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UV photoemission from Pt (111) and Pt(S) [6(111) $\times$ (100)] surfaces

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Résumé. — Les faces (111) et [6(111) $\times$ (100)] du Pt sont étudiées par photoémission UV directionnelle dans la gamme d'énergie d'excitation 10,2-26,8 eV. Les spectres de photoélectrons émis normalement à la face simple sont discutés en fonction du schéma de bandes calculé ; les courbes de dispersion des états initiaux suivant la direction ΓL sont déterminées expérimentalement. Avec la face vicinale on observe un élargissement des structures électroniques et une augmentation de l'émission près du niveau de Fermi.

Abstract. — Directional UV photoemission spectra have been obtained from a Pt (111) surface and its vicinal [6(111) $\times$ (100)], in the excitation energy range 10.2 to 26.8 eV. The results from the plane surface are discussed in terms of a calculated band structure, and experimental energy dispersions for the initial bands along the ΓL direction are constructed. The presence of steps produces a broadening of the spectral features and an increase of emission near the Fermi level.

Due to its fundamental and technological importance, adsorption on Pt has been the subject of a large number of experimental studies. In particular, it has been found that stepped surfaces were much more reactive in the adsorption process than the flat surfaces [1, 2]. In order to determine if this enhanced reactivity may be a consequence of a peculiar surface electronic structure, we have investigated the valence band structure using angle resolved U.P.S. of clean simple (111) and vicinal [6(111) $\times$ (100)] Pt crystal surfaces. Up to now, only one angle integrated U.P.S. study has been reported on this system [3]. This letter presents our preliminary results of the first measurements performed with the angle-resolved technique.

For the present experiments, two improvements were made to the ultra-high vacuum spectrometer described previously [4]. The normal incidence grating was replaced by a grazing incidence holographic grating (Jobin-Yvon LHT 30) in order to extend the photon energy range above 21.2 eV. A cryopump (Balzers KRY 200 U) was added to the vacuum chamber to maintain a residual pressure of about 5×10^{-10} torr during experiments.

The [6(111) $\times$ (100)] surface consists of (111) terraces, 6 atomic rows in width, separated by mono-atomic steps of (100) orientation [5]. Crystal prepara-

tions were made by B. Lang of Université L. Pasteur, Strasbourg, France. *In situ* cleaning was performed by repeated ion-bombardment, annealing and heat treatment in oxygen [5]. Surface cleanliness was checked by Auger spectroscopy.

The energy distribution curves (EDC) of photoelectrons collected along the surface normal from Pt (111) are displayed in figure 1 for photon energies $\hbar\omega = 10.2, 13.5, 16.8, 21.2$ and 26.8 eV. The product of total crystal photocurrent and scan time per unit energy was kept constant for all the curves.

Keeping in mind the dispersion scheme along the corresponding ΓAL direction of the $\mathbf{k}$ space, calculated by Smith [6] (Fig. 2a), the split structures labelled b-c on the spectra can be directly connected to the emission from the two upper filled d bands A_3 split by the spin-orbit coupling. The final states for these transitions are in the A_1 free-electron-like empty band originating at the L_1 point, the location of which was experimentally [6] determined to be 6 eV above the Fermi level. Additional information on this final band can be obtained from the evolution of the b-c spin-orbit-splitting *versus* excitation energy. The splitting is maximum for $\hbar\omega = 21.2$ eV and then cancels out for $\hbar\omega = 26.8$ eV, indicating a transition between the initial point Γ_{12} , where the two upper A_3 d bands join up, and the Γ_{15} band edge of the A_1 free-electron-like final band. This Γ_{15} point is thus determined to be at 25.5 eV above E_F .

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Fig. 1. — EDC of photoelectrons emitted normally to the clean Pt(111) surface. Vertical bars indicate energy locations of the structures, a : stationary structure, b and c : spin-orbit-split structures (see text).

Fig. 2. — (a) Model band structure for Pt after Smith (ref. [6]). (b) Experimental dispersion curves along the ΓL direction. Full circles correspond to measured structures in figure 1. Dashed lines a, b, ... correspond to the quasi-free-electron final band shifted downwards by respective $\hbar\omega$, 10.2, 13.5, 16.8, 21.2 and 26.8 eV.

In order to obtain experimental dispersion curves from our measurements, we have drawn empirically the quasi-free-electron band between the two critical points L_1 and Γ_{15} . The component of the momentum

normal to the surface $\mathbf{K}_\perp$ (in our case $\mathbf{K}_\parallel = 0$) of the electron states involved in a photoemission process is then determined by vertical transitions allowed for each excitation energy. In spite of this crude extrapolation one can hope for a relatively good confidence in the $\mathbf{K}_\perp$ values, since errors in the final energy band are reduced for the initial bands by the ratio of their respective slopes.

Figure 2b gives the experimental dispersion curves obtained. The dashed lines represent the quasi-parabolic empty band shifted downwards by the different photon energies used. The full circles on each line indicate, on the vertical scale, the energy location of the spectrum features, peaks or shoulders, observed at the corresponding $\hbar\omega$. Complete bands are constructed from these experimental points in analogy with the calculated band structure cited above.

In this framework, most of the features observed on the EDC of figure 1 can be related to direct inter-band transitions originating in the bulk electronic structure. With variable intensities, the five upper filled bands participate in photoemission and the experimental dispersion scheme obtained provides a good confirmation of Smith's band structure. Three features of the EDC however cannot be interpreted by this direct transition process. The first is the stationary shoulder, labelled « a » on figure 1, appearing in all spectra except for the 10.2 eV curve where it is probably masked by the large peak b. Located at about 0.2 eV below E_F , it cannot result from a $\mathbf{K}$ conserving transition due to the lack of available final states. Its relative intensity depends on the excitation energy and on the collection angle and reaches its maximum in the region $\theta = 30^\circ$ - 40° corresponding to the [110] crystal direction. The - 0.2 eV stationary structure has been detected as a predominant peak in integrated U.P.S. experiments on Pt [7, 8, 9] and has been then related to a large maximum located near 0.14 eV below E_F in the calculated [6] Pt density of states. In our angle resolved measurement it could be related to the same band region *via* a surface photoemission process. We remark that many of the FCC transition metals present a similar structure [7, 10, 11].

The second puzzling problem arises from the two well defined broad peaks centred at - 7 eV and - 10 eV on the 26.8 eV curve. In the ΓAL direction of the Brillouin zone these initial energies are much deeper than the d band and lie near and in the s band region which usually gives no contribution to photoemission from metals as a consequence of low photo-ionization cross sections.

No appreciable attenuation of these structures has been observed upon O or S adsorption. An hypothetic explanation could be an enhancement of secondary electron emission [13] or indirect transitions from the lowest occupied band, promoted by the presence of a high density of states empty band in the corresponding energy ranges. Such a f-like flat final band, crossing the parabolic free-electron band,

has been theoretically predicted [12] and experimentally observed [13] for Pd. A similar f-like band in Pt could be responsible for the two deeper structures detected on the 26.8 eV EDC. However, its energy extension of about 3 eV thus determined seems to be too large for a f-like band, even with a possible strong interaction with the free-electron band.

Let us consider now the vicinal

$$\text{Pt(S)} [6(111) \times (100)]$$

surface. For these experiments the crystal was positioned with the steps normal to the photon flux and to the electron analyser entrance axis, and a rotation θ of 9.5° made the (111) terraces perpendicular to the collection direction. Figure 3 shows the EDC recorded along the [111] axis, spectra from a flat (111) face are shown by dashed lines for comparison.

The main observations we make with this surface are : a no supplementary structure is detected, b broadening is clearly present, c the emission originating near the Fermi level is increased.

Thus our results show that there is no striking differences between vicinal and simple Pt (111) surfaces, like the Cu (111) case recently explored by Williams [14] *et al.* We have not seen the resonant surface structure theoretically predicted [15] as a sharp peak in the local density of states near 2.7 eV below the Fermi energy. But as the step edge atoms which participate in this extra structure are only 1/6 of the total surface atoms, the corresponding intensity may be too weak to be detected. Other experiments with higher step densities must be performed to rule out this doubt. A broadening of the bulk features has been also observed for Cu stepped surfaces [16]; we think it could be related to the smearing of the electronic structure generally observed when disorder is introduced. The last point, the variation of density of states near the Fermi level, is more puzzling.

Fig. 3. — EDC of photoelectrons emitted along the [111] direction, (—) vicinal surface, (---) simple (111) surface.

We can only underline its agreement with the angle integrated U.P.S. results obtained by Collins and Spicer [3] who also noted the particular sensibility of this electronic energy region to the geometrical surface structure.

Oxygen and sulphur adsorption experiments are currently undertaken with these surfaces.

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