Surface core-level shifts of some 4d-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 3d 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 4d 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 4d 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 1s and 3d core holes, respectively. The Z + 1 approximation is found to be well obeyed in the case of Ag whereas for the rest of the 4d 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 recently5–9 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 4d-metal single-crystal surfaces Rh(111), Rh(110), Pd(111), Pd(110), and Ag(111). Combining these results with earlier reports10–12 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 4d 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 accuracy13 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,
made 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 sur-
rounding of the core ionized atom. The commonly used
Z+1 model, in which the core hole is modeled by in-
creasing 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 SX700 monochro-
mator and a large hemispherical analyzer of SCIEN TA
type. The SCLS was measured for the 3d level in all
cases, as this is the core level with the smallest lifetime
breddening for all 4d metals. The experimental resolu
tion varied from around 0.15 eV for the lower photon ener-
gies 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 anneal-
ing in oxygen to remove residual carbon. Ag(111) sur-
faces 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 sur-
fase atoms. To desorb adsorbed hydrogen and CO, the
crystals were flashed to typically 700 K prior to each in-
dividual measurement of a 3d spectrum. This procedure,
the short duration of a measurement, and a pressure of
typically $6 \times 10^{-11}$ torr in the experimental chamber
mean that artifacts resulting from hydrogen contamina-
tion of the surfaces will be very small if existing at all.
All measurements were performed at a crystal tempera-
ture close to 100 K in order to reduce the phonon
breddening of the core-level spectra. For more details on
the Mo(110) and Pd(100) measurements, the reader is re-
ferred 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 be calculated accurately using ab initio
methods based on density-functional theory.

We have performed such calculations by the full-
potential linear-muffin-tin-orbital method 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 (LDA) to the ex-
change and correlation functional. The surfaces are
represented by seven-layer slabs using $c(2 \times 2)$ supercells
in the plane defined by the surface. Use of larger super-
cells, i.e., using a larger spatial separation of the core ion-
ized 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 sur-
faces between the present calculations and those of
Aldén, Skriver, and Johansson that avoid the use of super-
cells. 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 pro-
cess, 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). The crystal structure of Mo is bcc whereas all of
the other metals considered crystallize in the fcc struc-
ture. 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 calcu-
lations for a close-packed (111) surface for a hypothetical
fcc structure of Mo.

A common way 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).

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

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

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

$^a$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.

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

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

<table>
<thead>
<tr>
<th>metal</th>
<th>state</th>
<th>full calculation</th>
<th>initial-state approx.</th>
<th>screening contribution</th>
<th>$Z+1$ approx.</th>
<th>exp. data</th>
</tr>
</thead>
<tbody>
<tr>
<td>bcc Mo</td>
<td>$3d$</td>
<td>$-0.24$</td>
<td>$-0.08$</td>
<td>$-0.16$</td>
<td>$-0.11$</td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bcc Mo</td>
<td>$1s$</td>
<td>$-0.19$</td>
<td>$-0.04$</td>
<td>$-0.15$</td>
<td></td>
<td>$-0.33^a$</td>
</tr>
<tr>
<td>$-3.9%$</td>
<td>$3d$</td>
<td>$-0.28$</td>
<td>$-0.11$</td>
<td>$-0.17$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>fcc Mo</td>
<td>$1s$</td>
<td>$0.18$</td>
<td>$0.25$</td>
<td>$-0.07$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td>$3d$</td>
<td>$0.11$</td>
<td>$0.19$</td>
<td>$-0.08$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$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 fur-
furthhere 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 thermo-
dynamic model2,4,22,23. 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 mod-
els. As the present calculations are based on an all-electron method, which relaxes all core states as the po-
tential 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 ob-
tained 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_{3/2} core-level spectra for the three low-index surfaces of Pd measured at a photon en-
ergy of 390 eV where the spectra are very surface sensitive due to the kinetic energy of the emitted 3d_{3/2} elec-
trons 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 be-
comes 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 (111) (Ref. 26) surfaces of Pd. Comelli et al.28 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 earlier10 and con-
firmed 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.28 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

![Graph of Binding Energy vs. Intensity](image-url)
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\textsuperscript{26,27} to induce a large shift to higher binding energy of the surface Pd atom 3d 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 3d 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\textsuperscript{28} that the Pd 3d line shape is poorly described by the commonly used Doniach-Sunjic\textsuperscript{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 3d emission relative close to the peak position.

Reference 10 describes in detail how the 3d 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 3d 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,\textsuperscript{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 $-0.55 \pm 0.03$ 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 3d 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 $-0.28 \pm 0.05$ eV for Pd(111).

For Rh(111) and Rh(110), the much narrower 3d line shape and the fact that Rh 3d is much better described by a Doniach-Sunjic line shape make extraction of the SCLS considerably easier. Figure 2 shows how Rh 3d\textsubscript{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 $-0.50 \pm 0.02$ eV and $-0.64 \pm 0.02$ 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\textsuperscript{31} from spectra with worse resolution and statistics. Furthermore, the SCLS of $-0.62$ eV for Rh(100) reported by others\textsuperscript{12} is, as expected, intermediate between those of the (111) and (110) surfaces.

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

![Graph showing spectral data for Rh(111) and Rh(110)]

FIG. 2. Rh 3d\textsubscript{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.
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. The remaining fitting parameters are also close to those of the earlier study (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\textsubscript{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-3d 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. Third, a SCLS of 0.076±0.03 eV has been reported for polycrystalline Ag. 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 4d 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 concluded that this surface shows an unusual outwards relaxation of +3±1.5%, which should be compared to the inward relaxation of −0.6% calculated in. 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 4d-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. 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...
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 5d-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 4d 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 ls and 3d core holes, respectively, can be compared. Both of these tests indicate that the Z+1 approximation is excellent for Ag, whereas for the other 4d metals the error is of the order of 100 meV with an increasing trend as the 4d band becomes half filled.6 Calculations for Ru (Ref. 37) are consistent with this trend as are also calculations for the 5d elements by others.7 We believe that the observed behavior is due to the difference in screening orbitals for the different 4d metals. A core hole is for Ag screened primarily in a 5s orbital, for Pd in a combination of 4d and 5s orbitals, and for the remaining 4d elements primarily in a 4d orbital. Due to the less localized character of the 5s orbital, it is to be expected that the 5s screening electron will be much less sensitive than a 4d 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),7 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 4d 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 to 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 4d 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 4d character for the 4d elements to the left of Pd to having a large 5s 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 4d 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 5s 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. 3,37

**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 4d metals to the left of Pd, a behavior which was argued to be a consequence of the surface-induced narrowing of the 4d 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 4d 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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13. A number of other calculations have achieved a similar degree of agreement between experiment and theory using similar but not identical calculations. The calculated SCLS of −97 meV for Al(100) from Ref. 5 is in excellent agreement with the experimental value of −96 meV from Ref. 14; for Be(0001) the calculations of Ref. 15 reproduced the experimental finding of surface-related shifts of the outermost three layers reported in Ref. 16; and for elements where experimental values exist, the calculations of Ref. 7 for the most close-packed surfaces showed good agreement with these values.
25 Many of these initial-state models furthermore use simplifying models for describing the modification of the band structure at the surface (see, e.g., Refs. 3 and 4) in contrast to the present calculations where a full \textit{ab initio} band-structure calculation is performed.
34 E. Lundgren, J. Burchhardt, M. M. Nielsen, D. L. Adams, and J. N. Andersen (unpublished). In this study, special care was taken to avoid hydrogen adsorption on the surface by performing measurements at elevated temperature where hydrogen does not adsorb on Pd(100).
FIG. 4. The experimental and calculated 3d 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.