

## ENHANCED SCREENING OF CORE HOLES AT TRANSITION-METAL SURFACES

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*Ab initio* calculations based on density-functional theory were used to obtain surface core-level shifts for the 4d transition metals and silver in the initial-state model and in the full-impurity formulation, giving an unambiguous separation into initial state and screening terms. This shows that the screening of the core hole is substantially better at the surface than in the bulk for a transition metal. For Ag, an opposite and even larger effect is found, showing the central role of *d*-electron screening in the surface core-level shift of the transition metals.

Using X-ray photoemission experiments, the binding energies of the core electrons in a solid can be measured with high accuracy. It is well known that these are shifted for the surface atoms relative to those of the bulk. This effect is denoted the surface core-level shift (SCLS) and is a valuable probe of surface properties.<sup>1</sup> In exact terms, the measured quantity is the difference of two ionization energies:

$$\Delta_c = I_c^s - I_c^b, \quad (1)$$

where  $I_c^{s,b}$  denotes the energy required to remove one electron from the core state *c* of a surface or bulk atom. Each ionization energy is itself a difference of two total energies, namely, those before and after the core electron is removed. The theoretical determination of the SCLS is therefore within the capabilities of *ab initio* calculations based on density-functional theory (DFT), since these can accurately predict total-energy differences. This full treatment, while exact within the approximations used to solve the DFT equations, is computationally very demanding because the core hole destroys the periodicity of the lattice or the surface.

On the other hand, a number of popular models have attempted to pinpoint the relevant contributions to the SCLS. The most direct of these is the initial-state approximation<sup>2-4</sup> which assumes that the binding energy of a core state is simply given by the core eigenvalue before the electron is removed. This model can trace the basic trends across a transition-metal series to the reduced coordination of the surface atoms. However, it neglects all final-state effects which arise whenever the screening of the core hole is different at the surface and in the bulk. A different approach, sometimes denoted the thermodynamic model,<sup>4</sup> shows that the SCLS equals the difference of the impurity energies for a core-excited atom (denoted by  $Z^*$ ) at the surface and in the bulk.<sup>7,8</sup> By assuming that the response of the valence electrons to the core hole is similar to that when the nuclear charge is increased by one (the equivalent-core approximation),  $Z + 1$  is substituted for  $Z^*$  in the formulation. With this, the SCLS equals the heat of surface segregation for a  $Z + 1$  impurity<sup>7-9</sup> and is in principle accessible to thermochemical measurements, although direct

measurement of the segregation energy is difficult. To obtain a connection to more easily accessible quantities, it is a customary procedure to leave away certain correction terms associated with the impurity solution energy and to estimate the surface segregation energies as the difference of the  $Z + 1$  and  $Z$  metal surface energies.

A central difference of the two model descriptions is the treatment of the final-state screening effects. These are ignored in the first model, but are included to some degree in the surface-energy estimate. At present, the importance of final-state effects in metals is still a matter of controversy.<sup>2,5,6</sup> The aim of the present work is to study this matter systematically by a trend study of the 4d-row metals using *ab initio* calculations. This procedure can unambiguously separate initial-state and final-state contributions to the SCLS. A central point is the comparison of Ag with the true transition metals. Since Ag has a completely filled and exceptionally low-lying *d* shell, the screening properties are dominated by the *s* electrons, which behave differently than the electrons of a partly filled *d* shell. For this reason, we have elected to investigate the 4d metals despite the considerably larger amount of experimental data in the 5d's. The calculations show that for a true transition metal, the final-state screening is better at the surface than in the bulk. It gives a contribution of typically  $\approx 0.1$  eV to the initial-state prediction. For Ag and, to a lesser extent Pd, the screening at the surface is worse than in the bulk, leading to a positive screening contribution which to a large extent cancels the initial-state value. In addition, we find that the surface-energy estimate gives only rough qualitative agreement if the SCLS is expressed in terms of the surface energies of the equilibrium  $Z$  and  $Z + 1$  metals, due to a neglected term arising from the strong dependence of the surface energy on the lattice constant. We note that some preliminary results, which did not discuss the final-state results for Ag and the variation of the surface energy with the lattice constant, were presented in Ref. 10. Furthermore, a recent publication<sup>14</sup> has calculated the SCLS for the 4d and 5d transition metals (without Ag and Au) from *ab initio* total-energy differences, obtaining the expected good agreement to experimental values. However, these authors did not attempt a separation into initial-state and screening contribu-

tions. We consider this the relevant point towards understanding the various models of the SCLS.

The calculations were done using the full-potential linear muffin-tin orbital (FP-LMTO) method<sup>11</sup> to obtain self-consistent total energies and core eigenvalues for the bulk and low-index surfaces, the latter simulated by seven layer slabs. The local-density approximation (LDA) to DFT was used.<sup>12</sup> Details are the same as for a previous investigation of the 4d metal surfaces.<sup>13</sup> The study of trends was facilitated by treating all metals as fcc; for Nb and Mo, results for bcc surfaces were also obtained. The surface core-level shift in the initial-state description is obtained by simply comparing the core eigenvalues for the atoms in the outermost and center layers of the self-consistent slab. Hereby it is useful that the all-electron method used here relaxes all the core states while the potential is made self-consistent. To describe a core hole, the slab is made self-consistent under the constraint of single occupation of a selected core state of an atom which is either at the surface or in the center of the slab. The core hole is assumed to be completely screened so that an additional electron is added to the valence charge, making the slab neutral in overall. The impurity problem is treated by means of  $\sqrt{2} \times \sqrt{2}$  surface supercells. The SCLS including initial- and final-state effects is calculated directly as the difference of two impurity energies.

Figure 1 shows the calculated initial-state surface core-level shifts for the smooth surfaces of the 4d metals. The SCLS is defined here and in the following as the core-level binding energy of a surface atom minus that of a bulk atom. We remind that the single-particle *eigenvalue* of a core state with respect to the vacuum is negative, while the core-level *binding energy* is a positive number. Characteristic of the trends across the series is a decrease with increasing *d* occupation and a larger magnitude for rougher surfaces. Both trends are explainable in terms of a well-accepted model<sup>2-4</sup> which has been quantified within the tight-binding method. The density of states of a surface atom is narrowed due to the reduced coordination number. If the centers of the surface density of states were to coincide with that of the bulk, a surface-charge depletion would result near the start of the series and a charge surplus at the end. As the valence charge rearranges to obtain local charge neutrality, the electrostatic

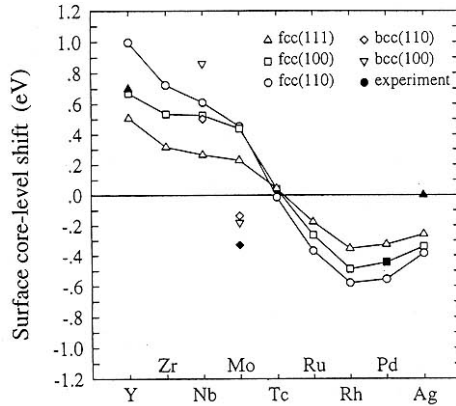


Fig. 1. Calculated surface core-level shifts of the 1s state of the 4d metals and Ag in the initial-state approximation. Values for the 3d-core states are lower by about 0.02 eV at the ends of the series and by  $\approx 0.08$  eV near the middle. Experimental values are shown for the Y hcp(0001) [Ref. 16], Mo bcc(110) [Ref. 15], Pd fcc(100) [Ref. 14], and Ag fcc(111) [Ref. 17] surfaces.

potential shifts the surface density of states downward (respectively upward), at the same time shifting the core levels. These properties are recovered in the *ab initio* initial-state results. For example, the dependence on the surface roughness (expressed by the surface and bulk coordination numbers  $C_s$  and  $C_b$ ) is very similar to the prediction from tight binding. As function of the  $d$  occupation, the *ab initio* SCLS shows smoother behavior than the tight-binding result.<sup>3</sup> Agreement to experiment is in general reasonable and shows the well-known trend across the series, as is seen from the points for Pd(100),<sup>15</sup> Mo(110),<sup>16</sup> and Y hcp(0001)<sup>17</sup> in Fig. 1. The overall trends and values are very similar to those measured for the 5d metals.<sup>4</sup> In the present context, an important point is that a major disagreement to experiment is found in the case of Ag, for which a recent measurement<sup>18</sup> of the fcc(111) surface obtained  $0.0 \pm 0.1$  eV, a value much closer to zero than the initial-state prediction. The discrepancy will be traced to final-state effects below.

In the initial-state result, Ag lies smoothly within the trend of the transition metals, whereas experiment suggests that from Pd to Ag the SCLS

should drop to nearly zero. This suggests that the neglected final-state effects play a different role for Ag. Table I compares the initial-state values to the results of slab impurity calculations with a true core hole in the 1s or 3d state. We have focused on the sequence Rh-Pd-Ag, but have also included Y as typical early transition metal and bcc Mo in order to compare to experiment. Noteworthy is that whereas the final-state screening contribution is small and negative for Y, Mo, and Rh, it is positive and almost completely compensates the negative initial-state value for Ag. The behavior for Pd is intermediate, in agreement with the fact that here the  $d$  band can only accommodate  $\approx 0.5$  electrons. When the final-state screening contribution is taken into account, the theoretical results for Mo and Ag come in close agreement with the experimental data.

The qualitative difference in the screening for Ag and the true transition metals can be explained as follows. In all cases, one extra valence electron moves from infinity to screen the core hole, making the system neutral again. For the true transition metals, the extra electron is taken up by the high-lying  $d$  states of the atom from which the core electron was emitted. This could be denoted

Table I. Comparison of surface core-level shifts at the Y fcc(111), Rh, Pd, Ag fcc(100), and the Mo bcc(110) surfaces as obtained from the initial-state model ( $\Delta_e^{\text{initial}}$ ) and from the full calculation as a total-energy difference [see Eq. (1)]. The third column is the difference of the first two and gives the part of the SCLS which is due to different screening of a core hole for a surface and bulk atom. Negative values here reflect that the screening at the surface is better than in the bulk.

State	Initial-state approximation	Full calculation	Final-state screening contribution
Y 1s	0.52	0.41	-0.11
Y 3d	0.50	0.38	-0.12
Mo 3d	-0.08	-0.24	-0.16
Rh 1s	-0.52	-0.65	-0.13
Rh 3d	-0.58	-0.62	-0.04
Pd 1s	-0.43	-0.30	0.13
Pd 3d	-0.49	-0.33	0.16
Ag 1s	-0.33	-0.08	0.25
Ag 3d	-0.36	-0.10	0.26

"intra-atomic" screening because the  $d$  states are strongly localized. Although this contribution is noticeable it is typically only a small correction. The screening is better at the surface because the surface-atom density of states at the Fermi level is enhanced, a well-known consequence of the reduced nearest-neighbor coordination. For Ag, on the other hand, the  $d$  shell is full and the extra electron must occupy the more extended  $s$  wave functions. Consequently this type of screening has a large "inter-atomic" component and is influenced by the presence of the surface. More graphically, in a transition metal the screening occurs within a radius which is shorter than the distance of the surface atom from the vacuum; for Ag, the radius is larger and the presence of the surface is sensed. The basic effect, that localized low-lying unoccupied states can strongly influence the screening on an atom, is also known for other systems, e.g., the Si(100) surface.<sup>19</sup> We expect the overall trends in the screening properties to be similar in the 3d and 5d series.

We note that the final-state screening contribution can be re-expressed using Slater's transition-state concept as applied to core levels.<sup>4,20</sup> The derivative of the total energy respective to the core occupation is given by the position of the core eigenvalue relative to the Fermi energy. From this, the screening correction to the initial-state surface core-level shift is approximately

$$\Delta_c - \Delta_c^{\text{initial}} \approx \frac{1}{2}(\Delta\epsilon_c^a - \Delta\epsilon_c^b), \quad (2)$$

whereby  $\Delta\epsilon_c^{a,b}$  is the positive energy by which the surface- or bulk-core eigenvalue drops relative to the Fermi energy when one electron is removed,  $\Delta\epsilon_c = \epsilon_c(2) - \epsilon_c(1)$ . Thus, a positive screening contribution to the SCLS (as in Ag) means that the surface-atom core level drops more strongly than in the bulk when deoccupied. This shows that the core-hole is screened more completely in the bulk. The reverse situation is found for the transition metals.

Based on the *ab initio* values, we now discuss the surface-energy model for the SCLS. Under the equivalent-core approximation, the SCLS is equal to the heat of surface segregation for a  $Z+1$  impurity, i.e., the difference of the surface and bulk impurity energies. As the  $Z+1$  impurity moves from the bulk to the surface, a portion of the surface is changed from that of the  $Z$  metal to that of the  $Z+1$  metal.

This suggests that the SCLS could be estimated as

$$\Delta_c \approx E_s^{Z+1} - E_s^Z, \quad (3)$$

where  $E_s^Z$  and  $E_s^{Z+1}$  are the surface energies per surface atom of the two relevant metals. A formal derivation of Eq. (3) has been given by an analysis involving a Born-Haber cycle, which assembles the impurity system in several steps from the pure constituents, together with subsequent neglect of terms associated with the intermetallic solubility.<sup>7,8</sup> Inherent to this description is that, as in Midema's theory,<sup>21</sup> crystals are assembled and disassembled at a fixed atomic volume, so that for a consistent description the two surface energies should be compared at the same lattice constant. However, when Eq. (3) is applied, each metal is usually taken at its own equilibrium lattice constant. We can investigate this question because, although the surface energy of crystalline metals is difficult to measure accurately, the *ab initio* calculation can provide it as well as its change with surface area. Figure 2 shows the estimate for the SCLS which is obtained when both surface energies are taken at the  $Z$ -metal lattice constant (squares) and when each is at its own equilibrium lattice constant (triangles). The additional "surface stress" term is seen to be a large contribution which can hardly be ignored in the theory. Note that this term increases the magnitude of the SCLS estimate at both ends of the series, consistent with a tensile (contractive) surface stress. For comparison, Fig. 2 also shows the initial-state SCLS for the fcc(001) surface. Considering that the full calculation gives a SCLS about 0.1 eV lower than the initial-state result for the transition metals, the overall agreement is clearly better when the surface stress term is included, especially near the beginning of the series.

In summary, the following picture of the initial- and final-state contributions to the surface core-level shift emerges. The initial-state SCLS is a difference of energy levels of the unperturbed system, while the screening correction is related to the downward shifts of the core levels with decreasing core occupation. The amount by which a deoccupied core level drops depends on how well the core hole is screened by the valence electrons. For the true transition metals, screening is mainly done by the localized  $d$  states on the atom with the core hole. We find that the screening at the surface is better than in the bulk

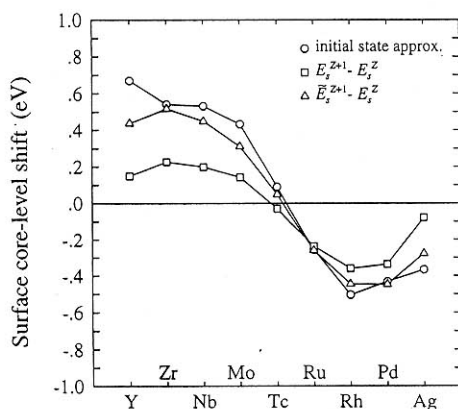


Fig. 2. For the fcc(100) surfaces, the comparison of the initial-state  $1s$  SCLS with the difference of the surface energies of each metal and its right-hand neighbor in the periodic table [compare Eq. (3)]. The results marked by triangles were obtained by evaluating the surface energy of the  $Z+1$  metal at the lattice constant of the  $Z$  metal.

for Y to Rh because density of states at the Fermi energy is higher. For a noble metal such as Ag, the screening is provided by more extended  $s$  states. At the surface this screening is less effective than in the bulk. This final-state effect compensates for the large SCLS obtained in the initial-state model, leading to a value which is close to zero. In addition, we find that the popular description of the SCLS in terms of the  $Z$  and  $Z+1$  surface energies neglects a large term due to the change of the surface energy with lattice constant.

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