Surface core-level shifts of some 4*d*-metal single-crystal surfaces: Experiments and *ab initio* calculations

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High resolution measurements are reported of the surface core-level shift of the 3*d* level for the Rh(111), Rh(110), Pd(111), Pd(110), and Ag(111) single-crystal surfaces. These measurements and earlier ones for the Mo(110), Rh(100), and Pd(100) surfaces are analyzed by *ab initio* calculations of the surface core-level shift. The calculations are found to reproduce well the trends of the experimental shifts with the 4*d* metal and with the crystal plane. The comparison between these experimental and theoretical results demonstrates the importance of proper inclusion of final-state effects for accurate calculations of surface core-level shifts. A core hole in a surface atom is found to be better screened than one in a bulk atom for the 4*d* metals to the left of Pd in the Periodic Table. The use of the $Z+1$ approximation to describe the core hole is investigated both by explicit use of this approximation and by performing calculations for 1*s* and 3*d* core holes, respectively. The $Z+1$ approximation is found to be well obeyed in the case of Ag whereas for the rest of the 4*d* transition metals it is less precise, introducing errors of typically 0.1 eV.

INTRODUCTION

Experimental determinations of the core-level binding-energy difference between an atom at the surface and in the bulk, the surface core-level shift (SCLS), have been performed for many years now, see, e.g., Refs. 1–4. It has been, and still is, a controversial issue whether the SCLS may be ascribed entirely to initial-state effects or if the screening of the core hole in the final state has to be taken into account. A major reason for this discussion is that *if* final-state effects were negligible, the electronic properties of the nonionized initial state could be derived in a rather straightforward way from the core-level shifts. The discussion and the wish to derive information on the initial-state properties from core-level binding-energy shifts has not been limited to SCLS's but has also extended to the more general case of core-level shifts induced by any change in the surroundings of the photoionized atom. Much of the reason why this debate still has not been settled is due to the fact that only very recently[5–9] has it become possible to perform *ab initio* calculations including the final-state screening of surface core-level shifts. Such calculations have the potential of allowing for an unambiguous separation of the SCLS into initial- and final-state contributions, thus allowing for an estimate of their relative importance. However, it is only in the calculations of Ref. 6 and in the present work that such a decomposition has been performed.

In the present paper we report experimental high resolution measurements of the SCLS for the 4*d*-metal single-crystal surfaces Rh(111), Rh(110), Pd(111), Pd(110), and Ag(111). Combining these results with earlier reports[10–12] gives a data set that covers the three low-index surfaces of Rh and Pd and the most close-packed surface of Mo and Ag, thus making it possible to study the variation with crystal face as well as with 4*d* element of the SCLS. The experimentally determined SCLS's are compared to results from density-functional-theory calculations with proper inclusion of a core hole in the final state. These *ab initio* calculations are found to reproduce the experimentally determined variation of the SCLS with a high accuracy[13] in all cases. Therefore, we

find it justified to discuss not only the total shifts but also the initial- and final-state effects, which, when combined, make up these total shifts. Based on this, we arrive at the main conclusion that differences in the core-hole screening in the bulk and at the surface may often be important in establishing the exact value of the SCLS; thus, there is no *a priori* justification for ascribing SCLS's to purely initial-state effects. The present results concerning the importance of final-state effects provide an indication that these effects are also of importance for the general case of chemical shifts induced by any change in the surroundings of the core ionized atom. The commonly used $Z+1$ model, in which the core hole is modeled by increasing the nuclear charge of the core ionized atom by one and adding an extra valence electron, is investigated by explicitly using this approximation in the calculations and also by performing calculations for a true core hole in different levels. From this it is concluded that the $Z+1$ approximation may lead to errors in the SCLS of the order of 100 meV for the true $4d$ transition metals, whereas for Ag, the approximation only introduces a very small error.

EXPERIMENTAL

The experiments were performed at beamline 22 at the MAX I synchrotron light source in Lund, Sweden. This beamline is equipped with a modified[17] SX700 monochromator and a large hemispherical analyzer of SCIENTA type.[18] The SCLS was measured for the $3d$ level in all cases, as this is the core level with the smallest lifetime broadening for all $4d$ metals. The experimental resolution varied from around 0.15 eV for the lower photon energies used for Mo $3d$,[11] to just above 0.2 eV for Rh, and to finally around 0.25 eV for the higher photon energies used for Pd (Ref. 10) and Ag $3d$. At these resolutions a typical measurement of a $3d$ core-level spectrum took about 10 min. The Mo, Rh, and Pd surfaces were cleaned by a combination of Ar^+ sputtering and annealing in oxygen to remove residual carbon. Ag(111) surfaces were prepared by depositing an Ag film on a Pd(111) or a Rh(111) surface at room temperature. Whereas these Ag films showed a clear low-energy electron-diffraction pattern characteristic of Ag(111), the background was distinctly higher than found for the rest of the investigated surfaces indicating that some disorder was present in these deposited Ag films. The cleanliness of the surfaces was checked by monitoring the core levels of likely contaminants (C, O, S) and by measuring the valence band at photon energies where the Cooper minimum of the $3d$ metals suppresses the substrate $4d$ valence-band emission. Adsorbed hydrogen cannot be detected directly by photoemission and may, as discussed in Ref. 10 for the case of Pd, cause problems because it induces a shift of the core-level binding energy of the surface atoms. To desorb adsorbed hydrogen and CO, the crystals were flashed to typically 700 K prior to each individual measurement of a $3d$ spectrum. This procedure, the short duration of a measurement, and a pressure of typically 6×10^{-11} torr in the experimental chamber mean that artifacts resulting from hydrogen contamination of the surfaces will be very small if existing at all. All measurements were performed at a crystal temperature close to 100 K in order to reduce the phonon broadening of the core-level spectra. For more details on the Mo(110) and Pd(100) measurements, the reader is referred to Refs. 11 and 10, respectively.

THEORETICAL

By definition the SCLS is the difference in the energy that it takes to remove a core electron from a surface and from a bulk atom, respectively. From that definition, it follows directly that the SCLS of a particular core level is the difference in total energy between a sample where the core hole in that particular core level is in a bulk atom and one where it is in a surface atom. Such differences in total energy can today[5–9,15] be calculated accurately using *ab initio* methods based on density-functional theory.

We have performed such calculations[8] by the full-potential linear-muffin-tin-orbital method[19] to obtain total energies and self-consistent core eigenvalues for the bulk and low-index surfaces of a number of $4d$ metals, using the local-density approximation[20] (LDA) to the exchange and correlation functional. The surfaces are represented by seven-layer slabs using $c(2\times2)$ supercells in the plane defined by the surface. Use of larger supercells, i.e., using a larger spatial separation of the core ionized atoms, for some selected cases indicated that the SCLS's were converged with respect to supercell size, a result that may be due to the fact that any errors in the total energy resulting from the finite size of the supercell will largely cancel when taking the difference between surface and bulk ionized systems. Further evidence for the supercell size being sufficient is given by the good agreement for the SCLS of the most close-packed surfaces between the present calculations and those of Aldén, Skriver, and Johansson[7] that avoid the use of supercells. To describe a core hole, the slab is made self-consistent under the constraint that an electron is missing in a particular core state (here $3d$ or $1s$) of an atom at the surface or in the center of the slab. Furthermore, because of the vertical nature of the core-level photoemission process, the geometry is kept the same as in the initial state before the core ionization took place and, as the core hole is assumed to be completely screened, an extra valence electron per core hole is added to the slab in order to maintain charge neutrality. To investigate the influence on the SCLS of changes in the interlayer distances, we have performed calculations for geometrically unrelaxed surfaces, i.e., the first interlayer distance is kept equal to the bulk value, as well as for relaxed surfaces, i.e., the first interlayer distance is chosen in such a way that it minimizes the total energy of the slab (without a core hole).[21] The crystal structure of Mo is bcc whereas all of the other metals considered crystallize in the fcc structure. To investigate the influence of the change in crystal structure, we have, in addition to the calculations for the close-packed bcc(110) MO surface, also performed calculations for a close-packed (111) surface for a hypothetical fcc structure of Mo.

A common way[2,4,5,22] of modeling the core hole is the so-called $Z+1$ approximation in which the influence of

TABLE I. The surface core-level shifts (eV) at the fcc (111) surfaces of Rh, Pd, and Ag as obtained from the full impurity calculation using a true core-hole state (column three) and from the initial-state model (column four). Column five shows the difference and gives the part of the SCLS which is due to different screening of a core hole for a surface and bulk atom. Column six shows the results of the $Z+1$ approximation and column seven gives experimental data. The used first-layer relaxation is indicated by the numbers below the chemical symbols (see text).

metal	state	full calculation	initial-state approx.	screening contribution	$Z+1$ approx.	exp. data
Rh	1s	−0.48	−0.36	−0.12		
0%	3d	−0.54	−0.42	−0.12		−0.50
Rh	1s	−0.38	−0.32	−0.06	−0.36	
−2.5%	3d	−0.42	−0.37	−0.05		−0.50
Pd	1s	−0.26	−0.34	0.08	−0.26	
0%	3d	−0.30	−0.39	0.09		−0.28
Ag	1s	−0.12	−0.19	0.08		
0%	3d	−0.14	−0.22	0.08		<0.1

TABLE II. The same data as in Table I for the SCLS (eV) at the fcc (100) surfaces of Rh, Pd, and Ag.

metal	state	full calculation	initial-state approx.	screening contribution	$Z+1$ approx.	exp. data
Rh	1s	−0.65	−0.52	−0.13	−0.57	
0%	3d	−0.62	−0.59	−0.03		−0.62[a]
Rh	1s	−0.67	−0.45	−0.12	−0.61	
−3.5%	3d	−0.64	−0.52	−0.12		−0.62[a]
Pd	1s	−0.30	−0.43	0.13	−0.24	
0%	3d	−0.33	−0.49	0.16		−0.44[b]
Pd	1s	−0.27	−0.42	0.15	−0.25	
−0.6%	3d	−0.32	−0.48	0.16		−0.44[b]
Pd	1s	−0.32	−0.48	0.16	−0.25	
+3.5%	3d	−0.38	−0.55	0.17		−0.44[b]
Ag	1s	−0.08	−0.33	0.25	−0.08	
0%	3d	−0.10	−0.36	0.26		

[a]See Ref. 12.
[b]See Ref. 10.

TABLE III. The same data as in Table I for the SCLS (eV) at the fcc (110) surfaces of Rh and Pd.

metal	state	full calculation	initial-state approx.	screening contribution	$Z+1$ approx.	exp. data
Rh	1s	−0.55	−0.61	0.06	−0.52	
−7.5%	3d	−0.63	−0.67	0.04		−0.64
Pd	1s	−0.43	−0.65	0.22		
0%	3d	−0.50	−0.71	0.21		−0.55
Pd	1s	−0.38	−0.56	0.18	−0.36	
−5.3%	3d	−0.44	−0.62	0.18		−0.55

TABLE IV. The same data as in Table I for the SCLS (eV) at the bcc (110) and fcc (111) surface of Mo.

metal	state	full calculation	initial-state approx.	screening contribution	$Z+1$ approx.	exp. data
bcc Mo	3d	−0.24	−0.08	−0.16	−0.11	
0%						
bcc Mo	1s	−0.19	−0.04	−0.15		
−3.9%	3d	−0.28	−0.11	−0.17		−0.33[a]
fcc Mo	1s	0.18	0.25	−0.07		
0%	3d	0.11	0.19	−0.08		

[a]See Ref. 11.

the core hole is approximated by increasing the nuclear charge by one and adding one valence electron. The $Z+1$ approximation is a vital ingredient in the so-called "thermochemical" models, which we discuss below. In order to investigate the accuracy of this approximation, we have used it with the *ab initio* calculations to calculate the SCLS for some of the surfaces. The $Z+1$ approximation is expected to become better as the core level gets more localized and we, therefore, in addition to the value calculated for the $3d$ level, which is the one that has been measured, also give the calculated SCLS for a core hole in the $1s$ level. These values for the $1s$ and $3d$ SCLS furthermore provide an additional test of the $Z+1$ approximation as the shift of these two core levels should be equal within the $Z+1$ approximation. Finally, it may be noted that the $Z+1$ approximation is fundamental when the segregation energy of a $Z+1$ impurity in the Z metal matrix is argued to be equal to the SCLS by a thermodynamic model[2,4,22,23]. In that connection it should be emphasized that, due to the vertical nature of core-level photoemission, the segregation energy of relevance for the SCLS is that of a substitutional $Z+1$ impurity of the same size as the Z atom. This segregation energy may differ from the thermodynamically relevant one, which is for a geometrically relaxed impurity. Furthermore, the precision of the derived values for the segregation energy is directly influenced by how well the $Z+1$ approximation is obeyed. The results of these calculations of the SCLS by total-energy differences are given in Tables I–IV.

In the so-called initial-state models,[2,3,24,25] the basic definition of the SCLS, and the total-energy-based picture based on that definition, is abandoned and instead the core-level shift is assumed to be equal to the shift of the orbital energies of the core levels between bulk and surface atoms. These methods ignore final-state effects in the SCLS, that is, differences in the screening of the core hole created by the differences in surroundings of the core hole at the surface and in the bulk of the material, which is why they are normally termed initial-state models. As the present calculations are based on an all-electron method, which relaxes all core states as the potential is self-consistently made, we may easily test this initial-state model for the SCLS simply by comparing the eigenvalues of the core states of bulk and surface atoms from calculations for a nonionized slab.[21] Values obtained in this way are also given in Tables I–IV.

EXPERIMENTAL RESULTS

In this section, we describe the experimental results focusing in particular on how the SCLS are extracted from the data. The analysis of most of the spectra are quite straightforward, however, for a few of the surfaces, the analysis becomes more involved due to small shifts and/or poorly described line shapes.

In Fig. 1 are shown Pd $3d_{5/2}$ core-level spectra for the three low-index surfaces of Pd measured at a photon energy of 390 eV where the spectra are very surface sensitive due to the kinetic energy of the emitted $3d_{5/2}$ electrons being close to that of the minimum in the escape depth curve. Large differences are obvious between the spectra from the different surfaces, clearly demonstrating that the SCLS and the surface-to-bulk intensity ratio are different for the three surfaces. It may be seen directly from Fig. 1 (and is also found by a decomposition of the spectra in bulk and surface components) that the surface-to-bulk intensity ratio decreases as the surface becomes more open, that is, for the sequence (111), (100), and (110). This behavior, which is found not only at 390 eV but for all photon energies, reflects the fact that the interlayer distance decreases as the surface becomes more open, which, neglecting all diffraction effects, means that a large number of bulk layers contribute to the spectra even though the probing depth is the same. It is also obvious from the raw spectra of Fig. 1 (and is also found by a detailed decomposition of the spectra, see below) that the SCLS is negative and that it increases as the surface becomes more open. This increasing trend is, however, not consistent with earlier measurements of the SCLS for the (100) (Ref. 10) and (110) (Ref. 26) surfaces of Pd. Comelli *et al.*[26] reported a value of only -0.24 eV for the SCLS of Pd(110), significantly smaller than the value for Pd(100) of -0.44 eV reported earlier[10] and confirmed in the present study, and also smaller than the value of -0.55 eV determined for the SCLS of Pd(110) in the present study (see below and Table III). On this discrepancy we note that the surface emission could not be resolved in the measurements by Comelli *et al.*[26] making any decompositions very difficult, whereas a surface-related structure is clearly seen in the present study; that any hydrogen or CO contamination of the surface will

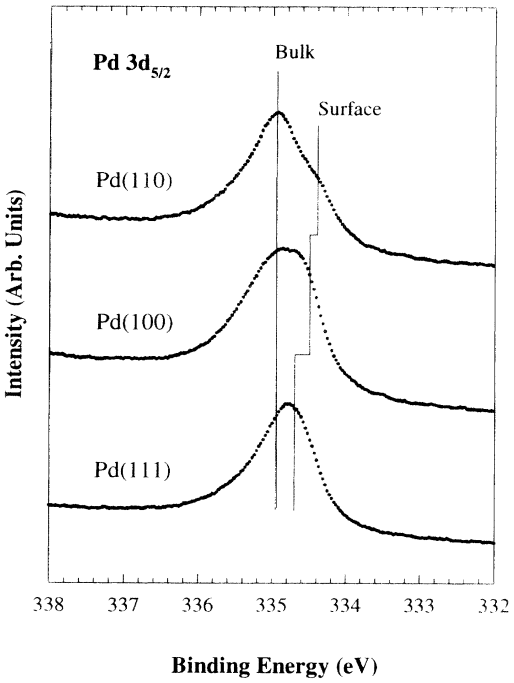

FIG. 1. Pd $3d_{5/2}$ spectra from the Pd(111), Pd(100), and Pd(110) surfaces measured at a photon energy of 390 eV. The binding energy of the bulk and surface emission is indicated.

reduce the SCLS of Pd (Refs. 10, 26, and 27); and finally that a larger SCLS for a more open surface is expected on general grounds, an expectation that is furthermore confirmed by the present calculations. For these reasons, we find it justified to disregard the determination of the SCLS of Ref. 26 and to state that also in the case of Pd is the SCLS larger for a more open surface.

The assignment of the surface emission has for all Pd surfaces been confirmed by following the relative intensities as the photon energy and thereby the surface sensitivity was varied, and by dosing the surface with hydrogen or CO, which is known[26,27] to induce a large shift to higher binding energy of the surface Pd atom 3*d* binding energy. Whereas these procedures unambiguously showed that the surface emission is at lower binding energy than the bulk emission, the large lifetime and vibrational broadening and the complicated line shape of the Pd 3*d* level presented some problems for extracting the SCLS. It is clear from the spectra of Fig. 1 that even for the 110 surface with the larger SCLS, the surface peak is not entirely resolved but only shows up as a shoulder towards lower binding energy. Thus, in order to obtain quantitative values for the SCLS of the Pd surfaces, some sort of decomposition procedure has to be applied. It has been shown previously[28] that the Pd 3*d* line shape is poorly described by the commonly used Doniac-Sunjic[29] line shape, which is based on a free-electron approach. In order to describe the line profile correctly, the detailed density of states of Pd has to be taken into account. In the analysis of the Pd spectra we have, therefore, mainly relied on different subtraction procedures in order to separate the bulk and surface contributions; however, consistent results were obtained from decompositions using Doniach-Sunjic line shapes even though these line shapes only provide a good description of the Pd 3*d* emission relatively close to the peak position.

Reference 10 describes in detail how the 3*d* spectra from Pd(100) may be analyzed by two different subtraction procedures. In the first method, one utilizes the strong variation with photon energy of the surface sensitivity of the 3*d* spectra of the Pd(100) surface to extract the surface and bulk peaks by simple subtraction of spectra measured at different photon energies. The second procedure is based on the assumption that the spectra consist of two parts with identical line shapes, one from the bulk and another from the surface emission. A simple iterative mathematical scheme, often used to decompose spin-orbit components,[30] may then be used to decompose the spectrum into its two parts; the two input parameters to this scheme being the binding-energy shift between the two peaks and their relative intensity. These subtraction procedures were found to also work excellently for the Pd(110) spectra, yielding a SCLS of -0.55 ± 0.03 eV for that surface, a value that is also consistent with decompositions based on Doniach-Sunjic line shapes. For the Pd(111) surface on the other hand, direct application of these procedures was unsuccessful in deriving an unambiguous value for the SCLS. As seen from Fig. 1, the 3*d* emission from the 111 surface consists of a structureless peak with maximum at a binding energy lower than that of the bulk peak from the 100 and 110 surfaces. This reveals that there is a SCLS toward lower binding energy but also that it is considerably smaller than the line width of the individual components. This makes the determined value for the SCLS dependent on the exact line shapes used in a fitting procedure and makes the subtraction procedures unstable. These problems may, however, be overcome by use of the line shapes determined from the (100) and (110) surfaces in fitting procedures utilizing as model functions either Doniach-Sunjic functions or the bulk line shape determined from the subtraction procedure *and* the knowledge of the bulk binding energy obtained from the two other surfaces. This leads to a SCLS of -0.28 ± 0.05 eV for Pd(111).

For Rh(111) and Rh(110), the much narrower 3*d* line shape and the fact that Rh 3*d* is much better described by a Doniach-Sunjic line shape make extraction of the SCLS considerably easier. Figure 2 shows how Rh $3d_{5/2}$ spectra from the (111) and (110) surfaces are excellently fitted by these model functions and a linear background to obtain SCLS's of -0.50 ± 0.02 eV and -0.64 ± 0.02 eV for Rh(111) and Rh(110), respectively. The assignment of surface and bulk peaks in Fig. 2 was further confirmed by CO and O adsorption, which was found to shift only the peak assigned to the surface. The presently determined value for the (110) surface is consistent with that obtained by others[31] from spectra with worse resolution and statistics. Furthermore, the SCLS of -0.62 eV for Rh(100) reported by others[12] is, as expected, intermediate between those of the (111) and (110) surfaces.

Figure 3 shows an experimental Ag $3d_{5/2}$ spectrum from Ag(111) and fits to this spectrum using Doniach-

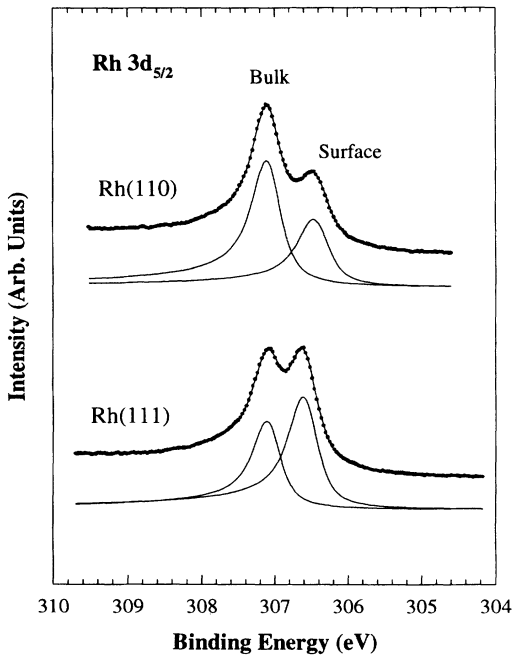

FIG. 2. Rh $3d_{5/2}$ spectra for the Rh(111) and Rh(110) surfaces measured at a photon energy of 380 eV for Rh(111) and 370 eV for Rh(110). Dots are experimental data, full lines are the individual surface and bulk components and the total fitted spectrum.

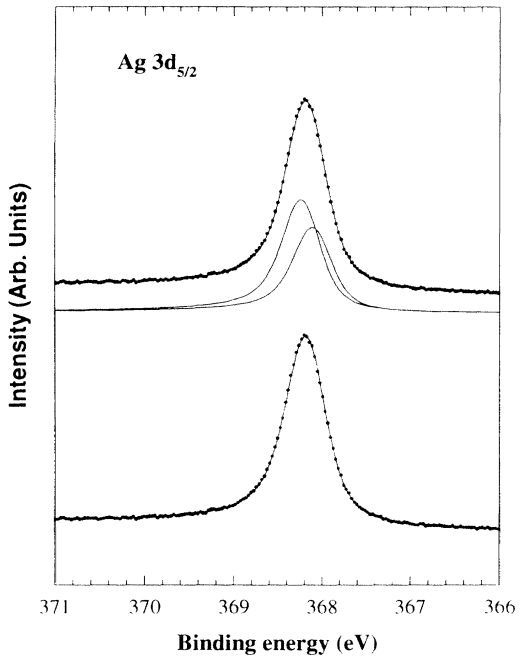

FIG. 3. Ag $3d_{5/2}$ spectrum from an Ag(111) surface measured at a photon energy of 450 eV fitted by either one or two Doniac-Sunjic lines. Dots are experimental data, full lines are fitted components and total fitted spectrum.

Sunjic line shapes and one or two lines, respectively. Considering first the one-line fit to the spectrum, we note that the binding energy determined for this single component is the same as the bulk binding energy reported for a polycrystalline Ag film from much more bulk sensitive measurements using Al Kα radiation for the excitation.[32] The remaining fitting parameters are also close to those of the earlier study[32] (Lorentzian 0.30 eV, asymmetry index 0.065), except for the Gaussian, which was 0.35 eV. This value for the Gaussian is consistent with what is expected from the resolution at 450 eV for the present beam line. In other words, it is possible to fit the Ag $3d_{5/2}$ spectrum using just a single line and physically reasonable fitting parameters. Thus, the SCLS of Ag(111) could be equal to zero. To obtain the two-line fit in Fig. 3, we have decreased the Lorentzian and Gaussian broadenings by 20 and 30 meV, respectively. The splitting between the two components, i.e., the SCLS, is for this particular fit 130 meV. The maximum SCLS which it is possible to accommodate by change of the Lorentzian and Gaussian broadenings without degrading the fit too much is about 150 meV, which would thus be a first upper limit on magnitude of the SCLS of Ag(111). We would consider this upper value as somewhat unlikely for a number of reasons. First, Ag-3*d* spectra measured at different photon energies and/or emission angles and thereby different surface sensitivities failed to reveal the changes that would be expected if a surface-related component had a shift of this magnitude. Second, in order to get a SCLS that differs from zero, we have to allow for a bulk binding energy different from that determined earlier from bulk sensitive measurements.[32] Third, a SCLS of 0.076±0.03 eV has been reported for polycrystalline Ag.[32] Based on these points, we argue that the SCLS of Ag(111) is below 100 meV and that it could actually be very close to zero.

DISCUSSION

Figure 4 shows a comparison between the experimental and the calculated values for the SCLS of the investigated surfaces. The calculated values are those obtained for the optimum first-layer relaxations given in Ref. 21 and in Tables I–IV. As seen from Fig. 4, the agreement between experiments and calculations is good. The trends of the SCLS with 4*d* element, as well as with crystal face, are reproduced well by the calculations and in many cases the calculations yield the experimental values to within 50 meV.

The values given in Tables I–IV show that the calculated SCLS depends on the exact value used for the first interlayer spacing. Comparing the SCLS value obtained using first interlayer distances equal to the bulk value and to the optimum value from Ref. 21, respectively, reveals differences of typically 50 meV between the two. It is thus clear that to obtain a complete quantitative agreement between theory and experiment a possible change of the first interlayer distance has to be included in the calculations. It is, therefore, tempting to suggest that the reason why the agreement is worse for Pd(100) and Pd(110) is due to the fact that these surfaces show an unusual geometrical first-layer relaxation, which is not reproduced by the calculations of Ref. 21. In the case of the Pd(100) surface, low-energy electron-diffraction studies[33,34] concluded that this surface shows an unusual outwards relaxation of $+3\pm1.5\%$, which should be compared to the inward relaxation of -0.6% calculated in.[21] As seen from Table II, using this value $+3\%$ for the first interlayer in the SCLS calculation actually improves the agreement to experiment for the Pd(100) surface. In the case of the Pd(110) surface, where no determinations of the first interlayer distance have been reported, it may be seen from Table III that using a nonrelaxed instead of an inwardly relaxed Pd(110) surface brings the calculated SCLS into better agreement with the experimental value suggesting that also the Pd(110) surface has a smaller inward first-layer relaxation than expected on the basis of the calculations in Ref. 21. It should be noted that the Pd(100) surface is not the only 4*d*-metal surface where a disagreement exists between first-layer relaxations determined from density-functional total-energy calculations and by low-energy electron diffraction (LEED), also for the Rh(100) surface the two methods disagree on the exact value of the first interlayer distance.[35] From the values for relaxed and unrelaxed Rh(100) in Table II it is, however, seen that the calculated SCLS of Rh(100) changes by only 20 meV for a first interlayer spacing change of 3.5%, thus we would expect no large change of the SCLS if an expanded first interlayer distance was used. Concerning this disagreement between the measured and the nonmagnetically calculated top-layer relaxations for Pd(100) and Rh(100), we note that the present calculations of the SCLS for Pd(100) seem to support that

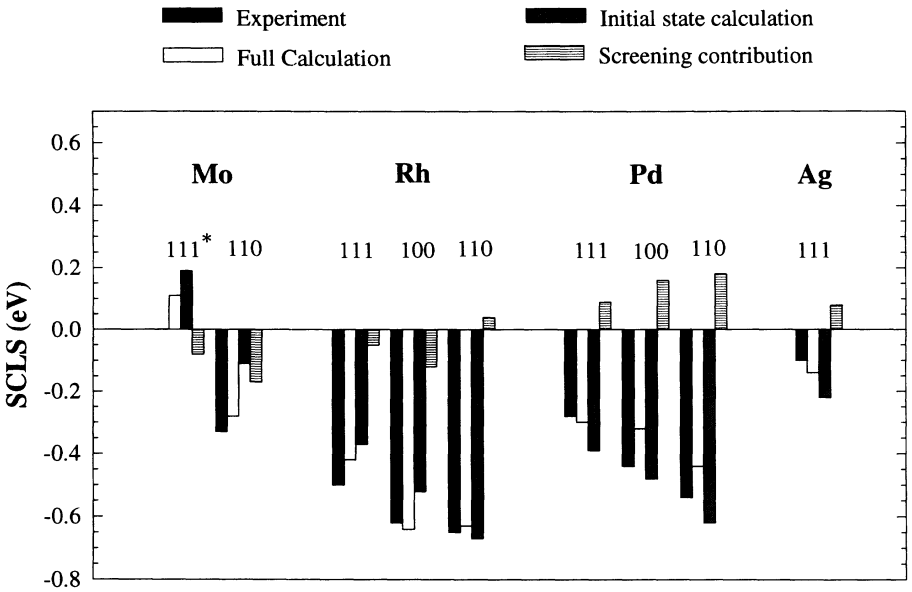

FIG. 4. The experimental and calculated 3*d* SCLS for the indicated surfaces. In the case of Ag(111), the experimental value indicated is the upper limit (−100 meV) of the SCLS, which we consider consistent with our measurements (see text). The SCLS's are calculated for the relaxed first interlayer distance given in Tables I–IV. For Mo we also give the values calculated for an fcc(111) surface. Also shown are decompositions of the SCLS into initial-state and final-state screening contributions.

the theoretical description presently shows a too large inward relaxation, whereas for Rh(100) the SCLS is too insensitive to the first interlayer distance to provide any help in resolving this issue. Both the theoretical and the experimental interlayer distances were carefully obtained and we believe technical problems can be excluded as source of the discrepancy. At this point, we choose to leave it as an open question what the origin of the outwards relaxation is. One interesting possibility, which is also suggested in Ref. 34, is that the surface atoms are magnetic and that therefore a spin-polarized calculation is required for a correct theoretical description.

In the case of Mo we give in Table IV the value for the most close-packed surface of the fcc and bcc structures, respectively. It is seen that the SCLS changes sign between these two crystal structures from negative for bcc to positive for fcc. A similar sign change has also been found between fcc and bcc structures of the isoelectronic 5*d*-metal W.[7] The reason for the negative experimental SCLS of Mo is thus related more to the crystal structure than to the number of 4*d* electrons.[36] The cause of the sign change between fcc and bcc is to be found in the initial-state energies, which change sign whereas the screening contribution has the same direction and is about equal for the two cases. It should be realized that a simple initial-state model,[2,3,24,25] which ascribes the SCLS to a narrowing and subsequent shift of the band structure of the surface atoms, is unable to predict this behavior. Actually, such a model would, for a half-filled band, predict no SCLS at all and in any case it would not distinguish between bcc and fcc. The details of the changes in the band structure from surface to bulk atoms and from fcc to bcc have to be known to predict this initial-state shift, that is, a full band-structure calculation has to be performed.

The precision of the $Z+1$ approximation can be investigated from the results in Tables I–IV in two ways. The SCLS calculated by explicit use of this approximation can be compared to the SCLS calculated for a true core hole and/or the SCLS's of the 1*s* and 3*d* core holes, respectively, can be compared. Both of these tests indicate that the $Z+1$ approximation is excellent for Ag, whereas for the other 4*d* metals the error is of the order of 100 meV with an increasing trend as the 4*d* band becomes half filled.[6] Calculations for Ru (Ref. 37) are consistent with this trend as are also calculations for the 5*d* elements by others.[7] We believe that the observed behavior is due to the difference in screening orbitals for the different 4*d* metals. A core hole is for Ag screened primarily in a 5*s* orbital, for Pd in a combination of 4*d* and 5*s* orbitals, and for the remaining 4*d* elements primarily in a 4*d* orbital. Due to the less localized character of the 5*s* orbital, it is to be expected that the 5*s* screening electron will be much less sensitive than a 4*d* electron to the exact nature of the core hole and thus obey the $Z+1$ approximation better. A similar argument may be invoked to explain why the calculations for Al(100),[5] which used the $Z+1$ approximation, still were able to achieve a very excellent agreement to experiment.[14] For true *d* elements we would, however, expect that the error involved in using the $Z+1$ approximation could be of the order of 100 meV. It should be realized that this defines only a lower limit for the error to be expected when surface segregation energies of $Z+1$ impurities in a Z metal are extracted from the measured SCLS.[2,4,22] In addition to the error caused by the $Z+1$ approximation, an additional error may arise from the fact that the $Z+1$ impurity relevant to core-level photoemission has the size of a Z atom.

Coming finally to the question of the relative importance of initial- and final-state effects, Fig. 4 and Tables I–IV demonstrate that the absolute magnitude of the screening contributions is small, typically 0.1 eV, for all of the investigated 4*d* metals. This, however, does not mean that this term can be neglected, in some cases its relative magnitude is large. For Mo, for example, the final-state contribution is 50% larger than the initial-state

contribution and has to be included to obtain good agreement to the experimental SCLS. Looking in more detail at the final-state contributions it is directly seen that the magnitude of these may change with the crystal face. Calculations for Ru (Refs. 8 and 37) show a picture similar that for Rh, that is, the final-state contribution is larger for the (100) than for the (111) and (110) surfaces. We have no simple explanation for this behavior but want to point out that it demonstrates that geometrical effects may also influence the magnitude of the final-state screening contributions. Therefore, it seems of importance to investigate the SCLS of more than one surface of a given metal when trying to draw general conclusions concerning the importance of final-state effects for that particular metal.

Ag and Pd are exceptional in having a positive final-state screening contribution, whereas the other 4*d* metal calculated here and also Y, Nb, and Ru (Refs. 8 and 37) all show a negative contribution. We believe that this change of sign of the screening contribution is related to the fact that the nature of the screening orbital changes from having mainly 4*d* character for the 4*d* elements to the left of Pd to having a large 5*s* component for Pd and Ag. The negative final-state contribution found for all the investigated metals except Pd and Ag means that the relaxation energy is larger for a surface than for a bulk atom, in other words, a core hole in a surface atom is, contrary to what is often assumed, better screened than one in a bulk atom. The enhanced screening of a core hole in a surface atom is due to the fact that the 4*d* density of states, in which the screening occurs, for a surface atom is higher than that of a bulk atom as a consequence of the band narrowing caused by the reduced coordination number at the surface. It is interesting to note that this more localized nature of the screening orbitals of a surface atom furthermore is consistent with the shorter core-hole lifetime of a surface than of a bulk Mo atom suggested in Ref. 11. For Pd and Ag where much of the screening occurs in a 5*s* orbital, this effect is no longer operative hence surface atoms are less well screened than bulk atoms. We believe that this difference in the nature of the screening orbital is also the explanation why the relative magnitude among the final-state contributions of the three surfaces shows a different pattern for Pd and Ag than for Rh and Ru.[8,37]

SUMMARY

In summary this work has reported experimental values for the SCLS of Rh(111), Rh(110), Pd(111), Pd(110), and Ag(111) surfaces and has demonstrated that these SCLS's may be calculated using density-functional theory together with LDA. Inclusion of final-state effects and of geometrical relaxations of the first interlayer spacing was found to be essential if an accuracy of the order of 50 meV is required for the calculated SCLS. The screening of a core hole was found to be more effective for a surface than for a bulk atom for the 4*d* metals to the left of Pd, a behavior which was argued to be a consequence of the surface-induced narrowing of the 4*d* band in which the screening occurs for these metals. The $Z+1$ approximation was found to be excellently obeyed for Ag, whereas it for the rest of the 4*d* elements introduces errors of the order of 0.1 eV. Initial-state calculations were found to be sufficient for reproducing the main trends, however, it was demonstrated that the details of the band structure may be important, i.e., a simple band-narrowing model does not always predict correctly the SCLS.

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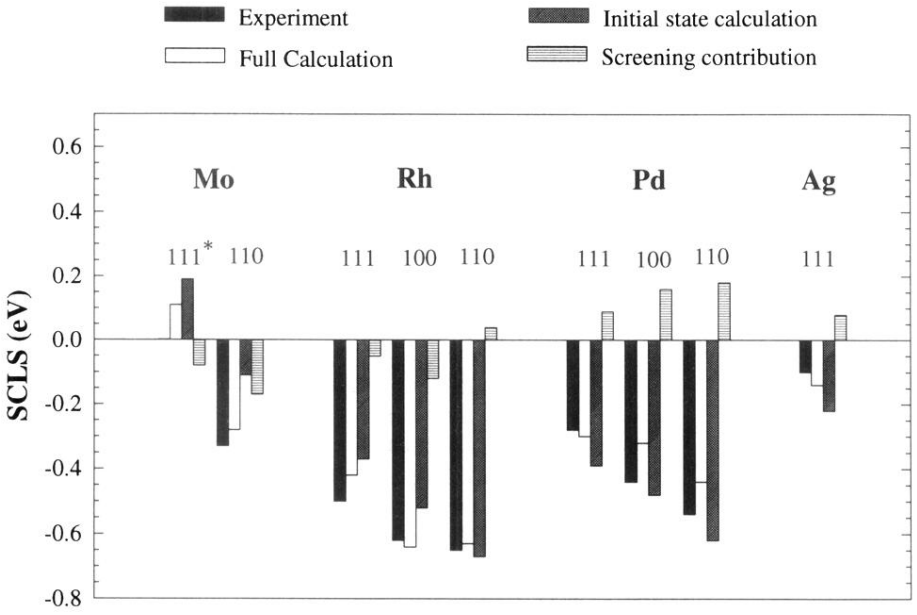

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