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

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**Abstract.** The surface core-level shift of the Pd(100) single-crystal surface has been measured from high-resolution Pd 3d core-level spectra. The surface atoms are found to have  $0.44 \pm 0.03$  eV lower binding energy than the bulk atoms. The result is compared with theoretical estimates.

### 1. Introduction

Measurements of surface core-level shifts (SCS) have an important role in the understanding of the electronic structure of surfaces. In many cases the binding-energy shifts between surface and bulk atoms can be related to both electronic and structural properties of the surface layer (see e.g. Johansson and Mårtensson 1983, Spanjaard *et al* 1985, Jugnet *et al* 1987). For metallic systems where the so-called  $Z+1$  approximation is applicable the SCS can be expressed in terms of surface energies representative of the initial and final state in the photoionization process (Johansson and Mårtensson 1980, 1983). For compound materials, adsorbate systems and interfaces this link between core-level binding energies and thermochemical entities has played an important role in understanding and quantifying phenomena like solution, segregation, and adhesion. Also for semiconductor materials much of the understanding of the electronic structure of the clean and adsorbate-covered surfaces has been achieved through accurate measurements of SCSs.

Determinations of the SCS have been made for a number of elements in the periodic table, e.g. the free electron metals, the 5d transition metals, the rare earth metals and several pure and compound semiconductors (see e.g. Jugnet *et al* 1987 and references therein). However, many important elements have still not been investigated. The reason for this is mainly that SCSs often are small even compared to the natural line widths and require a high experimental resolution in order to be accurately measured. This is especially a problem for the 3d and the 4d transition metals where the narrow core-levels (the 2p and 3d levels, respectively) have rather high binding energies for which an adequate experimental resolution has been difficult to achieve in the past.

In this letter we present an experimental study of the SCS for the Pd 3d core-level (binding-energy 335 eV) recorded from a clean Pd(100) surface. From our measurements we determine an SCS of  $0.44 \pm 0.03$  eV towards lower binding-energy. This result

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is in reasonably good agreement with theoretical predictions based on the Johansson-Mårtensson model (Johansson and Mårtensson 1980, 1983).

## 2. Experimental procedure

The experiments were carried out at beamline 22 at the MAX synchrotron radiation laboratory in Lund, Sweden. This beamline is equipped with a modified SX-700 plane-grating monochromator covering the photon energy range 20 to 1000 eV (Nyholm *et al* 1986). The experimental station includes all necessary equipment for the preparation and characterization of atomically clean surfaces and an electron energy analyzer for the recording of photoelectron spectra (Andersen *et al* 1991a). The electron energy analyzer is of the hemispherical type (mean radius 200 mm) using a multi-channel detector system. The spectra reported here were excited by photons with energies between 380 and 450 eV and the total instrumental resolution was in the range 0.2 to 0.3 eV.

The Pd surface was cleaned by argon ion sputtering and annealing as well as heating in oxygen in order to remove residual carbon. Cleanness was checked by photoemission measurements of the C 1s and O 1s core-level regions and also by recording the valence band emission at a photon energy of 120 eV where the Cooper minimum in the photoionization cross-section of the Pd 4d valence band greatly enhances the sensitivity to emission from contaminants. The surface structure was checked by LEED.

During these experiments it was observed that adsorption of hydrogen from the rest gas strongly reduced the intensity of the surface peak. This observation was made after prolonged (hours) exposure of the clean surface to the background pressure of about  $7 \times 10^{-11}$  Torr. Controlled exposures to hydrogen showed that about half a monolayer efficiently removes the surface peak from the clean metal. For the results on the clean surface reported here the adsorption of hydrogen did not impose any problems since the spectra were measured in less than 10 minutes, far below the time needed to contaminate the surface. The measurements were performed at or just above room temperature in order to further reduce hydrogen contamination.

## 3. Results

Figure 1 shows experimental Pd 3d spectra recorded at different photon energies. Already from the raw spectra it is obvious that both the  $3d_{3/2}$  and the  $3d_{5/2}$  spin-orbit component have a doublet structure. From the relative intensity variation as a function of excitation energy the component at lower binding energy can be identified as due to emission from the surface atoms. This is in accordance with the expected surface shift of Pd. The relative decrease of this component for higher and lower excitation energies follows the general behavior of the electron escape depth as a function of electron kinetic energy (Seah and Dench 1979). The intensity changes are, however, surprisingly strong which is believed to be due to photoelectron diffraction effects which enhances the surface emission at excitation energies around 390 to 400 eV. These observations were made for spectra recorded both with different photon energies and at different electron emission angles. Similar effects on surface to bulk intensity

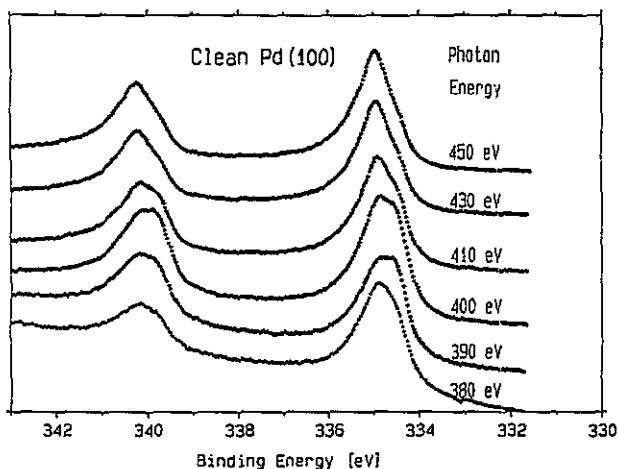


Figure 1. Pd 3d spectra from the Pd(100) surface recorded at different photon energies ranging from 380 to 450 eV.

ratios have been observed previously on other metals (see e.g. Jugnet *et al* 1987, p 710) and will not be further discussed here.

Figure 2 demonstrates the effect of hydrogen adsorption. The low binding energy structure clearly visible in the spectrum from the clean surface is completely removed in the spectrum from the hydrogen exposed surface. This observation has two important implications: firstly, since hydrogen is abundant in the rest gas in any ultra-high vacuum system care has to be taken in order to avoid prolonged measuring times if reliable data for the clean surface is aimed at. Secondly, the sensitivity of the low binding energy structure to the adsorption of hydrogen clearly shows the surface related nature of this spectral structure, lending further support to the identification of a surface core-level peak. This interpretation is consistent with results for other adsorbates on Pd (Andersen *et al* 1991b, Comelli *et al* 1991).

In order to determine the magnitude of the SCS for the clean Pd surface different methods of data analysis were used. Firstly, two different subtraction methods were applied in order to separate the surface and bulk contributions. Secondly, a numerical curve fitting procedure was used to model the measured spectra. In the latter case the surface and bulk components were described by asymmetric line profiles including both Lorentzian and Gaussian functions and the parameters controlling the detailed line shape were optimized for a best fit to the experimental spectra.

In the first subtraction procedure we take advantage of the fact that spectra recorded at different photon energies show very different bulk to surface intensity ratios. After removal of a linear background a spectrum dominated by the bulk peak is subtracted (using a proper scaling factor) from a spectrum with a high relative surface peak intensity so that the resulting spectrum contains only the surface contribution. Once the pure surface contribution has been obtained this spectrum can in turn be used to remove the small surface contribution in the bulk sensitive spectrum yielding finally the pure bulk spectrum. This procedure is illustrated in figure 3 for spectra recorded at 390 and 450 eV photon energies. The advantage of this simple method is that no assumptions on the detailed line shape has to be made. The only condition that has to be met is that the shape of the inelastic background does not

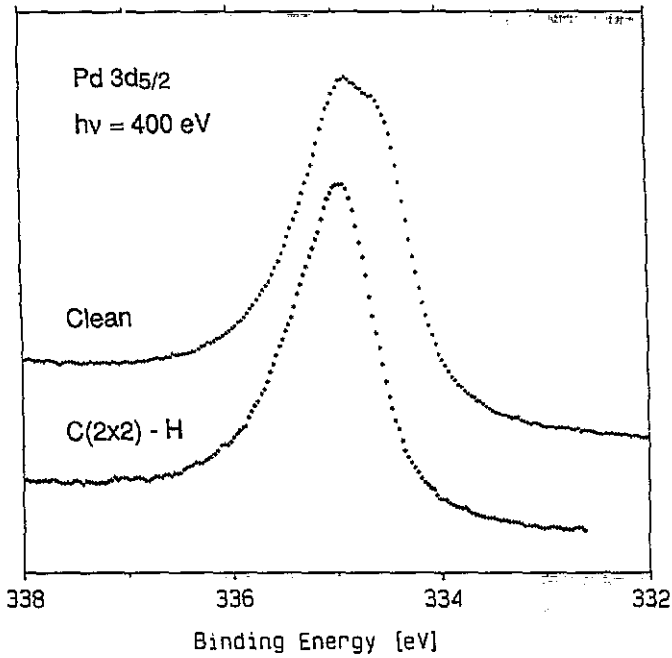


Figure 2. The Pd 3d<sub>5/2</sub> spectrum from the clean surface and after adsorption of hydrogen in a c(2 × 2) structure. The excitation energy was 400 eV.

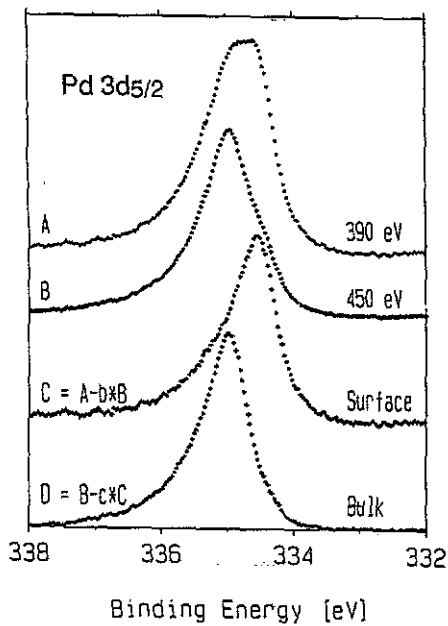


Figure 3. Decomposition of the Pd 3d<sub>5/2</sub> core-level into bulk and surface components using a simple subtraction procedure, see text.

differ too much between the two spectra. Once the separation into bulk and surface peaks has been made the magnitude of the SCS is easily obtained by determining the shift necessary to bring the peaks to overlap. This can be done with high accuracy since the two line shapes are found to be about equal.

The second subtraction procedure is based on the assumption that the measured spectrum consists of two parts with identical line shapes: one is the bulk related emission and the other the surface related emission. The only differences between these two contributions to the total spectrum are their binding energy and intensity. A simple iterative mathematical scheme can now be used in order to decompose the measured spectrum into its two parts† Two parameters enter the procedure, namely the binding energy shift, which in our case is the SCS, and the intensity ratio.

Applying these methods of analysis to the spectra shown in figure 1 we derive a SCS of  $-0.44 \pm 0.03$  eV. It should be noted that the two decomposition methods give identical results.

In a curve fitting procedure the large asymmetry of the Pd core-level peak poses some problems. It has previously been shown (Wertheim and Citrin 1978) that the commonly used Doniach–Sunjic line profile (Doniach and Sunjic 1970), based on a free electron approach, does not give a satisfactory description of the line profile for Pd. In order to describe the line profile correctly the detailed structure of the density of states has to be taken into account. It is, however, possible to obtain a good fit over a limited (about 1.5 to 2 eV) energy range centered at the peak position. The tails are then not well described but this type of fitting can still be used to derive reliable values for the SCS. The SCSs for all measured spectra were within  $-0.46 \pm 0.04$  eV. This is consistent with the results from the subtraction procedures described above, although we regard the subtraction procedures to be more accurate.

#### 4. Discussion

It is interesting to compare the experimentally determined SCS with theoretical predictions. Johansson and Mårtensson (1980) have shown that the SCS can be treated within the  $Z + 1$  model due to the metallic screening of the final core ionized state. Within this model the SCS may be given by the following expression (Johansson and Mårtensson 1983):

$$\text{SCS} = E_S(Z + 1) - E_S(Z) - [E_{\text{imp}}(Z + 1, Z) - E_{\text{imp,surf}}(Z + 1, Z)] \quad (1)$$

where the two first terms are the surface energies of the  $Z + 1$  and  $Z$  elements, in our case Ag and Pd, respectively. The last term is a correction containing the solution energies of a  $Z + 1$  impurity in the bulk and at the surface of a  $Z$  host, respectively.

Looking first to the surface energies we can use Miedema's semi-empirical scheme to obtain  $2100 \text{ mJ m}^{-2}$  for Pd and  $1250 \text{ mJ m}^{-2}$  for Ag (Miedema 1978a). Experimental values of  $1240$  (Tyson and Miller 1977) and  $1250 \text{ mJ m}^{-2}$  (Miedema 1978b) have been reported for the surface energy of Ag, in very good agreement with Miedema's theoretical values. Also recent *ab initio* calculations for Ag(100) (Erschbaumer *et al* 1991 and Methfessel *et al* 1991) give surface energies in excellent agreement with the

† This method has been widely used for decomposing (overlapping) spin-orbit components, see e.g. Nyholm and Mårtensson 1980.

values above. Thus, for Ag there are consistent experimental and theoretical values. For Pd, however, we are not aware of any experimental values and the calculated Miedema value of  $2100 \text{ mJ m}^{-2}$  does not quite agree with the calculation by Methfessel *et al* (1991) which gives  $0.88 \text{ eV/atom}$  (or  $1860 \text{ mJ m}^{-2}$ ).

Using the Miedema surface energies in equation (1), and neglecting the last term, we obtain a SCS of  $-0.40 \text{ eV}$  for the Pd(100) surface. If we instead use the calculated value for the surface energy of Pd (Methfessel *et al* 1991) we arrive at a SCS of  $-0.27 \text{ eV}$ . Both these values are in reasonable agreement with the present experimental result and we do not think that the comparison can be used to judge the accuracy in the surface energies.

The last term in equation (1) is difficult to estimate correctly since it involves the energy of a substitutional surface impurity. The bulk term can be obtained from Miedema's semi-empirical solution energies (Miedema *et al* 1977) which for an Ag impurity in a Pd host gives a value of  $-0.26 \text{ eV/atom}$ . The surface impurity term can be estimated in the following way. It has been found empirically that surface cohesive energies are about 80% of bulk cohesive energies (Allen 1972). It is a reasonable assumption that this scaling should also apply to the impurity term, which would replace the last term in equation (1) with  $0.2 \times E_{\text{imp}}(Z + 1, Z)$ . Thus the impurity term would modify the calculated SCS by  $0.05 \text{ eV}$ .

Tomanek *et al* (1982) have used a different approach to calculate a SCS for the Pd(100) surface. Starting with the bulk cohesive energies they derived surface energies in a broken bond picture including nearest neighbour and next nearest neighbour interaction. Neglecting the last impurity term in equation (1) the resulting SCS was calculated to be  $-0.3 \text{ eV}$ , again in reasonable agreement with the present experiment.

In a recent paper Comelli *et al* (1991) have measured the SCS for the Pd(110) surface to be  $-0.24 \text{ eV}$ . This value is surprisingly small when compared to the present result for the 100 surface, since one would expect the less dense 110 surface to have a larger shift. This expectation is in agreement with calculations of the SCS for Pd(110): using surface energies from Methfessel *et al* (1991) we obtain  $-0.45 \text{ eV}$  from equation (1) and the calculations by Tomanek *et al* (1982) give  $-0.4 \text{ eV}$ , i.e. larger shifts than for the 100 surface. Since the surface peak is clearly resolved in our spectra from the 100 surface, one would expect an even more accentuated surface peak to appear in spectra from the 110 surface. This is not the case in the data shown in the work by Comelli *et al* (1991). Further experiments are needed to resolve this apparent discrepancy between the measured SCSs for the 100 and 110 surfaces.

Finally, it should be mentioned that a SCS of  $+0.23 \text{ eV}$  has previously been reported for polycrystalline Pd (Erbudak *et al* 1983). This most astonishing result is in complete disagreement (both in sign and magnitude) with our experimental result and with that of Comelli *et al* (1991) and also with the theoretical models discussed above. It should be noted that equation (1) is known to give reasonably accurate values for the SCS for a large number of metals (see e.g. Johansson and Mårtensson 1983, Jugnet *et al* 1987).

## 5. Summary

In summary we have measured the SCS of the Pd(100) surface to be  $-0.44 \pm 0.03 \text{ eV}$  in close agreement with theoretical predictions based on the model of Johansson and Mårtensson. It was also found that the Pd 3d spectrum was very sensitive to the

adsorption of hydrogen. The SCS of Pd is one of the few measurements on single-crystal surfaces of the 4d metals, only Y(0001) (Barrett *et al* 1989) and Pd(110) (Comelli *et al* 1991) have been measured before. There also are data on a few polycrystalline materials (Rh (Erbudak *et al* 1983) and Ag (Citrin and Wertheim 1983)), but the present results clearly show the importance of measuring well characterized single-crystal surfaces. Further work is needed in order to get a complete and consistent picture of the SCSs of this transition metal series.

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