

Adlayer core-level shifts of admetal monolayers on transition-metal substrates and their relation to the surface chemical reactivity

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Using density-functional theory, we study the electronic and structural properties of a monolayer of Cu on the fcc(100) and (111) surfaces of the late 4*d* transition metals, as well as a monolayer of Pd on Mo bcc(110). We calculate the ground states of these systems, as well as the difference of the ionization energies of an adlayer core electron and a core electron of the clean surface of the adlayer metal. The theoretical results are compared to available experimental data and discussed in a simple physical picture; it is shown why and how adlayer core-level binding energy shifts can be used to deduce information on the adlayer's chemical reactivity.

Modern catalysts typically consist of more than one component, because the activity and selectivity required in a specific chemical process may be conveniently tuned by changing the catalyst's material composition.¹ While the requirements to a specific catalyst are usually quite obvious, a simple tool to analyze the reactivity of a multicomponent system, which could help in the design of new catalysts, is still missing, even when only a coarse scale is asked for. Recently, Rodriguez, Campbell, and Goodman investigated the core-level shifts of supported monolayers of Ni, Cu, and Pd by x-ray photoelectron spectroscopy (Refs. 2–4) in order to analyze the physical and electronic properties responsible for the particular catalytic properties of bimetallic surfaces.

The authors stress that parallel trends exist between the shifts of core-electron binding energies of surface atoms of the supported monolayers and the chemisorption properties of these systems. Furthermore, they note a correlation between changes in CO desorption temperatures and relative core-level shifts, and suggest that core-level measurements may be a powerful tool for examining the surface chemical reactivity.

We define the adlayer core-level shift (ACLS) as the difference of the ionization energies of an adlayer core level and a core level of a clean elemental crystal surface. The latter consists of the same element as that forming the adlayer. Thus, using the system Cu on Pd(100) as an example, the ACLS is

$$\Delta_{\text{ACLS}} = \tilde{I}_c^{\text{Cu/Pd(100)}} - \tilde{I}_c^{\text{Cu(100)}} = E^{\text{Cu/Pd(100)}}(n_c = 1) - E^{\text{Cu/Pd(100)}}(n_c = 2) - E^{\text{Cu(100)}}(n_c = 1) + E^{\text{Cu(100)}}(n_c = 2), \quad (1)$$

where \tilde{I}_c are the core-level ionization energies, with respect to the Fermi energies, and E are total energies of the ground state [two electrons in the core level ($n_c = 2$)] and the excited state [one electron in the core level ($n_c = 1$) and an additional electron at the Fermi level]. The upper indices identify the considered systems, namely, the adsorbed Cu monolayer on a Pd(100) substrate and the clean Cu(100) surface. It should be noted that the ACLS refers to an energy difference between *two surfaces* consisting of the same element, which

contrasts with the definition of surface core-level shift (SCLS), which is the energy difference of *surface and bulk* ionization energies. Therefore, it might appear plausible that screening effects experienced by the core hole may drop out in the ACLS. The above definition refers to Cu on Pd(100), but a transcription to other systems is obvious.

The analysis of Rodriguez *et al.*⁴ simply ignored final state screening contributions. Furthermore, they explained their results in terms of charge transfer between the surface and substrate atoms. For example, they argue that at a Cu monolayer adsorbed on an early transition metal (less than half occupied *d* band), some electron transfer takes place from the overlayer to the substrate, which will shift the Cu core levels towards higher binding energies (positive ACLS). Similarly, a Cu monolayer adsorbed on a late transition metal would *accept* electrons from the substrate. This would produce a negative ACLS and a stronger Cu-CO bonding.⁴

With respect to SCLS's, it is by now clear that the charge transfer picture and the initial-state approximation do not hold;^{5–7} however, whether this criticism also applies to ACLS's is not obvious. Nevertheless, there exist severe doubts that the analysis and interpretation of Rodriguez *et al.* can be trusted, although the idea to design a tool to investigate surface reactivities is most appealing.

In this work, we present a detailed density-functional-theory study of the trends in ACLS's for adsorbed metallic monolayers and show that also in ACLS's (similar to SCLS's), the final state screening contributions can be significant. We find practically no charge transfer *between* adsorbate and substrate. However, there is a noticeable internal polarization of the adlayer atoms. The results show that and why a correlation between ACLS's and surface reactivities exists.

We consider a monolayer of Cu on the fcc(100) and (111) surfaces of Ru, Rh, Pd, and Ag, as well as a monolayer of Pd on Mo bcc(110). Using Slater's transition-state concept to evaluate total energy differences, we obtain from Eq. (1),

$$\Delta_{\text{ACLS}} \approx -[\epsilon_c^{\text{Cu/Pd(100)}}(n_c = 1.5) - \epsilon_F^{\text{Cu/Pd}}] + [\epsilon_c^{\text{Cu(100)}}(n_c = 1.5) - \epsilon_F^{\text{Cu}}], \quad (2)$$

TABLE I. Relaxation of the outermost layer in percentage of the interlayer spacing in the substrate bulk.

Material	Surface relaxation	
	fcc(100)	fcc(111)
Clean Cu	-2.0	-2.4
Cu/Ru	-4.8	-2.8
Cu/Rh	-7.1	-5.0
Cu/Pd	-12.7	-9.3
Cu/Ag	-16.6	-10.9
Pd/Mo	-1.5 [bcc(110)]	

where $\epsilon_c^{\text{Cu/Pd}(100)}$ and $\epsilon_c^{\text{Cu}(100)}$ denote the Kohn-Sham eigenvalues of a particular core state of an adlayer Cu atom and a surface atom of clean Cu(100). The Fermi energies of the Cu/Pd(100) and Cu(100) slabs are $\epsilon_F^{\text{Cu/Pd}}$ and ϵ_F^{Cu} , respectively. In the initial-state approximation, the ACLS is given by Eq. (2) with $n_c=2$.

The electron density, surface atomic structure, total energies, core-electron eigenvalues, and ACLS's are calculated using the full-potential linear muffin-tin orbital method together with the local-density approximation of the exchange-correlation functional.⁸ Details of the method are described elsewhere.⁹ The surfaces are modeled by slabs which have a thickness of nine layers for the fcc(100) and bcc(110) systems, and seven layers for the fcc(111) ones. To describe the transition-state, self-consistent electronic structure calculations are performed under the constraint of charge neutrality, which implies that half a valence electron is added at the Fermi level. This describes the situation of an electronically fully relaxed final state and thus applies to systems which have a Fermi reservoir of electrons. The impurity problem of the localized core hole is treated by means of a supercell, such that the atom containing the core hole is surrounded by nonionized nearest neighbor atoms.

For a qualified theoretical analysis of ACLS's, it is important to use the correct ground state geometry. Thus, we have determined the surface relaxation of the outermost layer by minimizing the total energy, while keeping the interatomic distances of deeper layers as those obtained from bulk calculations. This approximation is well justified, because the change in the first interlayer spacing of the clean surface or

the distance between the adlayer and the first substrate layer would be less than $\pm 2\%$ of the ideal interlayer spacing if the two topmost layers are allowed to relax simultaneously. For example, we have obtained for the clean Cu(111) surface a 0.9% and a 0.6% contraction of the first and second interlayer spacings. This implies an increase of 1.5% of the first interlayer spacing if compared with the case where just the surface layer was allowed to relax (see Table I). Experimentally, a 0.7% contraction has been observed.¹⁰ Similarly, for Cu/Ru fcc(111), a contraction of 2.6% of the adlayer separation and a 3.1% contraction of the outermost Ru-layer separation has been obtained. The latter result implies an increase of only 0.2% of the adlayer separation if compared with the case in which just the adlayer was allowed to relax (see Table I). These numbers compared well with earlier calculations, which found 2.5% and 3.5% contractions for the adlayer and first substrate layer of Cu/Ru hcp(0001), respectively.¹¹ The results for the topmost layer relaxation calculations are summarized in Table I. In particular, for Cu/Pd and Cu/Ag, the surface relaxation is substantial, reflecting the fact that the covalent radius of Cu is significantly smaller than that of Pd and Ag. The Ru substrate is considered here in the fcc structure, because we do not expect that the difference between the fcc and hcp structures is important for the problems discussed in this paper. Obviously, the theory for Ru fcc(111) is compared with experiments for Ru hcp(0001).

Table II lists the ACLS's for Cu $2p$ electrons for a Cu monolayer on the fcc(100) and (111) surfaces of Ru, Rh, Pd, and Ag and for Pd $3d$ electrons for a Pd monolayer on Mo bcc(110). The agreement between calculated ACLS's and the few experimental data is good. In particular, it is better for the reported $3d$ level measurements than for the $2p$ level ones, which in turn have a substantially larger lifetime broadening. The theoretical results show that for a monolayer of Cu supported on late transition metals, the Cu core electrons are less strongly bound (relative to the Fermi level) than those of clean Cu. The magnitude of the ACLS increases with the filling of the substrate d band. The influence of the substrate is indeed significant: For Cu/Pd the Cu $2p$ electron is by 0.7 eV weaker bound than that of clean Cu. The results for Cu/Ag do not follow this trend, i.e., for these systems the magnitudes of the ACLS's are smaller than those of Cu/Pd,

TABLE II. Calculated adlayer core-level shifts (ACLS's) of Cu $2p$ and Pd $3d$ levels, their initial-state and screening contributions, and experimental data from Ref. 2. All values are in eV. For the definition of ACLS's see text and Eqs. (1) and (2).

Material	Surface	ACLS theory	Initial-state contribution	Screening contribution	ACLS experiment
Cu/Ru	fcc(100)	-0.42	-0.16	-0.26	
	fcc(111)	-0.42	-0.30	-0.12	-0.13 [hcp(0001)]
Cu/Rh	fcc(100)	-0.59	-0.46	-0.13	-0.43
	fcc(111)	-0.57	-0.53	-0.04	
Cu/Pd	fcc(100)	-0.69	-0.85	+0.16	
	fcc(111)	-0.67	-0.84	+0.17	
Cu/Ag	fcc(100)	-0.18	-0.46	+0.28	
	fcc(111)	-0.34	-0.53	+0.19	
Pd/Mo	bcc(110)	+0.90	+0.77	+0.13	+0.90

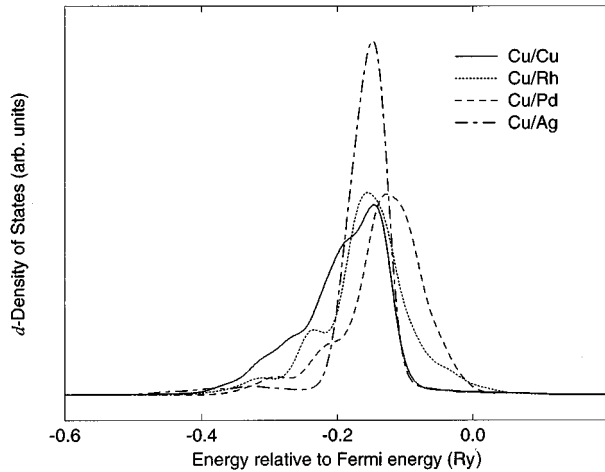


FIG. 1. Partial density of states (d contribution integrated over the muffin-tin sphere of the outermost atomic layer) for a clean surface of Cu fcc(100) (solid line) and for a Cu monolayer on Rh fcc(100) (dotted line), on Pd fcc(100) (dashed line), and on Ag fcc(100) (dot-dashed line).

Cu/Rh, and Cu/Ru. But the adlayer core levels are still at smaller binding energies than the corresponding levels at the clean Cu surface.

The trend of the calculated ACLS's is already present in the initial-state approximation (column 4 in Table II), but the difference between the total ACLS and the initial-state contribution, which is the screening contribution (column 5 in Table II), is obviously not negligible: For Cu/Ag(100) it amounts to 0.3 eV and reduces the initial state contribution by 60%.

We will first discuss the origin of the trend of the core-electron eigenvalues of the non-excited systems in their electronic ground states, i.e., the initial-state contribution to ACLS's. The theoretical analysis shows that the trend of the initial-state eigenvalues is due to a change in the surface potential caused by a rearrangement within the surface density of states (DOS): Electrons are transferred from the top of the d band of the Cu adlayer into sp DOS. This increases the bond strength between surface layer and substrate and still enables the system to maintain local charge neutrality. The sp electrons in turn spill out into the vacuum to reduce their kinetic energy, which implies an induced surface dipole moment which has the negative end at the vacuum side. The

emptying of the upper Cu $3d$ DOS at the surface is consistent with the shift of the surface d DOS towards the Fermi level.

Figure 1 displays the d contribution of the surface DOS at a clean Cu (100) surface and at the Cu monolayer adsorbed on the fcc(100) surface of Rh, Pd, and Ag. The mentioned shift to lower binding energies is clearly visible. The core electrons feel this reduced d electron density and also shift towards the Fermi level, i.e., to lower binding energies. Figure 2 displays the changes of the electron charges contained in the different muffin-tin spheres. We present the charges in "empty spheres" just above the surface in the vacuum, the differences of the charges contained in the spheres of the Cu layer and a sphere in Cu bulk, and differences of the charges contained in the spheres of the second layer, i.e., the top layer of the substrate, and the same atom in the bulk. The clean Cu surface is treated correspondingly, namely, as a Cu monolayer on a Cu substrate. In the top substrate layers (full circles in Fig. 2), the charges are very similar to those in the bulk: For Cu/Cu and Cu/Rh the deviations from the bulk charges are practically zero, for Cu/Ru there are slightly less electrons and for Cu/Pd and Cu/Ag there are slightly more electrons at the top substrate layer. Bigger changes are present in the surface layer: For all surface layers, the number of electrons is reduced and this reduction is nearly compensated by the electrons that we find in the "empty spheres" just outside the surface. These results confirm the above explanation, namely, that these systems ought to be described in terms of a rearrangement within (or polarization of) the adlayer DOS, as opposed to a charge transfer between the surface layer and the substrate.

In distinction to the Cu/ X results ($X = \text{Ru, Rh, Pd, and Ag}$), the calculations for a Pd monolayer supported on Mo bcc(110) reveal that the Pd $3d$ core electron is more strongly bound in Pd/Mo than in Pd fcc(100). Thus, for Pd/Mo, we find a positive ACLS. For Pd/Mo, the surface d band is broader than that of clean Pd, the bottom is dominated by Pd d states and the top by the tails of the d states of the Mo substrate. Local charge neutrality requires now a rearrangement of the d and sp electrons in a way that the surface d DOS shifts to higher binding energy. Similarly, inspection of the surface d DOS for the Cu/ X systems (see, e.g., Fig. 1) shows that the d band width for clean Cu is wider than for the Cu/ X systems. In this case, one argues that the narrower overlayer d DOS must shift to lower binding energies, so that local charge neutrality is maintained.

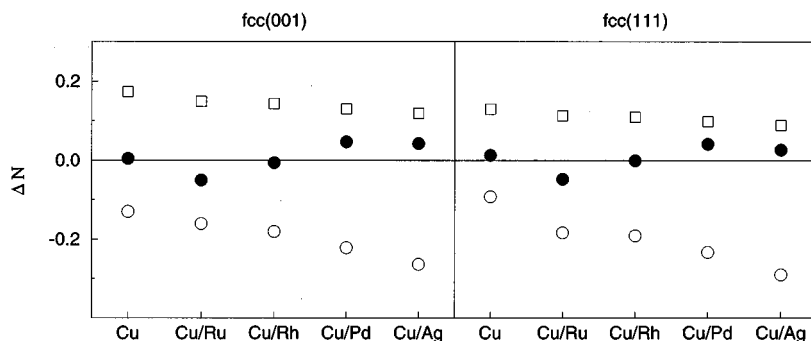


FIG. 2. Charge deficiency (negative ΔN) or charge increase (positive ΔN) on individual atomic sites, compared to the charge in the bulk metals. Full circles correspond to atoms in the interface, i.e., in the layer touching the adlayer or the second substrate layer for clean surfaces; open circles are for the adlayer or surface layer. Open squares are for the layer representing the vacuum-solid interface.

The ACLS's are sometimes substantially different to this initial-state effect; we note, however, that in the studied examples, the *sign* of the initial-state contribution and that of the total ACLS is always the same; in general, even this does not hold necessarily, but we expect that it will hold for most systems. We like to add that the screening contributions to ACLS's are particularly large for Cu, because noble metals have a low density of states at the Fermi level and thus the screening of a core hole by intraatomic polarization is rather inefficient. Thus, screening due to the surrounding atoms is important.

Both the initial state and the screening contributions to the ACLS probe the importance of *d* states at the Fermi level. A negative initial-state contribution means that the adlayer Cu (or Pd) atoms *d* band is shifted closer to the Fermi level (see Fig. 1), and a negative screening contribution means that screening of a core hole in the adlayer is better than for the surface atoms of clean Cu (or Pd). A positive screening contribution means that screening of a surface core hole is worse for the Cu (or Pd) adlayer atoms than for the clean Cu (or Pd) surface.

It is well known that the *d* states at the Fermi level determine the reactivity of surfaces (see, for example, Refs. 12–15): When there are *d* states at the Fermi level, strong chemical bonds can be formed with adsorbates,^{12,14} and Hammer and Scheffler have recently shown that a low DOS just below the Fermi level gives rise to an energy barrier hindering the dissociation of H₂, while a high DOS just below ϵ_F lowers or removes the energy barrier.¹⁵ Thus, the difference in H₂ dissociation barriers observed on pure Ni

and Cu surfaces arises due to the difference in the positions of the substrate *d* levels relative to the Fermi level on the two surfaces.¹⁵

The results presented here demonstrate that the shift of core-electron eigenvalues sensitively detect the shift of the valence *d* band. One important conclusion that can be drawn from this result is that as the *d* states at the Fermi level typically act as “frontier orbitals”¹³ in surface chemical reactions,¹⁴ ACLS's may indeed give important information on the changes of the surface reactivity induced by adsorbed metallic layers. Our above analysis, for example, suggests that the reactivity of a Cu monolayer on a rhodium (or Pd or Ag) substrate is higher than that of a clean Cu surface, and the reactivity of a Pd monolayer on Mo is lower than that of a clean Pd surface. It would be interesting to see if these predictions will be verified experimentally.

Note added. Recently, we learned that the Cu/Rh and Cu/Ru surfaces do indeed show higher chemical activities than clean Cu surfaces for the CO oxidation and cyclohexane dehydrogenation reactions, respectively.^{16,17} We are grateful to D.W. Goodman for this information.

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