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Surface core-level shifts of Ta(110) and W(110) versus alkali-metal-atom coverage: Implications for the alkali-metal–substrate interaction

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The change in the average surface-atom core-level shift (SCS) produced by submonolayer coverages of alkali adsorbates is quite small for both Ta(110) and W(110), less than 45 meV in magnitude. The small change of the measured SCS's as a function of coverage decisively supports the covalent-bonding picture of alkali adsorption proposed by Ishida and Terakura.

Sixty years of theoretical and experimental work devoted to the problem of alkali-metal chemisorption on metal surfaces testifies that a complete understanding of these systems has not been attained. Despite significant progress in theoretical and experimental techniques, there remain doubts as to a proper description of the alkali-metal-atom–metal-substrate interaction. While it is generally accepted that the alkali-metal valence s level is nearly fully occupied for coverages close to first-layer saturation, a consensus on the low-coverage description of the bonding is decidedly lacking. For example, in spite of nearly identical charge-density contours calculated for Na adsorbed on Al(100), the Na–Al-surface bonding at low coverage ($\leq \frac{1}{8}$ monolayer) has been described as both purely covalent¹ and highly ionic.² The interpretation of experimental data has also been a subject of controversy. Our earlier findings that Na, K, and Cs adsorbed on W(110) induce very small changes in the average surface core-level binding energy (BE) shift $\langle \text{SCS} \rangle$ at $\frac{1}{3}$ and 1 atomic-layer coverages, ($|\Delta_{\langle \text{SCS} \rangle}| < 30$ meV), was taken as an indication that the Langmuir-Gurney picture of charge transfer^{3,4} from the alkali-metal valence orbital to orbitals of the metal substrate must be abandoned.⁵ This elicited several responses designed to rescue the notion of charge transfer in these systems.^{2,6} In particular, Benesch and King⁶ (BK) suggested that charge transfer from the alkali-metal atom to the substrate is masked in the substrate surface-atom BE by a positive contribution to the change in SCS arising from the mere presence of the adsorbate atoms before any interaction with the substrate is allowed to take place. Charge transfer, BK argue, is then responsible for a compensating shift back to near the clean-surface BE.⁶

In order to characterize the nature of the alkali-metal-atom–transition-metal-substrate interaction more fully, we have measured the SCS's of both W(110) and Ta(110) surface atoms as a function of alkali-metal coverage between zero and one atomic layer. As for the two coverages for W(110) reported earlier, the alkali-metal-induced

variations in substrate surface-atom core-level BE's are remarkably small ($|\Delta_{\langle \text{SCS} \rangle}| < 45$ meV) for both substrates at all coverages. It is shown that within the BK model of core-level shifts, the results are more naturally interpreted in terms of covalent bonding between the substrate and the adsorbed alkali metal without recourse to charge transfer. The small magnitude of the measured shifts at all coverages strongly supports a covalent interaction of the alkali-metal adsorbate with the transition-metal surface at all coverages.

The photoemission data were obtained at the National Synchrotron Light Source using the AT&T Bell Laboratories—University of Oregon 6-m toroidal-grating-monochromator beamline. Spectra were obtained with a 100-mm Vacuum Science Workshop hemispherical analyzer. The single-crystal Ta(110) sample was cleaned by ion bombardment with 1.5-keV Ne^+ followed by numerous flashes to 2700 K. Alkali-metal deposition from well degassed SAES Getters sources occurred in a base pressure of 3×10^{-10} Torr onto a crystal cooled to 80 K. Photoemission spectra of the alkali-metal-covered Ta surface were collected at normal emission at a total system resolution of 80 meV, during which the base pressure was less than 1×10^{-10} Torr. Work-function data and alkali-metal core-level data were used to infer alkali-metal coverages on the Ta surface. Details of the sample preparation and data collection for deposition onto W(110) were described previously.⁵

Prior to concentrating on the substrate core-level shifts, we briefly examine the coverage dependence of the alkali-metal core levels as a function of coverage. A typical example of the $(n-1)p$ core-level spectra of all alkali metals studied on Ta(110) and W(110) is provided by the Na $2p$ spectra for Na/Ta(110) displayed in Fig. 1. With increasing coverage, the alkali-metal core-level feature increases in intensity and shifts toward lower binding energy. After the completion of the first adsorbate layer (\equiv one atomic layer \equiv saturation coverage θ_{sat}), another spin-orbit doublet grows in at a higher binding energy, as

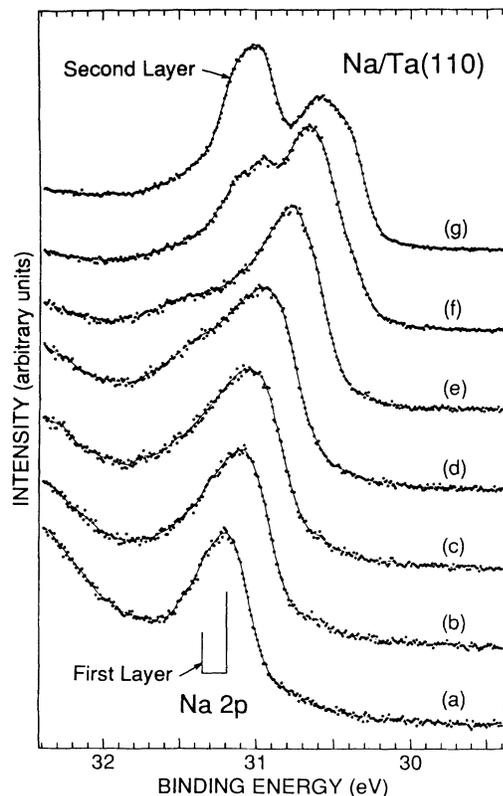


FIG. 1. The coverage dependence of the 2*p* photoemission spectrum of Na adsorbed on Ta(110).

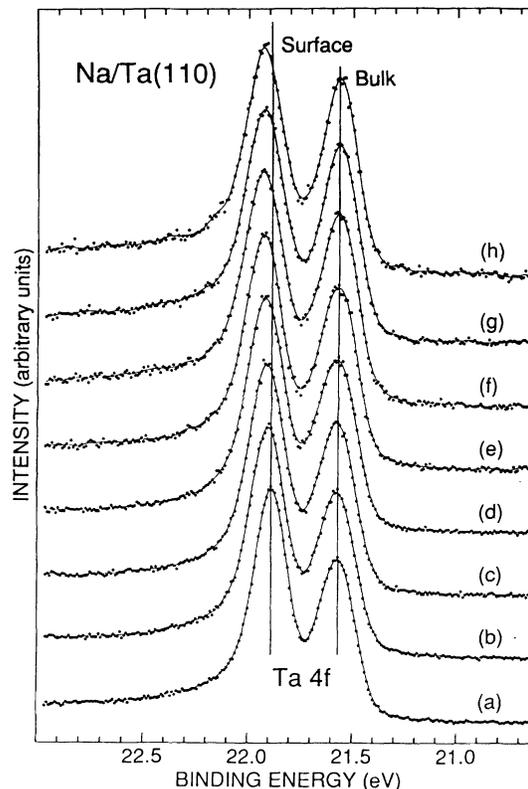


FIG. 2. The effect of Na adsorbate on the 4*f* spectrum from a Ta(110) surface. The fractional atomic-layer coverages are 0.00, 0.10, 0.20, 0.35, 0.45, 0.60, 0.75, and 1.05.

the second layer of alkali-metal atoms begins to form. The continuous shift of the first-layer binding energy, which is seen for adsorption on other transition metals and for other alkali metals as well,^{5,7} is due to the gradual decrease in the inter-alkali-metal spacing, which is principally the result of the repulsive dipole-dipole interaction between the adsorbed atoms comprising the ad-layer. Because of the coverage-dependent intralayer dipolar interaction and the eventual coverage-dependent formation of an alkali-metal *ns* conduction band, the alkali-metal core level is not a good indicator of the nature of the alkali-metal-substrate interaction.

On the other hand, the substrate core levels are well suited for probing the alkali-metal-substrate interaction since interactions between the surface atoms of the substrate are minimally affected by the adsorbed alkali-metal layer, especially in the case of highly cohesive metals like W and Ta. Data for Na/Ta(110), see Fig. 2, show that the Ta surface core level moves to slightly higher binding energy with increasing coverage, opposite to the shift expected for charge donation by the alkali metal. Figure 3 displays saturation-coverage substrate core-level data for Na, K, and Cs/W(110) and Na and Rb/Ta(110), where the magnitude of the change in average SCS, Δ_{SCS} , is either close to or at its maximum. The alkali-metal induced shifts for Ta are all positive at saturation coverage, while those for W are all negative. The largest change in Δ_{SCS} is +45 meV for Na/Ta(110). In Fig. 4, Δ_{SCS} vs alkali-metal coverage is displayed for both substrates. In

all five cases the change in SCS is initially positive. For W(110), Δ_{SCS} eventually turns over and becomes negative, while for Ta(110), it either levels off (Na) or decreases slightly toward saturation (Rb).

The quantity Δ_{SCS} is simply the average change in SCS for all of the atoms in the surface layer of Ta(110) or W(110). At low coverage, some surface atoms are perturbed by the alkali-metal atoms and some are not. In order to obtain a better idea of the change in SCS experienced by the surface atoms, which are actually affected by the adsorbed alkali metals, we divide Δ_{SCS} by the fractional coverage $\theta/\theta_{\text{sat}}$. The resulting quantity Δ_{SCS} is plotted in Fig. 5 vs fractional coverage. The curves in Fig. 5 were obtained from the smooth curves drawn through the data in Fig. 4. The relationship of Δ_{SCS} to Δ_{SCS} is analogous to the relationship between the dipole moment per adsorbed atom and the change in work function induced by the adsorbate layer. As evident in Fig. 5, Δ_{SCS} is relatively constant at low coverage ($\theta/\theta_{\text{sat}} < 0.2-0.3$) and decreases towards saturation for all five systems when the adsorbate atoms begin to chemically interact.

Before discussing the data, it is helpful to review the theoretical ideas related to alkali-metal-atom adsorption. Langmuir³ proposed that for an alkali-metal atom on a metal surface the alkali-metal *ns* valence level would be located above the Fermi level ϵ_F and thus be empty, having donated its charge to the conduction band of the sub-

strate. Since the alkali-metal ion is positively charged, the metal would then respond by producing a screening charge residing in orbits of the substrate atoms, at the surface of the metal. This idea was elaborated upon by Gurney,⁴ who realized that the hybridization between the alkali-metal ns level and the continuum of conduction-band states of the metal necessarily broadens the spectral weight of the ns level into a resonance by producing a

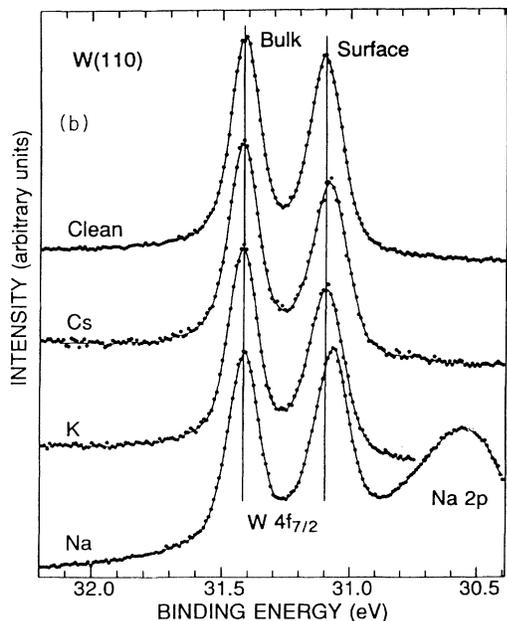
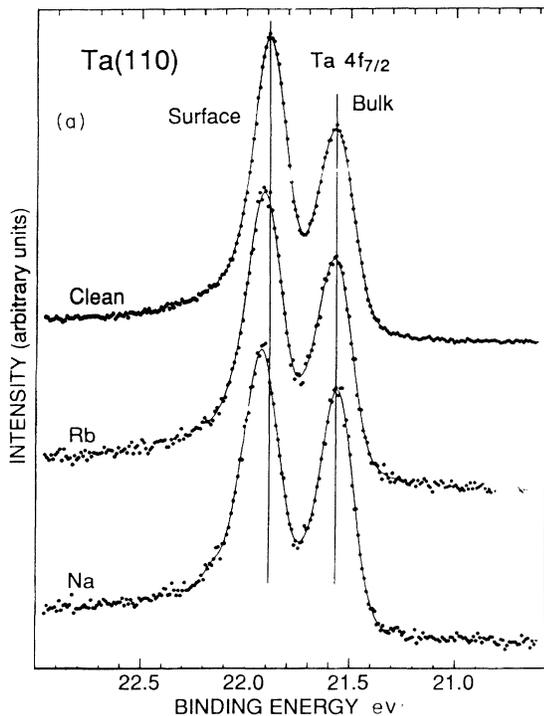


FIG. 3. $4f$ photoemission spectra of (a) Ta(110) and (b) W(110), for the clean surface and with one atomic layer (saturation coverage) of various alkali metals.

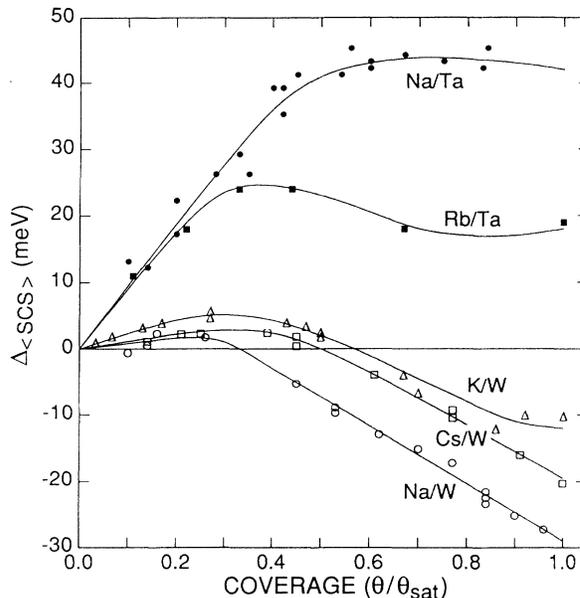


FIG. 4. Coverage dependence of the average alkali-metal-adsorbate-induced surface-atom core-level shift Δ_{SCS} for Ta(110) and W(110).

band of bonding states utilizing the lower half of the resonance and a band of antibonding states utilizing the upper half of the resonance. The position of the center ϵ_{ns} of the ns resonance with respect to ϵ_F in conjunction with the width of the resonance Δ_{ns} thus determines the ionicity of the adsorbed alkali-metal atom. For example, if $\epsilon_{ns} - \epsilon_F \gg \Delta_{ns}$, then the resonance is mostly empty, the alkali-metal atom is effectively ionized, and the bonding

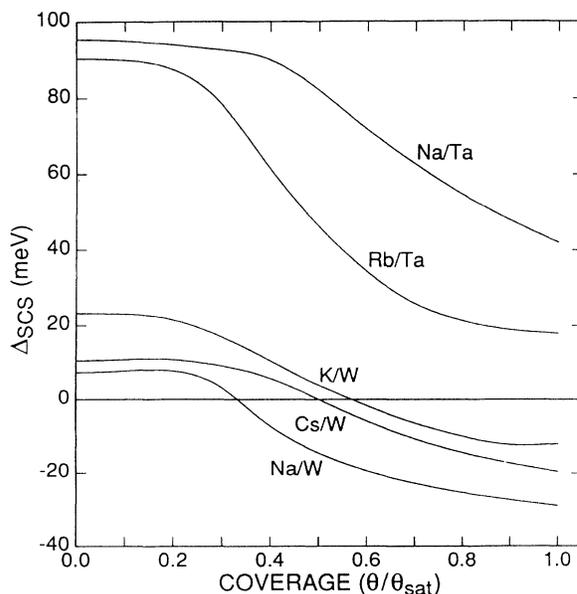


FIG. 5. Normalized alkali-metal-adsorbate-induced surface-atom core-level shift Δ_{SCS} for Ta(110) and W(110) (see text). The curves are derived from the fitted lines in Fig. 4.

may be regarded as an ionic. If, however, $\epsilon_{ns} = \epsilon_F$ then the resonance is half filled (with one electron), the alkali metal is natural, and the interaction between the atom and the substrate is wholly covalent. Gurney thus interpreted the initial decrease in work function of a metal upon alkali-metal adsorption as due to partial charge donation, leaving the ns resonance less than fully occupied. The Gurney model explains the decrease in dipole moment per adsorbed atom with increasing coverage as arising from interadsorbate dipole (depolarization) fields, which lower ϵ_{ns} with increasing coverage, causing the occupation of the resonance to increase (back donation) and eventually resulting in a largely covalent interaction between the alkali-metal atoms and the substrate.

Very recently, however, the Gurney concept has been questioned by Ishida and Terakura (IT) on the basis of a systematic evaluation of a set of first-principles calculations of alkali-metal atoms adsorbed at various coverages on both jellium and Al(100).^{1,8} In this work, IT pointed out that, in addition to the charge-transfer contribution to the work-function change, the only one considered by Gurney and almost everyone else since,⁹ polarization of the alkali-metal-atom charge density, which necessarily occurs as a result of hybridization of the ns level with the substrate orbitals, also contributes to a lowering of the work function even in the absence of charge transfer. By evaluating quantities such as the spatial charge density, bond-order density, electrostatic potential at the adatom site, and adatom dipole moment as functions of coverage, IT concluded that the s level is occupied by essentially unity charge—and hence the alkali-metal–substrate bond is highly covalent—at all coverages. Within the IT framework, the decrease in dipole moment per adsorbed atom with increasing coverage is due to a redistribution of charge from substrate–alkali-metal bonding orbitals to antibonding orbitals as the alkali-metal ns valence band is formed. However, it is clear from the electron-density distributions calculated by IT that the charge-density contours in the substrate–alkali-metal bonding region are fairly independent of coverage, and that a major part of the decrease in dipole moment per adsorbed atom occurs as a result of the contraction in size of the charge-density depletion region on the *vacuum* side of the adsorbed alkali-metal atom, away from the substrate surface atoms. One consequence of this nature of the charge redistribution is that the potential at the substrate surface atom is nearly *independent* of alkali-metal coverage. (See Fig. 3 of Ref. 1.)

We consequently consider the present experimental finding of very small shifts in the SCS of Ta(110) and W(110) at all coverages as the strongest confirmation of a near independence of charge density between adsorbed alkali-metal and substrate atoms as witnessed in the first-principles calculations. However, since core-level shifts are sensitive only to charge densities and not to the orbitals which the charge occupies, we must ultimately rely upon the quantitative assessment of the first-principles calculations to assess the degree of covalency in these systems. Although there have been a number of such calculations that provide some insight into the nature of the associated bonding, none to our knowledge has been ex-

PLICITLY carried out for the alkali-metal–adsorption cases that we have considered. However, for pedagogical reasons, it does seem plausible that calculations involving the (100) face of an Al substrate that have been carried out by IT can be used to gain insight into the nature of the bonding. It should be kept in mind, however, that the results of these comparisons do not include the substrate d electrons (which have been shown to be important in the bonding in a number of alkali-metal adsorptions),^{10,11} and are based on an approximate surface geometry that does not correspond to the geometry that was present in the experiment. As IT have shown, all measures of the degree of covalency of the alkali-metal–substrate interaction indicate a highly covalent interaction at all coverages. While some of IT's quantifications of covalency, such as the total charge associated with an alkali-metal atom, depend upon assigning a sphere of arbitrary size to represent the extent of the alkali-metal atom, other measures, such as the adsorbate-substrate bond-order density, have less arbitrariness associated with them. From these measures the interaction is clearly covalent. For example, at low coverage, explicit calculations¹² of the bond-order density β by IT demonstrate that β switches from positive to negative exactly at ϵ_F . With increasing coverage, the positive to negative crossover dips slightly below ϵ_F due to the occupation of substrate-adatom antibonding states as the alkali-metal intralayer-conduction s band forms. From the definition of β ,¹² this fact means that the partial density of states at ϵ_F switches from bonding to antibonding character as the coverage is increased from lower values to higher values, indicating a considerable covalency at lower coverage. In the Gurney model, the bond-order density at ϵ_F would be very positive at low coverage due to the large charge transfer to the substrate orbitals, and approach zero at ϵ_F as the covalency increases with coverage.

It has been suggested by Benesh and King⁶ that the near-zero shift of the substrate core levels Δ_{SCS} at low coverage is due to a near cancellation of the charge-transfer contribution Δ_{ct} and an environmental contribution Δ_{env} , which arises from the presence of the alkali-metal atoms before any alkali-metal–substrate interaction is considered. More specifically, BK break the change in substrate SCS into four contributions,

$$\Delta_{SCS} = \Delta_{env} + \Delta_{config} + \Delta_{ct} + \Delta_{relax} , \quad (1)$$

where Δ_{config} is a contribution from substrate intraatomic configurational changes (such as $6s$ to $5d$ charge redistribution) and Δ_{relax} is a change in final-state screening energy induced by the adsorbed alkali-metal layer. For Cs adsorbed on W(110) at a coverage of 0.67 atomic layers, BK calculate $\Delta_{env} = 190$ meV. Since the alkali-metal–substrate distance varies little with coverage,⁸ this value should be nearly independent of coverage.¹³ BK thus infer that at low coverages, charge transfer to the substrate nearly cancels this environmental shift. Since with increasing coverage the charge-transfer contribution in the Gurney model must decrease, BK then argue that

this decreasing contribution from charge transfer is itself nearly canceled out by an increasing contribution from Δ_{relax} as the metallic alkali-metal layer is formed at high coverage. (For all coverages, BK assume that Δ_{config} is negligible.) Within the confines of Eq. (1) it is very difficult to rationalize the actual coverage dependences shown in Fig. 5. The decrease in Δ_{SCS} at higher coverage requires that the change in Δ_{ct} due to back donation is always smaller than that due to Δ_{relax} , a most unlikely proposition especially since the surface-atom core-electron line shape does not change significantly with coverage. Even the fact that Δ_{env} and Δ_{ct} must cancel to the same extent for adsorbates as different as Na and Cs requires some explanation. In order to test the validity of the BK description, it is necessary to calculate the three major terms in Eq. (1) for different alkali metals and coverages to see whether it, in fact, reproduces the experimental observations.

It should be noted, however, that Eq. (1) is predicated on the assumption that charge transfer is the only possible response for an alkali-metal atom in close proximity to a metal surface. According to IT,¹ the actual response is the formation of an adsorbate-substrate covalent bond. BK ignore, as does the Gurney model in describing the work-function change, any contribution from the resulting interatomic hybridization. The BK expression, Eq. (1), must consequently be modified to include a covalent-bonding contribution Δ_{hybrid} so that the change in SCS should be written as

$$\Delta_{\text{SCS}} = \Delta_{\text{env}} + \Delta_{\text{config}} + \Delta_{\text{ct}} + \Delta_{\text{hybrid}} + \Delta_{\text{relax}}. \quad (2)$$

Within this expanded BK framework our measured changes are much more naturally explained through IT's description of covalent bonding in these systems. As with a possible charge-transfer contribution Δ_{ct} , Δ_{hybrid} also results in a negative contribution to Δ_{SCS} . This is easily inferred from IT's charge-density-difference contours in which the difference in charge density between the noninteracting alkali-metal-atoms-substrate system and the fully interacting system is considered. Since the contours correspond to the difference between the interacting and noninteracting adsorbate-substrate system, the potential resulting from them corresponds to the three initial-state terms in Eq. (2) not including Δ_{env} , namely, $\Delta_{\text{config}} + \Delta_{\text{ct}} + \Delta_{\text{hybrid}}$. In these contours, there is a buildup of electronic charge between the substrate atoms and the alkali-metal atoms due to the formation of the covalent bond, which is nearly independent of coverage. This buildup is responsible for a negative Δ_{hybrid} . For example, for Na on Al(100), Fig. 3 of Ref. 1 shows that Δ_{hybrid} is approximately -600 meV and virtually independent of coverage. Apparently, in the present case, the magnitude of Δ_{env} is nearly the same as Δ_{hybrid} . Since, within the IT model, Δ_{hybrid} and Δ_{env} are both nearly independent of coverage, the near lack of variation in SCS with coverage for all measured alkali metals on W(110) and Ta(110) naturally results. (The observed decrease in Δ_{SCS} for coverages greater than 0.3 may then be due to the additional final-state screening provided by the alkali-metal conduction band.) Within the Gurney mod-

el, one is now forced to conclude that the four quantities Δ_{env} , Δ_{ct} , Δ_{hybrid} , and Δ_{relax} all change in such a manner as to make their sum both small compared to the individual terms and largely independent of coverage, a possibility which seems exceedingly remote. However, a substantial cancellation between Δ_{env} and Δ_{hybrid} , the major terms, can be rationalized, because bond formation removes the nonphysical aspects of the charge distribution that is responsible for Δ_{env} .

While the IT description unquestionably accounts for our measured SCS changes in a more compelling manner than the Gurney model, it is perhaps somewhat nonintuitive for the covalent-bonding term Δ_{hybrid} to be negative. As an example, consider a simple homonuclear diatomic bond. In this case, there exists a positive contribution to the core-level BE shifts in either atom from the covalent hybridization since the effect of polarization away from a particular core, which occurs in the valence charge of that core's atom, dominates the polarization towards that core, which occurs in the valence charge of other atoms. In the present case for adsorbed alkali metals Δ_{hybrid} , as defined, turns out to be negative. This occurs because the predominant effect on the substrate surface-atom core levels in the formation of the chemical bond with the alkali-metal atom is the localization of the alkali-metal ns charge density in a region relatively close to the substrate core level compared to the atomic alkali-metal ns pre-bonding state, which exhibits a relatively large delocalization. In other words, within the present categorization of the contributions to Δ_{SCS} [Eq. (2)], the polarization of the substrate valence charge is secondary to the alkali-metal polarization in affecting the substrate core-level BE's as reflected in the Δ_{hybrid} term.

Although it is perhaps somewhat reckless to attempt to explain the details of our measured values of Δ_{SCS} , the similarity in the coverage dependence for all the measured alkali metals on W and Ta do invite comparison. As is clear from Fig. 5, Δ_{SCS} is initially positive for both systems and shifts in a negative direction at higher coverages. Within the IT model, the most immediate explanation of Δ_{SCS} vs coverage is that initially Δ_{env} and Δ_{hybrid} , which are roughly coverage independent, give the constant contribution below a coverage of ~ 0.3 – 0.4 atomic layers. However, upon formation of the alkali-metal overlayer conduction band at higher coverages, the screening energy in the final state begins to increase so as to make Δ_{SCS} vary in a negative direction. The graphs in Fig. 5 indicate that for W, Δ_{relax} at saturation is ~ -30 meV, while for Ta, Δ_{relax} at saturation is ~ -50 meV.

In summary, we have obtained data for alkali-metal induced variations in substrate SCS's for a variety of alkali metals adsorbed on W(110) and Ta(110). Any explanation of the measured shifts involving a large degree of charge transfer as in the Langmuir-Gurney model requires an unlikely balancing of several terms so as to result in very small shifts for all alkali-metal atoms at all coverages. In contrast, the near independence of the variations in SCS as a function of coverage are naturally explained in terms of Ishida and Terakura's model for alkali-metal-atom-metal-substrate bonding in which the interaction is highly covalent at all coverages. Our data

thus strongly confirm the correctness of IT's calculations and the covalent bonding picture of alkali-metal-atom adsorption. Finally, in agreement with our conclusions regarding the significance of the very small shifts in Δ_{SCS} vs alkali-metal coverage are the results of other very recent experimental investigations, which support the covalent-bonding model for low alkali-metal coverages on transition, noble, and simple metal surfaces.¹⁴

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¹³BK do calculate a larger environmental shift for higher Cs coverages. However, the coverage they consider, 0.5 monolayer, is much larger than the first-layer saturation coverage of 0.37 monolayer, and hence, not applicable to the experimental conditions.

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