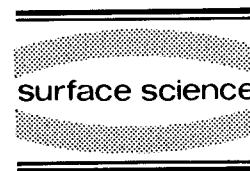




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Ab initio calculation of surface core-level shifts for transition metal surfaces

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Abstract

The surface core-level shift (SCLS) for a number of smooth surfaces of 4d-transition metals Mo, Rh, Pd and Ag was calculated within two different approaches using the full-potential LMTO method. The first approach, the initial state approximation, estimates the SCLS from the position of the core eigenvalues of atoms at the surface relative to those of the bulk. The second approach treats a surface or bulk atom with a core hole as an impurity by means of a supercell. This approach is in principle exact within the local-density approximation and thus includes final-state screening effects. The results show that the screening of the core hole is of different nature for Ag when compared to the transition metals.

The surface core-level shift (SCLS) at metal surfaces has been considered both experimentally and theoretically for several years [1,2]. 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 for a surface respectively a bulk atom. Each ionization energy is itself a difference of two total energies, namely, those before and after the core electron is removed. In principle, the SCLS can be obtained by calculating the total energies entering into this description, involving the treatment of

both a bulk and surface impurity problem. To avoid this complication and in order to obtain a simpler physical picture, two quite different approximate approaches have been used in order to interpret the data. The initial-state approximation explains the SCLS in terms of the energetical position of the core eigenvalues at the surface and in the bulk before an electron is exited [3,1]. This model can explain the basic trends which are observed for transition metals, as a consequence of the reduced coordination of the surface atoms and a valence electron redistribution to achieve a layerwise charge neutrality. It is clear, however, that the experiment does not measure the static core eigenvalue difference. Rather, the excitation process consists of the emission of a core electron, followed by the relaxation of the valence electrons to screen the resulting localized positive

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charge. It is the total-energy change of this relaxed system, respective to the unperturbed surface, which is imparted to the emitted electron. The degree of screening might well be different at a surface, leading to additional “final-state” contributions to the SCLS. In the thermodynamical model [4,5], both initial- and final-state effects are in principle included. It is assumed that response of the valence electrons to the core hole is very similar to the response when the nuclear charge is increased by one (the equivalent-core approximation). The SCLS is thus expressed in terms of impurity energies for a $Z + 1$ atom at the surface and in the bulk of the host metal with nuclear charge Z . The advantage of this approach is that the SCLS is expressed in terms of thermodynamic quantities; thus, the SCLS is in fact just the heat of surface segregation for the $Z + 1$ impurity [6].

The aim of the calculations is to determine the validity of the approximations used in the different model. On the one hand, the total energies for the exact impurity description can be calculated. Additionally, the single-particle core eigenvalues and quantities such as the surface energy are produced. The calculations were done using the full-potential linear muffin-tin orbital (FP-LMTO) [7] method, whereby surfaces were simulated by 7-layer slabs. The method recalculates all the core states in each iteration. To describe a core hole, the slab was made self-consistent under the constraint of single occupation of a selected core state at the surface or in the center of the slab in a $\sqrt{2} \times \sqrt{2}$ surface supercell. The core hole is assumed to be completely screened so that an additional electron was put into the valence states, making the slab neutral in overall.

A thorough discussion of the calculations will be given in a future publication [9]. One of the main results emerging from the comparison of the initial-state and full core-hole impurity calculations is that the screening in Ag is qualitatively different when compared to the true transition metals. In the latter, the final-state corrections lower the SCLS by typically 0.1 eV, in most cases a rather small correction. For Ag, the final-state contribution is much larger and cancels the initial-state SCLS to a large extent. The total value

Table 1

The surface core-level shifts at the bcc (110) surface of Mo and at the fcc (100) surfaces of Rh, Pd, and Ag as obtained from the full core-hole impurity calculation (column 1) and from the initial-state model (column 2); column 3 gives experimental data

| State | Impurity calculation | Initial-state approximation | Experiment |
|-------|----------------------|-----------------------------|------------|
| Mo 3d | −0.24 | −0.08 | −0.33 [10] |
| Rh 3d | −0.62 | −0.59 | — |
| Pd 3d | −0.33 | −0.49 | −0.44 [11] |
| Ag 3d | −0.10 | −0.36 | ≈ 0 [10] |

for Ag is obtained to be close to zero, in agreement with experimental data [10,3], only if final-state effects are included. The different nature of screening is explained as follows. In all cases, one extra valence electron moves in 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 “intra-atomic” screening is not sensitive to the environment because the d states are strongly localized. This is shown for Mo and Rh in Table 1, where a fairly well agreement between the full core-hole and the initial state calculation is seen. For Ag, the d shell is full and the extra electron must occupy the more extended s wavefunctions. Consequently this type of screening has a large “inter-atomic” component and is influenced by presence of the surface. This effect is especially pronounced for Ag in comparison to the other noble metals because the d band is more tightly bound. The measured SCLS are −0.24, −0.08, and −0.40 eV for polycrystalline Cu, Ag, and Au, respectively, and the s–d hybridization in Cu and Au seems to lead to similar behavior as that of a partly filled d band [3]. The behavior for Pd is intermediate, in agreement with that the 4d band can only accommodate ~ 0.5 electrons [8].

An interesting result was also found in the context of the thermodynamic model. As a standard approximation, it is usually assumed that the dominating contribution to the $Z + 1$ impurity surface segregation energy is the difference of the surface energies of the Z and $Z + 1$ metals. This expresses that the metal with the lower surface

energy will tend to move to the surface. The calculations show that the agreement of the SCLS to the difference of the surface energies of the $Z + 1$ and Z metal surface energies is only qualitative. The origin of the error is that the two surface energies should properly be compared at the same lattice constant, that is, at the lattice constant of the Z metal. Therefore an additional energy term should be included which is the change of the surface energy of the $Z + 1$ metal when it is expanded or compressed to the Z lattice constant. This increases the magnitude of the surface-energy difference at both ends of the series, indicating a tensile (contractive) stress in either case. Including the additional term then leads to good agreement across the whole series.

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