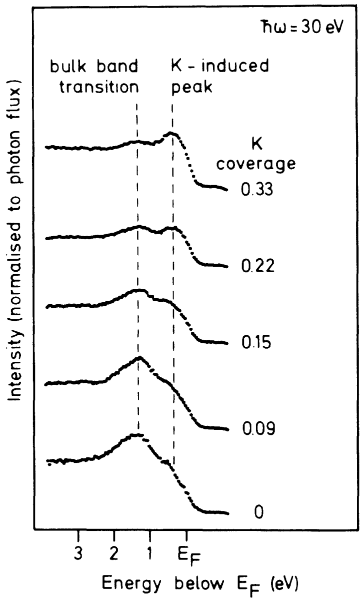

FIG. 3. Coverage dependence of the spectra from the $\bar{\Gamma}'$ point (second adsorbate SBZ). $h\nu = 30$ eV.

gap near the *K* point of the clean-surface SBZ.[13] For this reason we show in Fig. 3 photoemission spectra recorded at the $\bar{\Gamma}'$ point in the second (adsorbate) SBZ at $h\nu = 30$ eV as a function of K coverage, where this surface-state emission is weaker. Note the decrease in intensity of the feature about 1.3 eV below E_F, which is due to an interband transition, and the increase in intensity of the K-derived feature. We should also perhaps remark in passing that the valence-band photoemission spectrum of single-crystal aluminum is only really "flat" in angle-integrated photoemission or in the presence of contamination. As a result of these features, it is difficult to find a single photon energy where the complete dispersion curve of the K-derived state can be measured unhampered by substrate effects.

The experimental dispersion relation in Fig. 2 has a minimum at $\bar{\Gamma}$ and is, within the limits of experimental error, symmetric about the *M* point. We have also observed similar band shapes for Cs and Na on Al{111}.[14] This behavior is consistent with that of an *s*-derived band[15] and similar to Wimmer's calculations[16] for isolated alkali-metal-atom monolayers. Furthermore, its energy and shape are almost identical to that recently calculated for the Na 3*s*-derived band in the system Al{100}-Na by Benesh and Hester.[17] The observed dispersion thus supports our assignment of the K-induced feature at E_F in terms of a 4*s*-derived band. Moreover, we obtain some important information on the nature of the adlayer at high coverage, namely, that it has metallic character. The following discussion, however, concentrates necessarily on the coverage-dependent behavior of the observed feature.

As already mentioned above, a fully ionized adsorbed K atom at low coverages would be an obvious conclusion to be drawn from Fig. 1. The Penning study by Woratschek *et al.*[9] suggests, however, that even at the lowest coverages there is fractional occupation of a broadened 4*s* resonance. The intensity of the resonance in the Penning spectrum increases almost linearly with K concentration from zero coverage onwards. Although their data were taken on Cu{110}, one could reasonably expect the same behavior on Al{111}. What then is the reason for this discrepancy between the two experiments? We advance a possible explanation which derives from a combination of two effects. First, the relative cross section in the Penning experiment is indeed very much higher but only in the immediate vicinity of the Fermi level. In the Penning process, states close to E_F overlap more effectively with the 1*s* hole in the excited He atom. In a simple model this gives rise to an exponential decrease in the Auger deexcitation rate as a function of the square root of the binding energy.[18] The result is a narrow resonance just under E_F, the half-width of which does *not* change as coverage is increased, despite the fact that the effect of depolarization is seen in the work-function curve. A too simple an explanation of these data thus probably lends too much credence to the model calculations of Lang and Williams[2] which are certainly correct for jellium but not necessarily for a real metal. We suspect that in reality the *s*-derived states are very strongly hybridized with the metal *sp* band and smeared out over a much wider energy range. (In the case of copper there may even by some appreciable *s*-derived density of states below the *d* band; see the observation of Heskett *et al.*[6] referred to above.) This effect, combined with the low cross section, is likely to prevent a distinct feature from being observed in photoemission. At higher coverages, however, a second factor comes into play. On formation of an ordered overlayer, lateral interactions give rise to a band of *s* states which are concentrated in a small region of ϵ and $\mathbf{k}_\parallel$ space. The rapid increase in the intensity of the 4*s*-derived feature in photoemission after the onset is, apart from the still increasing K coverage, thus due to the growth of areas on the surface with the $(\sqrt{3}\times\sqrt{3})R30°$ structure. We therefore contend that the nonobservation of the 4*s*-derived feature at low coverages is not a result of 100% ionic bonding, although the ionic contribution to the bonding is still expected to be very high. The evidence for this comes not only from the data of Woratscheck *et al.* but also from the abrupt appearance of the photoemission peak: The depolarization effects are already apparent in the work-function curve *before* the 4*s*-derived feature appears.

Very recently Lamble *et al.* have measured the Cs (L_3) x-ray-absorption fine structure for the adsorption system Ag{111}-Cs.[19] they show that the Cs-Ag bond length increases from 3.2 to 3.5 Å as a function of increasing Cs coverage and conclude that a transition from predominantly ionic bonding to a more *covalent* state takes place. Only a direct probe of electronic structure will show whether the same situation pertains here as in the system Al{111}-K, i.e., an *s*-derived band dispersing across E_F indicating a *metallic* overlayer. On the other hand, the presence of substrate *d* electrons may indeed lead to strong covalent bonding as in the systems W {100}-Cs and Mo{100}-Cs.[20]

Another interesting aspect of the spectra reported in the present paper is the narrow width of the 4*s*-derived feature which is actually much narrower than the peak observed in the Penning spectra on Cu{110}. From the bulk band structure for aluminum, it is clear that there are no gaps in the projected bulk bands in the region of the SBZ at this energy. Hybridization with metal *sp* states must therefore also occur at high coverage but does not lead to very strong broadening. (One contributory factor to the linewidth—lifetime broadening—is of course also considerably weaker for a state so near to E_F.) This is an important observation because we suspect that the hybridization with metal *p* states gives rise to the observed photon energy dependence. A more complete data set from a variety of systems is required, however, before this point can be understood. Our preliminary data for Cs and Na on Al{111} indicate not dissimilar cross-sectional behavior to that reported here for K.

In summary, we report the observation of a 4*s*-derived state near E_F for K adsorbed on Al {111} but at photon energies considerably higher than that seen in the only previous photoemission study for adsorbed alkali-metal atoms. The coverage dependence, which is quite different from that reported in Penning spectroscopy from Cu{110}-K, is ascribed to the different energy-dependent matrix element in the latter experiment as well as to the effect of band formation. Finally, the present data clearly show that, whereas the isolated adsorbed alkali-metal atom is largely bound ionically, the full monolayer is characterized by metallic bonding.

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