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Electronic structures of clean and sulphur saturated Pt (100) surfaces

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Résumé. — Les mesures de photoémission uv angulaire ont été effectuées sur une surface de Pt (100) propre puis saturée de S adsorbé, avec des énergies d'excitation comprises entre 10,2 et 40,8 eV. Pour la surface propre, les résultats expérimentaux sont en bon accord avec la structure de bande du Pt calculée récemment par McDonald *et al.* L'adsorption de S introduit deux structures électroniques supplémentaires assez similaires à celles généralement observées dans la chimisorption des chalcogènes sur métaux de transition.

Abstract. — Angle-resolved uv photoemission experiments have been performed on clean and S saturated Pt (100) surface, in the photon energy range 10.2-40.8 eV. Empirical energy bands along the ΓX direction of the Brillouin zone are in good agreement with the calculated scheme for Pt given recently by McDonald *et al.* Adsorption spectra show two extra electronic structures, similar to those generally observed with chalcogen chemisorption on transition metals.

Angle-resolved uv photoemission (ARUPS) has become a common technique for determining the electronic structure of crystalline surfaces. Among metals, copper, silver and nickel are the most investigated. A considerable number of existing calculations for both clean and adsorbed surfaces of these metals have permitted fruitful comparisons between theory and experiments and also explorations of the capability of the technique. Similar studies with Pt are more seldom. Empirical valence band structures have been drawn for Pt (111) by Cinti *et al.* [1] and by Mills *et al.* [2], for Pt (100) by Thornton *et al.* [3]. One of the difficulties encountered in these studies was the determination of the final states participating in the interband transitions. We have found that by using the quasi-free electron conduction band given by Smith [4] our experimental dispersion relation $E(\mathbf{k})$ is in very good agreement with the valence band structure calculated recently for Pt by McDonald *et al.* [5]. On the other hand, chalcogen adsorption on Pt has been the subject of controversy. By angle-integrated UPS, Collins and Spicer [6] have found no oxygen resonant state on polycrystalline and two vicinal Pt surfaces at $\hbar\omega = 10.2$ and 21.2 eV. They suggested that the chemisorption bond of oxygen on platinum would be different from that on 3d transition metals, Ni and Fe, while Küppers and Ertl [7] argued the contrary. For sulphur adsorbed on Pt (100) surface, we have detected two extra electronic structures very similar to those observed previously for oxygen or sulphur adsorption on Ni (100) [8].

Experiments were carried out in an ultrahigh-vacuum spectrometer described previously [1]. The electron analyser was a CMA the aperture of which was partially obstructed in order to have

the full acceptance angle of 10° . The collection angle θ relative to the surface normal was varied by rotating the sample around an axis in the surface plane, arcs θ projecting onto the [001] azimuthal direction. By using a grazing incidence holographic grating (Jobin-Yvon LHT 30) and four discharge gases (H_2 , A, Ne and He), twelve resonance lines sufficiently strong for photoemission purpose were obtained in the photon energy range from 10.2 eV to 40.8 eV. *In situ* cleaning of the crystal was performed by heat treatment in oxygen and repetitive cycles of ion-bombardment-annealing [1] until no trace of contamination was detected by Auger electron spectroscopy (AES). After about one hour of exposition in the residual vacuum, a trace of CO appeared in AES spectra. Flash heating to 850 °C restored the clean surface. Sulphuration was performed by exposing the crystal to 5×10^{-7} torr of H_2S at room temperature. Surface saturation was indicated by the ratio of S 152 eV and Pt 237 eV AES peaks. No correction was applied to the presented spectra for the variation of the analyser resolution and transmission or for inelastic electrons.

Figure 1 shows the most significant energy distribution curves (EDC's) of photoelectrons emitted normally to the clean surface. The same product total photocurrent X scan time per energy

Fig. 1. — EDC's of photoelectrons emitted normally to the clean Pt (100) surface. Energy positions of the electronic structures are indicated by vertical bars; « a » and « b » : structures not originating from direct interband transitions (see text).

unit was kept for all spectra. For low photon energies ($h\nu \leq 18.5$ eV) the EDC's are composed of a dominant peak centred at about 0.5 eV below the Fermi level and of weak shoulders. At higher $h\nu$, a second peak appears around -4 eV. The rapid intensity decrease at the high binding energy side is probably due to the cut-off function of our analyser system.

Let us examine if the electronic structures, peaks or shoulders, appearing in these spectra originate from the three-dimensional density of states by direct interband transitions as generally observed in ARUPS. The valence band structure of platinum has been calculated by several authors : Anderson [9] by the RAPW method, Smith [4] using a combined interpolation scheme and more recently McDonald *et al.* [5] by a density functional formalism. Only Smith has given conduction bands up to 14 eV above the Fermi level. These empty final states have a quasi-free electron character and can be drawn empirically if critical points are deduced from the EDC's, as we did before for Pt (111) [1]. This is not the case here for Pt (100) and for the following interpretation we use Smith's conduction band [4]. In figure 2, the experimental results are compared with the band structure along the ΓX direction of the k space calculated for platinum by McDonald. Full circles indicate the energy positions of the experimental electronic structures, the peaks or shoulders of the EDC's in figure 1. The dashed lines correspond to the parabolic empty band of Smith shifted downwards by the corresponding photon energies. Each intersection point of the empty and filled bands corresponds to a possible direct interband transition. We see that nearly all the features of the spectra can be related to the three-dimensional density of states *via* direct interband transitions. The agreement between the experiments and the calculations of McDonald is fairly good, with deviations of less than 0.3 eV. The remaining structures which do not correspond to the three-dimension density of states belong to two stationary groups centred at about -0.5 eV and -1 eV below E_F and specified respectively by « a » and « b » on the EDC's of figure 1. Structure « a » is angle dependent, having its maximum at a collection angle equal to 30° and as it does not disappear upon adsorption (Fig. 3) an eventual surface state origin is ruled out. A Fermi edge would be detected in similar experimental conditions at an energy closer to E_F , less than 0.2 eV. For these reasons, we attribute it to a surface emission process from the high

Fig. 2. — Band structure for Pt along the ΓX direction of the Brillouin zone. Full lines : dispersion curves calculated by McDonald [5] ; dashed lines : Smith's conduction band [4] shifted downwards by respective $\hbar\omega$, 10.2, 13.5... 34.6 eV ; full circles : experimental results.

Fig. 3. — Variation of structure « a » with collection angle θ and with sulphur adsorption at $\hbar\omega = 21.2$ eV. Full lines : S saturated surface ; dashed lines : clean surface.

density of states region near E_F observed with many transition metals, in a similar way as with Pt (111) [1]. The peak labelled « b » can possibly be related to the (5×20) reconstruction of the Pt (100) clean surface prepared by ion bombardment and annealing. The main argument supporting this hypothesis is that this structure decreases considerably upon sulphur adsorption as indicated by the 40.8 eV and 26.8 eV curves in figure 4. It may also be favourably compared with the angle integrated UPS results of Helms *et al.* [10] who observed a difference in the spectra given by the classical reconstructed (5×20) surface and the unreconstructed one specially prepared by reaction of adsorbed CO with oxygen ions : the latter presented a sharp peak at -0.25 eV while the former had a softer one in the same energy region as our structure « b ».

The only other ARUPS study of Pt (100) surface is that of Thornton *et al.* [3]. Using synchrotron radiation these authors have measured the normal EDC's in the photon energy range from 6 to 32 eV and have drawn empirical dispersion relations. The final states used were deduced from a fitted Au conduction band [2], modified in order to take into account the differences in lattice constants and in E_F for the two metals. Agreement with the Anderson RAPW valence band [9] was qualitative, and except for the band 6, discrepancies were observed both in the energy positions and in the shape of the bands. As for supplementary structures, our interpretation is different from that of Thornton : they assigned the peaks near -4 eV to an intensity resonance of the one-dimensional density of states and the bulk density of states, while in our case these features follow interband transitions. We also note that Thornton *et al.* have not observed the structure we attribute to the reconstructed surface.

The EDC's of photoelectrons emitted normally to a surface saturated with adsorbed sulphur are reported in figure 4. Spectra of the clean surface are also shown by dashed lines, for comparison. Three main observations are given by these curves :

a) A broad but well defined extra electronic structure « c », centred at about 6.5 eV below E_F , is visible in all the spectra taken at $\hbar\omega \geq 26.8$ eV.

Fig. 4. — Normal emission spectra for sulphur adsorption. Full lines : S saturated surface ; dashed lines : clean surface.

b) A second well defined structure « d » appears on all the curves, at around 2 eV below E_F . Its energy position moves slightly with $\hbar\omega$.

c) Except for the structure attributed to the (5×20) surface, the other metal electronic features are weakly attenuated by sulphur adsorption. On the contrary, for $\hbar\omega$ in the 16.8 eV-21.2 eV range, an important additional emission emerges between -2 eV and -6.5 eV. Some of the metal structure are also slightly shifted.

This additional emission and these energy shifts restrict the use of classical difference curves for interpreting adsorption results. The two regular extra structures introduced by sulphur adsorption (peaks « c » and « d ») are very similar to the ones detected on Ni (100) surfaces [7]. This fact indicates that there is no fundamental difference in the chemisorption bonding of chalcogen with 5d and 3d transition metals, as has been suggested [6]. The deeper feature (~ -6.5 eV) can be readily attributed to the 3p bonding states of sulphur because of the correspondence with the ionization energy of S 3p orbitals and the analogy with previous studies of chalcogen adsorption on transition metals [7, 11, 12, 13]. As for the shallower level (~ -2 eV), its origin cannot be

straightforwardly determined. Its similarity with the -1.8 peak in ARUPS study of S and O adsorbed on Ni (100) [8] indicates that it would be due to the d metal states localized by the presence of adsorbate. This is perhaps the most interesting part of our adsorption results : the evidence of the presence of perturbed metal states which is rarely taken into account in the studies of the electronic character of adsorption.

References

- [1] CINTI, R., NGUYEN, T. T. A. and CAPIOMONT, Y., *J. Physique-Lett.* **40** (1979) L-377.
 - [2] MILLS, K., DAVIS, R. F., KEVAN, S. D., THORNTON, G. and SHIRLEY, D. A., *Phys. Rev. B* **22** (1980) 581.
 - [3] THORNTON, G., DAVIS, R. F., MILLS, K. A. and SHIRLEY, D. A., *Solid State Commun.* **34** (1980) 87.
 - [4] SMITH, N. V., *Phys. Rev. B* **9** (1974) 1365.
 - [5] McDONALD, A. H., DAAMS, J. D., VOSKO, S. H. and KOELLING, D. D., *Phys. Rev. B* **23** (1981) 6377.
 - [6] COLLINS, D. M. and SPICER, W. E., *Surf. Sci.* **69** (1977) 114.
 - [7] KÜPPERS, J. and ERTL, G., *Surf. Sci.* **77** (1978) L647.
 - [8] NGUYEN, T. T. A., CINTI, R. and CAPIOMONT, Y., *Surf. Sci.* **87** (1979) 613.
 - [9] ANDERSEN, O. K., *Phys. Rev. B* **2** (1970) 863.
 - [10] HELMS, C. R., BONZEL, H. P. and KELEMAN, S., *J. Chem. Phys.* **65** (1976) 1773.
 - [11] FISCHER, T. E. and KELEMEN, S. R., *Surf. Sci.* **69** (1977) 1.
 - [12] HAGSTRUM, H. D. and BECKER, G. E., *J. Vacuum Sci. Technol.* **14** (1977) 369.
 - [13] JACOBI, K., SCHEFFLER, M., KAMBE, K. and FORSTMANN, F., *Solid State Commun.* **22** (1977) 17.
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