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Unified behavior of alkali core-level binding-energy shifts induced by *sp* metals

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Thin overlayers of Na, K, Rb, and Cs on different *sp*-metal substrates have been investigated using photoelectron spectroscopy. The alkali core levels show clearly resolved binding-energy shifts between the surface layer, the intermediate layer(s), and the interface layer. The magnitude of these shifts depends on *sp* metal and on alkali metal. The layer-resolved core-level binding-energy shifts are well reproduced by models based on a thermodynamical description. For three-layer alkali films the core-level binding energy of the intermediate layer is found to exhibit a small but significant shift between different *sp*-metal substrates. A simple relationship between the core-level binding-energy shift for the interface layer and the difference in r_s value between the *sp* substrate and the adsorbate is shown to exist. [S0163-1829(97)07443-2]

INTRODUCTION

It has long been known that the core-level binding energy of an atom depends on the particular surroundings of the photoemitting atom. This so-called chemical shift effect has proven of great value for studies of molecules, surfaces, and solids as it often makes it possible to study separately not just the behavior of the different elements but also of the chemically inequivalent atoms of the same element that may be present in the sample. In addition to such utilizations of the core-level binding-energy shifts, the shifts themselves, i.e., the magnitude and sign of the binding-energy shift induced by a certain change of the surroundings, have attracted much attention. Experimental investigations of the systematics of core-level binding-energy shifts have contributed to an improved understanding of and incentive to calculate these chemical shifts in a number of systems. The large number of measurements of the binding-energy differences between bulk and surface atoms (the surface core-level shift, SCLS) has led to the development of various methods for calculating such shifts, see, e.g., Refs. 1–5. The present paper deals with a systematic experimental investigation of the core-level binding-energy shifts of alkali atoms induced by introducing *sp*-metal atoms in the surroundings of the alkali atoms. The experimental results lead to a surprisingly regular relation between the induced core-level shift and the difference in the r_s values for the alkali and the *sp*-metal valence electron gas.

As in previous investigations^{6–8} of core level binding energy shifts of alkali metals, the experimental method used to introduce *sp*-metal atoms as neighbors to alkali atoms is to deposit thin alkali films with a thickness of 3–4 layers on top of a single-crystal surface of the *sp* metal. In a nominally three-layer-thick alkali film, the neighbors of the innermost alkali layer atoms will partly be substrate atoms whereas the alkali atoms in the outermost and the intermediate alkali lay-

ers, respectively, will experience surroundings that are very similar to those on the surface and in the bulk, respectively, of a macroscopically thick alkali film. Because of this difference in the surroundings, alkali atoms in the various layers will have different core-level binding energies and the binding-energy shift between the interface and the intermediate layer atoms will directly reflect how strongly the particular substrate metal influences the core levels of the investigated alkali metal. In the present paper we report measurements of such layer-resolved alkali core-level spectra for a large number of three-layer Na, K, Rb, and Cs films on close-packed Na, Mg, and Be single-crystal surfaces and include also in the analysis previous spectra from alkali films on the Al(111) surface.⁶

Core-level binding-energy shifts in metallic systems can be related to certain thermodynamical parameters of the initial and the final state after photoionization of the system leading to so-called thermochemical models for core-level binding-energy shifts; see, e.g., Ref. 1. We have used such models for calculating the expected shifts in the present systems and find that they reproduce the observed trends reasonably well. Furthermore, the connection between the core-level shifts and certain thermodynamical parameters in combination with our experimental finding of a simple relationship between the shifts and the difference in the r_s values of the alkali metal and the *sp* substrate leads to the interesting conclusion that these thermodynamical parameters for the present systems have to obey a similar simple dependence on this r_s difference.

EXPERIMENT

The measurements were performed at the soft x-ray beamline 22 at the MAX I synchrotron radiation source. This beamline is equipped with a modified SX-700 monochromator⁹ and a large hemispherical electron energy

analyzer¹⁰ of SCIANTA type. The Mg, Al, and Be substrate crystals were cleaned by cycles of Ar⁺ sputtering, followed by annealing. The Na surface was obtained by depositing a thick film of Na on Al(111) producing epitaxial Na layers.¹¹ These Na layers also made it possible to measure the alkali-induced shifts of the Na core levels simply by measuring the shifts of the Na substrate core levels when depositing an alkali overlayer. The cleanliness of the surfaces and of the deposited alkali layers was checked by monitoring the core-level regions of possible contaminants, in particular, C and O. No contaminants could be detected in the final cleaning stages except for the Mg surface where a weak Pb signal was detected, which by using tabulated cross-section values¹² was estimated to correspond to an amount of less than 5% of a monolayer. The base pressure in the experimental chamber was 6×10^{-11} Torr and during evaporation the pressure increase was less than 1×10^{-10} Torr. The photon energies used for recording the Na $2p$, K $3p$, Rb $4p$, and Cs $4d$ levels were 110, 90, 39, and 110 eV, respectively. All depositions were made at 100 K in order to avoid any intermixing and alloy formation between the alkali films and the substrate. All measurements were performed at a sample temperature of 100 K in order to reduce phonon broadening.^{13,14}

RESULTS AND DISCUSSION

The large binding-energy shifts between emission from the first and the second alkali layers make it very easy to detect when the second layer starts growing as has been demonstrated in previous reports.^{6,7} We define one alkali layer as the amount deposited just before the emission from the second layer becomes visible. The alkali coverages quoted below are obtained simply by dividing the evaporation time by the time needed for deposition of one layer. We will for reasons of clarity in the following discussion often describe the alkali films as if they grew in a layer-by-layer fashion. However, it should be noted that the details of the growth mode for the alkali films are not important for the present experiments because even though most of the films do not grow by a layer-by-layer mode it is still possible to distinguish and assign the emission from alkali atoms with different surroundings. Since the nearest neighbors of alkali atoms in the middle layer of a nominally three-layer film are the same as in the bulk of a thick alkali film we denote these atoms as bulk atoms. Alkali atoms in the interface towards the substrate are denoted as interface atoms.

Complications that may arise when measuring layer-resolved core-level binding-energy shifts from alkali films such as changes in the magnitude of the shift when using different core levels,¹⁵ and the influence of the substrate surface index on the layer-resolved binding-energy shifts,⁸ have been discussed elsewhere. In order to minimize the effects of the detailed interface geometry, e.g., the substrate surface index, we have performed the measurements on alkali films deposited on the most close-packed surface of a specific substrate. Furthermore, when comparing binding energy shifts for a specific alkali metal we have always used the same core level, that is, for Cs the $4d$ level, for Rb the $4p$ level, for K the $3p$ level, and for Na the $2p$ level. It should also be noted that although the complications discussed above certainly are detectable, their magnitude is generally small compared to

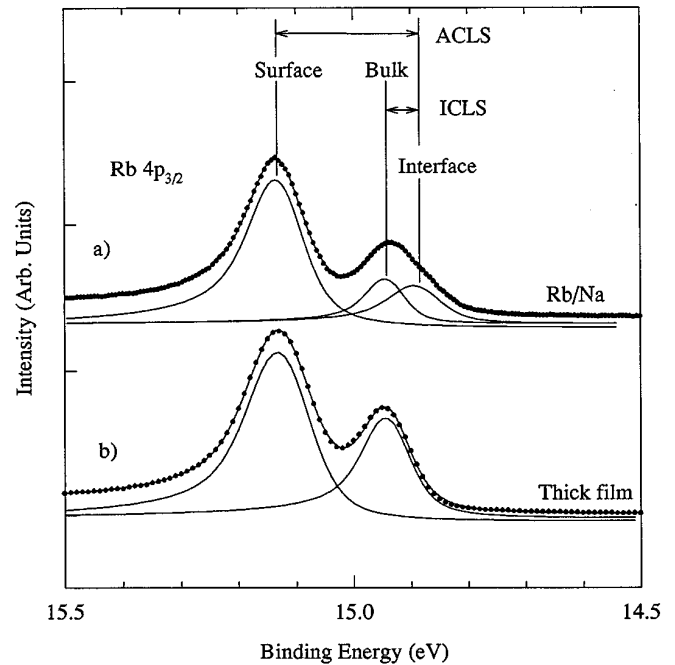


FIG. 1. (a) The decomposition of the Rb $4p_{3/2}$ spectrum for Rb deposited on Na for the three-layer situation (dotted line) into three shifted $4p_{3/2}$ components (full line) and the total spectrum (full line). (b) The decomposition of the Rb $4p_{3/2}$ spectrum for a thick Rb film (dotted line) into two shifted $4p_{3/2}$ components (full line) and the total spectrum (full line).

the shifts we discuss in this report.

As an example of core-level spectra of alkali metal films on sp -metal surfaces we show in Fig. 1 Rb $4p_{3/2}$ spectra from approximately three layers of Rb [Fig. 1(a)] on Na and from a thick Rb film [Fig. 1(b)]. The spectrum in Fig. 1(a) can be separated into three components, which correspond to electron emission from the surface, the bulk, and the interface layer, respectively, while the spectrum in Fig. 1(b) from a thick Rb film can be separated into two components, one from the bulk and one from the surface atoms. Similar behavior is found for all alkali films investigated. We define the interface core-level shift (ICLS) as the binding-energy shift between the interface and the bulk peaks and the adhesion core-level shift (ACLS) as the binding-energy shift between the interface and the surface peaks. (The reason for using the term adhesion core-level shift is that there is a close connection between this shift and certain adhesion energy differences; see, e.g., Ref. 16 and below.) As seen from Fig. 1(a) the ICLS for Rb on Na is quite small with a magnitude that is found to be approximately -50 meV. Such a small shift would normally be difficult to detect; however, comparison to the spectrum from the thick Rb film in Fig. 1(b) directly demonstrates the existence of a component at slightly lower binding energy than the bulk Rb peak. Furthermore, the thick Rb film spectrum provides a convenient reference for the line parameters to be used in the decomposition of the spectrum from the three-layer film, thereby making it possible to extract even such a small binding energy difference as 50 meV. It should be noted that for the majority of the systems measured the ICLS is considerably larger than that of Fig. 1(a), making it possible to determine it directly from the spectra

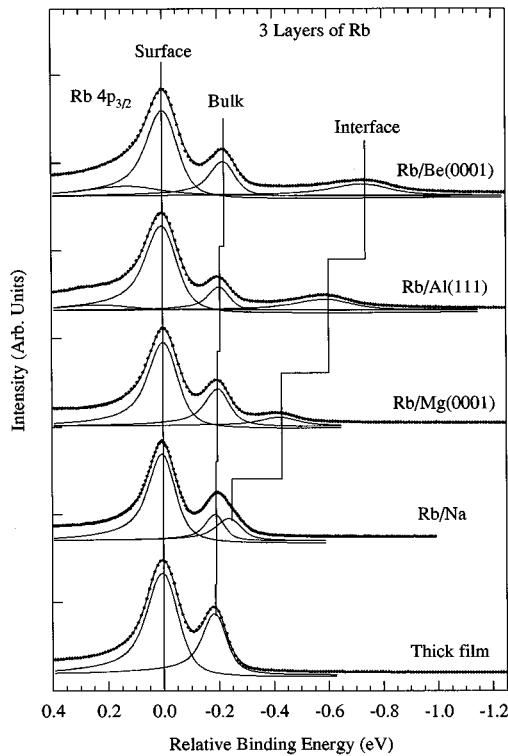


FIG. 2. Rb $4p_{3/2}$ spectra from approximately three layers of Rb on Na, Mg(0001), Al(111), Be(0001) as well as from a thick film of Rb. The weak components observed at higher binding energy than the surface peak for Rb on Al(111) and Be(0001) are due to emission from the Rb $4p_{1/2}$ spin-orbit component from the interface atoms.

without any need for a decomposition procedure.

In order to illustrate the influence of varying the substrate on the ACLS and ICLS we show in Fig. 2 core-level spectra from approximately three layers of Rb deposited on Na, Mg(0001), Al(111), and Be(0001) as well as a spectrum from a thick Rb film. The thick Rb film may be regarded as a three-layer Rb film deposited on a Rb substrate. The valence electron density of the substrate increases from the bottom towards the top of Fig. 2 and it is, therefore, seen that the ICLS and the ACLS of Rb increase with increasing electron density of the substrate, while the SCLS stays approximately constant. This dependence of the alkali core-level shifts on the substrate valence electron density is found for all of the investigated alkali-*sp*-metal interface systems. A qualitatively similar trend as observed in Fig. 2 has furthermore been observed in the case of alkali adsorption on 4*d* metals.⁷

Similar regularities and trends are also found when comparing the ICLS and the ACLS of different alkali metals deposited on the same substrate surface. In a previous publication⁶ dealing with the ICLS and ACLS of alkali films on Al(111) we have shown that these shifts increase as the alkali valence electron density is lowered, that is, as the atomic number of the alkali metal is increased. A similar behavior is found for alkali films deposited on the other *sp*-metal surfaces.

Before continuing a detailed discussion of the ICLS and the ACLS, which is the main theme of this paper, we will briefly comment on two interesting observations made from

Fig. 2; the increased linewidth of the interface peak and the apparent change in the SCLS with *sp*-metal substrate. These effects are not limited to Rb films but are generally observed in all of the investigated systems.

The broadening of the interface peak compared to the bulk and the surface peak is due to a combination of different effects. First, the existence of multiple sites in the interface layer may give an extra broadening. This is so because each different site may yield a separate core-level binding energy. In general, disorder at the interface layer may cause an extra broadening of the interface peak.^{13,16} Second, at the interface, the vibrational broadening is expected to be larger than for the bulk and the surface layers.^{13,14} Third, due to the different electronic structure of alkali atoms in the interface layer and the bulk and the surface layer, a broadening due to a decrease of the core-hole lifetime of an interface atom may occur. The lifetime of core holes in the outermost alkali *p* core levels would be particularly sensitive to changes in the valence electron structure as such holes can decay only via processes that involve the valence electrons. In agreement with this we have found that the deeper Cs $4d$ level is less broadened than the shallow Cs $5p$ level.¹⁷

The spectra in Fig. 2 have been aligned so that the binding energies of the surface components of the five spectra coincide. With this alignment, it can be seen that the binding energy of the bulk component, that is, of the intermediate Rb layer in the three-layer film, exhibits a trend of slightly decreasing binding energy with increasing substrate electron density. This decreasing trend is most likely caused by the influence of the substrate on the Rb atoms in the intermediate layer, that is, it is due to the core-level binding energies being dependent on the surroundings beyond the nearest neighbors. As can be seen from the binding energies of the interface peaks shown in Fig. 2 and as described above, Na, Mg, Al, and Be induce a lowering of the Rb $4p_{3/2}$ core-level binding energy. If the intermediate layer atoms in a three-layer Rb film are not completely isolated from the substrate, the result will be a shift of the core-level binding energy towards lower binding energy. In other words, the intermediate Rb layer will also exhibit an interface core-level shift. Furthermore, such a shift induced by the substrate is expected to show a trend similar to that of the ICLS, which is also what is observed. The largest decrease of the intermediate-layer binding energy, as compared to a true bulk layer, is observed for Rb on Be and is found to be approximately 30 meV, which is below 5% of the magnitude of the ICLS and ACLS. We want to point out that such a substrate dependent shift for the intermediate layer is found for all investigated alkalis and with a very small magnitude as exemplified in the case of Rb. In the following these very small shifts are not contained in our analysis and consequently we also term the intermediate layer as being bulk like.

Returning now to the discussion of the ICLS and ACLS, we give in Table I experimental values for these shifts from three layers of alkali metals deposited on close-packed *sp*-metal surfaces. It may be noted that Table I also includes the ACLS and ICLS of Na induced by the other alkali metals, and that these values are the only ones for interfaces towards a metal with a lower valence electron density. The values of Table I suggest as a qualitative rule that the mag-

TABLE I. Measured ICLS's and ACLS's in eV for Na, K, Rb, and Cs on the indicated metals.

	ICLS	ACLS
Rb on Na	-0.05	-0.24
Rb on Mg	-0.23	-0.42
Rb on Al	-0.39	-0.59
Rb on Be	-0.51	-0.73
Cs on Na	-0.13	-0.34
Cs on Mg	-0.35	-0.57
Cs on Al	-0.63	-0.83
Cs on Be	-0.67	-0.88
K on Na	-0.03	-0.25
K on Al	-0.36	-0.56
Na on Al	-0.18	-0.36
Na on K	+0.03	-0.16
Na on Rb	+0.04	-0.15
Na on Cs	+0.05	-0.14

nitude of the alkali core-level shift induced by an *sp* metal increases with the difference in the electron densities of the *sp* metal and the alkali metal. Concerning the direction of the shifts, Table I shows that deposition on a substrate with higher (lower) valence electron density than the alkali metal itself shifts the interface alkali core-level binding energy to lower (higher) binding energy than the bulk.

It is well known that the ICLS may be interpreted as the segregation energy to the interface of a $Z+1$ impurity in the Z metal host¹⁶ (we denote this way of interpreting the ICLS as the segregation model). From Table I it is seen that a $Z+1$ impurity in an alkali metal will segregate to the interface between the alkali metal and the substrate metal M , with increasingly higher segregation energy as the atomic number of the alkali metal is increased. Furthermore, the segregation energy to the interface of the $Z+1$ impurity in the Z metal host will increase as the substrate changes from Na to Mg to Al to Be.

The shift between the peak originating from emission from the alkali surface atoms and the peak from the interface atoms, the ACLS, is related to the difference in adhesion energy between the Z and the $Z+1$ atom per Z atom interface area on the same substrate^{7,16,18} (we denote this way of interpreting the ACLS as the adhesion model). This adhesion energy difference increases as we increase the atomic number of the alkali atom, and furthermore, it increases as we change the substrate from Na to Mg to Al to Be.

Not only are these measurements a source of information on thermodynamic properties, which may be difficult to obtain with other methods, but a reversal of the above relationships also allows for estimates of core-level binding-energy shifts from various thermodynamic parameters. To calculate the relevant thermodynamic quantities we use Miedema's semiempirical scheme.^{19,20} The complications due to the large size difference between the Z and $Z+1$ atoms in the case of Z being an alkali atom^{7,18} and to complications arising due to Miedema's scheme have been discussed elsewhere.⁷ The results from these calculations are presented in Figs. 3(a) and 3(b) together with the experimental results.

A model to estimate core-level binding-energy shifts in

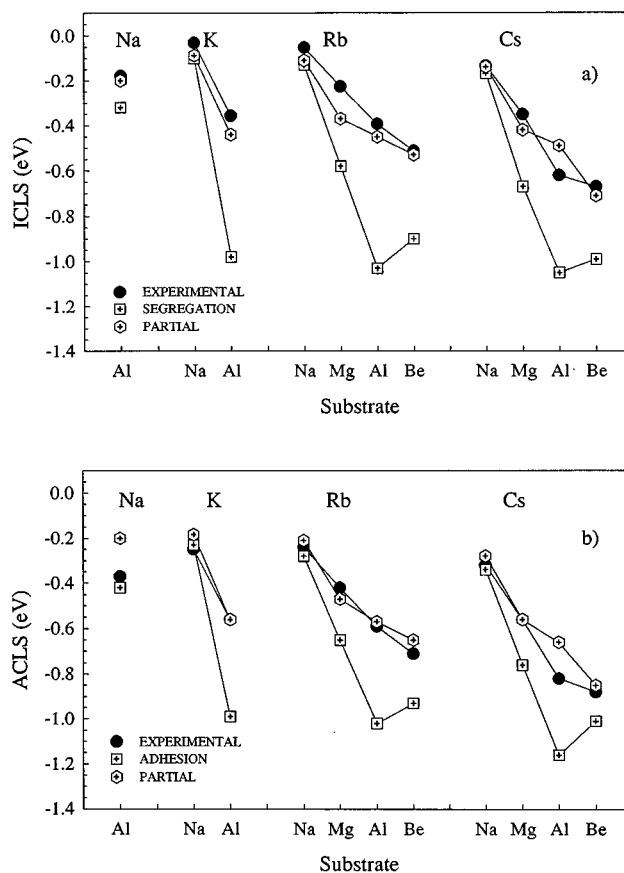


FIG. 3. (a) Measured and calculated ICLS for Na, K, Rb, and Cs on the indicated metals. (b) Measured and calculated ACLS for Na, K, Rb, and Cs on the indicated metals.

metallic alloy systems, which more explicitly takes into account the geometrical changes of the surroundings of the photoemitting atom, is the so-called partial shift model.²⁴ In this model each atom in the surroundings of the photoemitting atom is assumed to give an additive contribution to the binding-energy shift. In the case of a two-element system with elements Z and M this means that the binding-energy shift of the Z element is given by the sum of two or three terms, one term that takes into account how much the Z atom is coordinated to other Z atoms, a second term that takes into account how much the Z atom is coordinated to M atoms, and finally a third term, for a surface atom, that takes into account how much the Z atom is coordinated to vacuum. The results from the calculations²⁵ of the binding-energy shifts using the partial shift model for alkali deposition on close-packed surfaces, are included in Figs. 3(a) and 3(b).

As can be seen from Fig. 3, the agreement between the calculated values and the experimentally obtained values is surprisingly good for the partial shift model. The adhesion and segregation shift models reproduce the signs and the trends but yield larger deviations from the experimentally obtained values. The discrepancies are observed to be especially large in the case of alkali adsorption on Al, which most likely can be explained by errors in the solution energies calculated for these systems by Miedema's scheme.

Based on the measured core-level binding-energy shifts a qualitative rule may be established that says that the

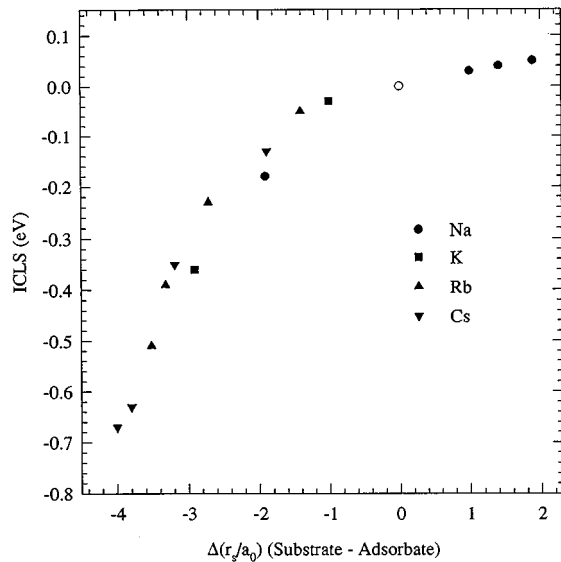


FIG. 4. Plot of the difference in r_s/a_0 value between the substrate and the alkali adsorbate vs ICLS for alkali deposition on various sp -metal substrates. $a_0 = 0.529 \times 10^{-10}$ m is the Bohr radius. The open circle at the origin indicates that the ICLS of a metal on itself is zero.

sp -metal-induced shift of an alkali core level increases with increasing difference in valence electron density between the sp metal and the alkali metal. This rule, however, is only qualitative and does not allow for quantitative predictions of the shifts. Somewhat surprisingly, it turns out that a predictive relation is found if one compares the ICLS against not the valence electron density itself but instead the r_s value of the electron gas. In Fig. 4 is shown the ICLS as a function of the difference in r_s value between the substrate sp metal and the alkali adsorbate. As can be seen from Fig. 4 all points fall very close to a smooth curve. Thus, Fig. 4 indicates that the ICLS (and the ACLS, as this is approximately the ICLS plus the surface core-level shift of the alkali metal) of the alkali core levels for the presently investigated systems depends, via a simple relationship, on the difference in r_s value for the alkali metal and the sp substrate. This is quite interesting as it means that the core-level shifts have a simple relation to parameters that are related to the *initial* state of the system. This does not mean that final-state effects are negligible as evident from the fact that the thermochemical models contain final-state effects and they agree well with experiments. However, one can argue that using r_s , which is solely an initial-state parameter, might still to some extent include final-state effects since the final-state relaxation energy should depend on the electron distribution in the initial state. Unfortunately it is not possible without *ab initio* calculations to distinguish the magnitude of initial- and final-state effects. Thus, without such calculations, it is not possible to explain the reason for the simple relationship observed in Fig. 4.

Because the variation of the r_s values in Fig. 4 spans the

whole range possible for alkali deposition on sp substrates it is most likely that measurements of the ICLS of an alkali sp -metal combination not included in the figure will yield a value that falls very close to the data assembled in Fig. 4. As there is a close relationship between the binding energy of interface alkali atoms and alkali atoms in a close-packed monolayer on the same surface, Fig. 4 also allows for predictions of the core-level binding energies of such monolayers on close-packed sp -metal surfaces. Furthermore, as the ICLS is equal to the segregation energy of a $Z+1$ impurity to the interface between the Z metal and the substrate, the relationship suggested by Fig. 4 must also be fulfilled by such segregation energies. As the ACLS to a good approximation is equal to the sum of the ICLS and the SCLS and as the SCLS of the alkali metals is almost independent of alkali metal, the ACLS, and thereby the adhesion energy difference which describes this shift, must also follow a similar simple curve.

It should be noted that the above relationship only applies to the alkali core-level binding-energy shifts induced by sp -metal substrates. We have previously^{7,8} reported core-level binding-energy shifts from thin alkali films deposited on various $4d$ -metal substrates. In the case of the $4d$ metals^{7,8} there is no simple relationship between the alkali core-level binding-energy shifts and the difference in r_s value between the alkali metal and the $4d$ metal (for the $4d$ metal we used the sum of the s and p densities for calculating the r_s values). For similar differences in r_s value a $4d$ metal induces a significantly larger shift of the alkali core level than an sp metal. It should furthermore be noted that the relation seen in Fig. 4 applies only to the alkali core level shifts and not to the shifts of the substrate core levels, except of course in the case when the substrate itself is an alkali metal.

SUMMARY

In summary, we have measured layer-resolved core-level binding-energy shifts for Na, K, Rb, and Cs on several different sp -metal substrates by high-resolution core-level spectroscopy. The experimental results can be reproduced quite well by models based on a thermodynamic description using as input parameters values calculated by Miedema's scheme. A strong correlation between the ICLS (and the ACLS) and the difference in r_s value between the alkali adsorbate and the sp substrate has been shown to exist.

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- ²⁰The adhesion energy in Miedema's formalism (Ref. 21) is given by
- $$E_{\text{adh}} = -\gamma_M - \gamma_Z + \gamma^{\text{chem}} + \gamma_{\text{mm}},$$
- where γ_M and γ_Z are the surface energies for the pure metals, γ^{chem} and γ_{mm} are the contributions from the interfacial energy where γ^{chem} is related to the energy of alloying, and γ_{mm} is the average grain boundary mismatch energy. The mismatch energy has been chosen to be 15% of the sum of the surface energies (Ref. 21). We have used surface energies from Ref. 22 and solution energies from Ref. 23.
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