Bonding between Alkali Atoms and Metal Substrates Probed by Soft-X-Ray Emission

K.-D. Tsuei and P. D. Johnson
Physics Department, Brookhaven National Laboratory, Upton, New York 11973
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We have studied the bonding of K and Cs to Ni and Cu metal surfaces by examining the soft-x-ray emission from the K $3p$ and Cs $5p$ core holes. The localization of the core hole allows a measurement of the coverage dependence of the valence states specifically associated with the alkali atom. The energy distribution of these states shows, certainly in the case of Ni, that the substrate d_{z^2} state plays a non-negligible role in the chemical bonding. Further for Ni, the quasi-two-dimensional metalization of the alkali overlayers was clearly observed.

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Alkali chemisorption on metal surfaces has been studied both experimentally and theoretically for many years. This interest reflects both the relative simplicity of the valence electron structure of the alkalis and also their technological importance in the promotion of catalytic reactions [1]. However, there is still considerable debate about the nature of the chemical bond between the alkali atom and the metallic substrate. Several papers have discussed whether the bonding is ionic or covalent [1-3] but few have examined the substrate role, especially in the case of the more complicated transition metals. The lack of discussion for adsorption on these latter substrates reflects partly the theoretical complexity of these systems and partly the lack of well-defined experimental observations. The work function change shows a universal trend. Electron energy losses are similar for alkalis adsorbed on both simple and transition metal surfaces [4]. Further, the core level binding energies of alkali atoms show the same monotonic decrease as a function of coverage on both transition and noble metal surfaces [5]. These observations have led to the suggestion that the substrate d bands do not play a significant role.

The existing spectroscopies used to probe the occupied valence states have been unable to identify the substrate role in the chemical bonding. Photoemission spectroscopy (PES) is often limited by background emission from the substrate. For alkali chemisorption systems, the bonding state of interest is close to the Fermi energy and smeared out by hybridization with the substrate [2,6]. It is thus difficult to observe the weak signal from the bonding state derived from an alkali s state on top of strong transition metal d-band peaks. Even on a simple metal such as aluminum in which the background emission is flat the alkali induced states cannot be observed below the work function minimum. This has led to the speculation that the alkali derived states are smeared out over a much wider energy range for low coverage than for high coverage [7]. Another experimental tool that has been applied to the study of alkali chemisorption systems is metastable-He deexcitation spectroscopy (MDS) [8]. This technique probes the electronic structure right at the solid-vacuum interface but it is unclear whether it will provide information on electronic states polarized towards the substrate.

In order to overcome the difficulties experienced by PES and MDS, we use soft-x-ray emission (SXE) or fluorescent decay from the alkali atom core holes. In the SXE process, a core hole is first created by either photon or electron excitation. The subsequent decay of this core hole may proceed via a radiative decay involving a valence electron. Thus the final state in SXE is the same as PES but now it provides information on the local valence density of states (DOS). Little substrate background emission is detected because of the local nature of the adsorbate core state.

The purpose of the present study was the investigation of the influence of the substrate d bands on the bonding to different alkalis. We report the SXE spectra from K and Cs adsorbed on Ni(111) and Cu(111). These substrates were chosen because their lattice constants are nearly identical, leading to electronic structures that differ only by the position of the d band with respect to the Fermi level. The SXE spectra are similar for different alkalis adsorbed to the same substrate but markedly different for Ni and Cu. We are able to provide clear evidence for the involvement of the d bands in the bonding.

In the present experiment the alkali core holes were created by an incident electron beam with 50 eV energy and the emitted photons detected with a grating spectrometer. The latter instrument which has been described elsewhere [9] operates in the normal incidence geometry. Photons were detected at an emission angle of 42° with the electron beam incident along the surface normal. Polarization effects were examined by rotating the crystal.

Alkalis were evaporated from commercial SAES getters. The deposition of alkalis and the measurements were made mostly at 310 K although a few coverages were also checked with the substrates cooled down to 130 K before deposition. No major difference was observed.

Low energy electron diffraction (LEED) studies show that K forms a (2×2) overlayer on Ni(111) corresponding to $\Theta=0.25$ [10], with Θ the density ratio of adsorbate to substrate surface atoms. At this coverage dynamic LEED [11] and surface extended x-ray absorption fine

structure (SEXAFS) [12] have determined the bond site as on top. The saturated monolayer (ML), approximately $\Theta=0.31$, represents an incommensurate hexagonal layer. At lower coverages, a ring pattern was observed, suggesting no island formation. LEED patterns of K on Cu(111) showed similar behavior. SEXAFS studies indicate that for (2×2)K on Cu(111) the adsorption site is also on top but the bond length is slightly longer [12].

The $3p$ SXE spectra for K adsorbed on Ni(111) are displayed in Fig. 1 as a function of coverage [13]. It will be seen that at the lowest coverage (0.03 ML) a peak ($P1$) is observed at a photon energy of 17.8 eV. At $\Theta=0.073$ a shoulder ($P2$) appears on the high energy side of $P1$ growing in intensity and becoming a sharp peak near saturation. The width of the sharp cutoff side of $P2$ ($\sim$0.5 eV) is close to the instrumental resolution for this energy range. Thus this cutoff represents the Fermi edge. At very low coverages this Fermi level cutoff cannot be observed. However, core level photoemission studies of Na adsorbed on Ni and Cu show a monotonic increase in the core level binding energy as the coverage decreases [3]. We hence extrapolate the approximate position of the Fermi level to the low coverage regime as indicated by the broken tick marks in Fig. 1. The binding energies relative to the Fermi energy are approximately 1.4 and 0.4 eV for $P1$ and $P2$, respectively. The integrated intensity is found to be proportional to the coverage. Shown in Fig. 2(a), the Cs $5p$ displays a similar behavior. The binding energies of the corresponding peaks $P1$ and $P2$ for Cs on Ni(111) are 1.1 and 0.25 eV, respectively.

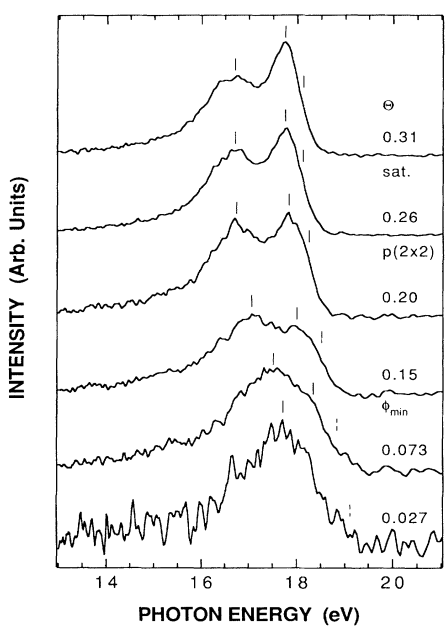

FIG. 1. SXE spectra from the fluorescent decay of K $3p$ core holes on Ni(111) at various coverages. The three tick marks at high coverages denote the peak positions of peaks $P1$, $P2$, and the Fermi level from low to high energies, respectively.

The spectra corresponding to the (2×2)K overlayers on both Ni(111) and Cu(111) are compared in Figs. 2(b) and 2(c). For Cu the sharp Fermi level cutoff was observed even at the lowest coverage probed (0.06 ML). The spectrum showed little variation as the coverage was changed. The low energy peak ($P1$) now only appears as a shoulder on the low energy side of $P2$ at the Fermi energy. The binding energy of $P2$ is 0.4 eV and that for $P1$, after subtracting a background tail from $P2$, is about 3.4 eV. The total integrated intensity for adsorption on Cu is again proportional to the coverage.

First principles theoretical calculations of alkali atom adsorption on a jellium surface as a function of coverage [5] indicate that, at low coverage, the alkali atom forms a bonding state with the substrate electrons. As the coverage increases the valence electrons between the neighboring alkali atoms start to overlap and band formation occurs. The calculation also predicts that the shape of the alkali induced occupied DOS is almost independent of coverage with a long tail extending towards higher binding energy. This state primarily has s symmetry. In addition, the integrated charge in the alkali core region is almost constant.

The coverage dependence of the SXE observed from alkalis adsorbed on the Cu surface compares favorably with these theoretical results. There is always a cutoff at the Fermi level and a long tail extending to higher binding energy. This reflects the sp-like character of the Cu states near the Fermi energy. The alkali atom bonds to these sp electrons. At low coverage, peak $P2$ can only be due to the interaction with the substrate. As the coverage increases, the overlap of the alkali overlayer states leads to the formation of a band which can cut through the Fermi energy and contribute to $P2$. Because the two effects contribute at the same energy it is impossible to

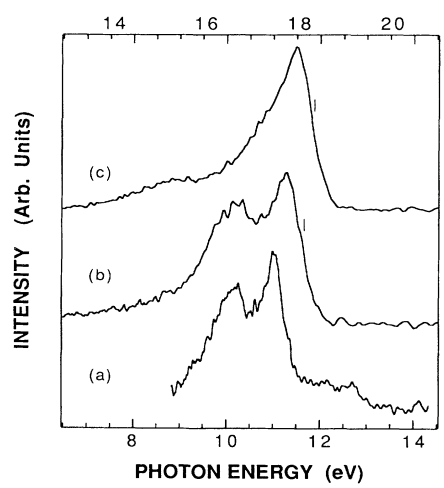

FIG. 2. Spectra of (2×2) overlayers of (a) Cs on Ni(111), (b) K on Ni(111), and (c) K on Cu(111). Note the energy scales are different for the Cs and K spectra at the bottom and top, respectively.

distinguish them. As noted above, the total integrated intensity is proportional to the coverage, suggesting no dramatic change in the charge in the core region, again in agreement with the calculated results.

Comparing the K SXE spectra obtained from the high coverage (2×2) structure on both substrates (Fig. 2) we associate peak $P1$ with the chemical bonding to substrate d states. K is known to sit on the on-top site on both surfaces and d bands with d_{z^2} symmetry occuring at binding energies of 1.1 eV for Ni(111) [14] and 3.6 eV for Cu(111) [15]. The intensity of $P1$ is relatively strong for Ni but weak for Cu because the Cu d orbitals are more localized and further away from the Fermi level. We recall that the K-Cu bond is slightly longer [12] and therefore the interaction between the K and the Cu d orbitals will be weaker than between the K and the Ni d orbitals. The desorption temperature for K is also lower from Cu than from Ni, indicating a weaker chemical bond. The different binding energies of $P1$ for K and Cs adsorbed on Ni(111) indicate different strengths of bonding to Ni d states for these two alkalis. Unlike the K/Cu case, $P2$ for K/Ni does not emerge until some finite coverage. It grows near the Fermi level as the overlap between the alkali atoms becomes more significant. This is the signature of two-dimensional (2D) band formation or metalization of the alkali overlayers. The band crosses the Fermi level similar to that observed for Li adsorbed on Be at saturation in an (inverse) PE study [16].

To offer further support for our assignment, we examine the polarization dependence of the SXE observed for (2×2)K on Ni(111) which is shown in Fig. 3 as a function of the photon emission angle with respect to the surface normal. The spectra are normalized to the total integrated area allowing a comparison of the relative intensity change of $P1$ and $P2$. We note that the intensity of SXE can be expressed, in a one electron picture, as $I \sim \omega \sum |\langle \Phi_c | \boldsymbol{\varepsilon} \cdot \mathbf{p} | \Psi_v \rangle|^2$, or, $I \approx \omega^3 \sum |\langle \Phi_c | \boldsymbol{\varepsilon} \cdot \mathbf{r} | \Psi_v \rangle|^2$, where $\boldsymbol{\varepsilon}$ is the polarization vector, Ψ_v denotes the occupied valence state, and Φ_c the core hole state. Because the initial core hole is localized, the observed spectrum is normally viewed as the local DOS modified by the ω^3 dependence.

In order to understand the polarization dependence of a 2D sp band decaying into a core hole, we may approximate the valence state by a 2D free electron wave $|\Psi_v\rangle = |\mathbf{k}_\parallel\rangle - |\Phi_{c_i}\rangle\langle\Phi_{c_i}|\mathbf{k}_\parallel^b\rangle$ where we have orthogonalized the plane wave to the core states. It is then easy to see that the matrix element, $\langle \Phi_c | \boldsymbol{\varepsilon} \cdot \mathbf{p} | \Psi_v \rangle \approx \boldsymbol{\varepsilon} \cdot \mathbf{k}_\parallel$, favors emission normal to the surface. For a bonding state perpendicular to the surface (z direction), on the other hand, decay into the p_z state is preferred due to the larger overlap. Emission will therefore be stronger parallel to the surface. This polarization dependence for the radiative decay involving in-plane and out-of-plane bonds has been observed in a bulk hcp crystal [17]. The relative intensity change of peaks $P1$ and $P2$ shown in Fig. 3 thus reflects

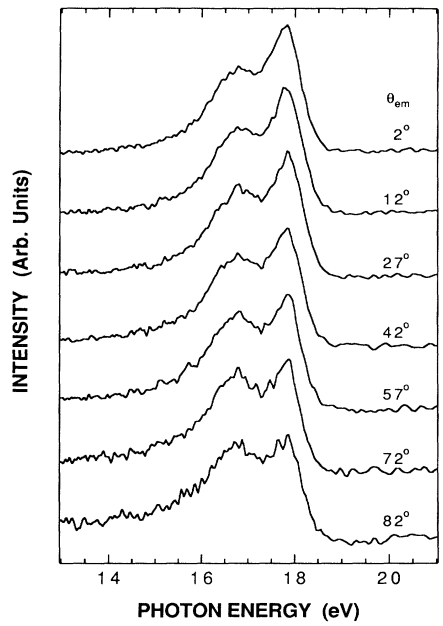

FIG. 3. Spectra of (2×2)K/Ni(111) at various photon emission angles with respect to the surface normal. These spectra are normalized to have equal areas.

their bond orientation. Presented elsewhere [18] a more detailed analysis of the angular dependence of the intensities provides ratios of the transition matrix elements. Transitions into the p_z core hole from the 2D band are larger than transitions into the p_{xy} core holes, reflecting the 2D band spatial distribution of the wave function which is strongly polarized towards the substrate by the chemical bonding.

The local DOS associated with bonding to the substrate and the formation of 2D bands can be analyzed quantitatively for K/Ni. With proper scaling and shifting the lowest coverage spectrum can be fitted to the low energy side of all higher coverage spectra. In Fig. 4, we plot the coverage dependence of the percentage of total emission of peak $P2$ after normalization to ω^3. Initially it grows exponentially approaching 23% close to saturation. In the earlier PE study of Li adsorbed on Be [16] it was determined that, at saturation, approximately 0.33 electron are occupied in the 2D overlayer band, i.e., similar to the present study. We also plot, as the solid line in Fig. 4, the percentage overlap of the $4s$ wave functions for two K atoms placed at a distance equal to the interatomic separation of a hexagonal K overlayer at the same coverage. In that each K atom within the hexagonal overlayer has six nearest neighbor K atoms, caution should be exercised in directly comparing the calculated overlaps with the observed intensity increase of $P2$. Further, the observed intensity will reflect only that component of any band formation falling below the Fermi level. However, the qualitative behavior of the experi-

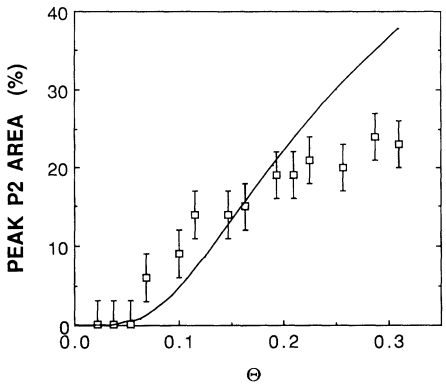

FIG. 4. Coverage dependence of the percentage of the peak $P2$ area after normalization to ω^3 for K/Ni(111). The solid line shows the percentage of the overlap of the $4s$ wave functions between two K atoms placed at a distance equal to the interatomic separation of a hexagonal K overlayer at the same coverage.

mental data is reproduced.

An alternative explanation of $P1$ is that it represents a pure substrate d state tunneling into the neighboring K core hole rather than emission from the bonding orbital. We notice that in all calculations there is an excess charge between the alkali atom and the substrate representing the chemical bonding. The overlap between this excess or hybridization charge and the K core hole is much larger than that of the unperturbed component of the substrate d_{z^2} orbital because the wave function of the latter decays exponentially toward the K atom. The MDS measurement of K/Ni(111) by Lee *et al.* [19] found an intense peak just below the Fermi level and a weaker peak at about 1 eV binding energy. They assign the latter peak as Penning ionization of Ni $3d$ orbitals. However, we note that these data have recently been reinterpreted [20].

In summary we have used a novel approach, SXE, to study alkali chemisorption on metal surfaces. This method provides complimentary information to PES and in some cases overcomes certain limitations of PES. Indeed the localization of the alkali atom core hole restricts the investigation to the local DOS associated with the adatom. In the present study SXE provides clear evidence for the involvement of the Ni d states in the bonding of an alkali atom. Further for Ni, the bonding to the substrate and that between neighboring adatoms can be separated and the metalization of the alkali overlayer is observed.

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