Alkali-Metal Adsorbates on W(110): Ionic, Covalent, or Metallic?

D. M. Riffe, G. K. Wertheim, and P. H. Citrin
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 6 November 1989)

The photoemission signal from the first atomic layer of W(110) is used to assess the nature of the interaction between the surface atoms of the metal substrate and the adsorbates Na, K, and Cs for coverages up to 1 atomic layer. Our results indicate that there is little or no charge transfer from the alkali metal to the W surface, even in the limit of low coverage. The satellite structure of the photoemission lines of the outermost p shell of the alkali metals confirms this conclusion. While contrary to the conventional picture of alkali-metal-charge donation, these findings fully support recent theoretical calculations.

PACS numbers: 79.60.Gs, 68.55.Gi

Ever since the work of Taylor and Langmuir[1] on the adsorption of Cs on W, the lowering of the work function of metals by alkali metals has been attributed to the formation of a dipole layer by donation of the outer s electron of the adsorbate to the conduction band of the substrate.[2] Although it was soon realized that broadening of the adsorbate s level modifies this purely ionic picture by introducing some degree of covalency,[3,4] the notion of charge donation has continued to provide the framework for the interpretation of a wide variety of experimental data, especially in the limit of low coverage.[5-10] Even calculations for an isolated Li atom adsorbed on jellium, in which distinct metal and alkali-metal states are not defined, were interpreted as showing that the transferred electron resides in the metal.[11] More recent band-structure calculations[12] of $c(2\times2)$Cs on W(100), however, lead to an entirely different conclusion. These show that the bonding is metallic and that the dipole layer resides in the polarized Cs valence electrons. Other theoretical work for Na on Al(001) (Ref. 13) and alkali-metal overlayers on jellium[14] also finds that the dipole moment arises from the polarization of the adsorbate, and demonstrates that the adatom charge is insensitive to coverage. These theoretical calculations thus contradict the intuitively appealing picture of charge donation by the strongly electropositive alkali metals, which has been the basis for the interpretation of so much experimental data. Significantly, while these data are consistent with expectations based on charge transfer, they do not discriminate against the predictions of the more recent theories.

In this Letter we report on measurements which clearly resolve this conflict by focusing not on the alkali metal, but on the outermost layer of the metal substrate. The well-resolved photoemission signal from the surface layer of W, which has been shown to be extremely sensitive to the interaction of the metal with adsorbates,[15,16] is the tool of this study. We demonstrate that high-resolution surface core-level photoemission measurements of W $4f$ as a function of coverage unambiguously support the metallic picture of the band-structure calculations.[12-14] Equally important, the measurements show that the ionic picture is not applicable even at low coverage.

The photoemission data were obtained at the National Synchrotron Light Source using the AT&T Bell Laboratories 6-m toroidal-grating monochromator on beam line U4A. Spectra were collected with a 100-mm Vacuum Science Workshop hemispherical analyzer operated with a resolution of 40 meV. The sample was a W(110) ribbon cleaned by standard techniques. Alkali-metal atoms were deposited from well-degassed SAES getter sources. Relative alkali-metal coverages were determined from exposure times and absolute coverages from low-energy electron diffraction (LEED) patterns, which indicate the formation of incommensurate hexagonal overlayers for first-layer coverages near saturation.[17,18] For Na, additional calibration points are provided by commensurate structures at $\frac{1}{3}$- and $\frac{2}{5}$-monolayer (ML) coverages.[17]

The coverage-dependent behavior of the alkali-metal adsorbate is typified by the $3p$ spectra of K in Fig. 1. The signal from the first atomic layer (curves a and b) is quite broad and shifts toward smaller binding energy with increasing coverage. The signal from the second monolayer (curve c) lies at greater binding energy and is so much sharper that the $p_{3/2}$-$p_{1/2}$ spin-orbit splitting of 240 meV is easily resolved. Beyond the second monolayer a new signal (curve d) appears at a somewhat smaller binding energy, which we believe is due to bulk K in random clusters, i.e., the growth follows the Stranski-Krastanov mode. This photoemission behavior is similar to that of alkali metals on other metallic[19,20] and semiconducting[21] substrates. The coverage dependence of the first-layer binding energy can be related through a Born-Haber cycle to the change in the adsorption enthalpy, as previously pointed out.[19] The other notable feature, the large linewidth of the $3p$ electrons in the first atomic layer, is due in part to vibrational broadening and in part to an interatomic Auger process involving an electron from the W d band. Note that a $3p$ hole in *atomic* potassium does not have an Auger decay channel because there is only one $4s$ electron. Dona-

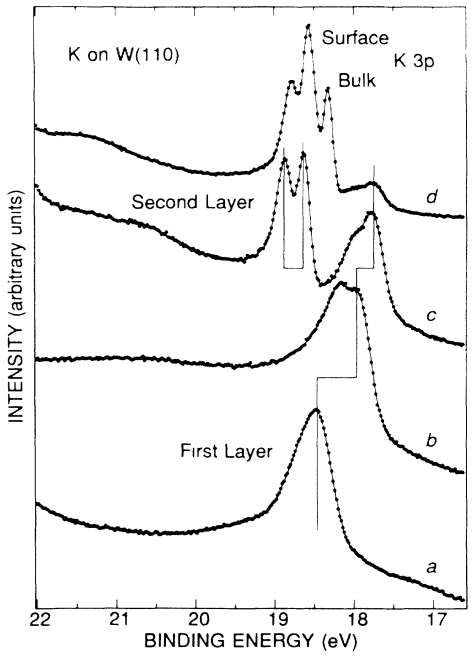

FIG. 1. Photoemission spectra of $3p$ spin-orbit doublet of K adsorbed on a clean W(110) surface with 1.412×10^{15} atoms/cm^2. In the case of the lower three curves the coverages are layerwise. In the case of the upper curve the majority of the adsorbate has formed large, randomly oriented clusters. Curve a, 2.1×10^{14}; curve b, 5.1×10^{14} corresponding to 86% of the densest coverage prior to forming the second layer; curve c, 1.0×10^{15} atoms/cm^2 corresponding to two monolayers; and curve d, 6.8×10^{15} atoms/cm^2 with two layers and random clusters.

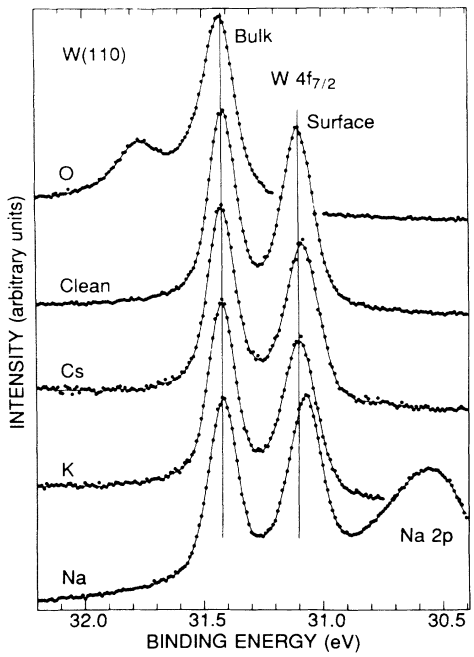

FIG. 2. Photoemission spectra of $4f_{7/2}$ electrons from clean and adsorbate-covered W(110). For O, the spectrum is for $\frac{1}{2}$-monolayer coverage. For Cs, K, and Na they correspond to the densest single-layer coverage, i.e., (5.2, 5.9, and 8.0)$\times10^{14}$ atoms/cm^2, respectively. For Na, emission from the Na $2p$'s is also evident.

tion of the outer s electron to the substrate would tend to suppress the Auger channel of the adsorbate atom.

The most significant results are obtained by photoemission from the W substrate. For clean W(110) the $4f$ surface-atom core-level shift (SCS) is -321 ± 3 meV.[22] The surprising finding is that the signal from the first atomic layer is barely modified by the deposition of alkali-metal atoms (see Fig. 2). At first-layer saturation coverage, Na, K, or Cs produce additional shifts of only -28, -12, and -20 meV, respectively (see Table I). Such small shifts are in very good agreement with band-structure calculations for the high-coverage-limit $c(2\times2)$Cs layer on W(100),[12] which predict that there is little if any charge transfer from the alkali metal to the W and no significant shift of the W $4f$ surface core levels. Note that the lack of shift cannot be due to an accidental cancellation of initial- and final-state effects, because charge added to the d band of W moves the Fermi level to a region with higher density of states, which would improve the screening and reduce the energy of the final state. The initial- and final-state shifts consequently have the same sign.

Results like those in Table I are not unique to W(110). Previous measurements of the SCS produced by alkali-metal adsorbates on other surfaces and metals[23,24] also failed to yield the expected large shifts to smaller binding energy. The work on Cs on W(100) (Ref. 23) resulted in only a small shift to smaller binding energy, but the data were complicated by surface reconstruction and the analysis by the presence of unresolved lines. In the work on K on Pt and Au,[24] small shifts to larger binding energy were obtained from the analysis of unresolved bulk and surface lines. The true implications of these results were not recognized, however, since charge transfer was taken for granted.

Our experimental findings extend the nonionic bonding picture to the low-coverage regime, where an ionic picture is still widely invoked.[5-10] As shown in Table I, an alkali-metal coverage equal to $\frac{1}{3}$ of saturation—where the dipole moment per adsorbed atom is much larger than at saturation and is still comparable

TABLE I. Adsorbate-induced shift of W(110) surface core-level binding energy (meV) for two coverages.

	$\frac{1}{3}$ saturation	Saturation
Cs	$+3\pm2$	-20 ± 3
K	$+5\pm2$	-12 ± 3
Na	0 ± 2	-28 ± 3
O	$+170\pm10$[a]	$+520\pm30$[a]

[a]For coverages equal to those of Cs.

to that of the low-coverage limit—produces an even smaller W $4f$ shift. If the dipole moment were due to charge transfer, a larger change in the SCS would be expected, even though the coverage is smaller. The SCS produced by the adsorption of highly electronegative atomic oxygen provides a means of quantifying this expectation. The average change in W(110) SCS varies linearly with O coverage, producing +170- and +520-meV shifts for coverages equal to $\frac{1}{3}$- and full-saturation Cs densities, respectively. We see, therefore, that the valence s electron of the adsorbed alkali metal is not transferred to the W surface atoms even at the lowest coverage.

Additional support for the conclusion that the W surface layer is largely unaffected by the adsorption of K is obtained from the intensity of the surface signal. In a small interval near the photon energy of 70 eV where the data were taken, the intensity of the surface signal is greatly enhanced by photoelectron diffraction.[25] This enhancement is very sensitive to the interatomic distances. Our observation of bulk and surface signals, which are both proportionately attenuated by the overlayer, therefore indicates that the adsorbate does not significantly alter the spacing of the W surface layer.

If the outer s electron is not transferred to the W substrate, it should be possible to demonstrate that it remains on the alkali-metal adsorbate atom. Proof can, in principle, be obtained from the alkali-metal s-electron photoemission spectrum. This has been accomplished at a coverage greater than $\frac{1}{3}$ of saturation for both K on Al (Ref. 10) and Cs on Cu,[26] systems in which the substrates have relatively featureless conduction bands near the Fermi level. A similar identification of the s-electron photoemission spectrum of alkali metals on W, however, is not possible because the much larger photoelectric cross section and sharp features of the W $5d$-derived conduction band obscure the spectral region of the alkali-metal s-electron contribution.[27]

Fortunately, the nature of the outer s electron can be assessed by looking at loss peaks associated with core-level emission from the alkali-metal atoms. Here we concentrate on K, since the loss peaks of Cs are obscured by the $\sim$1.7-eV spin-orbit splitting and those of Na by the W $4f_{7/2}$ emission (see Fig. 2). The K $3p$ data in Fig. 3 for coverages almost up to saturation of the first atomic layer show two distinct satellites. At low coverage, where the K atoms are well separated, there is a weak satellite at $\sim$1 eV. With increasing coverage the second satellite, which shifts to a final value of 2.7 eV at saturation, becomes dominant. Such satellites could, in principle, be produced by the excitation of the substrate, but then similar satellites with even greater intensity would be associated with the W lines. None are found. The satellites are therefore due to the shakeup of outer electrons associated with the K. The $3p$ electrons themselves are too tightly bound, leaving the $4s$ electron as the only source of these satellites. We assign the $\sim$1-eV satellite

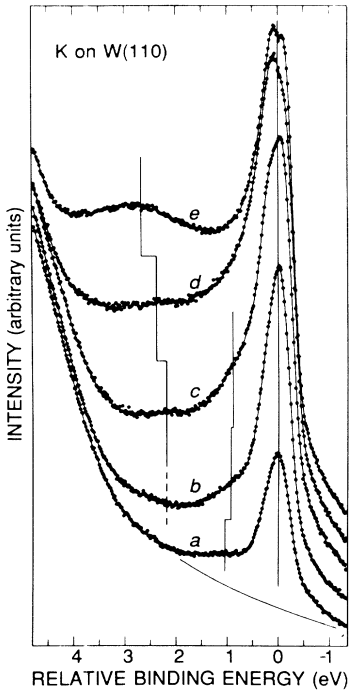

FIG. 3. Satellites of K $3p$ spectra on W(110). Spectra have been shifted to align the $3p$ doublet. Exposures for curves a–e correspond, respectively, to 0.17, 0.36, 0.50, 0.67, and 0.92 times those required to produce a single dense layer.

at low coverage to a single-ion $4s$ shakeup process, and the 2.7-eV satellite to a (surface) plasmon associated with the $4s$ band of a dense K layer. These results and their interpretation are similar to those obtained by electron energy-loss spectroscopy for Na on Al(111).[28] They are also consistent with the results of metastable-He deexcitation spectroscopy for K on Cu,[8] which showed that the K $4s$ electron is present even at low coverage.

The picture of the adsorbate-substrate interaction which emerges from this work is in agreement with those of recent band-structure calculations.[12–14,29] There is no donation of charge to the W conduction band at any coverage. At low adsorbate concentration the atoms form covalent bonds with the substrate. At high coverage the outer s electrons of the adsorbate form a half-filled conduction band. The interaction with the substrate is best described as metallic. The necessary corollary is that the dipole moment resides primarily on the adsorbate atom. The theoretical work has shown that this model accounts in detail for the change in work function and adsorption enthalpy with coverage, the very observations which provided the original motivation for the ionic model that the present work invalidates.

What are the implications of abandoning the ionic model on earlier work in which it was invoked to interpret data? Measured work functions are better accounted for by recent theory[29] than by the ionic model or its quantum-mechanical elaboration.[4] The fact that the cov-

erage dependence of the work function is quite similar for the alkali metals on diverse metallic substrates [including W(110)], typically showing a minimum just beyond half of saturation, shows that it does not depend on interaction with the substrate but arises from interaction of the adsorbate atoms themselves. Recent photoemission measurements[10] of K on Al, which invoked the ionic model to explain the lack of observable 4*s* intensity at low coverage, ignore the change in the nature and width of the 4*s* state with coverage. Finally, the coverage dependence of the bond length between Cs and Ag(111), derived from surface extended x-ray-absorption fine-structure measurements,[9] is suggested to arise from the change in the polarization of the Cs adatom, which is not spherical as assumed in Ref. 9.

In summary, we find that alkali-metal atoms adsorbed on W(110) transfer little if any charge to the substrate. Presumably this is also the case for other W surfaces, and in general for the other alkali metals on other metals. We conclude that at all coverages the change in work function produced by alkali-metal adsorbates on metals results from a dipole moment associated with the polarized adsorbate atom itself. For metals, one must consequently abjure the ionic model in favor of a metallic one, in full agreement with recent theoretical calculations for alkali-metal adsorbates.[12–14,29]

We are indebted to Professor P. J. Estrup for the use of the W(110) sample. The National Synchrotron Light Source at Brookhaven National Laboratory is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences (DOE Contract No. DE-AC02-76CH00016).

[1]J. B. Taylor and I. Langmuir, Phys. Rev. **44**, 423 (1933).

[2]I. Langmuir, J. Am. Chem. Soc. **54**, 2798 (1932).

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

[4]R. L. Gerlach and T. N. Rhodin, Surf. Sci. **19**, 403 (1970).

[5]G. Brodén and H. P. Bonzel, Surf. Sci. **84**, 106 (1979).

[6]L. Surnev, G. Bliznakov, and M. Kiskinova, Solid State Commun. **37**, 87 (1981).

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

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

[9]G. M. Lamble, R. S. Brooks, D. A. King, and D. Norman, Phys. Rev. Lett. **61**, 1112 (1988).

[10]K. Horn, A. Hohlfeld, J. Somers, Th. Lindner, P. Hollins, and A. M. Bradshaw, Phys. Rev. Lett. **61**, 2488 (1988).

[11]N. D. Lang and A. R. William, Phys. Rev. Lett. **37**, 212 (1976).

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

[13]H. Ishida and K. Terakura, Phys. Rev. B **38**, 5752 (1988).

[14]H. Ishida, Phys. Rev. B **39**, 5492 (1989).

[15]G. Treglia, M. C. Desjonquéres, D. Spanjaard, Y. Lassailly, C. Guillot, Y. Jugnet, Tran Minh Duc, and J. Lecante, J. Phys. C **14**, 3463 (1981); C. Guillot *et al.*, J. Phys. C **16**, 1555 (1983).

[16]J. F. van der Veen, P. Heimann, F. J. Himpsel, and D. E. Eastman, Solid State Commun. **37**, 555 (1981); J. F. van der Veen *et al.*, Solid State Commun. **40**, 57 (1981).

[17]V. K. Medvedev, A. G. Naumovets, and A. G. Fedorus, Fiz. Tverd. Tela (Leningrad) **12**, 375 (1970) [Sov. Phys. Solid State **12**, 301 (1970)].

[18]A. G. Fedorus and A. G. Naumovets, Surf. Sci. **21**, 426 (1970).

[19]G. Pirug, A. Winkler, and H. P. Bonzel, Surf. Sci. **163**, 153 (1985). K on Pt(111).

[20]T. K. Sham, G.-Q. Xu, J. Hrbek, and M.-L. Shek, Surf. Sci. **210**, L185 (1989).

[21]M. Domke, T. Madel, C. Laubschat, M. Prietsch, and G. Kaindl, Surf. Sci. **189/190**, 268 (1987).

[22]D. M. Riffe, G. K. Wertheim, and P. H. Citrin, Phys. Rev. Lett. **63**, 1976 (1989).

[23]P. Soukiassian, R. Riwan, J. Cousty, J. Lecante, and C. Guillot, Surf. Sci. **152/153**, 290 (1985).

[24]K. Dückers and H. P. Bonzel, Surf. Sci. **213**, 25 (1989).

[25]Tran Minh Duc, C. Guillot, Y. Lassailly, J. Lecante, Y. Jugnet, and C. Vedrine, Phys. Rev. Lett. **43**, 789 (1979).

[26]S. A. Lindgren and L. Walldén, Solid State Commun. **28**, 283 (1978).

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

[28]D. Heskett, K.-H. Frank, K. Horn, E. E. Koch, H.-J. Freund, A. Baddorf, K.-K. Tsuei, and E. W. Plummer, Phys. Rev. B **37**, 10387 (1988).

[29]W. Ning, C. Kailai, and W. Dingsheng, Phys. Rev. Lett. **56**, 2759 (1986).