The surface core-level shift of the Rh (100) single-crystal surface



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LETTER TO THE EDITOR

# The surface core-level shift of the Rh(100) single-crystal surface

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**Abstract.** High-resolution photoemission spectroscopy has been used to determine the surface core-level shift of the Rh(100) single-crystal surface. From the Rh 3d core level spectra the surface atoms were found to have 0.62±0.01 eV lower binding energy than the bulk atoms. The observed shift is in excellent agreement with recent theoretical calculations.

The sensitivity of the core-level binding energy of an atom to the atomic surroundings gives the possibility for studying the local geometrical and electronic environment of atoms, see, for example, references [1–4]. In particular, determination of surface core-level shifts (SCLS) is important for the understanding of the electronic structure of surfaces.

Accurate determination of the surface shift requires sharp core levels and high experimental resolution. Among the transition metals mainly SCLS of the 5d metals have been reported. The sharpness of the 4f levels of these metals and their low binding energies, 100 eV or less, energies for which beam lines with high energy resolution have been available at synchrotron radiation facilities, have made these core levels suitable for determining SCLS. However, in the past, high experimental resolution has been difficult to achieve at energies needed for studying the SCLS of 3d and 4d transition metals, the narrower core levels in these cases being the 2p and 3d levels, respectively. The SCLS results available for the 4d metals are data obtained by conventional x-ray photoemission spectroscopy on evaporated films and scraped samples [5, 6] and recent high-resolution synchrotron radiation measurements on single crystal surfaces [7–12].

In the present paper we report on an experimental study of the SCLS of the Rh(100) surface by recording the Rh 3d core level. From our data we determine an SCLS of 0.62±0.01 eV to lower binding energy relative to the bulk Rh 3d core level for this Rh single-crystal orientation.

The experiments were carried out at beamline 22 at the MAX synchrotron radiation laboratory, Lund University, Sweden. The spectra were recorded using a modified SX-700 plane grating monochromator, covering the photon energy range 20 to 1000 eV [13], in conjunction with a large hemispherical electron energy analyser [14]. The spectra reported here were measured at photon energies between 370 and 410 eV and at a total instrumental resolution of about 0.25 eV.

The Rh(100) sample was cleaned by $Ar^+$ sputtering, heating in oxygen and annealing in vacuum. Surface cleanliness was verified by monitoring the O 1s and C 1s core-level photoemission as well as the O 2p and C 2s levels in the valence band region. The surface structure was checked with LEED. The base pressure of the analysis chamber was about 5 ×

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$10^{-11}$ torr during the experiments. All spectra shown were recorded with the sample kept at room temperature.

Figure 1 shows the Rh 3d core-level spectrum as recorded at photon energy 370 eV. A doublet structure is clearly visible in the $3d_{5/2}$ spin–orbit component. The structure of the $3d_{3/2}$ component is less resolved due to additional broadening of this level through the Coster–Kronig decay process. Due to the smaller intrinsic width of the $3d_{5/2}$ component, with bulk binding energy 307.6 eV, the discussion of the SCLS of Rh(100) will be based on the experimental behaviour of this spin–orbit component.

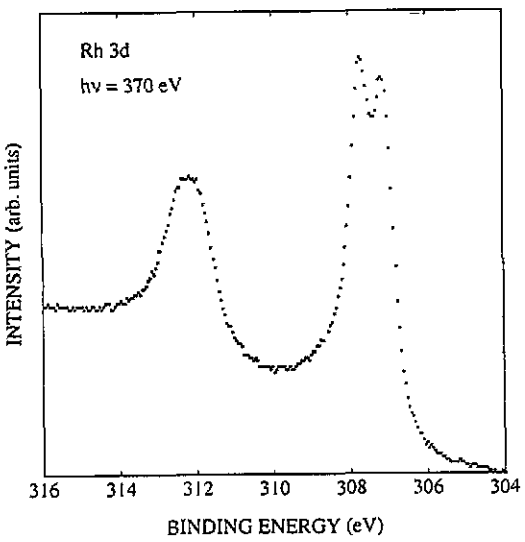


**Figure 1.** The Rh 3d core-level spectrum from the Rh(100) single-crystal surface as recorded at photon energy 370 eV.

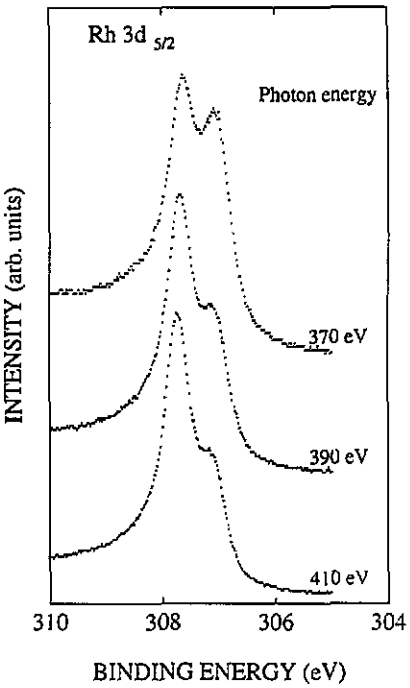


**Figure 2.** Development of the Rh $3d_{5/2}$ core-level spectrum as a function of photon energy. The photon energy ranges from 370 to 410 eV.

Figure 2 displays the development of the Rh $3d_{5/2}$ core-level emission as a function of photon energy in the range $h\nu$ = 370–410 eV. The relative decrease in intensity of the low-energy component as a function of increasing excitation energy identifies this component as being due to emission from the surface atoms. This intensity behaviour follows the general change in the electron escape depth as a function of the electron kinetic energy [15]. The behaviour of the Rh $3d_{5/2}$ core level at lower photon energies could not be studied due to the rapidly decreasing photoionization cross section of this core level closer to the threshold [16]. During the experiments it was observed that small traces of residual carbon or oxygen left on the surface after the cleaning procedure strongly reduced the intensity of the lower-binding-energy peak, providing additional evidence for this component being a surface-related feature.

The 3d SCLS of Rh(100) can be read directly from the 370 eV spectrum of figure 2 yielding a value of $-0.60\pm0.02$ eV. A decomposition of this spectrum into bulk and surface

components is given in figure 3. After subtraction of a linear background the spectrum was fitted using components being convolutions of a Gaussian and a Doniach–Sunjic [17] function. A total Gaussian full width at half maximum (FWHM) of 0.35 eV, including instrumental resolution and thermal broadening, was chosen. The corresponding Lorentzian FWHM was taken to be 0.32 eV and an asymmetry parameter of 0.13 was applied. These parameters gave consistently good fits throughout the series of spectra shown in figure 2 and the SCLS of Rh(100) was determined to be $-0.62\pm0.01$ eV. Because this SCLS fits so well with the estimate above ($-0.60\pm0.02$ eV) no attempts were made to optimize the fitting parameters. Other fits, using smaller Gaussian and larger Lorentzian linewidths also gave good fits and an SCLS of $-0.62\pm0.01$ eV. The observed SCLS of Rh(100) is slightly smaller than the corresponding shift of $-0.65\pm0.02$ eV measured at the unreconstructed Rh(110) surface [11]. In general, it is expected that the SCLS is larger at the less dense (110) surface.

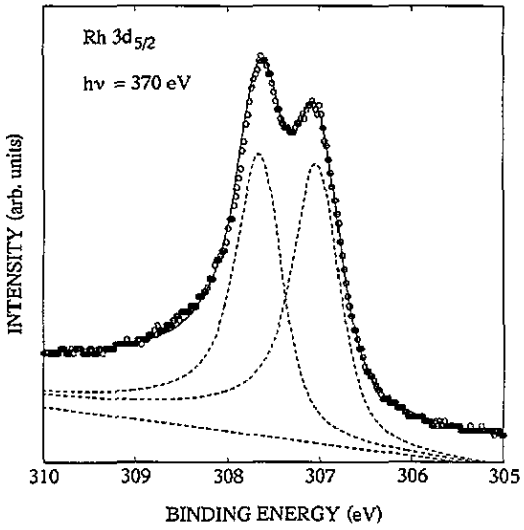


**Figure 3.** Decomposition of the Rh $3d_{5/2}$ core-level spectrum, measured at $h\nu$ = 370 eV, into bulk and surface components using linear background subtraction and a convolution of Gaussian and Doniach–Sunjic functions.

Theoretically, Johansson and Mårtensson [1, 18] have shown that by assuming a fully screened final state in the metallic case and applying the $Z+1$ approximation the SCLS may be written [1]

$$\text{SCLS} = E_s(Z+1) - E_s(Z) - E_{\text{corr}} \tag{1}$$

$E_s(Z+1)$ and $E_s(Z)$ are the surface energies of element $Z+1$ and $Z$, respectively. The last term is a correction term which contains the difference in solution energies of a $Z+1$ impurity in the bulk and at the surface of the $Z$ host. In our case the $Z$ element is Rh and the $Z+1$ element Pd. To our knowledge, no experimental values for the surface energies of Rh and Pd are available. The semi-empirical values of Miedema [19] give the following prediction of the SCLS for Rh(100) when the correction term of (1) is neglected

$$\text{SCLS} = (2100 - 2700)\ \text{mJ m}^{-2} = -0.29\ \text{eV/atom}.$$

More recent *ab initio* calculations by Methfessel *et al* [20] give the surface energies of Rh(100) and Pd(100) directly. From their values an SCLS of −0.38 eV is obtained. Both these theoretical estimates give an SCLS which is too low compared to our observation. Recently, we have become aware of new *ab initio* calculations by Hennig *et al* [21] where an impurity-like approach has been applied. These calculations give an SCLS of −0.62 eV for Rh(100) in excellent agreement with our experimental results thus indicating a much better accuracy in these calculations than in the earlier theoretical predictions.

In conclusion, we have measured the SCLS of the Rh(100) surface to be −0.62±0.01 eV. The experimental result is in excellent agreement with recent *ab initio* calculations.

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