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Structural dependence of the 5*d*-metal surface energies as deduced from surface core-level shift measurements

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Surface core-level shift measurements performed at the BESSY storage ring yield −0.41(2) eV for Os(0001) and 0.00(10) eV for Re(0001). An analysis of the surface shifts in the 5*d* transition series shows that the surface energy as a function of *Z* has a maximum at lower *Z* for the bcc phase than for the fcc-hcp phases, at W and between Re and Os, respectively.

INTRODUCTION

The increasing availability of synchrotron-radiation sources has resulted in the development of new methods for the characterization of solids and surfaces. One of these new tools is based on the investigation of surface core-level shifts (SCLS). Measurements of the SCLS gives information on many properties such as surface electronic structure, surface structure, reconstruction, surface defects, surface energies, surface segregation, adsorbate interaction, etc. (e.g., Refs. 1–3). For all of these purposes it is essential to know and properly understand the data on the pure and well-ordered metal surfaces.

Experimental results for all 5*d* transition metals except Os have previously been reported. In this work we report the first SCLS measurements for this remaining element performed on a single crystal Os(0001) surface. We have also made a redetermination of the SCLS for Re using a Re(0001) surface. Previous measurements for Re have been performed on less-perfect samples and show somewhat contradictory results.[3,4]

We have used the new data together with previously published surface shifts for the 5*d* transition metals to discuss the *Z* dependence of the SCLS. The experimental values are also compared to theoretical calculations. It has previously been shown that the surface core-level shift of a metal is closely related to the difference in surface energies between the *Z* and $Z+1$ metals.[5] This property of the SCLS is used to discuss the surface energies of the 5*d* metals. The observed trends of the surface shifts indicate that there are significant differences in the *Z* dependence of the 5*d*-metal surface energies depending on the crystal structure.

EXPERIMENT

The experiments were performed at the Toroidal Grating Monochromator TGM2 beamline at the synchrotron radiation laboratory BESSY (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung) in Berlin. Photon energies in the range 70–170 eV were used and the monochromator resolution was typically set to $E/\Delta E \leq 500$. The analyzer system was an angle-resolving spectrometer of the type ADES 400 (VG Instruments), and the typical resolution was set to approximately 100–150 meV. The overall resolution, determined experimentally by the width of the Fermi-level cutoffs was found to be 250–350 meV depending on the photon energy. The UHV system was equipped with the usual low-energy electron diffraction (LEED) and Auger-electron spectroscopy (AES) facilities to check the purity and the structure of the surface. The base pressure in the chamber was in the range of 5×10^{-11} mbar and the sample was cleaned by an annealing procedure up to 2000 °C just before each experiment. All measurements were performed at room temperature. The procedure to prepare the samples is described in detail in Ref. 6. In the case of rhenium the annealing procedure had to be done more carefully because of the sensitivity of this material to thermal stress.

RESULTS

Figure 1(a) shows the 4*f* spectrum of osmium obtained at normal emission using a photon energy of 110 eV. The spin-orbit splitting of the 4*f* level is 2.7 eV. The splitting of each spin-orbit component into surface and bulk peaks is clearly seen. The more intense feature at the low binding energy side is due to the emission from the first atomic layer. This can be seen by comparing the measured binding energies to available data for the bulk emission 50.7(1) (Ref. 7) and 50.8(1) eV (Ref. 8) obtained at x-ray photoelectron spectroscopy XPS energies. A large number of $4f_{7/2}$ spectra were measured in normal emission for different photon energies and the same polarization of the incident light ($\alpha=70°$ with respect to the surface normal). All these spectra show similar surface core-level shifts, but differences in the relative intensities of the emission features. This $\hbar\omega$-dependent intensity variation can be explained by the diffraction of the emitted photoelectrons. This topic will be discussed in a forthcoming paper.

The Os $4f_{7/2}$ spectra were analyzed by a least-squares fitting procedure, assuming model functions of the Doniach-Šunjić form for both peaks,[9] a linear background (this is sufficiently accurate within a small energy range[10]), and an instrumental broadening of Gaussian shape. The halfwidth of the Gaussian for each photon energy was determined from measurements of the Fermi edge. In a first run of the fitting program, the parameters

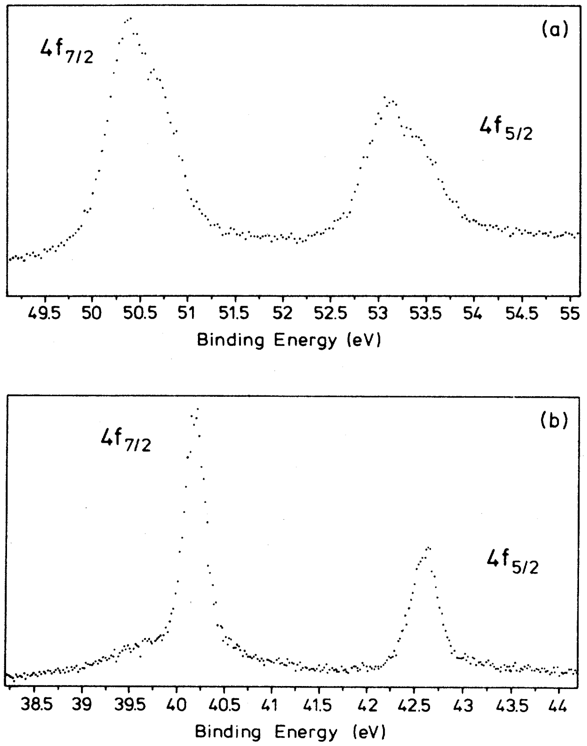

FIG. 1. Photoelectron spectra in normal emission within the range of the $4f$ core levels: (a) for Os(0001) excited with $\hbar\omega = 110$ eV. Note the clear splitting due to bulk and surface emission; (b) for Re(0001) excited with $\hbar\omega = 102$ eV.

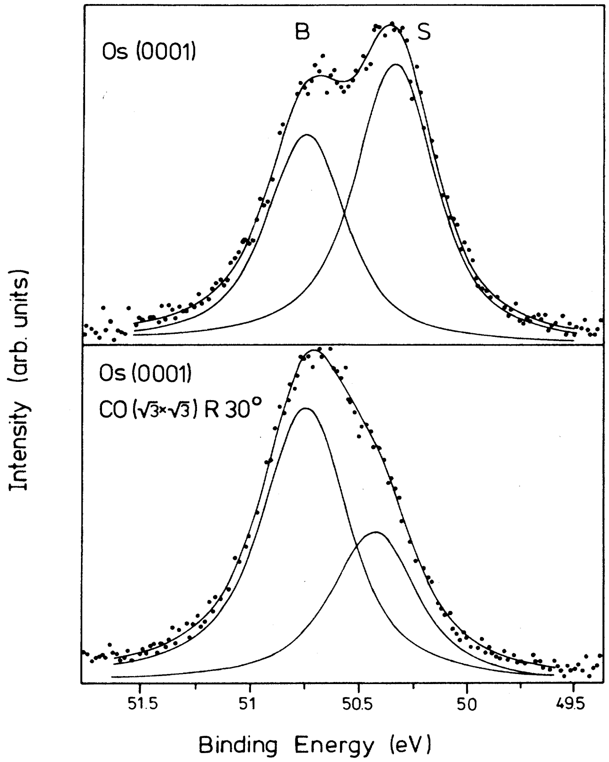

FIG. 2. Os(0001) $4f_{7/2}$ core-level spectra for a clean surface (upper spectrum) and a CO($\sqrt{3}\times\sqrt{3}$)R30° covered surface (lower spectrum). Surface emission (S) is strongly affected by adsorbates.

for the half-width Γ ($=2\gamma$) and asymmetry (α) were varied independently for the two peaks but the results showed no systematic differences between the bulk and surface peaks. In the following, these parameters were therefore set equal for the two peaks in order to reduce the number of free variables to eight only: the half-width Γ ($=2\gamma$), the asymmetry α, the intensity and energy position of the peaks ($I_1, \varepsilon_1, I_2, \varepsilon_2$) and two parameters for the linear background (A, B). A least-squares fitting procedure was used to determine the values of these parameters. The determined binding energies of the peaks are $E_{b,1} = 50.33(4)$ eV and $E_{b,2} = 50.74(4)$ eV and the SCLS $|\Delta_{c,\text{expt}}| = 0.41(2)$ eV. The asymmetry was determined to be $\alpha = 0.03(2)$ and for the halfwidth a value $\Gamma(=2\gamma) = 0.26(3)$ eV was obtained. These values fit well to the data for the neighboring $5d$ transition metals.[2] The lifetime broadening is in good agreement with a recently published value of $\Gamma = 0.27(2)$ eV,[11] and the binding energy $E_{b,2}$ corresponds to the previously reported bulk values.[7,8]

The origin of the different Os $4f$ peaks was further checked by an adsorption experiment. Figure 2 compares the $4f_{7/2}$ spectrum for the pure surface to that of a CO($\sqrt{3}\times\sqrt{3}$)R30° covered surface. For the pure Os surface the high intensity of the surface peak at the used photon energy is due to diffraction effects. From the spectra it is directly seen that the adsorption of CO significantly reduces this enhancement. Furthermore, it is seen that the adsorbed CO slightly reduces the magnitude of the SCLS. The reduction is determined to be $\Delta^{\text{ad}}_{c,\text{expt}} = -0.08(3)$ eV. To a first approximation the SCLS will be modified by the difference in heats of adsorption of CO for Os and Ir (the $Z+1$ element).[1,12,13] These heats of adsorption are 135(15) kJ/mol for CO on osmium[14] and 138(3) kJ/mol for CO on iridium.[15] For a coverage of $\theta = \frac{1}{3}$ the estimated adsorbate-induced contribution to the SCLS is $\Delta^{\text{ad}}_{c,\text{calc}} = 0.01(8)$ eV. The calculations thus predict a very small modification of the SCLS in agreement with experiment. For comparison it can be noted that for other $5d$ elements large adsorption-induced shifts have been observed [e.g., $\Delta^{\text{ad}}_{c,\text{expt}} = 1.3$ eV for CO on Pt (Ref. 16)].

In the case of rhenium the $4f$ region looks quite different from that of osmium [Fig. 1(b)]. Both spin-orbit-split peaks are narrow and there is no sign of a separation into surface and bulk features. There is, however, an additional broad feature in the direct neighborhood of the $4f_{7/2}$ level. This is due to emission from the $5p_{3/2}$ level.[7] Because of this additional peak we inspected mainly the $4f_{5/2}$ level instead. A number of spectra were recorded at different photon energies at normal emission. This was done in order to achieve different surface-to-bulk intensity ratios due to variations in the diffraction effects. No splittings were visible at any photon energy and the peak remained sharp and narrow. This directly shows that the surface shift must be small. Nevertheless, the spectra were analyzed in the same way as described for the Os $4f_{7/2}$ data. Fitting the spectra with two independent Doniach-Šunjić functions always resulted in one component which had an intensity of less than 0.1% of the other one. The best fit with one Doniach-Šunjić function is shown in Fig. 3(a). The resulting parameters are $E_B=42.6(1)$ eV, $\Gamma=0.16(2)$ eV, and $\alpha=0.05(2)$. The determined binding energy fits reasonably well to previously published bulk binding energies.[7,8]

In order to find the largest possible surface shift consistent with the present data, a number of numerical fits were also performed with different fixed splittings. Since the line shape is very close to symmetric this was done by fixing the positions of the two components symmetrically around the observed peak position. The introduction of a finite surface core-level shift results in a lower intrinsic linewidth for each component. Figure 3(b) shows the best fit for a separation of 0.125 eV. The parameters for this fit are $\Gamma=0.08$ eV and $\alpha=0.06$. Compared to the fit obtained with one peak it is seen that the tails of the spectrum are less well described. This is due to the smaller lifetime broadening obtained when fitting the spectrum with two shifted peaks. The effects of the lifetime broadening are most clearly seen at some distance from the peak due to the long tails of the Lorentzian function. In particular, the low binding-energy tail of the peak, which is unperturbed by the asymmetry, provides a sensitive measure for the Lorentzian width.

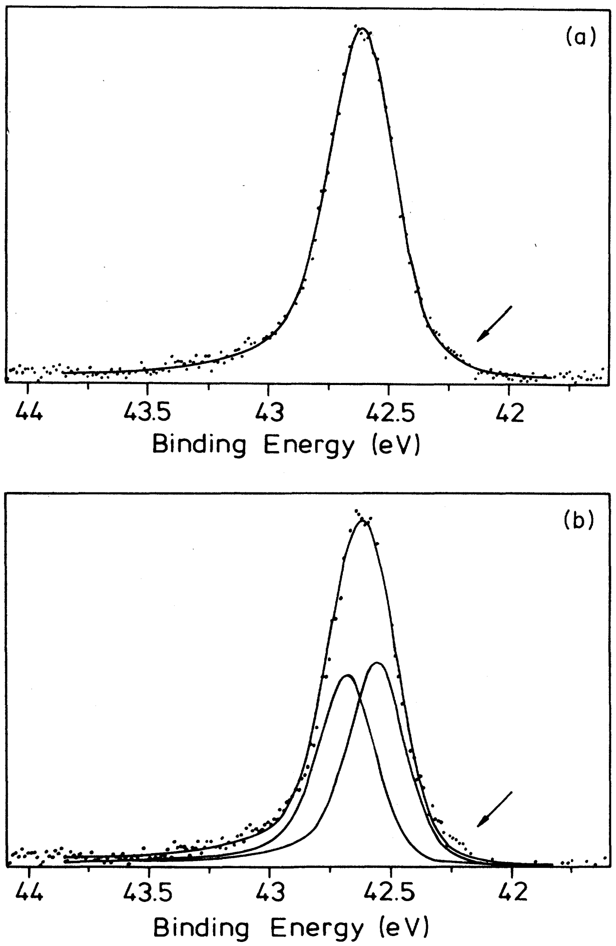

FIG. 3. (a) The Re(0001) $4f_{5/2}$ core-level spectrum is well described by *one* Doniach-Šunjić (DS) function (solid line). Describing the same spectrum by two DS functions, (b) yields a surface core-level shift smaller than 0.125 eV.

From this discussion we conclude that the shift used in Fig. 3(b) is too large and that the shift is close to zero. For zero surface shift a Lorentzian width of 0.2 eV is obtained. This width is consistent with the previous result from Ref. 11. It also shows the expected difference to the value obtained for Os in this work. These considerations of the lifetime width gives further support for the fit with a small surface shift. We therefore conclude that the SCLS should be less than about 0.1 eV.

DISCUSSION

With the present results there exist experimentally determined SCLS for all the 5d transition elements. It is therefore interesting at this stage to summarize these shifts and to investigate in detail how the SCLS depends on the atomic number Z. In Fig. 4 experimental shifts are plotted for the elements Yb to Au.[17–24] Most values (Ta–Au) refer to single crystal measurements. The Yb results are obtained from an epitaxial layer grown on top of a Mo(110) substrate.[17] For some elements several crystal phases have been investigated. In these cases the shifts for the most highly coordinated surfaces are used, i.e., fcc (111), hcp (0001), and bcc (110).

From Fig. 4 it is seen that there is a large positive shift for the first elements in the series, decreasing shifts for the following elements, a sign change in the middle of the series, and large negative shifts for the last elements.

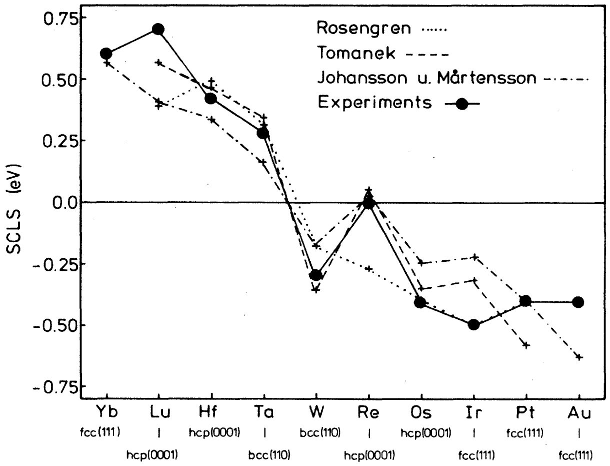

FIG. 4. Comparison of the experimentally determined SCLS of the 5d transition metals with the results of different theoretical approaches. Only values of the close-packed surfaces are included.

This general trend has been established before and has been interpreted in terms of the bonding-to-antibonding crossing in the filling of the 5*d* band states when passing the middle of the transition series. The presently added measurements for Re and Os, however, show in more detail how the shift varies in the middle of the series. It is seen that after the sign change which occurs between Ta and W the shift again becomes close to zero for Re. For Os the previous trend continues with increasing negative shifts.

For comparison, theoretically calculated surface core-level shifts have also been included in Fig. 4. The theoretical shifts are based on a general expression for the SCLS derived in Ref. 5. Taking the leading terms in this expression, the SCLS can be expressed as the difference between the surface energies of the Z and $Z+1$ elements, the $Z+1$ element representing the screened core-ionized final-state atom (equivalent core approximation)

$$\Delta E_c = \gamma_{Z+1} - \gamma_Z \ . \qquad (1)$$

In Eq. (1), a number of cross terms representing the interaction between the core-ionized site and the surrounding Z metal lattice have been neglected.[1] One term represents the chemical modification of the $Z+1$ site due to the surrounding lattice. One has also neglected the fact that the $Z+1$ atom, which is created in the photoionization process, has the geometry of the unperturbed Z-metal lattice. These additional terms are generally small. For the 5*d* transition metals the neglected terms will play some role for the first elements in the series. Around the middle of the series these terms will, however, be small. First of all, the chemical interaction is small as can be seen from alloying energies and from the fact that the Z and $Z+1$ metals form solid solutions with each other for these elements. Furthermore, the atomic radius is rather similar for the Z and $Z+1$ elements, leading only to small strain energies in the final state.

Using Eq. (1) one can obtain direct information about the variation of the surface energies over the 5*d* transition series. Especially when the SCLS has been studied for all the elements in the series, it is possible to obtain a consistent view of the surface energies. This is most interesting since the existing compilations of surface energies for metals reveal large uncertainties.

The results from three different numerical evaluations of Eq. (1) are shown in Fig. 4. In Ref. 5 the surface energies were estimated using the empirical finding that the surface energy of a metal is approximated equal to 0.2 times the cohesive energy. In a more detailed calculation of the SCLS, it is necessary to let this factor depend on the surface structure, etc. Tománek *et al.*[25] derived such factors in a broken bond picture including nearest-neighbor and next-nearest-neighbor interaction. The shifts in this case, however, are also directly related to the difference in cohesive energies between the Z and $Z+1$ metals, the only difference being that slightly different factors are used. The derived curve is therefore quite similar to the one obtained in Ref. 5. In the work by Rosengren and Johansson,[26] a related approach was employed. However, a major difference in this case is that they used surface energies which had been calculated from tight-binding calculations.

It can first be noted that all the theoretical curves reproduce the overall trend of the surface core-level shift. However, there are differences in the middle of the series. The kink in the experimental curve around Re is only reproduced by the theoretical results from Refs. 5 and 25, i.e., by the calculations which are based on experimental cohesive energies. In these calculations the kink is a direct consequence of the Z dependence of the cohesive energy. Plotting the cohesive energies of the 5*d* metals as a function of Z, it is seen that, to a first approximation, this forms a parabolic function with a maximum value for W. However, it can also be seen that there is a plateau in the curve for Re and Os with very similar values for these two elements (see, e.g., Ref. 27). If the surface energy is taken as a certain fraction of the cohesive energy, the same type of curve is obtained for the surface energy and Eq. (1) will produce a zero shift for Re.

The cohesive energy of a metal represents the difference in total energy between the atom in the metallic state and the free atom in its atomic ground state. The energy of this atomic state may be quite different from the energy of the configuration average state which corresponds to the situation in the metal. In this way, the cohesive energy contains contributions which are of a purely atomic origin. The cohesive energies of the 5*d* transition metals have been calculated by Davenport *et al.*[27] using a linear augmented-Slater-type-orbital method. They obtained a paraboliclike function for the Z dependence of the cohesive energies when these were related to the same type of $d^n s^1$ multiplet average atomic state for all elements. They estimated, furthermore, the atomic contributions to the cohesive energy and concluded that the kink at Re is of atomic origin. The expected proportionality between the surface energy and the cohesive energy should apply when these atomic effects are corrected for, since these do not represent contributions to the bonding strengths in the metal. The calculated kink in the SCLS for the elements W-Re therefore seems to be an artifact of the atomic contribution to the cohesive energy.

This is most interesting since the calculated behavior is indeed reproduced by experiment. We therefore have to seek an alternative explanation for the behavior of the SCLS for Re and Os. As a possible explanation for this behavior, we note that Ta and W are bcc metals while the other elements form fcc or hcp metals. Using Eq. (1) we obtain from the experimental surface shifts a direct measure of the difference in surface energy between the Z and $Z+1$ metals. The sign change of the SCLS between Ta and W implies that the surface energy has a maximum for W. The zero shift for Re, on the other hand, implies that [again using Eq. (1)] Re and Os have very similar surface energies. This indicates that the maximum occurs between Re and Os instead. We therefore propose that the behavior of the surface shift is due to significant differences in the Z dependence of the surface energy as a function of Z for the 5*d* transition metals depending on the crystal structure. For the bcc structure (Ta and W are bcc metals) the maximum occurs for W. For the metals in the fcc-hcp structures, however, the maximum is not reached until between Re and Os.

The existing compilations of experimental surface energies are not at all accurate enough to check the conclusions above. There is, however, some theoretical support at least for the maximum in cohesive energy for W (in the bcc structure). Posternak *et al.*[28] calculated the surface core-level shift for W in a ground-state picture, i.e., they calculated the orbital energy shift between the bulk and the surface. They obtained in this way a zero shift. The orbital energy is closely related to the derivative of the total energy with respect to the occupation number of the orbital (compare the transition-state theory). Using the $Z+1$ approximation, the zero shift implies that the derivative of the total energy per atom with respect to a change in the atomic number Z is the same for a bulk and a surface atom. This implies in turn that

$$\frac{\partial \gamma}{\partial Z} \approx 0 \qquad (2)$$

for W. In this way, the calculations give direct support for the conclusion above, that the surface energy has an extremum for W. To our knowledge, there exist no corresponding calculations for the fcc-hcp metals which could be used to check the proposal that the surface energy reaches its maximum at a higher Z for these structures.

CONCLUSIONS

Surface core-level shift measurements are reported for the Os(0001) and Re(0001) surfaces yielding shifts of $-0.41(2)$ and 0.00(10) eV, respectively. With these measurements, the 5*d* series is completed in the sense that experimental surface shift measurements have been reported for all the 5*d* transition metals. Using these data, the trend as a function of Z of the SCLS has been considered. It is seen that there is a rather complex variation in the middle of the transition series with a negative shift for W, zero shift for Re, and again a negative shift for Os.

The general trend of the experimental shifts is well reproduced by calculations based on a theoretically derived relationship between surface core-level shifts and surface energies for the Z and $Z+1$ metals. It is found that using simple relationships between surface energies and experimental cohesive energies, the detailed shape of the SCLS curve around Re is reproduced. It is, however, shown that this agreement is accidental. The correct behavior of the surface energies for these elements is caused by atomic contributions to the cohesive energies, which should have been corrected for in a more detailed derivation.

It is proposed instead that this behavior is due to the fact that Ta and W are bcc metals whereas the other elements form fcc or hcp crystals. Analyzing the surface shifts in terms of surface energies shows that there is a maximum surface energy for the bcc metal W. For the 5*d* metals in the hcp or fcc structure the maximum surface energy is reached at a higher Z value between Re and Os.

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