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Surface core-level spectroscopy of Cu(100) and Al(100)

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We present experimental and theoretical results for the surface core-level binding-energy shifts of Al(100), representative of an *sp* metal, and Cu(100), representative of a transition metal. Our analysis of these results leads to a unified interpretation for the different behavior of *sp* and transition metals. The *d*-electron contribution to smaller surface core-level binding energies is elucidated.

The binding energy of core electrons is a probe of the electronic configuration of the ionized atom. Due to the broken symmetry at the surface of a solid, the atoms of the topmost layer have an electronic structure modified with respect to the bulk and their core-level binding energies (BE's) are expected to be shifted from the bulk position.¹⁻⁴ Angle-resolved x-ray photoemission spectroscopy (ARXPS) has been widely applied to study the electronic structure of surface atoms as compared to that of the bulk.¹⁻⁴ The first surface-atom core-level (SCL) shifts were reported by Houston, Park, and Laramore⁵ and afterwards were observed for many other metals.⁶ For *sp* metals, SCL shifts are, with a few exceptions,⁷ toward higher BE's.⁸ Systematic trends, correlated with the position of the atom in the Periodic Table,⁹ have been found for *d* and *f* metals. Several models have been proposed to interpret the SCL effects, in particular for *d*-electron metals; see, for example, Refs. 4, 10, and 11 and the review of Egelhoff.¹² These theories predict a trend for the SCL shifts that depends on the *d*-electron count, i.e., on the predominance of *d*-electron bonding, or on the surface-broken symmetry (bond-breaking models). However, recent experiments on Os(0001), Re(0001),¹³ Ba polycrystalline films,¹⁴ and Y(0001) (Ref. 15) indicate that accurate first-principles calculations are needed to understand the SCL mechanisms. Johansson and Mårtensson¹⁶ have given a semiempirical relationship for SCL shifts for metals based on the use of the equivalent-core approximation. They relate the SCL shift to the cohesive energies of the original and the equivalent core metal and to the solvation energy of an equivalent core impurity; their relationship leads to both positive and negative SCL shifts. Our purpose in the present paper is to relate the SCL shifts to the fundamental aspects of the different electronic structure of surface and bulk atoms. We have studied these basic aspects for a 3*d* metal (Cu) and an *sp* metal (Al). The SCL shifts measured on

(100)-oriented Cu and Al single crystals are interpreted in the framework of molecular orbital, self-consistent-field (SCF) wave functions for clusters modeling Al(100) and Cu(100).

We show that SCL shifts of Al to higher BE's and of Cu to lower BE's arise from two canceling initial-state contributions to the core-level BE. For both Al and Cu, there is a shift of the core-level BE's which arises from the diffuse, primarily *sp* conduction-band, charge density due to the surroundings of the ionized atom.^{17,18} This shift lowers the BE's depending on the coordination of the ionized atom and leads to an SCL shift to a higher BE because the surface atoms have lower coordination. However, for Cu (but not for Al) there are also BE shifts because of the hybridization and promotion of *d* electrons with the *sp* band. This hybridization reduces the *d*-electron count of both bulk and surface atoms and it raises the BE's. In this paper, we show that the *d* hybridization effect dominates for Cu and the SCL shift is negative. We also show that final-state effects are similar for both bulk and surface atoms and do not change the sign and magnitude of the SCL shift.

ARXPS spectra were taken using a small-spot monochromatized XPS system, Perkin-Elmer mod. 5500. The resolution of this system, as measured on the Ag 3*d*_{5/2} line, was 0.35 eV. Cu and Al single crystals, 99.999 and 99.9999% pure, respectively, were prepared with exposed (100) surfaces which were electropolished. The samples were in an ARXPS chamber, held at a pressure of 1×10^{-10} torr. The surfaces were cleaned by mild sputtering and heating ($\sim 450^\circ\text{C}$ for Al and $\sim 700^\circ\text{C}$ for Cu). This surface preparation produces very good surfaces on an atomic scale.^{19,20} The XPS spectrometer was calibrated using the Fermi edge E_F measured at takeoff angles, θ , and 10° and 80° , where 10° is the grazing exit; E_F was the same for both takeoff angles.

Figure 1 shows the Al(100) 2*p* XPS spectra for $\theta = 10^\circ$

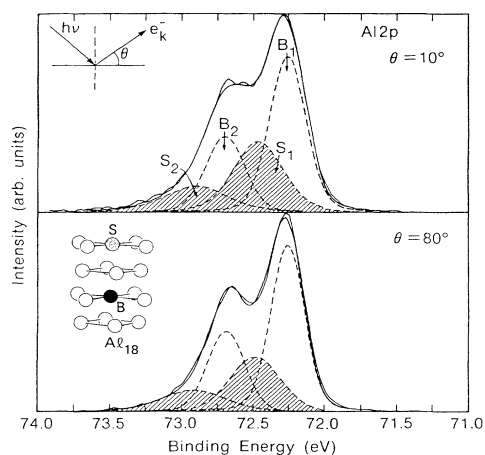


FIG. 1. The surface, S_1 and S_2 , and bulk, B_1 and B_2 , components of the $2p_{3/2}$ - $2p_{1/2}$ doublet of the Al(100) XPS spectra. The dashed lines are the decomposition of the observed, solid line, spectra; the Al₁₈ cluster is shown.

and 80°. The grazing-angle spectra are unambiguously broadened toward higher BE. Moreover, the Al $2p_{1/2}$ -Al $2p_{3/2}$ spin-orbit splitting is significantly quenched in the $\theta=10^\circ$ spectrum, indicating the rise of two extra core lines at ~ 72.4 and 72.8 eV. In the decomposed spectra shown in Fig. 1, the lines labeled S_1 and S_2 are assigned to SCL states while the lines B_1 and B_2 are attributed to photoelectrons from bulk atoms. The measured SCL shift is ~ 0.20 eV. The only constraints imposed in our decomposition are that there would be two pairs of peaks, S_1 and B_1 and S_2 and B_2 , and that the BE difference of these two pairs would be the same, $S_1 - B_1 = S_2 - B_2$. All other parameters, including peak position, $S - B$ separation, intensity, and full width at half maximum (FWHM) were found by obtaining the best fit to the data.

These results are confirmed by resonant photoemission data for the Al(100) single crystal. In this case however, the spectra were not carefully decomposed and the shift was ambiguously interpreted.²¹ However, our spectral decomposition gives a $2p_{3/2}/2p_{1/2}$ intensity ratio for both the S and B lines very close to 2, the theoretical value. Moreover, the difference between the fitted bulk and sur-

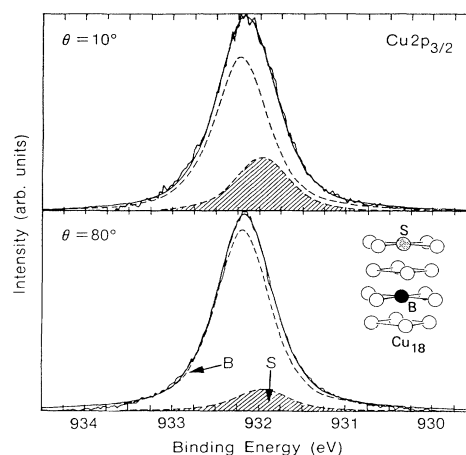


FIG. 2. The surface component S of the Cu(100) $2p_{3/2}$ XPS spectra is at lower BE than the bulk component B .

face BE's are similar for the 80° and 10° spectra consistent with the physical origin of bulk and surface peaks. Finally, the broadening, or FWHM, of the S and B lines determined from our decomposition are similar for the 10° and 80° cases, but with the surface peaks somewhat broader.

Similar measurements on the Cu(100) surface lead to completely different results. Figure 2 shows the Cu $2p_{2/3}$ core line of Cu(100) at $\theta=10^\circ$ and 80°. The Cu(100) spectra at $\theta=10^\circ$ exhibits a broadening to lower BE, with respect to the spectra at $\theta=80^\circ$. This broadening, in agreement with the current literature,³ has been attributed to the SCL shift. For the grazing exit at 10°, the Cu $2p_{3/2}$ peak has been decomposed into bulk (B) and surface (S) contributions, see Fig. 2; peak S is shifted downward by ≈ 0.2 eV with respect to peak B . Table I summarizes the parameters of the decomposition; they are similar to those reported for polycrystalline samples.³ A shift in the same direction, i.e., toward lower BE, was also observed in the Cu $L_{2,3}M_{4,5}M_{4,5}$ Auger lines measured at $\theta=10^\circ$ compared to the same Auger transition measured at $\theta=80^\circ$. Also consistent with data reported in literature is the narrowing observed for the $3d$ valence band states measured at grazing takeoff angles.²²

TABLE I. Typical results of the spectral decomposition for the bulk and surface components at $\theta=80^\circ$ and 10° for Cu $2p_{3/2}$ and Al $2p_{3/2,1/2}$ core levels using a BE resolution of ≈ 0.35 eV.

θ	BE (eV) Bulk (B)	BE (eV) Surface (S)	$E_b^{\text{surf}} - E_b^{\text{bulk}}$ (eV)	FWHM (B) (eV)	FWHM (S) (eV)	Gauss.% (B)	Gauss.% (S)	I_S/I_B Intensity ratio ^a
Cu $2p_{3/2}$								
80°	932.2	931.95	-0.24	0.75	0.75	35	45	0.12
10°	932.2	931.95	-0.24	0.75	0.75	35	40	0.34
Al $2p_{3/2}$								
80°	72.26	72.48	+0.22	0.28	0.42	86	100	0.45
10°	72.28	72.48	+0.20	0.30	0.42	83	85	0.62
Al $2p_{1/2}$								
80°	72.69	72.91	+0.22	0.30	0.51	94	79	0.45
10°	72.72	72.92	+0.20	0.32	0.51	94	59	0.62

^a I_S/I_B is the intensity ratio of the deconvoluted surface and bulk components.

We have used a molecular-orbital cluster-model²³ analysis to interpret the SCL BE shifts for Al(100) and Cu(100). The Al₁₈ and Cu₁₈ clusters (Fig. 1) were chosen because they contain a bulk and a surface atom with their twelvefold and eightfold coordination, respectively; an unreconstructed surface is represented with bond distances taken from the bulk. The two atoms in the X₁₈ cluster which have the proper bulk and surface coordinations are treated including all their electrons explicitly. The remaining 16 environmental atoms are treated using pseudopotentials²⁴ for the core electrons. The cluster molecular orbitals are expanded into large basis sets of atomic orbitals to reduce basis-set-superposition artifacts.²⁵

The core-level BE's or ionization potentials were obtained in two ways. Initial-state effects only were obtained from SCF wave functions for the neutral ground state using Koopman's theorem (KT). Final-state effects were taken into account by taking the difference of the total SCF energies of the neutral and ionic states, the Δ SCF method. The Δ SCF BE's include the cluster representation of the screening of the core hole. It has been shown that the KT-initial-state effects make the largest contribution to the core-level BE shifts for atoms in different environments. The large final-state relaxations, or screening, are similar for these different atoms; see Ref. 26. We shall see that this is also the case for the SCL shifts. For Al₁₈ and Cu₁₈, the orbitals for all the electrons were varied to obtain wave functions denoted full SCF. For Cu₁₈, we also obtained wave functions where certain orbitals were constrained to have their free-atom character in the cluster. This was done in order to show the importance of the Cu *d* electrons for the core-levels BE's.

The initial-state, KT, BE's for the 1*s* ionization are summarized in Table II; the results for the other *ns* core ions, 2*s* for Al and 2*s* and 3*s* for Cu, are similar. We give the bulk- and surface-atom BE's as shifts from the KT BE for a free atom:

$$\Delta E_b(\text{KT}) = E_b(\text{KT}; X_{18}) - E_b(\text{KT}; \text{free atom}), \quad (1)$$

where E_b denotes the BE. We also give, in Table II, the difference between the surface- and bulk-atom BE's, $E_b^{\text{surf}} - E_b^{\text{bulk}}$. A negative $E_b^{\text{surf}} - E_b^{\text{bulk}}$ indicates that the BE for a bulk atom is larger than the BE for the surface atom, or that there is an SCL shift to lower BE. Finally, we give $E_b^{\text{surf}} - E_b^{\text{bulk}}$ for the Δ SCF BE's. These $E_b^{\text{surf}} - E_b^{\text{bulk}}$ or SCL shifts have the same sign as the KT $E_b^{\text{surf}} - E_b^{\text{bulk}}$ although they are somewhat smaller in mag-

nitude. Thus the direction and general size of the SCL shifts are determined by initial-state effects which we now consider.

For Al(100), the KT 1*s* BE's for both bulk and surface atoms are smaller than the BE for the free atom. However, the twelvefold coordinated bulk atom has its BE shifted lower by ≈ 1.0 eV, while the eightfold coordinated surface atom has its BE shifted lower by only ≈ 0.2 eV. These shifts are entirely consistent with studies of core level BE's in Li and Al clusters¹⁷ where it has been shown that there is a monotonic relationship between the BE and the coordination of the ionized atom. This monotonic dependence of BE on coordination was shown to arise from the conduction-band charge density around the ionized atom.¹⁸ The different shifts of the BE's of bulk and surface atoms lead to a higher BE for the surface atom; KT $E_b^{\text{surf}} - E_b^{\text{bulk}} = 0.74$ eV. The situation is entirely different for Cu. The KT BE's for both surface and bulk atoms are larger than the free-atom BE. Further, the surface atom shifts to a lower BE than the bulk atom. The cluster results are in qualitative agreement with the observed shifts of the surface Al atom 2*p* level to higher BE, and the Cu 2*p* level to lower BE. Our X₁₈ clusters describe the important differences of the local environments of the surface and bulk atoms. A more extended cluster which describes the detailed features of the surface and bulk band structure would be required for quantitative agreement with experiment.

The 4*sp* conduction band of Cu should affect the bulk and surface BE's much as the 3*sp* conduction band does in the case of Al. However, Cu is different from Al because the Cu 3*d* electrons can also affect the BE's. The 4*sp* and 3*d* effects have been separated for Cu using constrained orbital variations for the Cu₁₈ cluster.²⁵ In the first case, the 28 1*s* to 3*d* electrons of the bulk and surface atoms in Cu₁₈ have been fixed as they are in the free atom; for these two atoms, only one electron, the 4*s*, has been allowed to vary. This constraint, denoted frozen core, prevents the Cu *d* electrons from participating in bonding, and forces Cu to be like a simple metal. With the frozen-core constraint, the shifts of the BE's of the surface and bulk Cu atoms have the same direction as found for Al, see Table II. For the second constrained variation, frozen Ar core, only the 18 1*s* to 3*p* electrons of the bulk and surface Cu atoms are frozen; the 10 3*d* electrons as well as the 1 4*s* electron are varied, and the Cu is allowed to be a transition metal atom. The 1*s* BE of the twelvefold coordinated bulk atom increases by 3.9 eV and the BE of the eightfold coordinated surface atom increases by 2.6 eV over the frozen-core case where the *d* electrons are fixed. Now both the bulk and the surface BE's are larger than for the free atom and the results are very similar to the full-SCF results. The reason for these changes is that the *d* electrons hybridize with the 4*sp* electrons in order to participate in the chemical bonding. The number of *d* electrons promoted from the bulk atom is larger than from the surface atom because the bulk atom bonds with more neighbors. The spatially contracted *d* orbital has an electrostatic potential which reduces the BE of the core electrons. When a fraction of a *d* electron is promoted to the spatially diffuse 4*sp* conduction band, the core BE becomes

TABLE II. Bulk and surface atom KT BE's, in eV, for the Al₁₈ and Cu₁₈ core levels, see Eq. (1). For the difference between the BE's for surface and bulk, $E_b^{\text{surf}} - E_b^{\text{bulk}}$, the Δ SCF value is given in parenthesis after the KT value. For Cu₁₈, two frozen-core results are given as well as the full SCF, see text.

		ΔE_b bulk	ΔE_b surface	$E_b^{\text{surf}} - E_b^{\text{bulk}}$
Al ₁₈	Full SCF	-0.97	-0.23	+0.74 (+0.63)
Cu ₁₈	Full SCF	+1.03	+0.40	-0.63 (-0.38)
	Frozen core	-2.56	-2.01	+0.55
	Frozen Ar core	+1.34	+0.63	-0.71

larger. The surface-atom BE is smaller than the bulk-atom BE because fewer $3d$ electrons have been promoted into the spatially diffuse $4sp$ conduction band.

In summary, the SCL shifts result from two initial-state effects. One is due to the diffuse conduction-band charge density and occurs for both sp and transition metals. This charge density leads to a decrease of the KT core-level BE's which is monotonically related to the coordination of the ionized atom; the higher the coordination, the larger the decrease of the BE. This effect gives an SCL shift to

higher BE. The second effect occurs only for transition metals and is caused by the promotion of the d electrons into the diffuse sp conduction band. This promotion increases the core-level BE. It also depends on the coordination of the atoms; the effect is smaller for atoms with lower coordination. Hence, it is in the opposite direction to the first effect. While final-state screening modifies the quantitative value of the SCL shift, the dominant contributions to this shift arise from these two canceling initial-state effects.

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