RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 11 15 APRIL 1987-I

Potassium-induced empty electronic states on Ag(110)

W. Jacob, E. Bertel, and V. Dose
Max-Planck-Institut für Plasmaphysik—EURATOM Association,
D-8046 Garching bei München, Federal Republic of Germany

(Received 24 December 1986)

The unoccupied level structure of K and Na adsorbed on a Ag(110) surface has been probed by inverse photoemission. A peak is observed initially ~3 eV above E_F, which shifts in energy towards the Fermi level as a function of increasing coverage. The dispersion of this feature is consistent with a p_z character of the observed empty state. For $\Theta > 0.3$ new structures appear in the spectra indicating the formation of a metallic layer. Energy position, coverage dependence, and dispersion of the unoccupied level are in striking agreement with predictions made on the footing of previous ultraviolet photoemission spectroscopy, electron energy-loss spectroscopy, and theoretical results.

The promotional effect of alkali-metal coadsorbates on many catalytic reactions has stimulated intense investigations of the changes in electronic structure induced by submonolayer coverages of alkali-metal atoms. Langmuir[1] assumed a complete transfer of the alkali-metal *s* electron to the metal leading to a totally ionic alkali-metal ground state at low coverages. This view was questioned already by Gurney,[2] who argued on the basis of quantum-mechanical considerations that the alkali-metal *s* level should be broadened upon adsorption into a partially occupied surface resonance. The surface resonance model was later refined by a number of workers (e.g., Refs. 3–5) who were able to reproduce in their model calculations most of the characteristic behavior found in experimental studies of alkali-metal adsorption systems. The degree of *s*-level occupancy at low alkali-metal coverages remained, however, an intriguing problem, because no alkali-metal *s*-derived feature could be detected in ultraviolet photoemission spectroscopy studies of metal surfaces with less than half-monolayer alkali-metal coverages. It is only quite recently that metastable quenching spectroscopy has provided evidence for significant contributions of the K 4*s* level to the density of occupied states close to E_F in the low coverage limit of the system K/Cu(110).[6]

On the other hand, electron energy-loss spectroscopy (EELS) data on a variety of systems showed a prominent loss feature. This energy loss is strongly coverage dependent and changes from 3 eV at low alkali-metal coverages to about 1 eV at roughly half a monolayer.[7–10] Although collective excitations have been proposed to explain this loss even for the small coverage limit, the experimental data seemed to be more consistent with an interband transition from an occupied level involving alkali-metal *s*-character to an alkali-metal *p*-derived empty state.[8,9] Combining angle-resolved ultraviolet photoemission data with EELS measurements Soukiassian *et al.*[11] postulated an unoccupied state for the system Cs/W(100) which shifts from 2.5 eV above the Fermi level in the zero coverage limit to just above E_F at half a monolayer coverage and above. As such an unoccupied state was hitherto inaccessible to direct observation, this model of an $s \rightarrow p$ interband transition and the implied initial- and final-state shifts remained rather speculative.

In the present study we applied inverse photoemission spectroscopy (IPE) on the system K/Ag(110) and observed for the first time unoccupied K-induced levels, their shift as a function of coverage, and their dispersion $E(k_\parallel)$. The experiments were carried out in a stainless-steel ultrahigh vacuum system with base pressure below 10^{-8} Pa. The Ag(110) surface was cleaned by argon sputtering and annealing cycles. The quality of the Ag(110) surface was checked by the observation of high-quality oxygen-induced $(n \times 1)$ LEED patterns.[12] A potassium source using SAES alkali-metal dispensers mounted in a heated glass collimator tube was employed for dosing K onto the sample. The photons were detected in a Geiger-Müller counter with CaF_2 window and iodine gas filling as described by Dose.[13] The instrumental response function has a full width at half maximum (FWHM) of about 0.8 eV. Work function changes were measured by means of the diode method. Coverages were monitored via the induced work function changes and calibrated against thermal desorption spectra. A monolayer is defined by the number of the topmost (ridge) silver atoms, i.e., 8.45×10^{14} cm^{-2}. Using a metallic radius of 2.32 Å for K (Ref. 14) we obtain 5.4×10^{14} cm^{-2} for a close-packed overlayer, which consequently corresponds to $\Theta_K = 0.64$. The minimum in the work function is associated with a coverage $\Theta_K = 0.3$. Finally, it should be mentioned that the Ag(110) surface shows a (1×2) reconstruction already at very low alkali-metal coverages.[15] Therefore, an absolute calibration using the induced LEED structures is not possible.

Figure 1 shows a series of IPE spectra taken at normal electron incidence as a function of potassium coverage. The spectrum of the clean Ag(110) surface has been discussed elsewhere.[16] Already at a K coverage of $\Theta_K = 0.08$ the silver features are noticeably reduced, but a new peak appears at 2.8 eV above E_F. Up to a coverage of $\Theta_K = 0.2$, i.e., $\sim \frac{1}{3}$ of the coverage corresponding to a close-packed metallic K layer, this peak grows in intensity and shifts towards the Fermi level. A further increase in coverage results in rapid attenuation of the K-induced feature, which continues to drop down in energy until for $\Theta_K = 0.34$ it remains stationary right at the Fermi level. As the intensi-

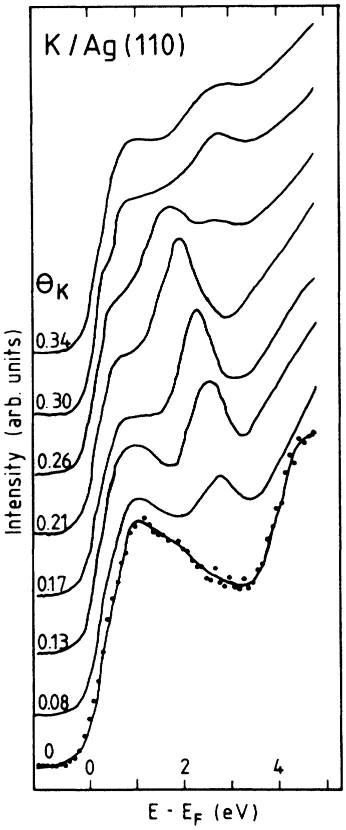

FIG. 1. IPE spectra of K/Ag(110) as a function of potassium coverage Θ_K. The spectra are recorded at normal electron incidence. Data points are shown for the IPE spectrum of clean Ag(110) in order to characterize the quality of the spectra.

ty of the transition goes through its maximum at $\Theta_K = 0.21$ a second peak emerges at 2.7 eV. The intensity of this peak grows with increasing K coverage but remains at constant energy. Figure 2 displays the observed energy shifts as a function of coverage.

Figure 3 shows a series of IPE spectra taken at various angles of electron incidence θ for a K coverage of $\Theta_K = 0.2$. The potassium-induced feature is seen to disperse from 1.9 eV at normal incidence to 2.3 eV at $\theta = \pm 30°$. In Fig. 4 the measured peak energy is given as a function of $k_{\parallel}$ in the ΓKLU direction of Ag(110). Around $\bar{\Gamma}$ the dispersion can be fitted by a parabola if an effective mass of $m^*/m = 2.5$ is assumed.

Discussing the present results and comparing them to previous work on alkali-metal adsorption in the submonolayer range we emphasize the following points: (a) Figure 1 presents the first direct observation of the alkali-metal-induced unoccupied state just above the Fermi level which was inferred from the EELS measurements on a variety of alkali-metal adsorption systems.[7-11] (b) The decrease in energy of this unoccupied state with increasing coverage shown in Fig. 2 is in striking agreement with the behavior anticipated by Soukiassian and co-workers[11] for the analogous state in Cs on W(100). Even the coverage at which this state approaches the Fermi level is the same in both systems, namely, 50% of the close-packed metallic layer where the work function minimum occurs. This similarity might seem fortuitous were it not for the many EELS results revealing the same pattern in a large number of other alkali-metal systems. (c) The dispersion observed in Fig. 3 and displayed in Fig. 4 is consistent with an unoccupied band of either s or p_z character. As the alkali-metal s-derived band should be partly occupied[6] the corresponding empty states should appear close to the Fermi level. Ac-

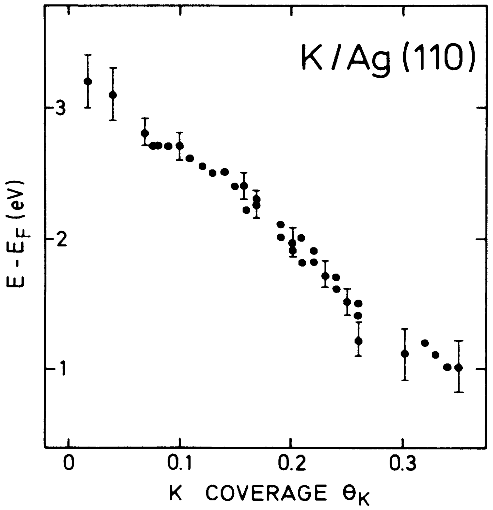

FIG. 2. Energy position of the K p_z-derived unoccupied level in K/Ag(110) as a function of K coverage.

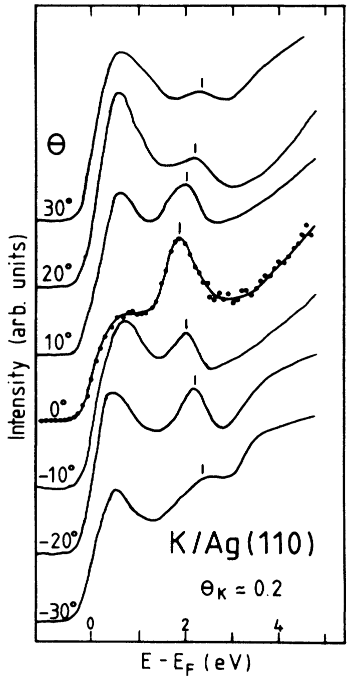

FIG. 3. Dispersion of the K p_z-derived unoccupied level at a potassium coverage $\Theta_K = 0.2$. θ is the polar angle of electron incidence in the ΓKLU azimuth of the Ag(110) surface.

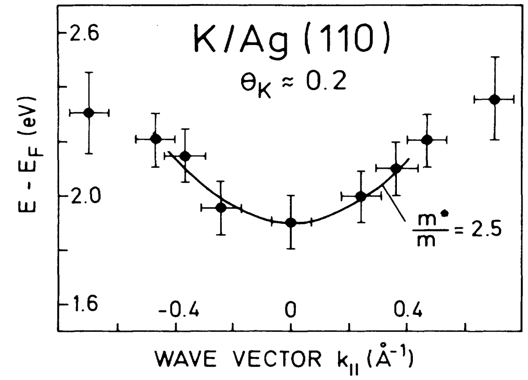

FIG. 4. Energy vs $k_{\parallel}$ plot of the K p_z-derived unoccupied state for a K-coverage $\Theta_K = 0.2$. From the parabola drawn through the data points around $\bar{\Gamma}$ an effective mass of $m^*/m = 2.5$ is deduced.

cordingly, we assign the dispersing peak to the p_z band. Such an assignment is in keeping with the interpretation of the prominent low coverage loss as an $s \rightarrow p$ transition.[8,9]

Wimmer[17] calculated the band structure for a free hexagonal monolayer of potassium and obtained a similar parabolic dispersion for the s and the p_z band around $\bar{\Gamma}$ but with the effective masses being somewhat different. The s-band dispersion can be approximated with an effective mass of $m^*/m \sim 0.8$, whereas the corresponding parameter for the p_z band is $m^*/m \sim 1.2$. It is surprising that dispersion is observed in the present study at coverages which correspond to only $\frac{1}{3}$ of a close-packed layer. However, the unoccupied K $4p$ wave function has a considerable spacial extension which could result in a sufficient overlap to produce the measured dispersion. From Fig. 4 an effective mass of $m^*/m \sim 2.5$ can be deduced. This is a considerable increase in effective mass as compared to Wimmer's calculation[17] and it is just what one would expect for the larger interatomic distances at the lower coverage in the present measurement. Of course the band structure observed here is expected to be modified by the mixing with substrate states. Our preliminary data suggest, however, that the deviation from the unsupported layer band structure may be restricted more or less to quantitative variations, leaving the essential qualitative features unchanged. (d) The new feature emerging at $\Theta_K \approx 0.25$ in Fig. 1 about 1 eV above the p_z band is tentatively associated with K $3d$-derived levels. The smaller spacial extension of the $3d$ wave function as compared to the $4p$ orbital would then account for the relative insensitivity of its energy position towards changes in coverage.

We point out that a coverage of $\Theta_k = 0.25$ corresponds to $\frac{1}{3}$ of a close-packed layer. This is the coverage at which Woratschek *et al.*[6] observe an increase in metastable deexcitation intensity for K on Cu(110). The accompanying decrease in FWHM of the K $4s$-derived feature is attributed by these authors to the formation of a metallic layer and the corresponding outward movement of the K atoms.[18] A similar process could give rise to the appearance of the K $3d$-related peak in the present IPE spectra.

In summary, we observe unoccupied states in alkali-metal adsorption systems which show coverage-dependent shifts consistent with previous EELS results. The observed dispersion behavior is qualitatively similar to calculated band structures and allows identification of p_z- and d-derived features. The changes observed in IPE with increasing coverage parallel complementary observations obtained by other spectroscopies and are consistent with a transition from partly charged alkali-metal atoms to a metallike layer already at $\frac{1}{3}$ of the coverage corresponding to a close-packed metal layer.

---

[1] I. Langmuir and K. H. Kingdon, Phys. Rev. **21**, 381 (1923).

[2] R. W. Gurney, Phys. Rev. **47**, 479 (1935).

[3] N. D. Lang and A. R. Williams, Phys. Rev. Lett. **37**, 212 (1976); Phys. Rev. B **18**, 616 (1978); **27**, 2019 (1983).

[4] K. F. Wojciechowski, Acta Phys. Polon. **33**, 363 (1968).

[5] E. Wimmer, A. J. Freeman, J. R. Hiskes, and A. M. Karo, Phys. Rev. B **28**, 3074 (1983).

[6] B. Woratschek, W. Sesselmann, J. Küppers, and G. Ertl, Phys. Rev. Lett. **55**, 1231 (1985).

[7] S. Andersson and U. Jostell, Faraday Discuss. Chem. Soc. **60**, 255 (1975).

[8] S. A. Lindgren and L. Wallden, Phys. Rev. B **22**, 5967 (1980).

[9] P. Soukiassian, R. Riwan, and Y. Borensztein, Solid State Commun. **44**, 1375 (1982).

[10] L. Surnev, G. Rangelov, E. Bertel, and F. P. Netzer, Surf. Sci. (to be published).

[11] P. Soukiassian, R. Riwan, J. Lecante, E. Wimmer, S. R. Chubb, and A. J. Freeman, Phys. Rev. B **31**, 4911 (1985).

[12] H. A. Engelhardt and D. Menzel, Surf. Sci. **57**, 591 (1976).

[13] V. Dose, Appl. Phys. **14**, 117 (1977).

[14] C. T. Campbell, Surf. Sci. **167**, L181 (1986).

[15] B. E. Hayden, K. C. Prince, P. J. Davie, G. Paolucci, and A. M. Bradshaw, Solid State Commun. **48**, 325 (1983).

[16] W. Altmann, V. Dose, and A. Goldmann, Z. Phys. B **65**, 171 (1986).

[17] E. Wimmer, J. Phys. F **13**, 2313 (1983).

[18] J. P. Muscat and I. P. Batra, Phys. Rev. B **34**, 2889 (1986).