

Top-site adsorption for K on Cu(111) and Ni(111) surfaces

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Surface-extended x-ray-absorption fine-structure (SEXAFS) measurements have been obtained from $p(2 \times 2)$ overlayers of K on Ni(111) and Cu(111) surfaces. The data show that at 65–70 K, potassium occupies the atop site on both substrates, with chemisorption bond lengths of 2.92 ± 0.02 Å on Ni and 3.05 ± 0.02 Å on Cu. The identical adsorption site and small change in bond length, only slightly larger than that predicted from the difference in Cu and Ni lattice constants, are consistent with the expected dominance of adatom-adatom interactions in these near-saturation metallic adlayers. The inability to obtain SEXAFS data from K at lower coverages on these surfaces and at these temperatures, indicative of disorder/multisite occupation, is further evidence of a relatively weak alkali-metal substrate interaction even in the dilute-adatom, nonmetallic-overlayer regime.

I. INTRODUCTION

Alkali-metal adsorption on metal surfaces has received much attention recently because of the unexpected structures observed for near-saturation coverages on primarily close-packed substrates. In particular, it has been observed that alkali-metal adatoms often adsorb on top of substrate atoms instead of in hollow sites,^{1–5} as was previously expected on the basis of other chemisorption systems.⁶ Much of the interest in this phenomenon has arisen because of the debate over how alkali metals bond to metal surfaces.^{7–10} This issue is particularly pointed because alkali-metal adsorption has long been considered one of the simplest forms of chemisorption. Since how an

adatom bonds to a surface is closely related to where it bonds, there is interest in studying what effect the electronic structure of the substrate might have on the geometric structure of the adsorbate.

In this work we have used surface-extended x-ray-absorption fine-structure (SEXAFS) measurements¹¹ to determine the adsorption geometry of $p(2 \times 2)$ potassium overlayers on the (111) surfaces of Cu and Ni. These two fcc metals are nearly identical in geometry, but their electronic structures are different. If d -band participation in the adatom-substrate chemisorption bond is important, this should be manifest in a significant change in bond length, adsorption site, or both.

The $p(2 \times 2)$ overlayer on K on Ni(111) has been stud-

ied recently using low-energy electron diffraction (LEED), finding that K occupies the atop site.² No previous site determination for K on Cu(111) has been reported to our knowledge.

II. EXPERIMENT

The Ni and Cu crystals were aligned by Laue diffraction and mechanically polished to within 0.25° of the (111) direction. They were cleaned by successive cycles of 1.5-keV Ne⁺ bombardment and annealing at 600°C. Dosing with K was performed from a thoroughly degassed getter source which was shuttered to obtain accurate exposures. LEED characterization of the $p(2 \times 2)$ overlayer on Ni(111) showed it to be uniform over the whole crystal. The $p(2 \times 2)$ pattern was well formed at room temperature and became better defined upon cooling the substrate. Potassium adlayers on both Ni (Ref. 12) and Cu (Ref. 13) form incommensurate structures at coverages just above and just below the commensurate $p(2 \times 2)$ structure. Defining the absolute K coverage for the $p(2 \times 2)$ structure¹⁴ as 0.25 monolayers (ML) [a single monolayer here is the number of Ni or Cu atoms in a (111) surface], our observation of sharp $p(2 \times 2)$ superlattice spots on Ni(111) indicates that our sample coverage lies within the range of $0.25 \pm 0.01_5$ ML. Saturation occurs at approximately 0.31 ML on both substrates.^{12,13} Lower coverage surfaces, calibrated against the $p(2 \times 2)$ surface using K/substrate Auger intensity ratios and x-ray-absorption edge jumps, were also prepared. The temperature at which the crystals were dosed was approximately 60°C, after which they were quickly cooled using a copper braid attached to a cryogenic cold finger at 15 K. In the present experiments, sample temperatures could be cooled no lower than about 65 K.

The SEXAFS experiments were carried out using the AT&T Bell Laboratories X15B beamline at the National Synchrotron Light Source at Brookhaven National Laboratory. Such measurements from alkali-metal overlayers are inherently difficult because the surfaces are extremely reactive and because relatively long measurement times (several hours) are needed for the accumulation of high-quality data. The X15B beamline¹⁵ contains several features which minimize these difficulties. The beamline is Be windowless and has variable incident-angle collimating and focusing mirrors which bracket a fixed-exit monochromator, so that monochromatic x rays can be focused onto the sample with reasonably high efficiency. SEXAFS data were obtained using a solid-state fluorescence detector windowed around the K $K\alpha$ fluorescence line. The strong Ni $K\alpha$ fluorescence from the substrate, excited by the third harmonic of the Ge(111) monochromator crystals, falls outside the analyzer window but still contributes significantly to the overall counting and saturates the detector. This problem was eliminated by increasing the angle on the Pt-coated collimating mirror to 1.35°, effectively converting it to a low-pass photon energy filter. The resulting count rates of K $K\alpha$ radiation were low, typically 100 Hz, but the edge jump (i.e., signal to background) exceeded 400%.

The ultrahigh vacuum chamber in which the experi-

ments were performed had a base pressure in the high 10^{-11} -Torr range, of which the principal component was hydrogen. Partial pressures of other gases were more than an order of magnitude lower. After cleaning the crystal, impurity concentrations were below detectable levels in the Auger-electron spectra. The upper limit of O contamination, in the form of CO after dosing with K, was 1% of the K coverage. Surface cleanliness was monitored during the SEXAFS measurements using the structure in the near-edge region, which was extremely sensitive to the presence of contamination. No substantive changes were observed during the course of the 2–3 h used in accumulating multiple 30-min scans.

III. RESULTS

For K -edge x-ray absorption, the SEXAFS amplitude function $A(k)$ is proportional to $|\epsilon \cdot \mathbf{r}|^2$, where ϵ is the electric vector of the incident radiation, and \mathbf{r} is the direction of the chemisorption bond.¹⁶ Identifying the atop adsorption site in these measurements is particularly straightforward, therefore, because $A(k)$ goes to zero when the incident polarized radiation is normal to the surface, i.e., ϵ (lying in the horizontal plane) is then perpendicular to \mathbf{r} . [Such behavior in SEXAFS data has been observed for atop adsorption of Cl on Si(111) and Ge(111) surfaces¹⁷.] In the present experiments, data were taken at normal and at 30° grazing incidence angles.

Figure 1 shows the grazing and normal incidence potassium K -edge absorption data for the $p(2 \times 2)$ phase on Ni(111) at 70 K. The strong polarization dependence is clearly apparent, with the SEXAFS oscillations being prominent only at grazing incidence. Figure 2 shows the k^2 -multiplied SEXAFS $\chi(k)$ obtained by subtracting a smoothly varying polynomial background from the raw data, normalizing the amplitude of the oscillations to the edge jump, and converting from energy in eV to wave vector k in \AA^{-1} .¹⁶ The grazing incidence data show SEXAFS over the full energy range, while at normal in-

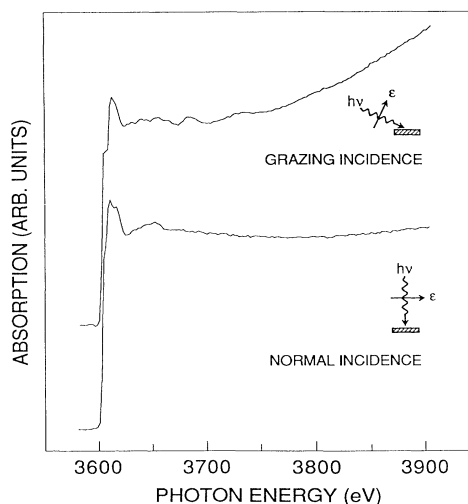


FIG. 1. Raw x-ray-absorption potassium K -edge data for the Ni(111)- $p(2 \times 2)$ -K surface at grazing and normal incidence angles.

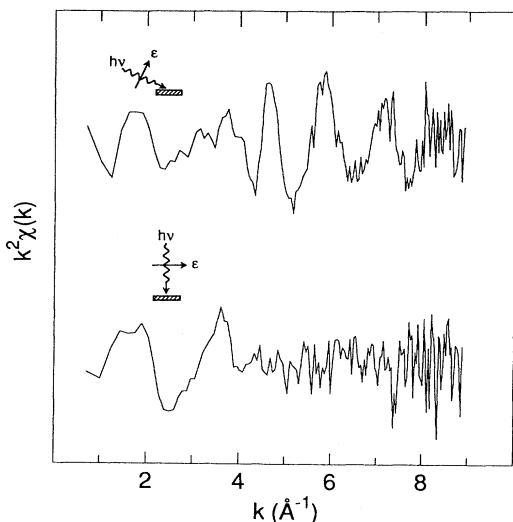


FIG. 2. Background-subtracted, edge-normalized, k^2 -multiplied SEXAFS for Ni(111)- $p(2 \times 2)$ -K.

vidence there are no oscillations $> 4 \text{ \AA}^{-1}$. The structure below 4 \AA^{-1} ($< 60 \text{ eV}$), evident at both incident angles, will be seen to arise largely from the second-neighbor shell.

The Fourier transforms of the $k^2\chi(k)$ data in Fig. 2, truncated at $\sim 2.5 \text{ \AA}^{-1}$, are shown in Fig. 3. A large peak dominates the grazing incidence transform near 2.6 \AA (uncorrected for the phase shift), while the normal incidence transform, plotted on the same scale, is featureless above the noise level around this distance. From the above discussion, the clear absence of a first-neighbor peak in the normal incidence data is direct proof that K must occupy the atop site.

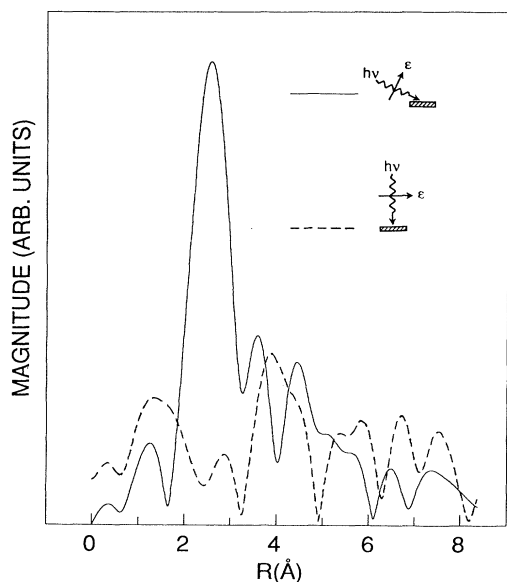


FIG. 3. Fourier transforms of the data in Fig. 2. The lack of a first-neighbor peak in the normal incidence data indicates atop adsorption for K.

To obtain distance information, we use standard EXAFS analysis procedures¹⁶ to remove residual low-frequency background and high-frequency noise components. These are readily identified by their strong sensitivity in amplitude and position with changes in background, data range, and statistical quality. The first-neighbor peak at 2.6 \AA is unaffected by these factors, but the smaller peak at $\sim 3.6 \text{ \AA}$, which we identify with the second-neighbor shell, is dependent on them (although much less so than a noise component). This behavior of the second-shell peak is a consequence of our having truncated a part of the SEXAFS associated with that shell, namely the oscillation at 2 \AA^{-1} (the data at such low k cannot be used in the analysis because EXAFS involves scattering from only the higher-energy core-dominated potentials¹⁶). Despite this inherent limitation on distance information from the second shell, we will see that its inclusion in the analysis provides useful insight into the interaction between K and the substrate. The filtered data, obtained by placing a window function around both shells ($1.6\text{--}4.4 \text{ \AA}$) and inverting the result back into momentum space, is shown as the solid line in Fig. 4.

Determining accurate bond lengths requires reliable absorbing and backscattering phase shifts, so we have used empirical values from the model compound CuCl, cooled to 80 K to avoid anharmonic distortions.^{11,16} The choice of this compound is based on its chemical stability, its simple and well-characterized crystal structure, and the fact that Cu and Cl differ in Z from Ni and K by only 1 and 2, respectively, resulting in a small ($\sim 0.01 \text{ \AA}$) and correctable change in bond length¹¹ (confirmed by comparing calculated values using K-Ni versus Cl-Cu FEFF5 theoretical phase shifts¹⁸). Using this phase shift, the filtered data were least squares fitted with two shells. The result is shown as a dashed line in Fig. 4. The K-Ni(111) first-neighbor bond length obtained from the

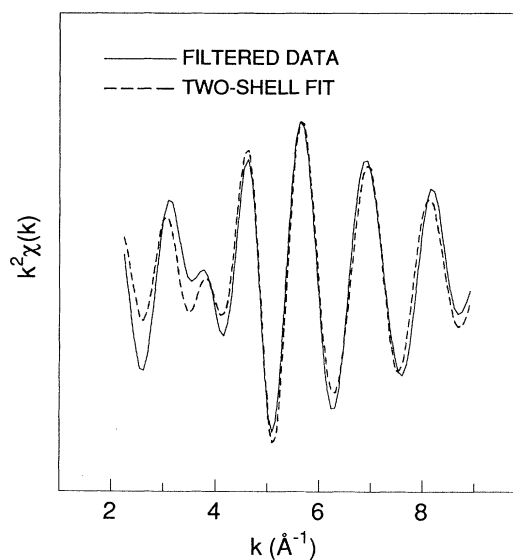


FIG. 4. Comparison of the SEXAFS-filtered data with results of a two-shell fit. The filter encompassed the peaks at 2.6 and 3.6 \AA in Fig. 3.

fit is $r_1 = 2.92 \pm 0.02 \text{ \AA}$. (This value is identical to that obtained in a standard one-shell analysis, i.e., there is no effect of the second shell on r_1 .) Deviations between the fit and data are largest at low k , where the effect of excluding the large oscillation at 2 \AA^{-1} is most significant. Accordingly, the value of $r_2 = 4.1 \text{ \AA}$ for the six second-neighbor surface Ni atoms is not reliable.

The reason for including the second shell in the analysis of the grazing incidence data becomes clear in Fig. 5, where the relative contributions from these two shells in the fit are compared. The difference in amplitude functions is striking, reflecting a large Debye-Waller-like damping in the second shell at higher values of k . This arises from the additional contribution of in-plane vibrations in $A_2(k)$, which are much weaker in $A_1(k)$. It is the unavoidable combination of lost higher- k information, coupled with the omission of structure at lower k , which is responsible for the unreliable determination of r_2 .

SEXAFS measurements have also been performed at other K coverages and Ni(111) temperatures. Below 0.13 ML, i.e., at less than 50% of the $p(2 \times 2)$ coverage, no measurable SEXAFS above 4 \AA^{-1} was observed, indicative of a disordered or incommensurate overlayer. Between ~ 0.2 – 0.3 ML, i.e., within $\pm 20\%$ of the $p(2 \times 2)$ coverage, SEXAFS characteristic of the atop site was readily apparent [despite the fact that the $p(2 \times 2)$ spots either split or broaden at coverages only $\sim 4\%$ (0.01 ML) above or below 0.25 ML, respectively]. The first-neighbor bond length in these other systems varied only slightly with temperature and coverage. In particular, at 0.23 ML and 145 K, r_1 increased to 2.99 \AA ; at 0.28 ML and 120 K, r_1 increased to 2.97 \AA .

The largest change with coverage and increasing temperature was not in r_1 but in $A_1(k)$, which decreased by as much as a factor of 2.5. The observed decrease was

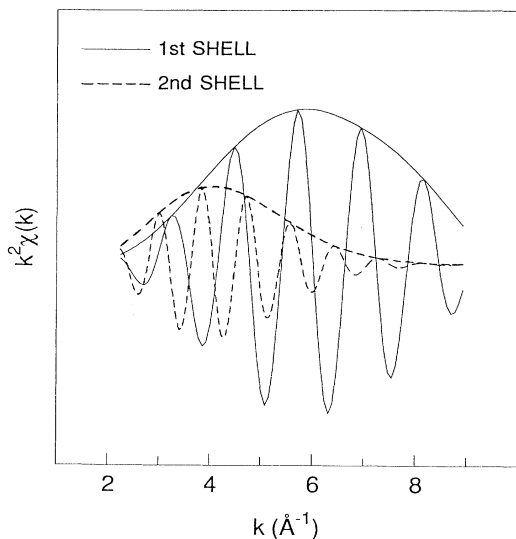


FIG. 5. Individual first- and second-neighbor contributions to the fit shown in Fig. 4. Note the significantly shifted amplitude function of the second shell due to enhanced vibrational motions.

uniform over the whole energy range, not just at higher k as would be expected from Debye-Waller-like damping. This indicates a lowering of the effective coordination of Ni around the K atoms. Since K still shows only atop adsorption at these higher temperatures, the amplitude reduction must be due to a lowering of the “SEXAFS-active” fraction, i.e., those K atoms contributing to the observed SEXAFS. The reasons for this are discussed in Sec. IV.

The SEXAFS experiments for K on Cu(111) at 65 K were carried out and analyzed identically to those for K on Ni(111). The polarization-dependent $k^2\chi(k)$ data are shown in Fig. 6, indicating that the K atom also occupies the atop site on Cu(111) at this coverage and temperature. The smooth line superposed on the grazing incidence spectrum is the two-shell fit to the filtered data, analogous to that in Fig. 4. With the CuCl model compound, we determine the K-Cu first-neighbor bond length to be $r_1 = 3.05 \pm 0.02 \text{ \AA}$.

IV. DISCUSSION

A. Atop adsorption site

The fact that potassium adsorbs in the atop site for both Ni(111) and Cu(111) surfaces may not seem surprising, since this site has now been reported for Cs/Cu(111),¹ Cs/Ru(0001),³ Rb/Al(111),⁴ and K/Al(111).⁵ However, in the absence of more complete information such hindsight can be misleading. For example, the result for Cs/Cu(111), obtained with fewer beams than typically used in more current LEED studies, had been viewed with caution during the nine or so years it stood standing as the only system in which an alkali-metal adatom was assigned to occupy an atop site. It is only within a short and very recent period of time that

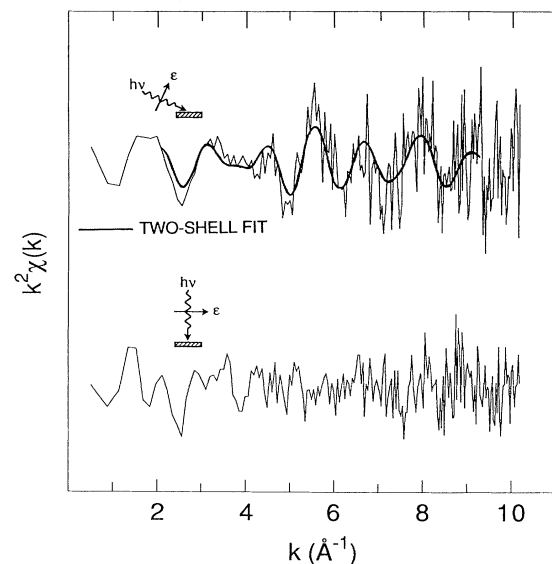


FIG. 6. Same as Fig. 2, but for the Cu(111) $p(2 \times 2)$ -K surface. The result of a two-shell fit, similar to that in Fig. 4, has been superposed on the grazing incidence angle data.

reports have appeared of such unexpected adsorption behavior for alkali-metal adatoms in other systems. The role of the substrate electronic structure, and in particular that of the d electrons, should also not be taken for granted, despite the apparently similar behavior reported for Al(111) (Refs. 4 and 5) and Ni(111).² More careful inspection reveals that atop adsorption on Al(111) occurs only at low temperatures; at room temperature, an energetically more stable configuration evolves whereby the alkali metal intermixes with the Al. Therefore, it is not obvious that the same atop adsorption site should be found for substrates of different $3d$ electronic configuration at both room and low temperatures.

What can be learned about the factors influencing atop adsorption of alkali-metal adatoms? Based on the present and previous work, several general observations can be made. (1) All systems in which atop sites have been identified involves closest-packed fcc(111) and hcp(0001) metal substrates. (2) Atop sites have been seen only for the larger alkali metals; Li and Na have yet to be included in this category. (3) All the alkali-metal coverages exhibiting atop adsorption have been at or near saturation values. Collectively, these findings indicate that there is a very small lateral variation of the adsorbate-substrate potential, i.e., atop adsorption reflects a very shallow minimum for the lowest-energy configuration. This is not a new picture, of course, since the dominance of alkali-metal adatom-adatom over adatom-substrate interactions is already well established.^{19,20} At low coverages, strong dipolar repulsions typically lead to incommensurate structures; at higher coverage, spatial proximity leads to formation of metallic overlayers. What appears to be new is how this picture ties into the recent findings of atop adsorption, namely, that a set of fairly restrictive conditions are required—*large* alkali-metal adatoms at *near-saturation* coverage on very *weakly corrugated* surface potentials.

There are three results from this work which support the views that adatom-adatom repulsive interactions are dominant, that the potential minimum for atop adsorption is shallow, and that, accordingly, the balance between adatom-adatom versus adatom-substrate interactions to achieve atop adsorption is indeed very delicate. The first is our observation of much larger vibrational displacements in the 0.25-ML second-shell SEXAFS data. This is a direct indication of enhanced in-plane motion resulting from a wide and shallow potential well. The second is our inability to observe any measurable SEXAFS for K on Ni(111) at <0.13 ML, even at 70 K. This reflects the fact that the main hindrance to lateral motion of the adatoms is simply the presence of other adatoms. The third is the unusual thermal behavior of this system. As noted above, the uniform decrease in the SEXAFS amplitude at all values of k indicates a reduced “SEXAFS-active” fraction of K atoms. The absence of an apparent bond-length shortening with increasing temperature rules out an anharmonic effect.¹⁶ This thermal behavior is again related to the very flat potential well in which the atop-site atoms reside. As the temperature increases, the small but available free surface area can accommodate thermally excited adatoms into nonatop sites,

even at these relatively low temperatures of 120–145 K. Some Boltzmann fraction of adatoms now occupy a distribution of other sites, whose SEXAFS signatures destructively interfere and reduce the overall SEXAFS amplitude of the remaining atop adatoms. It would be interesting to study this behavior more systematically as a function of temperature and coverage.

Very recent calculations for predicting adsorption sites as a function of coverage have been performed for Na and K on Al(111).²¹ These results show that for Na, the threefold hollow adsorption is the most energetically favorable at low coverage, and that the atop site is the least energetically favorable one at any coverage, consistent with experimental findings at low temperatures (at higher temperatures, an intermixed configuration is most favorable). For K, the results predict a similar behavior at low coverage, but near saturation the atop site becomes essentially degenerate in energy with the hollow site, again consistent with experiments at low temperature. Given the delicate balance of factors that must be considered, these theoretical findings are most impressive. Similar calculations applied to systems not yet experimentally studied are eagerly anticipated.

B. Adatom-substrate bond length

Before discussing what might be learned about the adatom-substrate interaction from bond lengths measured in the present and previous work, two points should be mentioned. First, the bond length determined here for the Ni(111) $p(2\times 2)$ -K surface, 2.92 ± 0.02 Å at 70 K, differs from that obtained using LEED,² 2.82 ± 0.04 Å at 120 K, and angle-resolved photoelectron fine structure (ARPEFS),²² 3.02 ± 0.01 Å at 130 K.²³ Since we observe that the K-Ni(111) distance only increases with increasing temperature and different coverage (2.99 ± 0.02 Å at 0.28 ML and 120 K, 2.97 ± 0.02 Å at 0.23 ML and 145 K), the smaller bond length obtained with LEED cannot be due to such differences in sample preparation or measurement conditions; they may, however, be contributing factors in the ARPEFS data. Because systematic studies of temperature and coverage have not yet been performed, and because systematic errors in the LEED and ARPEFS measurements remain a possibility, the discrepancies are still unresolved. In the following discussion, these small differences²³ will not affect our conclusions.

The second point relates to the description of the alkali-adatom-metal-substrate bond as being primarily ionic, covalent, or metallic. These simple terms are historically and pedagogically useful for discussing earlier theoretical models, but more recent experimental²⁵ and theoretical²⁶ work indicates that there are different interpretations in assigning the origin and orbital parentage of the charge that is localized between the adatom and metal substrate. Regardless of how the interpretations may vary about the alkali-adatom-metal-substrate bond, there is agreement nonetheless that the debate centers around the fact that this bonding changes in going from low- to high-coverage regimes. Since it is also agreed that the alkali-metal adlayer is metallic at higher or near-

saturation coverages, the discussion simplifies into how the bonding changes in the low-coverage regime. It has been assumed that a straightforward test of this is to look for changes in alkali-adsorbate–metal-substrate bond length as a function of coverage. We now show that such a test requires more care than had been appreciated.

Surface bond length changes involving *electronegative* adsorbates have previously been correlated with simple concepts of ionic or covalent bonding²⁷ (such terms are less contentious for these adatoms). It was shown that (i) for a given substrate, surface, and adsorption site, bond lengths *increase* with *increasing adatom electronegativity*, indicative of greater ionicity, and (ii) for a given adatom-substrate pair, bond lengths *increase* with *increasing coordination number*, again consistent with greater ionicity (recall that covalent bonds are shorter and more directional to optimize orbital overlap, while ionic bonds are longer and less directional to optimize Coulombic interactions). Now, in the case of *electropositive* adatoms, the first trend, (i), cannot be tested because the electronegativities of the alkali metals are too similar. Trend (ii), however, can be tested. For the cases of K/Al(111) (onefold vs sixfold),⁵ K/Ni(111) and K/Ni(100) (onefold vs fourfold),^{2,28} Na/Al(100) and Na/Al(111) (fourfold vs sixfold),^{29,24,4} and Cs/Ru(0001) (onefold vs threefold),³ the higher-coordinated site *always* has a longer bond.

It should now be apparent that in looking for a correlation between alkali-adsorbate coverage and a change in bonding—specifically, for a given alkali-adsorbate and metal substrate, bond lengths *decrease* with *decreasing coverage*, indicative of increasing “ionicity”—two important factors must be considered before a meaningful trend can be established. First, the coverage change must occur over a sufficiently wide range to sample the low-coverage regime, and second, there must be no corresponding change in coordination which goes in the same direction as the trend being tested. Of the approximately two dozen alkali-metal systems studied thus far, only three have reported variations in coverage with sufficiently high precision to infer reliable information. For Cs/Ru(0001),³ the coverage increases from 0.25 to 0.33 ML, which does not include the low-coverage region. Furthermore, the coordination increases from one to three. [Interestingly, the higher coordination site at higher coverage is opposite to the calculations²¹ for K/Al(111).] For Cs/Ag(111),⁷ the coverage increases from 0.15 to 0.3 ML, which covers both high and low regions, and a 0.3-Å bond-length increase was reported. Unfortunately, the coordination was not determined. Finally, for Na/Al(111),²⁴ the coverage changes from 0.16 to 0.33 ML, and the sixfold coordination remains the same. Significantly, with both provisos satisfied in this particular example, *no* change in bond length was observed. Therefore, the sum of these results is that no definitive evidence yet exists for a substantive change in alkali-adsorbate–metal-substrate bonding in going from low- to high-coverage regimes.

It is precisely because we were looking for a clear-cut change in site and/or bond length with coverage that we attempted to study K on Ni(111) and Cu(111) surfaces at <0.13 ML. Even if the adsorption site was different at

lower coverage, the coordination could only be larger than the onefold value measured at 0.25 ML. From the correlations discussed above, the bond length would then *increase* with higher coordination at *lower* coverage, exactly *opposite* to simple expectations based on an increasingly “ionic” alkali-adsorbate–metal-substrate bond. Unfortunately, as noted above, this test could not be made at 65–70 K.

The last comparison involves bond lengths between K/Ni(111) and K/Cu(111). The same measurement technique, coverage, adatom, and coordination in these systems should allow differences in alkali-adsorbate–metal-substrate bonding to be reliably identified. Taking the different lattice constants into account and adding the uncertainties in the individual bond-length determinations gives a 0.06 ± 0.04 -Å longer bond length for K-Cu(111). This suggests somewhat greater adatom-substrate interaction involving the unfilled Ni $3d_{z^2}$ orbitals relative to that in Cu, consistent with recent x-ray-emission work.³⁰ Given our picture for the dominance of adatom–adatom over adatom–substrate interactions, however, it is difficult to attach much significance to this result.

V. CONCLUSIONS

A little more than a year ago, there was a single report of atop adsorption for an alkali-metal atom on a metal surface. Since then, five more systems (including the present study) have been found to exhibit similar behavior. The fact that this result runs counter to that of any other known adsorbate on a metal surface is significant; that it occurs for an alkali metal—one of the oldest studied and “simplest” adsorbates—demands that conventional wisdom and perceived understanding of alkali-metal adatom bonding should, at the least, be reevaluated. Indeed, the renewed discussions over how such bonding should be described at low adatom coverage are in keeping with this view. The difficulties in discussing the alkali-metal-substrate bond due to limitations or inadequacies in the language do not prevent experimental and theoretical progress from being made. Instead, they simply force more careful consideration of the problem.

In the present work, we have focused attention on the factors generally related to atop adsorption behavior and concluded that a delicate balance of coverage, substrate corrugation, and adatom size is required. We have also argued that there presently exists no definitive experimental evidence for a change in alkali-metal-adatom bond length in going from low- to high-coverage regimes. Future coverage- and temperature-dependent studies of alkali-metal-adatom bond lengths and coordination numbers on more corrugated surfaces should clarify this problem.

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