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Core-level photoemission from alkali metals on Ru(001)

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We report soft-x-ray photoemission results on the core-level binding energies of Li, Na, K, and Cs adsorbed on Ru(001). For all four alkali metals, the saturated alkali-metal–Ru interface core level and the second- (surface-) layer core-level binding energies differ by as much as 0.85–1.25 eV. Surface versus bulklike core-level shifts are reported for Li, K, and Cs, which are 0.55 eV for Li and ~0.25 eV for the other two. For increasing coverages of Li, Na, and K in direct contact with Ru, there are significant decreases in the core-level binding energies, the total shift ranging from ~ −1.25 eV for Li to ~ −0.80 eV for K; the shift for Cs is small and the reasons for the deviation are discussed. A comparison between our observations and the prediction from the thermodynamic model of Johannson and Mårtensson is also given.

I. INTRODUCTION

We have carried out a comparative study of the systems Li, Na, K, and Cs adsorbed on Ru(001), with the hope of deriving physical and chemical trends across the alkali-metal group. The objective of this paper is to document and summarize our observations on the coverage dependence of the core-level photoemission spectra of these alkali-metal overlayers. A brief report on this aspect of our work has been given,[1] and some detailed results on the K $3p_{3/2}$ and the Cs $5p_{3/2}$ core levels are given elsewhere.[2-5] The overall features observed are (i) layer-resolved binding energies for all four alkali-metal overlayers, and (ii) a decreasing binding energy upon increasing the coverage of Li, Na, and K at the interface in direct contact with Ru. It may be noted that layer-resolved binding energies have also been reported by other workers for Cs/Si(111)(1×2) and K/Pt(111).[6-9] Binding-energy shifts of K single adlayers on Pt(111) and Ru(001) have been studied with low-energy resolution.[7-9] Results will be compared when appropriate. To our knowledge, coverage-dependent Li and Na core-level shifts have not been reported by other workers.

II. EXPERIMENT

The results to be shown were obtained in two runs at the National Synchrotron Light Source (Upton, NY), with the use of the U14 Plane Grating Monochromator. The data to be presented here were obtained with photon energies between 35 and 105 eV. The base pressure of the ultrahigh-vacuum chamber was typically about $(1-2)\times10^{-10}$ Torr. An angle-resolving electron-energy analyzer (Vacuum Generators, Inc. VG-ADES-400) was used in run I, normally with a pass energy of 10 eV or an energy resolution of 0.18 eV. A double-pass cylindrical mirror analyzer (CMA, Perkin Elmer, Physical Electronics PHI-15-255G) was used in run II, with 0.15 eV resolution. In run I, *p*-polarized light was incident at ~45° relative to the sample normal, and the photoelectrons were detected at ~50° away from the sample normal in the other direction. In run II, the incident angle was ~60° and the sample normal was ~30° relative to the CMA axis. The coverage-dependent core-level shifts were not affected by the type of analyzer and the geometry used. We shall report photoemission spectra normalized to a stored beam current of 100 mA.[10]

After Ar-ion sputtering, the Ru(001) surface was cleaned by several cycles of oxygen and flashing to 1500 K. Alkali-metal overlayers were evaporated from SAES Getters dispensers, and the background pressure did not rise above 5×10^{-10} Torr during evaporation. The coverages were varied by briefly heating a multilayer, deposited at a sample temperature below 200 K, to various temperatures in the range ~800 to ~300 K to achieve partial desorption. The alkali metals could be desorbed by heating the sample to ~ 1450 K, and a clean surface was obtained without residual traces of alkali metals. In run I, low-energy electron diffraction (LEED) was performed to aid in the preparation of submonolayers prior to photoemission. The cleanliness of the overlayers was judged by photoemission and thermal desorption. Thermal desorption of overlayers prepared under a similar manner in a separate chamber showed very small levels of contamination which did not affect the photoemission spectra.[11]

III. RESULTS

We shall first present some Na $2p$ and Li $1s$ core-level spectra in Figs. 1 and 2. Their coverage dependence will then be summarized graphically in Fig. 3. The core-level spectra of K $3p$ and Cs $4d$ will be shown in Figs. 4 and 5, respectively.

Figure 1 shows the coverage dependence of the Na $2p$ core level: curves 2–4 show that the binding energy decreases with increasing coverage in the layer adsorbed directly on Ru. [The full range of such a decrease will be better seen in Fig. 3(b)]. Further increase in coverage results in the emergence of a second-layer Na core level at 31.15 eV, or 0.60 eV larger binding energy with respect to the interface (curve 5). We also see the continuation of a small decrease in the binding energy of the Na/Ru interface core level after the second Na layer sets in (compare curves 4 with 5 and 6). Estimates of Na coverages up to a fully saturated first layer [~ 1 monolayer (ML), curve 4] are based on the following: (i) a distinct $(\sqrt{3}\times\sqrt{3})R30^\circ$ LEED pattern observed for curve 3 corresponds to $f=\frac{1}{3}$ with reference to a Ru(001) surface atomic density $f=1$ for 1.572×10^{15} atoms/cm^2; (ii) the photoemission peak area, after a linear background subtraction, is approximately proportional to the coverage in this regime. For curve 2 the estimated value $f=0.23$ is in harmony with $f=0.25$ expected for an ideal (2×2) overlayer. For curve 4 the estimated $f=0.56$ is larger than the value $f=0.44$ expected for an ideal $(\frac{3}{2}\times\frac{3}{2})$ overlayer, but lies close to the saturated first layer value $f=0.53$ reported previously.[12,13] These coverage estimates support the assignment of curve 4 as ~ 1 ML, that is, a single atomic layer in which the Na-Ru direct interaction is saturated. For curve 5 the coverage of ~ 1.5 ML is estimated from the relative peak heights of the Na/Ru interface core level and the second-layer Na core level.[14] It may be noted that the photoemission intensities for the thicker overlayers are smaller than expected. This may be attributed to the increasing importance of surface- and bulk-plasmon losses, which become especially evident in the multilayer (curve 7) as broad peaks around ~ 4 and ~ 6 eV towards higher binding energy relative to the main Na $2p$ peak. Other multielectron excitation processes, as well as changes in "escape probability," may also come into play.

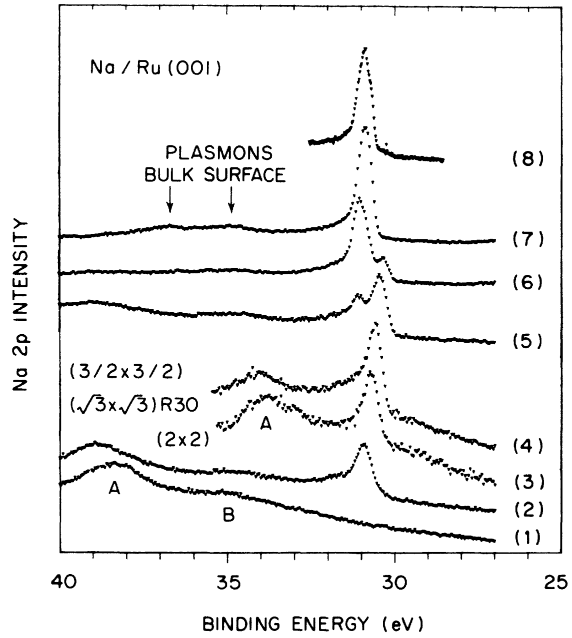

FIG. 1. Na $2p$ photoemission for varying Na coverages on Ru(001), excited by $h\nu=55$ eV except where noted. Curve (1), clean Ru background, run I; curve (2), $f=0.228$, distinct (2×2) LEED pattern, run I; curve (3), $f=\frac{1}{3}$, distinct $(\sqrt{3}\times\sqrt{3})R30^\circ$ LEED pattern, $h\nu=50$ eV, run I; curve (4), $f=0.56$, ~ 1 ML, $(\frac{3}{2}\times\frac{3}{2})$ LEED pattern, $h\nu=50$ eV, run I; curve (5), ~ 1.5 ML, run I; curve (6), thin multilayer, run I; curve (7), multilayer, run I; curve (8), multilayer with a total-energy resolution of <0.2 eV, run I. $f=1$ denotes 1.572×10^{15} atoms/cm^2. 1 ML means a single atomic layer saturated in an alkali-metal–Ru direct interaction. The peaks labeled A and B are final-state peaks.

Figure 2 shows the behavior of the Li $1s$ core level. As in the case of Na, the Li $1s$ binding energy decreases towards the Fermi level as the coverage in the first layer is increased, as seen in curves 1–3. However, the decrease in the Li/Ru interface core-level binding energy, after the emergence of the second-layer Li $1s$ peak (curve 4), is significantly greater than that for Na on Ru. An additional feature is that, unlike Na $2p$, the Li $1s$ bulk-like core level, lying at 55.0–54.95 eV in curves 5 and 6, is

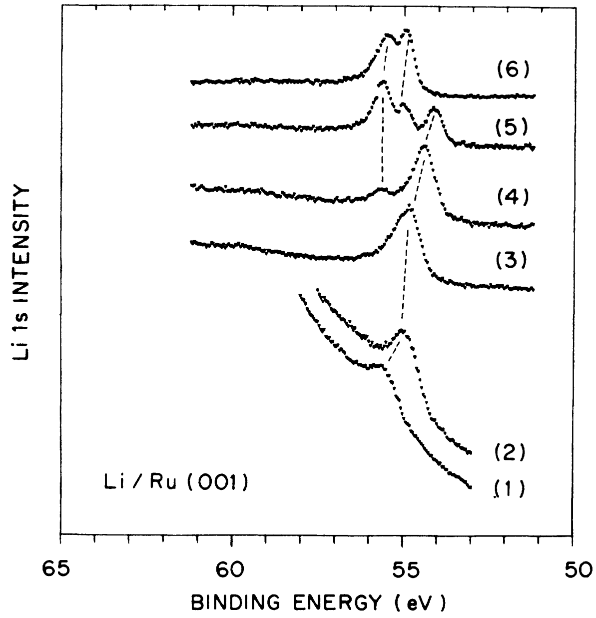

FIG. 2. Li $1s$ photoemission for varying Li coverages on Ru(001), excited by $h\nu=80$ eV unless otherwise stated. Curve (1), ~ 0.36 ML, $h\nu=75$ eV, run II; curve (2), ~ 0.78 ML, $h\nu=75$ eV, run II, curve (3), ~ 1 ML, run I; curve (4), ~ 1.2 ML, run I; curve (5), thin multilayer, run I; curve (6), multilayer, run I. 1 ML means a single atomic layer saturated in an alkali-metal–Ru direct interaction. The dashed lines trace the evolution of various origins of the core level.

well separated from the surface peak at 55.55–55.50 eV. For lack of definitive LEED patterns, the coverages quoted in Fig. 2 are only estimates based on the assignment of curve 3 as ~ 1 ML, and the scaling of the photoemission peak areas after background subtraction. If curve 3 is assumed to correspond to a reported saturation value of $f=0.46$,[15] then curves 1 and 2 correspond to $f=0.16$ and 0.34, respectively.

Figure 3 summarizes graphically the coverage dependence of both Li 1*s* and Na 2*p* on Ru(001), including additional data not shown in Figs. 1 and 2. For Na at the lowest coverage, $f\sim 0.05$, that we have investigated, a rather deep binding energy of 31.25 eV is found. We do not know if this might be due to defects. The coverages between 2 and 3 ML in the graphs correspond to the "thin multilayers" referred to earlier (Fig. 1, curve 6 and Fig. 2, curve 5) and are estimates based on the attenuation of the interface core levels. The bulklike overlayers are located at 5 ML only for the graphical presentation.

Figure 4 shows the general features of K 3*p* on Ru (001). The peak position shifts by ~ -0.7 eV (towards the Fermi level) from $f=0.13$ in curve 1 to $f=\frac{1}{3}$ or ~ 1 ML in curve 4. The surface core level appears at ~ 0.85 eV higher binding energy relative to the interface core level in curve 5. However, the K 3*p* spectra are actually complicated by a spin-orbit splitting of approximately 0.23 eV as shown by detailed analysis of spectra acquired with high-energy resolution.[4,5] It is shown that, for each spin-orbit-component, the binding-energy difference between the surface and the interface (in the presence of the second K layer) core levels is ~ 1.0 eV, and the surface core level lies at ~ 0.25 eV (higher binding energy) relative to the bulk core level. For the data in Fig. 4, we have assumed that curve 4, with a well-defined

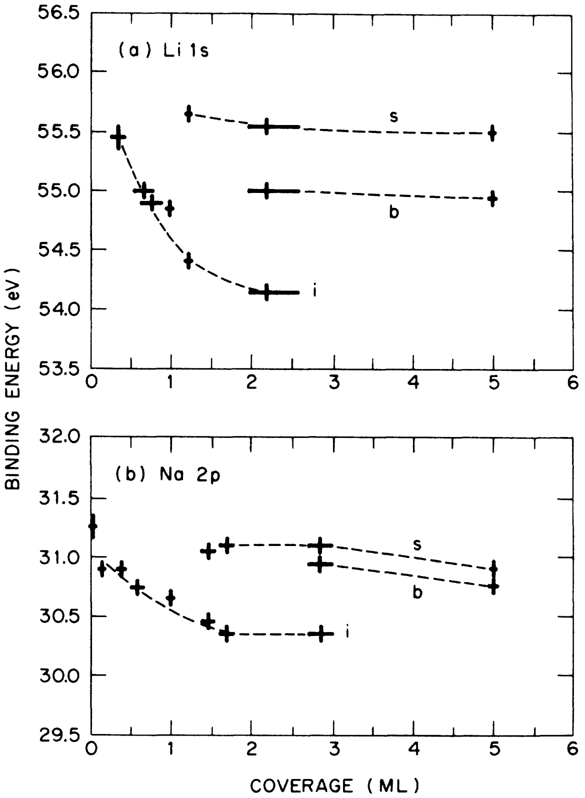

FIG. 3. Coverage dependence of Li 1*s* and Na 2*p* core-level binding energies: *i*, interface; *s*, surface; *b*, bulklike. 1 ML means a single atomic layer saturated in alkali-metal–Ru direct interaction. For thick Na, the 2*p* peak energy is taken to correspond to the surface core level, and the shoulder at 0.15 eV smaller binding energy. [Fig. 1, curve (8)] is taken to be the bulk core level.

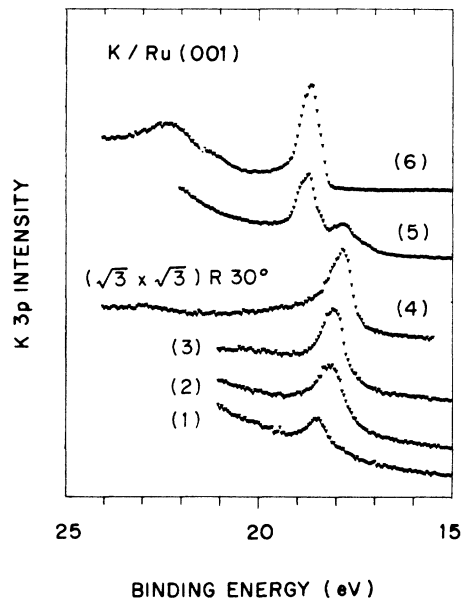

FIG. 4. K 3*p* photoemission excited by $h\nu=40$ eV. Curve (1), $f=0.10$, run II; curve (2), $f=0.24$, fuzzy (2×2) LEED pattern, run II; curve (3), $f=0.26$, run II; curve (4), $f=\frac{1}{3}$, ~ 1 ML ($\sqrt{3}\times\sqrt{3}$)R30° LEED pattern, run I; curve (5), thin multilayer, run II; curve (6), multilayer, run II.

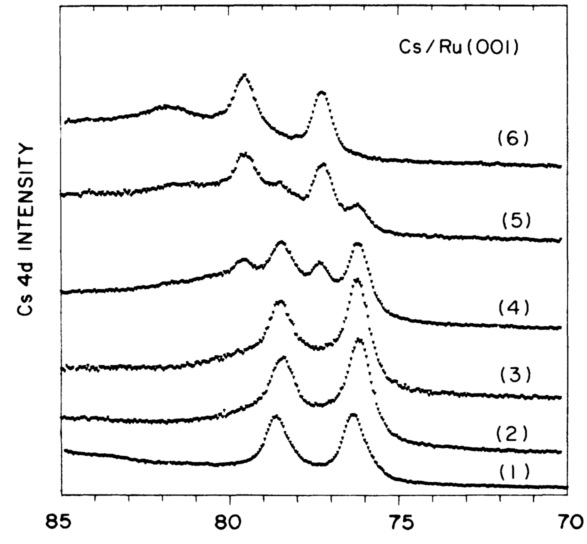

FIG. 5. Cs 4*d* photoemission for varying Cs coverages on Ru(001), excited by $h\nu=100$ eV unless otherwise stated. Curve (1), $f=0.134$, $h\nu=105$ eV, run II; curve (2), $f=\frac{1}{4}$, distinct (2×2) LEED pattern, run I; curve (3), $f=0.26$, LEED pattern ($\sqrt{3}\times\sqrt{3}$)R30° plus rings, run I; curve (4), ~ 1.5 ML, run I; curve (5), thin multilayer, run I; curve (6), multilayer, run I.

$(\sqrt{3}\times\sqrt{3})R\,30°$ LEED pattern, corresponds to $f=\frac{1}{3}$.

Figure 5 shows the evolution of the Cs $4d$ core level. In contrast to the other alkali metals, the shift between $f=0.13$ and 0.25 is only -0.15 eV, and then the binding energy stays essentially constant at 76.15 eV for the layer in contact with Ru. However, as in other alkali metals, the second-layer Cs $4d$ core level is well resolved from the interface core level, lying at 1.1 eV higher binding energy in this case. This is consistent with the Cs $5p$ data obtained by He I excitation, showing a second-layer $5p$ level at 1 eV higher binding energy relative to the interface.[2,3] The present experimental energy resolution does not permit us to resolve the Cs $4d$ surface and bulk core levels. However, previous Cs $5p$ data have revealed a surface versus bulk core-level shift of $+0.24$ eV.[3]

IV. DISCUSSION AND COMPARISON

We shall first compare our observations with the predictions of the thermodynamical model of Johansson and Mårtensson.[16] Then we shall discuss the factors contributing to the observed trends. An important physical factor that emerges is the variation in the valence (filled and lowest unfilled) orbitals of the alkali-metal group.

A. Comparison with the model of Johansson and Mårtensson

Table I summarizes the observations that can be compared with simple applications of the thermodynamical model of Johansson and Mårtensson.[16] We shall compare the bulk binding energies (with respect to the Fermi level), the surface core-level shifts relative to the bulk, and the binding-energy differences between the submonolayers (for low coverages) and the bulk. Previous results on K and Cs overlayers are also included. We make such a comparison because there is a widespread interest in the use of the thermodynamical model and we would like to identify the various uncertainties we have experienced in its application.

In the Appendix we give the notations and the details of the calculations. In our calculation we use the relevant atomic excitation energies,[17,18] tabulated sublimation energies,[19] differential heats of solution calculated semiempirically,[20] and tabulated values of heats of adsorption calculated semiempirically.[21]

Some observations can be made from Table I. We first compare the experimental and calculated bulk core-level binding energies $E_B^F(Z)$. It is seen that the discrepancy for Li is quite significant. We think that this is partly due to the error involved in the use of the equivalent-core approximation to simulate the extra-atomic final-state screening in free Li.[18] For Li it is expected that the equivalent-core approximation may result in a greater error. Let us consider the step involving $E_B^V(Z)-I(Z+1)$ When a Li $1s$ electron is removed, the Li ion with an electron configuration $1s2s$ is left in triplet or singlet state. Here we have used the smaller $E_B^V(Z)$ corresponding to leaving the ion in a triplet state. Then an electron is added to the $2s$-like orbital to simulate the major effect of extra-atomic final-state screening. Here we lower the energy of the atomic system by the ionization potential of the $2s$ electron of Be. This may only roughly account for the direct Coulomb interaction when there are few electrons in the system. Moreover, this does not properly account for the exchange interaction between the screening electron and the remaining $1s$ core electron (or the $1s$ core hole), because the electron which is being added is interacting with a filled $1s$ shell. Now suppose we consistently ignore the effect of spin-dependent interactions. That is, let us ignore the $1s$-$2s$ exchange interaction and take the average of the triplet and singlet ionization energies for $E_B^V(Z)$.[17] Hence $E_B^V(Z)$ is 65.36 eV and the calculated $E_B^F(Z)$ becomes 55.13 eV, an improvement in the right direction. Of course, there are also other sources of error involved, in general, in the predicted values of $E_B^F(Z)$, such as the heats of solution calculated sem-

TABLE I. Observed and calculated core-level binding energies (in eV) for alkali-metal overlayers. $E_B^F(Z)$ and $E_B^F(Z,\text{surf})$ denote the bulk and surface core-level binding energies, respectively. $E_B^F(Z,\text{sub})$ denotes the binding energy of a small submonolayer ($f>0.1$) of alkali metal Z. All binding energies are referenced to the Fermi level. The details of the calculation are given in the Appendix. The values for Na are uncertain because of the small magnitude of the surface core-level shift, and are thus given in parentheses.

	$E_B^F(Z)$		$E_B^F(Z,\text{surf})-E_B^F(Z)$		$E_B^F(Z,\text{sub})-E_B^F(Z)$	
	Obs	Calc.	Obs.	Calc.	Obs.	Calc.
Li $1s$	54.95	54.18[a]	0.55	0.18	$+0.50$	0.29
Na $2p$	(30.75)	30.45[a]	(0.15)	0	~-0.15[b]	-0.03
K $3p_{3/2}$	18.20[c]	17.92[a] to 18.20[d]	0.25[c]	0.10	~0	-0.43
Cs $5p_{3/2}$	12.00[e]	11.38[a] to 11.66[d]	0.24[c]	0.13	-0.77[c]	-0.40
Cs $4d_{5/2}$	77.25–77.01[f]	e	e	0.13	-0.85 to -0.60[f]	-0.40

[a] Value calculated from approximating the atomic excitation energy with $E_B^V(Z)-I(Z+1)$; see Ref. 18 and the Appendix.

[b] We confine our discussion to coverages $f>0.1$; hence the Na $2p$ binding energy of 31.25 eV at $f\sim0.05$ is not included here.

[c] References 3 and 4 for K, Ref. 3 for Cs.

[d] Value calculated from the atomic excitation energy given in Ref. 17; also see Ref. 18 and the Appendix.

[e] Numbers are omitted for lack of relevant information.

[f] The first value assumes that the maximum in the Cs $4d_{5/2}$ peak of thick Cs corresponds to the bulk core-level binding energy. A lower limit (the second value) to the bulk core-level binding energy would be 77 eV, if the peak maximum is dominated by the surface contribution and if the 0.24-eV surface core-level shift determined in Ref. 3 is used.

iempirically. A more subtle point is that the use of $E_{\text{coh}}(Z+1)$ elements have different crystal structures.

We shall next compare the calculated and the experimental surface core-level shifts. Surface core-level shifts for Na, K, and Cs have been reported.[22,23] We shall discuss the problems encountered in the application of the thermodynamical model. From Table I it is seen that the discrepancy for Li is quite large. In our calculation we have taken the surface energy $E_{\text{surf}}(Z)$ as $0.2E_{\text{coh}}(Z)$. It may be asked if this is the source of the error and if experimental values should be used instead. However, in using the available experimental surface energies,[24,25] an ambiguity immediately arises. The experimental values are not obtained for a well-defined surface, and hence the surface energy per atom is an uncertain quantity. This is compounded by the complication that Li and Be have different crystal structures. Nevertheless, in the case of Na, where similar difficulties arise, the observed surface core-level shift has been correlated with the difference in the Z and $Z+1$ surface energies.[23] Now if the Be surface energy is assumed to correspond to that for a (0001) hcp surface, and the experimental Li surface energy is assumed to correspond to that of the bcc (110) face, the Li surface core-level shift is roughly $E_{\text{surf}}(\text{Be})-E_{\text{surf}}(\text{Li}) \approx 0.17$ eV.[26] There are other instances where similar difficulties arise but are obscured. For example, the large surface core-level shift of -0.5 eV for Be has been rationalized by modifying the Be cohesive energy by the addition of the optical energy for Be $s^2 \rightarrow$ Be sp.[27] However, we think that the additional term is not warranted, since the cohesive energy already includes the effects of different electron configurations between the atomic and solid systems.

From Table I the agreement between the calculated and the observed values for $E_B^F(Z,\text{sub})-E_B^F(Z)$ ranges from fair to poor. The poor agreement might be partly due to errors in the calculated values for $E_B^F(Z)$, and partly to the errors in the semiempirical heats of adsorption.[21] This is illustrated as follows for Li and Cs. Noting the uncertainties mentioned above in using $E_{\text{coh}}(Z)$ and in the E_{sol} values, we may use Eq. (A1) of the Appendix and the observed bulk core-level energies to obtain $E_{\text{coh}}(Z)-E_{\text{coh}}(Z+1)+E_{\text{sol}}(Z+1$ in $Z)$. Then, $E_B^F(Z,\text{sub})-E_B^F(Z)$ would be $+0.467$ and -0.736 eV for Li and Cs, respectively, with the use of 65.36 eV for $E_B^V(\text{Li})$ and with 12.30 eV as the atomic excitation energy for Cs.[17]

In summary, we have outlined that various ambiguities arise in calculating alkali-metal core-level binding energies and their shifts from the available thermodynamical quantities in the model of Johansson and Mårtensson. (On the other hand, the model can be powerful in other applications.[28–30]) Despite these uncertainties, it is noteworthy that the trends and the sign of energy shifts are correctly predicted, except for $E_B^F(\text{K},\text{sub})-E_B^F(\text{K})$.

B. Surface versus bulk core-level binding energy

The most surprising observation of the surface core-level shifts is the large shift observed for Li. We shall discuss the factors which contribute to this, especially the role of the spatial extent of the valence orbital.

The mechanisms for surface core-level shifts have been discussed or reviewed in the literature.[28–30] An extension of the surface band-narrowing concept might lead to the expectation that free-electron-like metals should show only small surface core-level shifts.[28] For Be the unusually large (and negative) surface core-level shift can be associated with the up-shifted non-free-electron-like surface local density of states obtained theoretically.[31] For Li, however, we have no knowledge of the surface-electronic density of states. For lack of detailed knowledge, we cannot give definitive explanations, but shall only discuss the various mechanisms which may be operative. In addition to the as-yet-unknown behavior of the surface band, we note that a decrease in intra-atomic repulsion between the core electron and the valence electrons at the surface can lead to a positive surface core-level shift. It may be asked if this can be the result of electron redistribution ("spill-out") at the surface, which should be more pronounced for Li than for other alkali metals because of its higher conduction-electron density.[32] Another factor for the larger surface core-level shift for Li 1*s* is the smaller spatial extent of the 2*s* valence orbital and hence a larger 1*s* $-$2*s* interaction. The qualitative effect may be seen in the variation of the two-electron integral $F^0(\text{core},ns)$, where "*ns*" denote the valence orbital.[30,33,34] The trend is $\text{Li} > \text{Na} > \text{K} > \text{Cs}$. This is necessarily oversimplified because of the neglect of the screening due to other electrons and the modifications of the wave functions in the solid state. But the trend should remain.

We also note that a reduction in extra-atomic final-state screening at the surface would contribute to a positive surface core-level shift. Theoretical work on the Cu 3*s* core level has shown that final-state relaxation at the (100) surface is 0.3 eV smaller than that in the bulk.[35] At present, there is insufficient knowledge to permit generalizations to other types of metallic systems. We raise this as a possibility in the hope that theoretical work will be done. It should be noted that the spatial extent of the final-state screening charge, if we may think in terms of the "excited-atom" model,[36] depends on the spatial extent of the *ns* (unfilled) orbital as well. Hence it is again for Li that the extra-atomic screening energy is the largest.[34] Then, even a small fractional change from the bulk to the surface can become significant.

C. Core level of alkali-metal layer in contact with Ru

The significant decrease in binding energies of Li, Na, and K submonolayers and interface layers, upon increasing coverage, contrasts with the lack of a large change for Cs. We confine our discussion to fractional coverages greater or equal to 0.1.[37] The decrease in binding energy is the largest for Li, being -1.2 to -1.3 eV. The total change of the Na 2*p* binding energy is -0.65 eV if we consider $f > \sim 0.1$. Our observation of a ~ -0.80-eV shift for K 3*p* on Ru is in good agreement with the -0.7-eV shift observed for the K 2*p* core level on Pt(111) and Ru(001).[6–8] As for Cs on Ru(001),[38] no shift larger than 0.2 eV has been observed for Cs 4*d* and 5*p* on Si(111).[5]

For the Li adlayer the interface binding energy continues to shift even after the second layer has started growing. This may suggest a continuation of the incorporation of Li atoms into the Li/Ru interfacial layer. The saturated single layer, with a fractional coverage $f=0.46$,[15] corresponds to an average Li-Li separation of 4 Å, while that in pure bcc Li is only 3 Å. Therefore further incorporation of Li adatoms is not unlikely. For Na the core-level binding energy also continues to decrease beyond ~ 1 ML, although the decrease is less than that for Li. At 1 ML the average Na-Na distance is close to the bulk value.

We shall attempt to relate some of our observations to what is known theoretically. It will be clear that a systematic theoretical investigation is needed in order to interpret the results in a conceptually satisfactory manner. A general behavior is that the binding-energy change, when it occurs with increasing coverage, is in a direction away from, and not towards, the bulk binding energy. This is the opposite of what might be expected from direct adatom-adatom interaction. Hence the binding energy is dominated by bonding with the substrate that changes with coverage.

It has been demonstrated, for Li and Na on a jellium substrate,[39] as well as for $c(2\times2)$ Cs on W(001),[40] that bonding occurs through valence-electronic hybridization. Moreover, Na adsorption is thought to be neutral even at low coverages.[39] As the Na fractional coverage increases from 0.2 onward, the electron-depletion region on the side of the adatom recedes from the core site. This might be correlated with the upward movement of the core-level binding energy as the Na coverage increases. For Li the successive changes in the calculated coverage-dependent electronic structure is less clear (because of the coverage range studied), although the electron-depletion region on the adatom side tends to become more delocalized as the coverage increases. This may also lead to an increase in Coulomb repulsion between the core and valence electrons as the Li coverage increases.

The negative shift of the Cs adatom core level, with respect to the bulk, might be interpreted as consistency with the theoretical result that the potential near the Cs adatoms in $c(2\times2)$ structure is less attractive than that in an unsupported Cs monolayer.[40] Theoretical work has not addressed the question of coverage dependence for a Cs adlayer. However, our interpretation is that, after the electron hybridization which results in an upward shift of the core level towards the Fermi level, the coverage-dependent electron redistribution does not have a large effect at the core, for the coverages reported here.

In considering final-state effects, we note that in the extra-atomic screening of ionized Cs the screening charge is likely to take on partial 5*d* character. The atomic optical excitation energy from the Cs ground state $5p^6 6s$ to the excited state $5p^5 6s^2$ is 12.3 eV, while the excitation energy to $5p^5 6s 5d$ is 14.07–14.70 eV.[17] The proximity in excitation energy leads to some configuration mixing in the final state, and the modifications of the wave functions in the solid tends to enhance such mixing. For the $Z+1$ element Ba, valence 5*d* states have been reported for the solid.[41] For Cs in contact with Ru it has been suggested that 5*d* electrons participate in the decay of 5*p* core holes.[3] If a greater 5*d* screening is involved for Cs on Ru, relative to bulk Cs, a larger relaxation energy will result because the 5*d* orbitals are more localized than the 6*s*. This will contribute to the negative core-level shift as well.

Finally, some remarks will be made on how our observations should *not* be interpreted. The energy shifts upon increasing coverage cannot be attributed to a transition from "ionic" to metallic bonding.[42] A fractional K coverage $f>0.16$ (Fig. 4, curve 2 and beyond) should be above the coverage for "ionic" adsorption;[43,44] yet the binding-energy shift persists. Our fractional coverage $f=0.13$ for Cs/Ru might be thought to be "ionic,[45]" yet there is no large (>0.2 eV) core-level shift between this and higher Cs coverages. Hence, even if some common notions about "charge transfer" from alkali-metal adatoms were correct, the binding-energy shifts that we are concerned with require other explanations.

V. SUMMARY

The main photoemission results can be summarized as follows.

(1) Layer-resolved binding energies: The observed energy difference between the saturated alkali-metal–Ru interface core level and the second-layer core level is 1.25 eV for Li, 0.85 eV for Na, 0.90 eV for K,[4] and 1.1 eV for Cs. Further coverage increase leads to a bulklike core level shifted by -0.55 eV in the case of Li; for K and Cs, the shifts between the surface and bulklike levels are ~ 0.25 eV, as extracted by curve fitting to high-resolution spectra.[3–5]

(2) Core-level binding-energy decrease of the layer in direct contact with Ru(001), upon increasing alkali-metal coverage from $f\sim0.1$ onward: The total shifts observed are -1.2 to -1.3 eV for Li, -0.65 eV for Na, ~ -0.80 eV for K, but only -0.15 eV for Cs.

We have suggested possible explanations in terms of core–valence-electronic interactions.

Note added. The question has been raised as to whether intermixing occurs between Li and Ru. While we have observed no indications of intermixing between the alkali metals and Ru, direct experimental investigations geared to settling this point are in order.

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APPENDIX

In the well-known thermodynamic model of Johansson and Mårtensson,[16] the core-level binding energy $E_B^F(Z)$ of atom Z in the condensed phase, with respect to the Fermi level, can be written as

$$E_B^F(Z)=E_{\mathrm{coh}}(Z)+[E_B^V(Z)-I(Z+1)] \\ -E_{\mathrm{coh}}(Z+1)+E_{\mathrm{sol}}(Z+1 \text{ in } Z)\ , \qquad \text{(A1)}$$

where $E_{\mathrm{coh}}(Z)$ and $E_{\mathrm{coh}}(Z+1)$ are the cohesive energies of elements Z and $Z+1$, respectively, $E_B^V(Z)$ is the binding energy of the core level in the free atom, $I(Z+1)$ is the first ionization potential of the $Z+1$ free atom, and $E_{\mathrm{sol}}(Z+1 \text{ in } Z)$ is the differential heat of solution of the $Z+1$ element in the Z solid (negative being exothermic). The term $E_B^V(Z)-I(Z+1)$ is an approximation to the atomic excitation energy;[17,18] that is, the energy required to excite the core electron into the lowest unfilled orbital of the relaxed ion.

Equations analogous to (A1) can easily be written for the core-level binding energies of the surface, $E_B^F(Z,\mathrm{surf})$, and of the submonolayer, $E_B^F(Z,\mathrm{sub})$.[16] Hence the surface versus bulk core-level shift is

$$E_B^F(Z,\mathrm{surf})-E_B^F(Z) \\ =-0.2[E_{\mathrm{coh}}(Z)-E_{\mathrm{coh}}(Z+1)+E_{\mathrm{sol}}(Z+1 \text{ in } Z)]\ , \qquad \text{(A2)}$$

where the surface quantities are taken to be 80% of those for the bulk.[16] Alternatively, $0.2E_{\mathrm{coh}}(Z)$ is taken to be the surface energy of the Z solid.

The energy shift of small submonolayer with respect to the bulklike level is

$$E_B^F(Z,\mathrm{sub})-E_B^F(Z)=E_a(Z/\mathrm{Ru})-E_a((Z+1)/\mathrm{Ru}) \\ -[E_{\mathrm{coh}}(Z)-E_{\mathrm{coh}}(Z+1) \\ +E_{\mathrm{sol}}(Z+1 \text{ in } Z)]\ , \qquad \text{(A3)}$$

where E_a denotes the heat of adsorption at low coverage.

The values of $E_{\mathrm{coh}}(Z)-E_{\mathrm{coh}}(Z+1)+E_{\mathrm{sol}}(Z+1 \text{ in } Z)$ for Li, Na, K, and Cs, are, respectively, $(1.651-3.358+0.795)$ eV$=-0.912$ eV, $(1.112-1.525+0.393)$ eV$=-0.02$ eV, $(0.9224-1.843+0.416)$ eV$=-0.505$ eV, and $(0.7929-1.856+0.425)$ eV$=-0.638$ eV, with the use of Refs. 17 and 18. Thus the calculated bulklike core-level binding energies are 54.175 eV for Li 1s, 30.474 eV for Na 2p, 17.920 eV for K 3$p_{3/2}$, and 11.385 eV for Cs 5$p_{3/2}$, from Eq. (A1) and Refs. 17 and 18. The surface versus bulk core-level shifts calculated from Eq. (A2) are 0.182, 0, 0.101, and 0.128 eV, respectively, for Li 1s, Na 2p, K 3$p_{3/2}$, and Cs 5$p_{3/2}$. The values of $E_B^F(Z,\mathrm{sub})-E_B^F(Z)$ calculated from Eq. (A3) are as follows: $(2.9538-3.5742+0.912)$ eV$=0.292$ eV for Li, $(2.849-2.9008+0.02)$ eV$=-0.032$ eV for Na, $(3.471-4.403+0.505)$ eV$=-0.427$ eV for K, and $(4.144-5.180+0.638)$ eV$=-0.40$ eV for Cs.

It may be noted that, although we have the experimental values for $E_a(Z/\mathrm{Ru})$ in Eq. (A3), we use Miedama's semiempirical values because experimental values for $E_a((Z+1)/\mathrm{Ru})$ are still lacking.

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[11] Typical contamination levels for Na are as follows: for CO, $f<0.017$; for CO$_2$, $f<0.002$; for H$_2$O, $f<0.001$; here $f=1$ corresponds to the Ru(001) surface atomic density. These estimates are obtained by calibration with CO/Ru.

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[14] We assume that one atom in the surface layer attenuates the signal from one atom in the interface layer. Hence the coverage $(1+x)$ ML is determined from $\mathcal{I}_s/\mathcal{I}_i=x/[x\exp(-y)+(1-x)]$, where $\mathcal{I}_s/\mathcal{I}_i$ is the peak-height ratio of the second layer to the interface core level, x is the fractional coverage in the second layer, $y=d/(l\cos 50^\circ)$, d is the thickness of the second layer, and l is the photoelectron mean free path. We have used $d=2.4685$, 2.9875, and 4.2744 Å for Li, Na, and Cs, respectively, corresponding to their bcc (110) interlayer spacings. The kinetic energies of the Li 1s, Na 2p, and Cs 5p photoelectrons in our data are in range ~15 to ~25 eV. For mean free path l ranging from 5 to 15 Å, the calculated values of x do not vary too much. For Li, Fig. 2, curve 4, x ranges from 0.245 to 0.265. For Na, Fig. 1, curve 5, x ranges from 0.437 to 0.513. For Cs, Fig. 5, curve 4, x ranges from 0.453 to 0.546.

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