A method for the experimental determination of surface photoemission core-level shifts for 3d transition metals

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A method is presented to determine the photoelectron surface core-level shift (SCLS) of 3d transition metals using x-ray photoelectron spectroscopy. The experimental difficulties arising from the relatively large broadening of photoemission lines in the 3d transition series can be overcome by the analysis of the angular dependence of photoemission spectra. The proposed method has been demonstrated using well-defined single-crystal surfaces of copper. The observed values of the SCLS for copper are compared with those predicted by both *ab initio* calculations and a macroscopic atom model. The experimental determination of SCLSs opens alternative routes for collecting thermochemical data for surfaces/interfaces. © *2005 American Institute of Physics*.
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I. INTRODUCTION

During the past two decades considerable progress has been achieved in understanding the physics of core-level photoemission from surface atoms of pure metals. It is now firmly established that atoms at a metallic surface yield a photoelectron response different from that in the bulk, i.e., shifted peak position, different singularity index, and lifetime and phonon broadening. Theoretical and experimental studies of broadening and asymmetry of the surface peak have mainly focused on W,[1] Ta,[2,3] and alkali metals (Ref. 4 and references therein), demonstrating a higher singularity index and broadening for photoelectron emission from surface atoms. A lot of attention has been paid to the investigation of the shift of the surface peak position with respect to the bulk peak position (see Ref. 5 for a review) because it could be used to obtain thermochemical data of the surface, such as the surface and segregation energies. Johansson and Martensson[6] demonstrated that the main contribution to the core-level shifts of a metal with atomic number Z is the cohesive energy difference between metal $Z+1$ and Z. This implies that the difference between the surface and the bulk photoelectron peak positions is related to the segregation energy of metal $Z+1$ as an impurity to the surface of metal Z.[7] Surface energies, segregation energies, and related properties such as work of adhesion are of importance for the rapidly developing field of surface and interface engineering. Since no methods for precise and direct experimental measurement of surface and segregation energies of crystalline materials are currently available, the measurement of photoelectron shifts is potentially a powerful tool for the collection of thermochemical data for metallic surfaces that otherwise only could be obtained theoretically using both *ab initio*[5] and semiempirical[8] models. Extensive experimental and numerical studies of surface core-level shifts (SCLSs) were carried out for many pure metals, especially from the 4d and 5d transition series (see Ref. 5 and references therein). The experimental attempts to determine SCLSs in 3d metals are very few and inconclusive.[9,10] This is due to the relatively complex photoelectron spectrum of these metals, i.e., the large intrinsic peak widths (of the order of the expected shift or more) that hinders unambiguous peak separation when resolving these spectra by curve fitting.

In this paper a method is presented for the determination of the SCLS of 3d transition metals from measured photoelectron spectra. One of the earliest works on SCLSs (Ref. 9) demonstrated a method for the determination of SCLSs (for polycrystalline evaporated Cu films) from photoelectron spectra recorded at several observation angles. The underlying idea is that the observation angle determines the analysis depth of the photoelectrons, and thus spectra, with different surface contributions, recorded by varying the observation angle. By analyzing the spectra simultaneously, the surface and the bulk contributions can be distinguished. The work ignores the substantial differences in singularity indices and broadening for bulk and surface peaks was ignored. By taking into account today's knowledge of core-level photoemission from metallic surfaces, the method can be improved significantly. In addition it will be shown that the condition of the surface, i.e., roughness, crystallographic orientation, imperfections, etc., can have major influence on the results.

The method is demonstrated here using x-ray photoelectron emission spectra recorded from clean, crystallographically perfect, single-crystal copper surfaces. Three differently oriented copper surfaces were investigated: (111), (100), and (110). The values for the SCLSs obtained from these x-ray photoelectron spectroscopy (XPS) measurements are compared with those determined using a semiempirical "macroscopic atom" model and with *ab initio* calculations.

II. EXPERIMENT

A. X-ray photoelectron spectroscopy

The XPS analysis was performed with a PHI 5400 ESCA system equipped with a dual anode x-ray source

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(Mg/Al) and a spherical capacitor analyzer (SCA). The x-ray source was operated at 15 kV and 400 W generating a nonmonochromatic incident Mg x-ray radiation (Mg $K\alpha_{1,2}$ =1253.6 eV). The energy scale of the SCA was calibrated according to a procedure described in Ref. 11. The instrument was set at a constant analyzer pass energy of 35.75 eV when measuring the C 1*s* and the O 1*s* photoelectron lines and at 8.95 eV when measuring the Cu 2*p* and Cu 3*s* photoelectron lines. The spectra from the C 1*s* and O 1*s* photoelectron lines were recorded with a step size of 0.2 eV and those of the Cu 2*p* and 3*s* photoelectron lines with a step size of 0.1 eV. The electrons emitted from the sample were detected at angles θ of 20°, 30°, 45°, and 60° (with respect to the sample surface). The elliptic analysis area of the sample surface is given by $1.1 \times 1.1/\sin\theta$ mm.

Although the application of a nonmonochromatic Mg $K\alpha$ radiation increases the instrumental broadening (as compared to a monochromated source), the overall peak shape is well described[12] by means of the Doniach–Sunjic (DS) peak form.[13] It has been proved that such a peak form is a physically justified model for the profile analysis of the photoelectron spectra of pure metals. The Cu $2p_{3/2}$ photoelectron emission line investigated in this work was chosen because it is fully separated from the Cu $2p_{1/2}$ and is less broadened than the 3*s* emission line. The surface sensitivity (the intensity ratio between surface and bulk contributions) when using Mg $K\alpha$ radiation is also higher for photoelectrons emitted from the 2*p* than from the 3*s* shell.

B. Copper single crystals

Three different copper single-crystal surfaces were studied: Cu (100), (110), and (111). These Cu single crystals with a purity of 5*N* were prepared using the Czochralski method (Surface Preparation Laboratory, Zaandam, the Netherlands). The single-crystal samples, with a diameter of 10 mm and a thickness of 2 mm, were polished on one side with 50-nm oxide particle suspension in the final step. The orientation of the crystal surfaces was verified using the Laue method and was within 0.5°.

Copper was chosen because the value expected for the SCLS is relatively large (see estimates given in Sec. IV C). In addition, the copper surfaces studied do not exhibit surface reconstruction[14] and the surface of copper can be cleaned and recovered in UHV.

Prior to the XPS measurements the Cu single-crystal surfaces were sputter cleaned (with 1-keV Ar^+ for 15–30 min) and then annealed for 5 min at 800 K in an UHV chamber directly coupled to the XPS equipment (base pressure $\leqslant 1 \times 10^{-7}$ Pa). This procedure was repeated twice. The annealing treatment is necessary to recover the Cu surface, which becomes damaged by the sputter-cleaning process. The level of oxygen and carbon contamination was monitored during the XPS measurements by recording their 1*s* photoelectron lines; the oxygen and carbon levels were below the detection limit of about 0.01 monolayer. After the XPS measurement the orientation and the quality of the Cu single crystal were verified with a scanning electron microscope (Jeol JSM 6500F) by means of electron backscattering diffraction (HKL Technology). The results indicate that the surface crystallinity after annealing has been restored fully.

TABLE I. Surface-to-bulk intensity ratio k according to Eq. (1) for the Cu $2p_{3/2}$ photoelectron line of Cu (100) and Cu (111) single-crystal surfaces at different take-off angles θ (λ=0.785 nm taken from Ref. 15).

θ (°)	$k_{(100)}$	$k_{(111)}$
20	0.80	0.97
30	0.50	0.59
45	0.33	0.39
60	0.26	0.31

III. DATA ANALYSIS

A. Estimation of surface contribution to photoelectron emission spectra

The takeoff or observation angles θ (measured with respect to the sample surface) were chosen such that a sufficient change in the relative contributions of the surface and bulk intensity is achieved. Estimates of these relative contributions can be made with a simple approximation by considering the surface layer as just the upper monolayer of atoms. The layer directly below the surface is considered as bulk, i.e., all the atoms are considered as fully surrounded by nearest neighbors. First, the (111) and (100) surfaces are considered, leaving the case of the (110) surface for later discussion. If d is the thickness of a surface layer and λ is the electron inelastic mean free path (IMFP), then the photoelectron intensity ratio k of surface to bulk contribution is given by

$$k = \frac{I_{\mathrm{surf}}}{I_{\mathrm{bulk}}} = \int_0^d e^{-z/(\lambda \sin\theta)} dz \Big/ \int_d^\infty e^{-z/(\lambda \sin\theta)} dz = e^{d/(\lambda \sin\theta)} - 1. \quad (1)$$

A considerable change in the relative contribution of the surface layer intensity to the Cu $2p_{3/2}$ peak is expected within the take-off angle range of 20°–60° for Mg $K\alpha$ radiation (see Table I). In these calculations, the effect of photoelectron diffraction (which may cause variations of up to 75% of the maximum intensity[16]) has been ignored. Thus Eq. (1) cannot be used to calculate the precise intensity ratios for the surface of a single crystal. In this work Eq. (1) is only used to consider the trend between the surface-to-bulk intensity ratio and the photoelectron take-off angle.

The nearest-neighbors approximation allows separation of the upper surface layer (some of the nearest neighbors are missing) from the bulk atoms (all the nearest neighbors are present). For (111) and (100) surfaces, the atoms in the surface layer miss three and four nearest neighbors, respectively. In the case of a (110) surface the atomic arrangement is more complex. Besides an upper surface layer, where the atoms miss five nearest neighbors, a subsurface layer (immediately below the surface layer) can also be identified where the atoms miss one nearest neighbor. The latter implies that a two-peak description of the photoemission line from the (110) surface is too simple, since the contribution of the subsurface layer is not included (see discussion in Ref. 3).

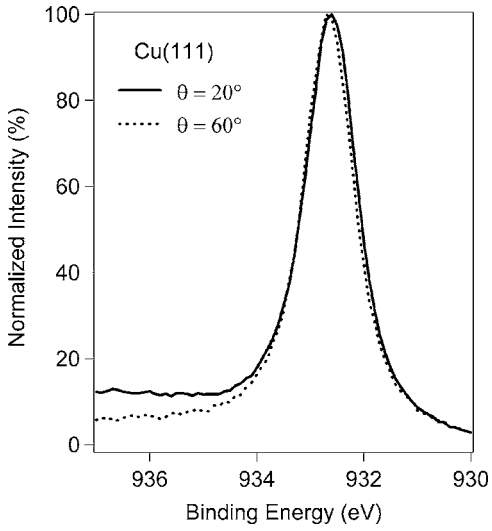

FIG. 1. Cu $2p_{3/2}$ photoelectron spectra recorded from a Cu (111) single-crystal surface at two different take-off angles θ, showing an increase of the extrinsic losses as well as a slight but significant shift of the spectrum to lower binding energy at a grazing angle.

B. Analysis of photoemission spectra

As a first step in the analysis of the photoelectron spectra the satellites due to the nonmonochromatic nature of the x-ray source were removed. Then the contribution to the background of the photoelectron spectrum of electrons that suffered extrinsic energy losses was computed by adopting the universal Tougaard profile.[17] After subtraction of this background profile an extrinsic energy-loss contribution still remains, as is evident from Fig. 1. The intensity of the background tail of the peak rises with an increasing value of the binding energy, while the intrinsic losses as described by Doniach and Sunjic (see below) are expected to steadily decrease with increasing binding energy. Thus, in addition to the universal Tougaard background profile, it is necessary to include an extra extrinsic energy- loss component in the profile fitting that depends on the photoelectron emission take-off angle. This extra component is approximated by a linear function near the position of the peak maximum.[18]

In the profile analysis of the photoelectron spectra a DS peak shape was used,[13]

$$I(E) \propto \frac{\Gamma(1-\alpha)}{[(E-E_0)^2+\gamma^2]^{(1-\alpha)/2}} \times \cos\left[\frac{\pi\alpha}{2}+(1-\alpha)\tan^{-1}\left(\frac{E-E_0}{\gamma}\right)\right], \quad (2)$$

where $I(E)$ is the photoelectron intensity as a function of the binding energy E, α is the singularity index or asymmetry parameter, γ is the lifetime broadening, and E_0 is the peak maximum in the absence of lifetime broadening. The last-mentioned parameter does not represent the position of the symmetric part of a peak (see Ref. 13 for details), thus, for the analysis of the surface core-level shifts, the broadened DS-peak maximum is taken as the peak position, i.e.,

$$E_{\max} = E_0 - \gamma\cot\left(\frac{\pi}{2-\alpha}\right). \quad (3)$$

The singularity index α reflects the nature of the screening charge and varies between 0 (i.e., the DS-peak shape becomes Lorentzian) and its maximum allowed value of 0.5 (see Sec. IV B for details).

The surface and bulk contributions are difficult to resolve from the measured photoelectron spectra due to the large intrinsic peak width for 3d transition metals. The peak width is larger than the surface shift and therefore surface and bulk contributions merge into one broad peak. The different asymmetry of the surface and bulk photoelectron peaks adds to the complexity of the problem. Any unconstrained fitting of a single 3d-metal photoelectron spectrum with two peaks is likely to end up with physically meaningless values for the peak positions, intensities, etc. This can be overcome by considering a series of spectra recorded with different surface sensitiveness. Previously, Citrin *et al.*[9] applied *simultaneous* fitting of several spectra observed at different take-off angles with some of the parameters constrained. In that work, the asymmetry and broadening of the surface peak were forced to be equal to the bulk values, while the intensities and positions were allowed to change. However, it has been shown[1–4] that the surface peaks of metals have significantly different asymmetry and broadening than the bulk ones.

Therefore, the photoelectron spectra recorded at four different take-off angles (after subtraction of satellites and background signal, see above) were analyzed simultaneously by least-square fitting of the surface and bulk peaks. When fitting these two peaks, the parameters of the surface peak (i.e., intensity, position, broadening, and singularity index) were set independent of their counterparts of the bulk peak. However, the position, broadening, and asymmetry of the bulk peak, as well as these for the surface peak, were kept the same for all the take-off angles. The surface-to-bulk intensity ratios were obtained by integrating the fitted peaks with a DS shape over the binding-energy range (930–938 eV). The range is selected to cut off the nonlinear extrinsic background contribution.

IV. RESULTS AND DISCUSSION

A. Surface and bulk photoelectron emission peaks of Cu

The photoelectron emission spectra of clean and recovered Cu (100), (110), and (111) single-crystal surfaces and one sputter-damaged Cu (111) surface were analyzed, as described in Sec. III. The surface and bulk peaks of a Cu (100) surface as obtained by simultaneous fitting of photoelectron emission spectra recorded at four different take-off angles are shown in Fig. 2. In Table II the values are given for the surface-to-bulk intensity ratio as determined from the surface and bulk peaks resolved from the measured photoelectron spectra. These values decrease with increasing photoelectron take-off angle θ for both the Cu (100) and (111) recovered surfaces. However, such a trend is not observed for the surface-to-bulk intensity ratio for the Cu (110) recovered and

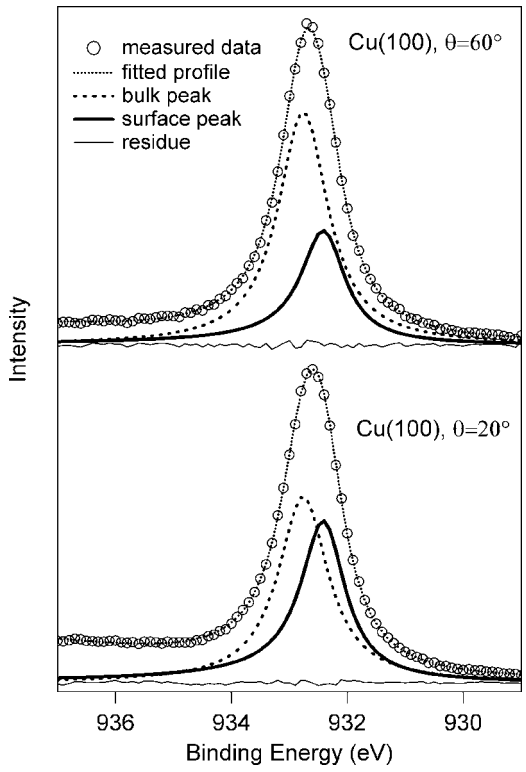

FIG. 2. Cu $2p_{3/2}$ photoelectron spectra (after Tougaard background and satellite subtraction) recorded from a Cu (100) single-crystal surface at two different take-off angles θ. The surface and bulk peaks as resolved from simultaneous fitting of a series of photoelectron spectra are shown.

the Cu (111) sputter-cleaned surfaces. These findings indicate that the applied model (i.e., a single surface layer on top of the bulk material) is not appropriate for the Cu (110) recovered and the Cu (111) sputter-cleaned surfaces.

The results for the sputter-cleaned surface demonstrate the importance of a perfect surface structure. Thus, only in experiments with a well-defined single-crystal surface layer is it possible to determine a reliable value of the SCLS. In this context it is noted that surfaces of polycrystalline materials are also not suitable for the determination of a value of the SCLS due to (i) the contribution of subsurface layers for various orientations, (ii) the possible differences in photoemission peak parameters between different orientations, and (iii) the presence of grain boundaries, in particular, for the case of thin films where the grain size is usually very small.

B. Asymmetry and broadening of surface peaks: (111) and (100) Cu surfaces

The measured asymmetry parameters for Cu (111) and (100) surfaces show the same behavior as was found in the 5d transition series[1,3] and for alkali metals,[4] i.e., higher surface singularity index as compared to the bulk singularity index. It can be shown that the singularity index depends on the screening charge as follows:[19]

$$\alpha = \sum_l \frac{q_l^2}{2(2l+1)}, \tag{4}$$

where q_l is the partial screening charge, i.e., the amount of charge screening the core hole with orbital momentum l (for the screening of a single core hole it holds: $\Sigma_l q_l = 1$). The values of the singularity index are within the range from 0 to 0.5. The maximum value is reached for a solely *s*-like ($l=0$) screening charge. With increasing contribution of *p*- or *d*-wave scattering the singularity index decreases. Thus, the rise in the singularity index at the surface reflects the decrease in momentum of the screening charge. For example, reduced *sp*-hybridization at an alkali metal surface is thought to be responsible for a sharp rise of the surface singularity index.[4] The values of the singularity index for Cu (111) and (100) surfaces obtained in this work (Table III) approach 1/18—the minimum value for screening electrons with *s*, *p*, and *d* symmetries. The bulk value of the singularity index is closer to zero indicating a decreased role of *s*- or *p*-like electrons in screening a core-level hole within the bulk.

A reduction of the core-level line broadening of 0.07 ± 0.03 eV is observed when the photoelectrons are emitted from the surface of both Cu (111) and (100), see Table III. Such a line broadening reduction has not been reported for 4d and 5d transition metals, instead broader surface peaks were observed.[1–3] The interpretation of the Cu $2p_{3/2}$ photoemission peak broadening is not straightforward because several components including lifetime and phonon broadening, and subsurface contribution may have played a role.

TABLE II. Surface-to-bulk intensity ratios k resolved from simultaneous fitting of a series of photoelectron spectra recorded from Cu single-crystal surfaces at different photoelectron take-off angles θ (see Sec. III B for details).

θ (°)	$k_{(111),\text{annealed}}$	$k_{(100),\text{annealed}}$	$k_{(110),\text{annealed}}$	$k_{(111),\text{damaged}}$
20	0.95	0.87	0.41	0.63
30	0.50	0.63	0.59	0.51
45	0.74	0.60	0.30	0.45
60	0.47	0.50	0.43	0.57

C. Surface core-level shifts for (111) and (100) Cu surfaces

The surface core-level shifts of metallic surfaces can be related to thermochemical parameters such as surface segregation energies and the work of adhesion. The equivalent core approximation (based on the assumption that the screening of a core-level hole effectively increases the positive charge of a nucleus by one) is used to relate the photoelectron surface core-level shift (SCLS_Z) of a metal with atomic number Z to the surface segregation energy of an impurity with atomic number $Z+1$ in that metal (with atomic number Z).[20]

$$\text{SCLS}_Z = E_{\text{surf}} - E_{\text{bulk}} = \gamma_{Z+1 \text{ in } Z}^{\text{surf segr}}, \tag{5}$$

where E_{surf} and E_{bulk} are the core-level electron binding energies of the surface and bulk atoms, respectively, and $\gamma_{Z+1 \text{ in } Z}^{\text{surf segr}}$ is the segregation energy of impurity $Z+1$ from the bulk Z to the surface. Segregation energies can be estimated using either *ab initio* calculations (linear muffin-tin orbitals method[21,22]) or with a semiempirical macroscopic atom model.[8,23] The advantage of using a macroscopic atom model, as compared with *ab initio* calculations, is that it can be easily applied to complex systems. Development of this

TABLE III. Surface core-level shift (SCLS), broadening γ, and singularity index α of surface and bulk peaks resolved from simultaneous fitting of a series of photoelectron spectra recorded from Cu single-crystal surfaces (see Sec. III B for details).

Cu surface	SCLS (eV)	γ_{bulk} (eV)	α_{bulk} (a.u.)	γ_{surface} (eV)	α_{surface} (a.u.)
(100), recovered	−0.35(5)	0.52(2)	0.00(2)	0.44(3)	0.06(3)
(111), recovered	−0.35(5)	0.51(2)	0.00(1)	0.45(3)	0.04(3)
(110), recovered	−0.36(6)	0.52(2)	0.01(2)	0.45(4)	0.03(4)
(111), sputter cleaned	−0.33(7)	0.53(3)	[a]	0.43(5)	0.09(7)

[a]Reached the physically allowed lower limit of zero.

method is therefore important for applied materials science.[24,25]

For Cu, the SCLS_Z is related to the segregation of Zn (the $Z+1$ impurity) from the bulk to the Cu surface. The *ab initio* calculations for surface segregation energy of Zn in Cu result in −0.24 eV for Cu (111) and −0.19 eV for Cu (100) surfaces, but with an uncertainty up to 0.2 eV.[22]

In the macroscopic atom model the segregation energies depend on the surface energies and interfacial enthalpies as follows:[8]

$$\gamma_{A\text{ in }B}^{\text{surf segr}} = \gamma_A^{\text{surf}} - \gamma_B^{\text{surf}} - (1 - f_{B\text{ surf}}^{A})H_{A\text{ in }B}^{\text{int}}. \tag{6}$$

Here $H_{A\text{ in }B}^{\text{int}}$ is the enthalpy of mixing of metal A in metal B, and $f_{B\text{ surf}}^{A}$ indicates the degree of contact of the Wigner–Seitz (WS) cell of the A impurity with surrounding B neighbors at the surface of B, the same factor within the bulk of B is equal to 1. The values of $H_{A\text{ in }B}^{\text{int}}$ are also determined with the macroscopic atom model and are given in Ref. 8. The surface segregation energy of Zn in Cu becomes

$$\gamma_{\text{Zn in Cu}}^{\text{surf segr}} = \gamma_{\text{Zn}}^{\text{surf}} - \gamma_{\text{Cu}}^{\text{surf}} - (1 - f_{\text{Cu surf}}^{\text{Zn}})H_{\text{Zn in Cu}}^{\text{int}}. \tag{7}$$

The surface energy (per surface atom) of a pure metal can be estimated[8] with

$$\gamma_A^{\text{surf}} = f_{\text{vacuum}}^{\langle A\rangle} c_0(\gamma^* V^{2/3}) - \text{RT}, \tag{8}$$

where γ^* is the atomic interface energy between metal A and a vacuum, V the molar volume at temperature T, c_0 the proportionality constant between the surface area of a mole of atomic cells and $V^{2/3}$ ($c_0 = 4.5\times10^8$ in this work; the average of the values for a perfect sphere of 5.1×10^8 and a cube of 4.1×10^8), and $f_{\text{vacuum}}^{\langle A\rangle}$ is the fraction of the WS-cell's surface area exposed to vacuum. This last parameter depends on the type of the surface plane. For a fcc lattice the exposed fraction of WS cell is fully determined by the missing nearest neighbors, e.g., for a (111) surface 3 out of the 12 neighbors are missing, thus $f_{\text{vacuum}}^{\langle A\rangle,(111)} = 1/4$.

The segregation energy is mainly determined by the difference in the surface energies of two metals. The interface term usually accounts for no more than 20% of the total value of the segregation energy. The surface energy in Eq. (8) depends on the values of $\gamma^* V^{2/3}$. These are obtained by extrapolating the surface energies of liquid metals to absolute zero or by using enthalpies of evaporation,[8] because no other means of obtaining surface energies for crystalline metals are available.

The experimentally determined surface core-level shifts for Cu (111) and (100) surfaces are shown in Table IV together with predictions based on *ab initio* calculations from Ref. 22 and the macroscopic atom model as discussed above. No dependence on the surface orientation of the surface core-level shift of Cu has been observed experimentally. The predicted values (from *ab initio* calculations and the macroscopic atom model), however, suggest surface orientation dependence, but the uncertainty in these values is too large to be conclusive. The uncertainty for the surface core-level shift as obtained by *ab initio* calculations has a maximum value of 0.2 eV.[22] The uncertainty of these values estimated with macroscopic atom model is about 0.3 eV. The agreements and discrepancies between values for the surface core-level shift obtained experimentally and predicted with *ab initio* calculations and macroscopic atom model will be discussed next.

The SCLS values for close-packed single-crystal surfaces of 5d transition metals, i.e., (111) for fcc and (110) for bcc, as measured and predicted by both *ab initio* calculations

TABLE IV. Surface core-level shifts (SCLSs) of Cu (111) and (100) single-crystal surfaces according to model calculations and determined experimentally.

Method	$\text{SCLS}_{(111)}$ (eV)	$\text{SCLS}_{(100)}$ (eV)
Ab initio calculations (Ref. 22)	−0.24±0.2	−0.19±0.2
Macroscopic atom model	−0.18±0.3	−0.24±0.3
Experiment	−0.35±0.05	−0.35±0.05

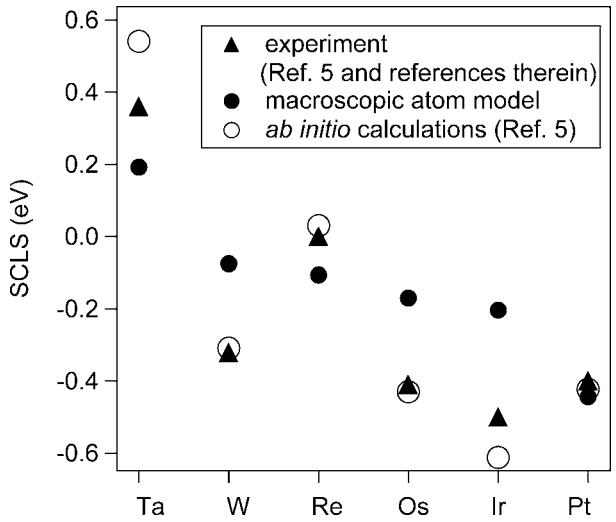

FIG. 3. Measured and calculated values for the surface core-level shifts (SCLS-) of the close-packed single-crystal surface of 5d transition metals, i.e., (111) for fcc and (110) for bcc.

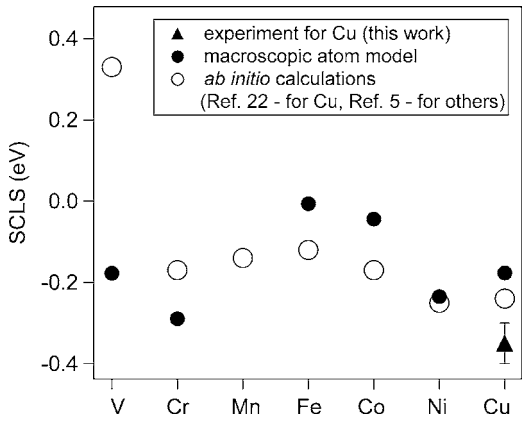

FIG. 4. Measured and calculated values for the SCLSs of the close-packed single-crystal surface of 3d transition metals, i.e., (111) for fcc and (110) for bcc.

and the macroscopic atom model, are compared in Fig. 3. These metals show rather narrow photoelectron peaks and the surface contribution can be resolved easily as a completely separate surface peak is present in most cases, provided that sufficient energy resolution is utilized (usually achieved by applying synchrotron radiation). Agreement within 0.1–0.2 eV exists between the SCLS values according to *ab initio* calculations (Ref. 5 and references therein) and those determined experimentally. Differences of 0.2–0.3 eV occur when comparing the SCLS values estimated on the basis of macroscopic atom model [Eqs. (6) and (8)] with the experimentally determined values for the 5d transition metals.

A similar comparison of the SCLS values is made for the close-packed single-crystal surfaces for 3d transition-metal series, i.e., (111) for bcc and (110) for bcc, see Fig. 4. However, in this case an experimental result is only available for Cu, which is obtained in this work. The values for the SCLS as estimated by both *ab initio* calculations and the macroscopic atom model are about 0.1 eV higher when compared with the experimentally determined values (cf. Table IV). This is well within the estimated uncertainty range of 0.2–0.3 eV. The large discrepancy for *V* can be explained by the relatively sharp drop in molar volume for the next $(Z+1)$ element, i.e., Cr. Data for Mn are not considered because of its complicated crystallographic structure. To confirm the trend seen for SCLS values from the both ab initio calculations and the macroscopic atom model (Fig. 4), experimental data of other metals of the 3d series are required.

V. CONCLUSIONS

A method for experimental determination of surface core-level photoemission shifts in 3d metals was demonstrated using copper as an example. The method is based on the analysis of the angular dependence of photoemission spectra. It was shown that a well-defined single-crystal surface is a necessary condition for a successful determination of surface core-level shift. The experimentally determined values of the SCLS for Cu (-0.35 ± 0.05 eV) are within the uncertainty range (0.2–0.3 eV) of both *ab initio* calculations and the macroscopic atom model predictions for surface segregation energies of Zn in Cu. The method of SCLS determination for a 3d transition metal demonstrated here together with evolving theoretical descriptions can help in understanding the thermochemical properties of metallic surfaces and interfaces and allow the development of the methods for the prediction of the adhesion properties.

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