Eur. Phys. J. D **29**, 57–61 (2004)
DOI: 10.1140/epjd/e2004-00008-4

THE EUROPEAN PHYSICAL JOURNAL D

Photoelectron spectroscopy on Pt atoms and clusters deposited on C(0001)

K. Fauth[1,2,a], N. Schneider[1], M. Heßler[1,2], and G. Schütz[1,2]

[1] Experimentelle Physik IV, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany
[2] Max Planck Institut für Metallforschung, Heisenbergstr. 3, 70569 Stuttgart, Germany

Received 22 June 2003 / Received in final form 25 November 2003

Abstract. An experimental photoelectron spectroscopy study is presented highlighting several aspects of importance for the study of deposited metal clusters and particles with photoemission. It is shown that the Fermi level is the correct energy reference for the core level binding energies. The choice of different deposition conditions, well within the range of soft landing, has a strong impact on the outcome of the spectroscopic experiments. Single adatoms as well as clusters deposited with some excess energy display relatively narrow core level spectra at much lower binding energies than previously reported, even when atomic mass selection is not performed. In contrast, single sized Pt_{19} clusters, deposited onto a thin Ar film before being exposed to the graphite surface show spectral broadening and shifts to higher binding energies. We discuss our results in terms of the cluster substrate interaction and the influence of deposition conditions on the metal adsorbate structure.

PACS. 36.40.-c Atomic and molecular clusters – 36.40.Cg Electronic and magnetic properties of clusters – 36.40.Mr Spectroscopy and geometrical structure of clusters – 73.22.-f Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals

Core level photoelectron spectroscopy has a long standing history in the investigation of the electronic properties of metal clusters on surfaces [1–3]. One of the driving motivations for this research is the wish to elucidate the evolution of the electronic structure of clusters by monitoring the size dependence of their photoelectron spectra from the isolated atom to the bulk. Both, gas phase and deposited clusters also exhibit interesting catalytic and magnetic properties that are intimately related to their underlying electronic structure.

The investigation of mass selected clusters with photoelectron spectroscopy in the gas phase has been extensively explored with great success in the last 15 years [4]. These experiments are, however, limited to the use of lasers as excitation sources. Hence, there is a considerable restriction in the accessible binding energy range and only the most weakly bound valence electron states can be probed.

The study of core level spectra and strongly bound valence states is therefore still restricted to particles grown or deposited on surfaces. Thus, the interaction with the surface represents an additional degree of freedom and will inevitably affect the photoelectron spectra of the clusters. The graphite surface has been considered an ideal substrate for such investigations on small metal particles, since due to its two-dimensional nature, the interactions are believed to be small. The typical finding of core level binding energies in excess of those in the corresponding bulk materials is most often interpreted in terms of the electrostatic energy of the photoemission final state [5]. While in the classical discussion [5] the size dependent core level binding energies are well accounted for, more recent high resolution valence electron measurements suggested a refinement of this model by explicitly taking into account the time dependence of the neutralization process after photoionization of the adsorbed clusters [6].

However, the metal particles investigated are typically grown at surface defect sites [3,6] where the interaction e.g. to Pt adatoms and small clusters is considerable and, as we have recently shown [7], contributes significantly to both, a shift of the core level binding energies towards larger values and a broadening of the photoelectron spectra. Low temperature cluster deposition experiments offer the opportunity to investigate the metal adsorbate species under better defined conditions on the C(0001) terraces.

Another important aspect for the interpretation of photoemission results is to establish the proper energy reference serving as an adequate zero for the electron binding energy. In the limit of small interaction, as might be expected to be the case for clusters on the C(0001) terraces,

---

[a] e-mail: `fauth@physik.uni-wuerzburg.de`

it has been argued [8] that the vacuum level rather than the substrate Fermi energy should represent the proper energy reference. This description is adequate e.g. for physisorbed atoms or molecules on graphite and has been demonstrated to apply also in the case of Na clusters grown on cryogenic Kr films [9].

We will demonstrate in the present communication that the same does not hold in the case of Pt adatoms and small clusters on the C(0001) surface. Instead, the interaction is sufficiently strong to establish a common Fermi reference level. Furthermore, by varying the cluster deposition conditions, we find evidence for the fact that in the case of very small clusters it is the cluster structure and adsorption geometry rather than the precise cluster size which plays the key role for the position and shape of the spectra obtained.

Atomic Pt and Pt cluster ions were generated and deposited under UHV conditions using a laser vaporization cluster source and deposition setup the details of which will be described elsewhere [10]. Briefly summarized, the cationic species generated after the vaporization are electrostatically extracted from the primary molecular beam and guided towards the deposition spot with a combination of differentially pumped DC and rf ion guide devices. Atom by atom mass selection is provided by means of a quadrupole mass filter (QMF). Broader mass distributions are deposited by operating the QMF and the rf octopole ion guide as high and low pass mass filters, respectively [11]. At the substrate the ions possess a kinetic energy of about 3.5 eV (Pt_1) and 5 eV (Pt_{19}), respectively, with an energy spread of less than 2 eV. All cluster depositions can therefore be safely regarded as soft landing processes [12]. The cluster coverage is determined by monitoring the cluster ion current on the substrate.

The experimental results presented here were obtained during two different beam times at the U49/2-PGM1 beamline of the BESSY II synchrotron radiation source [13]. In both cases the cluster source was attached to an electron spectrometer chamber equipped with a hemispherical electron analyser. Pt $4f$ spectra were recorded at a photon energy of 400 eV, chosen such as to provide a large photoionization cross section [14] and a smooth, structureless background from the graphite substrate. The total instrumental resolution ΔE was set to 200 meV (adatoms) and 250 meV (clusters), respectively. The valence electron spectra were acquired using 100 eV photon energy ($\Delta E = 90$ meV). Additional spectra taken to ascertain the absence of contaminant species were routinely taken at a higher energy of 650 eV and lower energy resolution to increase the sensitivity. Energy calibration was carried out independently with the help of the well-known [15] binding energy of the C1s line in graphite (284.4 eV) and by higher resolution measurements of the Fermi edge from the (rare gas covered) graphite surface [7], the two methods agreeing to within less than 50 meV. Experimental binding energies are referenced to the substrate Fermi level.

We used pyrolithic graphite (HOPG, ZYB grade) as substrate for cluster deposition. Before each deposition, a clean surface was obtained by cleavage in a preparation chamber at $\approx 1 \times 10^{-9}$ mbar, after which the samples were quickly transferred to the main chamber, maintained at 1×10^{-10} mbar. For cluster deposition the substrates were held at cryogenic temperatures. In what follows we will consider results obtained for three different types of samples, Pt_1, Pt_{19} and $Pt_{10\ldots40}$, prepared on C(0001) under different conditions as described below.

Pt monomers were deposited (atomic Pt density: 4.4×10^{13} atoms/cm^2) and investigated in the presence of a preadsorbed monolayer of Ar ($T \approx 14$ K). Since we have observed the Pt monomers to still diffuse within rare gas monolayers when irradiated by the intense synchrotron beam [7] this procedure is the only way to capture their photoelectron spectra while residing on the C(0001) terraces. Pt_8 clusters were also seen to be mobile, at least around the desorption temperature of the Ar monolayer (≈55 K) [7], the larger clusters investigated here were immobile up to temperatures of at least 80 K, judging from the temperature independence of their photoelectron spectra. The Pt_{19} clusters were deposited (5.8×10^{12} clusters/cm^2, corresponding to ≈5% of an atomic monolayer) onto a thin Ar film, 4–5 monolayers in thickness, which was desorbed before taking the photoelectron spectra. Since they are deposited into the Ar film the clusters assume the substrate temperature before being exposed to the HOPG surface. By contrast, mass distributed cluster samples ($Pt_n, 10 \lesssim n \lesssim 40$) were deposited at $T \approx 60$ K without a rare gas layer present. Under these "harder landing" conditions the kinetic and internal cluster energies are available to initiate and facilitate structural relaxation of the clusters before reaching thermal equilibrium with the substrate. Without the Ar films, the ion current is not a reliable measurement of the coverage, since we found the sticking coefficient to be considerably reduced. The coverage was therefore estimated by a comparison of the Pt $4f$ photoelectron intensity to the previous cases and determined to amount to ≈15% of an atomic monolayer. We will see below, that the above choice of different cluster deposition conditions does indeed lead to observable differences in the Pt $4f$ photoelectron spectra.

Before we analyze the spectroscopic results in more detail, however, we present in Figure 1 the expected binding energy position for the Pt adatom levels based on the assumptions of Citrin and Wertheim [8]. Neglecting all initial and final state interactions and given the Pt ionization potential (IP) of 8.96 eV [16] as well as the graphite work function of $\Phi_C = 4.6$ eV [17], we should expect the lowest lying valence electron signature of Pt adatoms to appear roughly 4.3 eV below the graphite Fermi level [18]. Likewise, the expected Pt $4f_{7/2}$ position can be estimated by decomposing the $4f$ ionization into two steps as follows: the excitation $4f^{14}5d^{9}6s^{1} \longrightarrow 4f^{13}5d^{10}6s^{1}$ amounts to 68.5 eV [19] and yields a valence system isoelectronic to the atomic Au ground state (including a $(Z_{\mathrm{Pt}}+1)$-core). In the spirit of the $Z+1$ approximation [20] we thus add the IP of atomic Au (9.43 eV [16]) to arrive at the full ionization energy of 77.9 eV, resulting in an electron

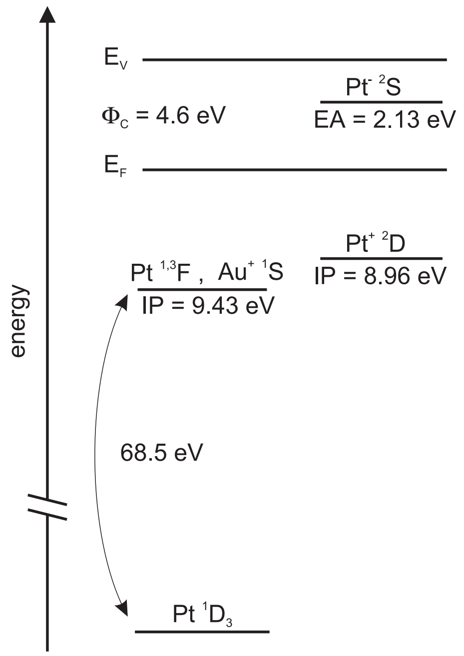

Fig. 1. Schematic diagram illustrating the expected position of the Pt $4f_{7/2}$ level in a photoemission, spectrum, neglecting all initial and final state interactions. ^{1}D$_3$ denotes the atomic Pt ground state ($5d^96s$), ^{1,3}F the (neutral) core excited states ($4f^{13}5d^{10}6s$), isoelectronic to the Au atomic ground state (($Z+1$)-approximation), which has an ionization potential of 9.43 eV [16]. The Pt$^-$ ^{2}S state is the first electron affinity level of the Pt atom.

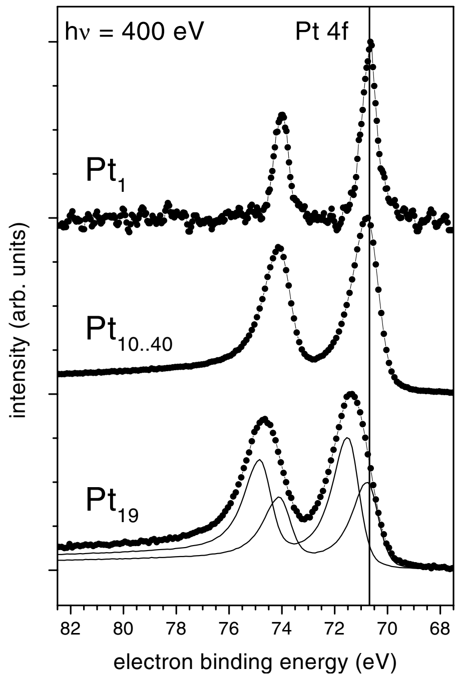

Fig. 2. Pt $4f$ spectra ($\hbar\omega = 400$ eV), obtained from Pt atoms within a monolayer of Ar (Pt$_1$) on HOPG, a size distributed cluster ensemble deposited at 80 K (Pt$_{10...40}$) and a size selected Pt$_{19}$ cluster sample soft landed on Ar after desorption of the Ar film.

binding energy of 73.3 eV with respect to the substrate Fermi level.

We note that while the IP of atomic Pt is larger than Φ_C, the electron affinity (EA) is considerably smaller. This situation should then lead to the formation of an "impurity" state pinned in the vicinity of the Fermi level [21]. In this respect the present situation is similar to the one of Cu atoms ($\mathrm{IP_{Cu}} = 7.726$ eV, $\mathrm{EA_{Cu}} = 1.235$ eV [16]). Indeed, the Cu $4s$ related signature of Cu atoms immobilized on the graphite surface by a Xe monolayer has been found to appear near E_F [22]. Its relatively narrow width documents both, the smallness of the hybridization matrix elements of the impurity state with the graphite band states [21] as well as the small graphite DOS near the Fermi level.

Experimentally, we find the Pt $4f_{7/2}$ adatom peak [7] at the very small binding energy of 70.7 eV, as can be seen in Figure 2. It is furthermore interesting to note that the width of the adatom $4f$ peaks amounts to only 0.55 eV (FWHM) and is thus largely accounted for by considering the instrumental resolution and the Lorentzian lifetime $2\gamma \approx 0.35$ eV [23].

Nearly the same binding energy is found for the mass distributed cluster sample, which was deposited without a preadsorbed rare gas layer. In contrast to the typical finding of increased core level binding energies for small metal particles on graphite [2,3,24], we note that the Pt adatoms and the "harder landed" clusters display reduced binding energies compared to bulk Pt (71.1 eV [25]), the value of 70.7 eV actually matching the range typically found at the surfaces of Pt crystals (negative surface core level shift) [26]. This correspondence indicates that the electronic structure should also be related.

The $4f$ line shape of the Pt$_{10...40}$ clusters displays the typical asymmetry found in metallic Pt as well as a significant secondary electron background. A Doniach-Šunjić analysis indicates an asymmetry parameter $\alpha = 0.16$. The Gaussian and Lorentzian contributions to the lineshape are very similar to the adatom case which implies that the width of the Pt $4f$ peaks arises mainly from the low energy excitations while the cluster size distribution does not contribute significantly. The asymmetry parameter for the clusters is smaller than in bulk Pt ($\alpha = 0.2$) [27], but too large to be accounted for by electronic excitations in the graphite alone. We therefore conclude that an additional density of states is formed close to E_F upon deposition of the clusters, in accordance with our valence electron spectroscopic results shown below.

Despite mass selection, the $4f$ spectrum of the Pt$_{19}$ sample displays a considerable shift towards higher binding energies and an additional spectral broadening with respect to the previous case. Since this difference in spectral behavior cannot be related to the cluster sizes in the different samples it must relate to the changed conditions during cluster deposition. The main difference here is the presence of the Ar film during the deposition of the Pt$_{19}$, efficiently dissipating both, the kinetic and internal energies of the clusters before they come into contact with the graphite substrate. Upon landing in a rare gas matrix, different structural isomers may be formed [28] resulting in a variety of adsorption geometries after the desorption of the Ar film.

Qualitatively, we find that the shift and broadening of the Pt_{19} spectrum is well described by convoluting the $\mathrm{Pt}_{10\ldots40}$ data with a Gaussian centered at 0.52 eV (shift) and a FWHM of 800 meV. Despite this broadening, the Pt_{19} related $4f$ binding energy and peak width are still smaller than what is found for small Pt aggregates grown by vapor deposition on a graphite surface [29]. In this case, as we have previously shown [7], the interaction with defects plays an essential role for the additional shifts and broadenings. Here, the Gaussian broadening could represent the variations in electronic level structure and substrate coupling associated with the various possible cluster and adsorption geometries. It is not obvious, however, to understand the overall binding energy shift from such considerations. Neither does it deliver an explanation of the narrower spectra in mass distributed cluster samples unless we consider fundamental differences in the cluster geometries as a result of the different deposition conditions.

The low binding energy onset of the two cluster spectra coinciding, the broadening could as well be related to a Pt $4f$ binding energy depending on the atomic positions. Indeed, the Pt_{19} spectrum can still be well represented by considering only a pair of $\mathrm{Pt}_{10\ldots40}$-like spectra (relative amplitudes 3:2), one component of which is shifted by 0.74 eV towards higher binding energies (see Fig. 2). As discussed in some more detail below, we take this an indication that the clusters deposited onto the bare substrate form flat islands on the C(0001) surface, while the Ar assisted soft landing leads to the preservation of more three-dimensional cluster geometries, thus providing inequivalent Pt sites.

We finally turn to our valence photoelectron results summarized in Figure 3. The inset gives an overview over the entire valence band region with and without an argon film condensed on the graphite surface. Spectra (a) to (e) are restricted to a smaller binding energy range near E_F. Curve (a) demonstrates, that upon Ar coverage, the substrate Fermi edge emerges in normal emission spectra [30], serving as a convenient energy reference. Spectra (b) and (c) show the low binding energy region of the bare graphite and after the deposition of the $\mathrm{Pt}_{10\ldots40}$ clusters, respectively (no Ar present). The corresponding difference spectrum is given in curve (d), showing the added spectral density due to the deposited clusters. The Pt cluster induced intensity spreads over more than 2 eV and drops rapidly when approaching E_F.

In order to inspect the low intensity region near E_F more closely, we have plotted as curve (e) the ratio of the spectra obtained before and after cluster deposition, respectively. Due to the smoothly decreasing substrate intensity, the cluster induced spectrum is the more amplified the more E_F is approached. While the spectral shape is clearly distorted, the plot shows that the enhancement of the spectral weight persists up to the Fermi level. We thus argue that due to hybridization the Pt $5d$ related states are redistributed in energy up to the Fermi level, which is therefore the adequate reference for the electron binding energies.

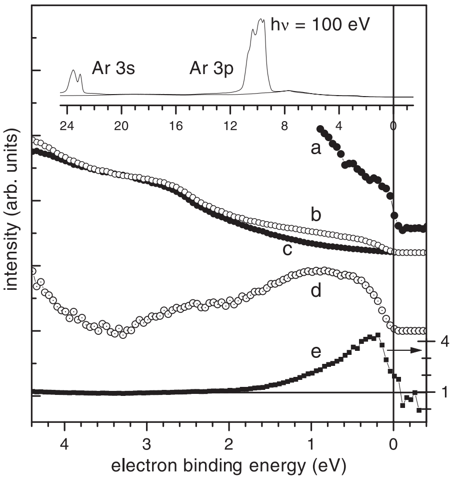

Fig. 3. Valence electron spectra at $\hbar\omega = 100$ eV. Inset: valence region overview of the bare and Ar covered HOPG substrate, respectively. (a) Fermi edge spectrum of the Ar covered substrate. Near $\mathrm{E_F}$ spectra before (c) and after (b) deposition of the $\mathrm{Pt}_{10\ldots40}$ clusters, respectively; (d) difference curve (b) – (c); (e) is curve (b) divided by curve (c), normalized to unity around $E_B = 3.5$ eV. It emphasizes the spectral changes in the region closest to E_F. The arrow indicates that the scale to the right applies for curve (e).

It is worthwhile noting that low temperature tunneling spectra of Pt clusters [31] deposited on graphite display more narrow peaks than the spectral intensity observed here. On the other hand, similar experiments on Ag particles [32] have shown such peak positions to vary as a function of tip position above the clusters. The integrating character of photoelectron spectroscopy might therefore be better suited to study the total density of states of adsorbed clusters. The broad energy distribution of the cluster related states suggests that the hybridization with the graphite electronic states is considerable. Under such conditions the electronic structure of $3d$ transition metal adsorbates has been shown by both, calculations [33,34] and recent experiments [35] to be strongly modified, leading to an enhanced effective d-electron count. Within a simple model calculation, Cini et al. have produced a similar result [36] and obtain a reduced but nonvanishing d-like density of states at E_F. They additionally find that most of the remaining empty d spectral weight is shifted away from E_F and forms a hybridized resonance state. This model was found to account well for observed X-ray absorption resonance shifts in small Pd particles [2,36]. It is thus very conceivable that a similar mechanism is operational in our Pt clusters, increasing the effective Pt $5d$ occupation and leading to an electronic configuration in the clusters which resembles the one at Pt surfaces. Such an effect should be the more pronounced the more atoms actually participate in the cluster substrate interface. While this necessarily involves all single Pt adatoms, we conclude from our photoemission data that the more energetic cluster deposition produces more two-dimensional Pt islands exhibiting small Pt 4*f* binding energies, while the Ar assisted soft landing results in more three-dimensional clusters. Our results therefore indicate, that the cluster shape rather than the precise cluster size has the largest impact on the resulting photoelectron spectra. In contrast to metallic single crystalline surfaces, where the deposition of small metal clusters leads to the formation of monolayer islands even when employing the rare gas assisted soft landing method [37,38], both situations appear possible on graphite. In any case, the smallness of the Pt 4*f* binding energies is irreconcilable with the charged final state picture both, in its static [5] or dynamic [6] version. In particular the negative core level shifts exhibited by the Pt adatoms and $Pt_{10...40}$ clusters indicate a substrate induced modification of the electronic ground state. Further experiments on clusters of various sizes will be necessary to further corroborate the above assignments.

In conclusion, we have presented an experimental study of Pt atoms and clusters deposited onto the C(0001) basal plane of graphite. Single adatoms and clusters deposited with moderate excess energy exhibit 4*f* core level binding energies smaller than in bulk Pt, strongly contrasting the typical results obtained for particles grown by vapor deposition. The valence electron spectra show that the cluster induced states extend up to the substrate Fermi level, which is therefore the natural energy reference for the core level binding energies. The smallness of the core electron binding energies is explained to result from considerable cluster surface interactions, leading to electronic configurations comparable to the situation at bulk Pt surfaces. By contrast, the deposition of size selected Pt_{19} clusters into Ar layers results in broadened 4*f* spectra having their spectral weight shifted to higher binding energies, even after desorption of the rare gas. This finding is attributed to the formation of more compact clusters, where less atoms participate in the formation of the cluster substrate interface. The possible formation of multiple structural isomers at the surface may well additionally contribute to the observed peak shape.

It is a pleasure to acknowledge O. Rader and W. Gudat for the opportunity to use their photoelectron spectrometer and the BESSY staff, especially D. Batchelor, P. Bressler, R. Follath and G. Reichardt and for their excellent support.

References

1. R. Unwin, A.M. Bradshaw, Surf. Sci. **77**, 219 (1978)
2. M.G. Mason, Phys. Rev. B **27**, 784 (1983)
3. G.K. Wertheim, S.B. DiCenzo, D.N.E. Buchanan, Phys. Rev. B **33**, 5384 (1986)
4. U. Boesl, W.J. Knott, Mass Spectrom. Rev. **17**, 275 (1998)
5. G.K. Wertheim, S.B. DiCenzo, S.E. Youngquist, Phys. Rev. Lett. **51**, 2310 (1983)
6. H. Hövel, B. Grimm, M. Pollmann, B. Reihl, Phys. Rev. Lett. **81**, 4608 (1998)
7. K. Fauth, M. Heßler, D. Batchelor, G. Schütz, Surf. Sci. **529**, 397 (2003)
8. P.H. Citrin, G.K. Wertheim, Phys. Rev. B **27**, 3176 (1983)
9. S.L. Qiu, X. Pan, M. Strongin, P.H. Citrin, Phys. Rev. B **36**, 1292 (1987)
10. K. Fauth, S. Gold, M. Heßler, G. Schütz, Rev. Sci. Instrum. (submitted)
11. K.J. Boyd, A. Lapicki, M. Aizawa, S.L. Anderson, Rev. Sci. Instrum. **69**, 4106 (1998)
12. S. Fedrigo, W. Harbich, J. Buttet, Phys. Rev. B **58**, 7428 (1998)
13. `http://db-exp.bessy.de/info/beamlines/u492pgm1/u492pgm1.html`.
14. J.-J. Yeh, *Atomic calculations of photoionization cross sections and asymmetry parameters* (Gordon and Breach, Langorne, 1993)
15. P. Bennich, C. Puglia, P.A. Brüwiler, A. Nilsson, A.J. Maxwell, A. Sandell, N. Mårtensson, P. Rudolf, Phys. Rev. B **59**, 8292 (1999)
16. *CRC Handbook of Chemistry and Physics*, 80th edn. (Boca Raton, 1999)
17. T. Mandel, M. Domke, G. Kaindl, C. Laubschat, M. Prietsch, U. Middelmann, K. Horn, Surf. Sci. **162**, 453 (1985)
18. Even in the absence of direct interaction the binding energy is lowered by image charge screening, see e.g. reference [17]
19. J.T. Costello, E.T. Kennedy, B.F. Sonntag, C.L. Cromer, J. Phys. B **24**, 5063 (1991)
20. S. Hüfner, *Photoelectron spectroscopy* (Springer, Berlin, Heidelberg, New York, 1996)
21. P.W. Anderson, Phys. Rev. **124**, 41 (1961)
22. F. Patthey, M.H. Schaffner, W.D. Schneider, B. Delley, Phys. Rev. Lett. **82**, 2971 (1999)
23. M.C. Desjonquères, D. Spanjaard, Y. Lassailly, C. Guillot, Solid State Commun. **34**, 807 (1980)
24. V. Vijayakrishnan, A. Chainani, D. Sarma, C. Rao, J. Phys. Chem. **96**, 8679 (1992)
25. NIST Standard Reference Database 20, Version 3.4 (Web Version: `http://srdata.nist.gov/xps/`)
26. R.C. Baetzold, G. Apai, E. Shustorovich, R. Jaeger, Phys. Rev. B **26**, 4022 (1982)
27. G. Apai, R.C. Baetzold, E. Shustorovich, R. Jaeger, Surf. Sci. **116**, L191 (1982)
28. C. Félix, private communication
29. P. Marcus, C. Hinnen, Surf. Sci. **392**, 134 (1997)
30. F. Patthey, M.-H. Schaffner, W.-D. Schneider, B. Delley, Surf. Sci. **454-456**, 483 (2000)
31. A. Bettac, L. Köller, V. Rank, K.-H. Meiwes-Broer, Surf. Sci. **402-404**, 475 (1998)
32. H. Hövel, Appl. Phys. A **72**, 295 (2001)
33. D.M. Duffy, J.A. Blackman, Phys. Rev. B **58**, 7443 (1998)
34. R. Pandey, B.K. Rao, P. Jena, J.M. Newsam, Chem. Phys. Lett. **321**, 142 (2000)
35. K. Fauth, S. Gold, M. Heßler, G. Schütz, Chem. Phys. Lett. (submitted)
36. M. Cini, M.D. Crescenzi, F. Patella, N. Motta, M. Sastry, F. Rochet, R. Pasquali, A. Balzarotti, C. Verdozzi, Phys. Rev. B **41**, 5685 (1990)
37. K. Bromann, C. Félix, H. Brune, W. Harbich, R. Monot, J. Buttet, K. Kern, Science **274**, 956 (1996)
38. R. Schaub, H. Jödicke, F. Brunet, R. Monot, J. Buttet, W. Harbich, Phys. Rev. Lett. **86**, 3590 (2001)