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Clean surface studies by photoelectron diffraction analysed within a single scattering theory

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Résumé. — Nous montrons qu'il est suffisant de traiter la diffraction de photoélectrons dans un formalisme de diffusion simple pour rendre compte de la dépendance azimutale observée de l'intensité photoémise par les niveaux $4f_{7/2}$ de W(100), et ce, même dans la gamme des basses énergies cinétiques pour lesquelles les émissions de volume et de surface sont bien séparées. Nous démontrons aussi qu'il est hasardeux de remplacer les fonctions d'onde f exactes par des fonctions s , même si cela peut conduire à de bons résultats dans quelques cas particuliers. Enfin, la comparaison entre résultats expérimentaux et théoriques concernant la reconstruction de W(100) permet d'envisager l'utilisation de la diffraction de photoélectrons comme outil d'étude de possibles réarrangements des atomes des surfaces propres.

Abstract. — We show that a single scattering treatment of photoelectron diffraction is sufficient to account for the observed azimuthal dependence of the intensity of the W(100) $4f_{7/2}$ photoemission, even in the low kinetic energy range for which bulk and surface emissions are well separated. We also demonstrate that replacing the exact f wave functions by an s one is quite hazardous even though it might give good results in some cases. Finally, in view of the agreement between experimental and theoretical results on the reconstruction of W(100), we can be optimistic in the use of photoelectron diffraction to study clean surface atom rearrangements.

1. Introduction.

Core level photoelectron spectroscopy is a very sensitive probe of the chemical environment of the atom which undergoes the optical excitation. Among the data available from this type of experiment, two quantities have been more particularly investigated: the variation of the intensity of the lines with the angle of observation and the photon energy (photoelectron diffraction: PhD) [1-3] and the binding energy shift of the surface levels relative to the bulk one [4-13]. Historically, Liebsch was the first to prove that photoelectron diffraction could be used for the determination of the surface structure of adsorbates [14]. Indeed, the symmetry of the adsorption site is directly given by the symmetry of the azimuthal pattern [1]. The precise determination of distances requires a comparison of the experimental

data with the calculated patterns. Whereas the first calculations have been performed using a multiple scattering theory [14], Kono *et al.* [15] have shown that a single scattering model was sufficient to explain the experimental data, at least for kinetic energies larger than 200 eV. The study of clean surfaces, which requires kinetic energies in the range 20-200 eV, is much more complicated since there are several types of emitters: surface, first underlayer, ..., bulk atoms. However, these emitters having their own geometrical environment, their core level lines should not appear strictly at the same energy. Therefore, if the various lines can be resolved, one should be able to obtain experimental patterns specific of each type of emitter. The core level binding energy shift between surface and bulk atoms

being of less than 1 eV, such surface studies will only be possible for very narrow lines such as the 4f levels of transition metals of the 5d series [4-13]. One can wonder yet whether the single scattering treatment of the diffraction is still adequate for such small kinetic energies. The aim of the present paper is first to check the validity of these calculations in the particular case of azimuthal patterns of the 4f levels of W(100) and then to investigate its sensitivity to atomic displacements (relaxation, reconstruction). In view of the good agreement between experimental and theoretical results, we also give the calculated curves for the other two low index faces of this metal.

2. Single scattering formalism.

If indeed Kono *et al.* [3, 15] were the first to use a single scattering treatment to interpret their PhD experiments, this model had already been used by Mc Donnell *et al.* [16] to study the angular anisotropy of the Auger emission. The corresponding theoretical model was first developed by Liebsch [14] and

Lee [17] in the particular case of a spherical s initial state and then extended to the case of any initial state by Fujikawa [18]. Here, we will first derive the formula of Fujikawa in a slightly different manner. Then, although we are interested in f initial states, we will show how it simplifies in the case of an s state to recover the Kono *et al.* formula. Actually, we will also use this last formula to check the validity of the Kono *et al.*'s conjecture according to which it can account for the emission from core levels belonging to filled shells which have a spherically symmetric charge distribution [15].

Let us now briefly give the main steps of the derivation of the general formula. The photoelectron wave function $\psi(\mathbf{R})$ at the detector located at $\mathbf{R}$ is given by :

$$\psi(\mathbf{R}) \propto \int d_3\mathbf{r} G(\mathbf{R}, \mathbf{r}) \mathbf{p} \cdot \mathbf{A} \psi_i(\mathbf{r}) \quad (1)$$

where $\psi_i(\mathbf{r})$ is the core orbital of the photoexcited electron, $\mathbf{A}$ the vector potential, $\mathbf{p}$ the momentum operator and $G(\mathbf{R}, \mathbf{r})$ is the propagator of the emitted electron :

$$G(\mathbf{R}, \mathbf{r}) = G_0(\mathbf{R}, \mathbf{r}) + \sum_j \iint d_3\mathbf{r}' d_3\mathbf{r}'' g_0(\mathbf{R}, \mathbf{r}') T_j(\mathbf{r}', \mathbf{r}'') G_0(\mathbf{r}'', \mathbf{r}) \quad (2)$$

where G_0 is the propagator of the photoexcited electron for an isolated emitter, T_j is the T -matrix describing the diffusion of the electron by the neighbour j at distance R_j from the emitter and g_0 is the free electron propagator ; they are given, in Hartree units, for $R > r'$ and $r'' > r$ and outside the range of the potential of the emitter, by :

$$G_0(\mathbf{r}'', \mathbf{r}) = -2ik \sum_{\ell m} Y_{\ell m}(\hat{\mathbf{r}}'') Y_{\ell m}^*(\hat{\mathbf{r}}) h_{\ell}^{(1)}(kr'') e^{i\delta_{\ell}^0} \mathcal{R}_{\ell}(kr) \quad (3)$$

$$g_0(\mathbf{R}, \mathbf{r}') = -2k \sum_{\ell m} Y_{\ell m}(\hat{\mathbf{R}}) Y_{\ell m}^*(\hat{\mathbf{r}}') \frac{e^{i(kR - \ell \frac{\pi}{2})}}{kR} j_{\ell}(kr')$$

where $Y_{\ell m}$ are the spherical harmonics, j_{ℓ} the spherical Bessel functions, $h_{\ell}^{(1)}$ the Hankel functions of the first kind, $\mathcal{R}_{\ell}(kr)$ the regular solution of the radial Schrödinger equation of the emitter atom, δ_{ℓ}^0 the corresponding phase-shift and k the wave vector. With these notations, $G_0(\mathbf{R}, \mathbf{r})$ for $R \gg r$ is obtained by

using the first term of the asymptotic development of $h_{\ell}^{(1)}(kR) \simeq \frac{-i e^{i(kR - \ell \frac{\pi}{2})}}{kR}$. To treat the diffusion by

a spherical potential centred at site j , it is convenient to use functions centred at this site. First we take advantage of the invariance of g_0 with respect to the translation $\mathbf{R}_j$, i.e. $g_0(\mathbf{R}, \mathbf{r}') = g_0(\mathbf{R} - \mathbf{R}_j, \mathbf{r}' - \mathbf{R}_j)$ which can be written, since $R \gg R_j$:

$$g_0(\mathbf{R}, \mathbf{r}') \simeq -2 \sum_{\ell m} (-i)^{\ell} Y_{\ell m}(\hat{\mathbf{R}}) \frac{e^{+ik(R - \hat{\mathbf{R}} \cdot \mathbf{R}_j)}}{R} Y_{\ell m}^*(\widehat{\mathbf{r}' - \mathbf{R}_j}) j_{\ell}(k|\mathbf{r}' - \mathbf{R}_j|) \quad (4)$$

Then we rewrite the spherical wave $Y_{\ell m}(\hat{\mathbf{r}}'') h_{\ell}^{(1)}(kr'')$ outgoing from the emitter in terms of spherical waves incoming on the neighbour j [19] :

$$Y_{\ell m}(\hat{\mathbf{r}}'') h_{\ell}^{(1)}(kr'') = \sum_{\ell' m'} \mathcal{G}_{\ell m \ell' m'}^j j_{\ell'}(k|\mathbf{r}'' - \mathbf{R}_j|) Y_{\ell' m'}(\widehat{\mathbf{r}'' - \mathbf{R}_j}) \quad (5)$$

with :

$$\mathfrak{G}_{\ell m \ell' m'}^j = 4 \pi \sum_{\ell'' m''} i^{\ell - \ell'' - \ell'} h_{\ell''}^{(1)}(kR_j) Y_{\ell'' m''}^*(\hat{R}_j) G(\ell m, \ell'' m'' | \ell' m')$$

where $G(\ell m, \ell'' m'' | \ell' m')$ is the Gaunt coefficient given by :

$$G(\ell m, \ell'' m'' | \ell' m') = \int d\Omega Y_{\ell m}(\hat{r}) Y_{\ell'' m''}(\hat{r}) Y_{\ell' m'}^*(\hat{r}). \quad (6)$$

Since the diffusion potential has a spherical symmetry, the T operator only acts on the radial part of the incoming spherical wave. Then, taking into account the well-known relation :

$$\iint r_j'^2 r_j''^2 j_\ell(kr_j') T(r_j', r_j'') j_\ell(kr_j'') dr_j' dr_j'' = - \frac{e^{i\delta_\ell^j} \sin \delta_\ell^j}{2k} \quad (7)$$

where $r_j^{(')} = |\mathbf{r}^{(')} - \mathbf{R}_j|$, and δ_ℓ^j is the phase shift due to scatterer j , one finds :

$$\psi(\mathbf{R}) \propto \frac{-2e^{ikR}}{R} \sum_{\ell m} \left\{ (-i)^\ell Y_{\ell m}(\hat{R}) + i \sum_j e^{-ik\hat{R} \cdot \mathbf{R}_j} \sum_{\ell' m'} (-i)^{\ell'} Y_{\ell' m'}(\hat{R}) \mathfrak{G}_{\ell m \ell' m'}^j e^{i\delta_{\ell'}^j} \sin \delta_{\ell'}^j \right\} M_{\ell m, i} \quad (8)$$

with

$$M_{\ell m, i} = \int d_3\mathbf{r} Y_{\ell m}^*(\hat{r}) \mathcal{R}_\ell(kr) \mathbf{p} \cdot \mathbf{A} \psi_i(\mathbf{r}) e^{i\delta_\ell^i}.$$

In the dipole approximation and for an initial state $\psi_i(\mathbf{r}) = R_{\ell_i}(r) Y_{\ell_i m_i}(\hat{r})$

$$M_{\ell m, i} = M_{\ell m, \ell_i m_i} \propto \int Y_{\ell m}^*(\hat{r}) \mathcal{R}_\ell(kr) \hat{\varepsilon} \cdot \hat{r} R_{\ell_i}(r) Y_{\ell_i m_i}(\hat{r}) r^3 dr d\Omega. \quad (9)$$

Then, making use of the relationship

$$\hat{\varepsilon} \cdot \hat{r} = \frac{4\pi}{3} \sum_{m=-1}^{m=+1} Y_{1m}^*(\hat{\varepsilon}) Y_{1m}(\hat{r}) \quad (10)$$

$$\left. \begin{aligned} M_{\ell m, \ell_i m_i} &\propto (-i)^\ell e^{i\delta_\ell^0} \sum_{m'=-1}^{m'=+1} Y_{1m'}^*(\hat{\varepsilon}) G(\ell_i m_i, 1 m' | \ell m) \tilde{\rho}_k(\ell, \ell_i) \\ \tilde{\rho}_k(\ell, \ell_i) &= \int \mathcal{R}_\ell(kr) R_{\ell_i}(r) r^3 dr \end{aligned} \right\} \quad (11)$$

with

and finally :

$$\psi(\mathbf{R}) \propto \frac{e^{ikR}}{R} \sum_{\ell m} M_{\ell m, \ell_i m_i} \left\{ Y_{\ell m}(\hat{R}) + i \sum_j e^{-ik\hat{R} \cdot \mathbf{R}_j} \sum_{\ell' m'} (-i)^{\ell' - \ell} Y_{\ell' m'}(\hat{R}) \mathfrak{G}_{\ell m \ell' m'}^j e^{i\delta_{\ell'}^j} \sin \delta_{\ell'}^j \right\} \quad (12)$$

Note that the Gaunt coefficient in $M_{\ell m, \ell_i m_i}$ is 0 except for $\ell = \ell_i - 1$ and $\ell = \ell_i + 1$ which are then the only transitions allowed.

The photocurrent is given by :

$$\frac{dI}{d\Omega} = R^2 \text{Im} \left(\psi^*(\mathbf{R}) \left| \frac{\partial \psi}{\partial r} \right|_{\mathbf{r}=\mathbf{R}} \right)$$

which, using (Eq. (5)) leads to :

$$\frac{dI}{d\Omega} \propto k \left| \sum_{\ell m} M_{\ell m, \ell_i m_i} \left\{ Y_{\ell m}(\hat{R}) + 4i\pi \sum_{j \neq 0} e^{-ikR_j \cos \vartheta_j} \sum_{\ell'' m''} Y_{\ell'' m''}^*(\hat{R}_j) h_{\ell''}^{(1)}(kR_j) (-i)^{\ell''} \sum_{\ell' m'} (-1)^{\ell - \ell'} Y_{\ell' m'}(\hat{R}) e^{i\delta_{\ell'}^j} \sin \delta_{\ell'}^j G(\ell m, \ell'' m'' | \ell' m') \right\} \right|^2 \quad (13)$$

where ϑ_j is the scattering angle, or angle between $\hat{R}$ and $\hat{R}_j$. Equation (13) is equivalent to the equations derived by Fujikawa [18] and Sagurton *et al.* [21]. This formula is the exact single scattering solution in a spherical wave description. It greatly simplifies if kR_j is sufficiently large. Indeed, in this case, $h_{\ell}^{(1)}(kR_j)$ can be replaced by the asymptotic development given above. Then, using the formula [22] :

$$Y_{\ell m}(\hat{R}_j) Y_{\ell' m'}^*(\hat{R}_j) = \sum_{\ell'' m''} Y_{\ell'' m''}^*(\hat{R}_j) G(\ell m, \ell'' m'' | \ell' m') \quad (14)$$

and the condition that $(\ell + \ell'' - \ell')$ should be even, one finds :

$$\frac{dI}{d\Omega} \propto k \left| \sum_{\ell m} M_{\ell m, \ell_i m_i} \left\{ Y_{\ell m}(\hat{R}) + \sum_{j \neq 0} \frac{e^{ikR_j(1 - \cos \vartheta_j)}}{R_j} f(\vartheta_j) Y_{\ell m}(\hat{R}_j) \right\} \right|^2 \quad (15)$$

in which $f(\vartheta_j)$ is the usual scattering factor :

$$f(\vartheta_j) = \frac{4\pi}{k} \sum_{\ell' m'} e^{i\delta_{\ell'}} \sin \delta_{\ell'} Y_{\ell' m'}(\hat{R}) Y_{\ell' m'}^*(\hat{R}_j) \quad (16)$$

which is equivalent to Fujikawa formula.

Note that this formula is valid for any initial state but can be still simplified if one considers an s initial state ($\ell_i = 0$). Actually, in that case, the only possible transition is towards $\ell = 1$ and the matrix element becomes :

$$M_{1m, 00} \propto -i e^{i\delta_1^0} Y_{1m}^*(\hat{\varepsilon}) \tilde{\rho}_k(1, 0). \quad (17)$$

Using once again equation (10) one obtains the formula valid for a s initial state

$$\frac{dI}{d\Omega} \propto k \tilde{\rho}_k^2(1, 0) \left| \left\{ \hat{\varepsilon} \cdot \hat{R} + \sum_{j \neq 0} \hat{\varepsilon} \cdot \hat{R}_j \frac{e^{+ikR_j(1 - \cos \vartheta_j)} f(\vartheta_j)}{R_j} \right\} \right|^2 \quad (18)$$

which is the formula initially derived by Kono *et al.* [15].

3. Application to the study of the 4f core level emission from W surfaces.

Let us now apply this formalism in the particular case of the 4f core levels ($\ell_i = 3$) of W. Then, due to the above mentioned selection rule, the allowed final state has angular momentum $\ell = 2$ or $\ell = 4$. One can show that the latter is negligible in the energy range where the maximum surface sensitivity is obtained. This can be qualitatively understood if one assumes that the final state is a plane wave. Actually, in this case, the ratio of the radial matrix elements, which is given by :

$$\frac{\tilde{\rho}_k(4, 3)}{\tilde{\rho}_k(2, 3)} = \frac{\int_0^\infty r^3 j_4(kr) R_3(r) dr}{\int_0^\infty r^3 j_2(kr) R_3(r) dr},$$

can be estimated to be of the order 10^{-1} (see Appendix). Note however that this ratio is energy dependent so that the transition towards $\ell = 4$ state can become non-negligible, and even predominant, at larger energies. Here, we will thus neglect this $\ell = 4$ optical transition so that equation (15) can be rewritten :

$$\frac{dI}{d\Omega} \propto \sum_{m_i = -3}^{m_i = +3} k \left| \sum_{m = -2}^{m = +2} M_{2m, 3m_i} \left\{ Y_{2m}(\hat{R}) + \sum_{j \neq 0} \frac{e^{ikR_j(1 - \cos \vartheta_j)}}{R_j} f(\vartheta_j) Y_{2m}(\hat{R}_j) \right\} \right|^2. \quad (19)$$

In order to calculate azimuthal patterns, for a given energy, the radial matrix element factorizes so that (19) becomes

$$\frac{dI}{d\Omega} \propto \sum_{m_i = -3}^{m_i = +3} \left| \sum_{m = -2}^{m = +2} Y_{1m-m_i}^*(\hat{\varepsilon}) G(3m_i, 1(m-m_i) | 2m) \times \left\{ Y_{2m}(\hat{R}) + \sum_{j \neq 0} \frac{e^{ikR_j(1 - \cos \vartheta_j)}}{R_j} f(\vartheta_j) Y_{2m}(\hat{R}_j) \right\} \right|^2 \quad (20)$$

with $|m - m_i| \leq 1$.

We have performed the calculations for the three low index faces of W taking into account [16] :

— the inelastic effects as an isotropic attenuation $e^{-\gamma L(L_j)}$ of the electronic amplitude, ($1/2 \gamma$: electron mean free path, $L(L_j)$: distance from emitter to the surface (via the j -th scatterer))

— and the thermal vibrations via a Debye-Waller factor.

We have taken the following parameters (see Fig. 1) :

- polar angle : $\theta = 30^\circ$
- angle between the polarization vector $\hat{\epsilon}$ and the surface normal : $\alpha = 22^\circ 5'$
- and photon energy : $h\nu = 65$ eV.

These parameters correspond to the experimental conditions in the particular case of W(100) (see Sect. 5). The scattering factor is calculated from the potential of Christensen and Feuerbacher [23], which is assumed to be the same for bulk and surface atoms. The surface potential barrier between vacuum and bulk is taken into account by allowing a slight refraction effect changing the emergence angle ϑ of the photoelectron inside the solid to ϑ' in vacuum according to the relation :

$$\sin^2 \vartheta = (1 + V_0/E_k) \sin^2 \vartheta' ,$$

where V_0 is the value of the inner potential ($V_0 = -14$ eV) and E_k is the kinetic energy of the electron inside the metal. In our calculations we limit the summations over j in equation (20) to terms where $L_j \leq \gamma^{-1}$. At the kinetic energies of the photoelectrons in our experiments (~ 30 eV), $\gamma^{-1} \approx 10$ Å so that the emission comes mainly from the first layers. In practice, only relatively small clusters are needed in the calculations (~ 33 atoms) : we have checked that increasing the allowed values of L_j beyond γ^{-1} , although it slightly changes the relative intensities of the structures, does not modify their angular positions. In a first step, the three surfaces are assumed to be unrelaxed and unreconstructed. Since the bulk (B), subsurface

(S_2) (at least for (111) and (100) faces) and surface (S_1) emissions can be distinguished experimentally, we have plotted separately the azimuthal patterns for the ($B + S_1 + S_2$), B and S_1 emissions in figures 2(a, a', a''), 2(b, b', b'') and 2(c, c', c'') respectively. $\varphi = 0^\circ$ corresponds to the $\langle 001 \rangle$, $\langle 00\bar{1} \rangle$, $\langle 1\bar{1}0 \rangle$ directions for the (110), (100), (111) surfaces respectively. Obviously, these patterns reflect the symmetry of the corresponding faces. The surface emission is less anisotropic than the bulk one. Actually, under these experimental conditions, most of the atoms giving rise to forward scattering (which is predominant) are suppressed for surface emitters. Let us point out that, although equation (20) has been first derived a few years ago [18], it had never been applied in practice to an experimental case with $\ell_i \neq 0$, at least to our knowledge. Indeed, most experiments have been performed on s core levels, except for the Cu p levels. However, in this last case, Kono *et al.* [15], arguing that these p-levels being filled have a spherical charge distribution, have proposed to still use the formula valid for an s initial state (Eq. 18). This approximation enabled these authors to interpret satisfactorily their experiments. More recently, Sébilleau *et al.* [24] have used the same approximation in the case of the W(100) 4f core levels with the same success. In view of equations (18) and (20) which look quite different, one can wonder to what extent this approximation is general. In order to

Fig. 1. — Schematic representations of the experimental geometry defining the angles used in the main text (a) and of the single scattering model (b).

Fig. 2. — Polar plots of the theoretical azimuthal dependence of W(110) : (a, b, c), W(100) : (a', b', c') and W(111) : (a'', b'', c'') 4f_{7/2} core photoelectron intensities for the total (a, a', a''), bulk (b, b', b'') and surface (c, c', c'') emissions, calculated from Fujikawa formula (neglecting the $f \rightarrow g$ transition) for the following conditions : $\theta = 30^\circ$, $\alpha = 22^\circ 5'$, $h\nu = 65$ eV.

check this point, we have also calculated the azimuthal patterns for the two other low index faces of W within this approximation. The corresponding results are shown in figure 3. One sees at first glance that although the agreement between figure 2 and figure 3 is good in the case of W(100), it is less satisfactory for W(110) and non existent for W(111). In view of these results, one can conclude that it is more advisable to use the exact formula (20), even for filled inner shells, although in some particular cases, the simplified formula (18) might give satisfactory results.

Finally, let us remark that the azimuthal patterns are very sensitive to the experimental conditions. To illustrate this point, we give in figure 4 the azimuthal patterns of 4f levels of W(110) for an other set of parameters [25] : $\theta = 45^\circ$, $\alpha = 20^\circ$, $h\nu = 70$ eV.

Fig. 3. — Polar plots of the theoretical azimuthal dependence of W(110) (a, b, c), W(100) (a', b', c') and W(111) (a'', b'', c'') 4f_{7/2} core photoelectron intensities for the total (a, a', a''), bulk (b, b', b'') and surface (c, c', c'') emissions calculated from Kono *et al.* formula (s initial state) for the following conditions : $\theta = 30^\circ$, $\alpha = 22^\circ 5'$, $h\nu = 65$ eV.

4. Sensitivity to atomic surface displacements.

It is well known that most of the transition metal surfaces undergo a surface relaxation, i.e. the first interlayer spacings differ from the values they would have in bulk metals. This effect is very weak for the most close-packed surfaces but may become significant for the open ones. On the other hand, in some experimental conditions (temperature, presence of adsorbates...) these surfaces may reconstruct. Thus, W(100) presents a c(2 × 2) LEED pattern at low temperature which can be explained by alternate

Fig. 4. — Polar plots of the theoretical azimuthal dependence of W(110) 4f_{7/2} core photoelectron intensities for the total (a, α), bulk (b, β) and surface (c, γ) emissions calculated for an f initial state for two sets of parameters :
— a, b, c : $\theta = 30^\circ$, $\alpha = 22^\circ 5'$, $h\nu = 65$ eV
— α, β, γ : $\theta = 45^\circ$, $\alpha = 20^\circ$, $h\nu = 70$ eV [25]
---- unreconstructed surface ; — reconstructed surface.

lateral displacements of surface atoms along the $\langle 11 \rangle$ direction (« zig-zag » reconstruction [26, 27]). It has also been suggested that W(110) is not the perfect termination of the bulk but that the surface plane, while retaining its crystallographic structure, is rigidly displaced along the $\langle 10 \rangle$ direction relative to the first underlayer [28]. Although this assertion is questionable for the clean surface, there are good reasons to admit that it is verified when hydrogen atoms are present at the surface [29]. Therefore, in the hope of using PhD as a tool to study clean surface crystallography, one should check its sensitivity to such surface atomic displacements.

Let us first present our results for the relaxation of the (100) face of W. They are shown in figure 5a, b, c, for three values of the relaxation : 0 %, 5 % (experimental value for W), 10 % (experimental value for Ta [30]). Actually, the potentials and lattice parameters of W and Ta being very similar, our results can also be applied to the case of Ta, for the same photoelectron kinetic energies. In view of this figure, the effect is too weak to be used as a tool for a precise determination of so small relaxations.

Fig. 5. — Influence of relaxation (a, b, c) and zig-zag reconstruction (α , β , γ) on the theoretical azimuthal dependence of W(100) $4f_{7/2}$ core photoelectron intensities for the total (a, α), bulk (b, β) and surface (c, γ) emissions calculated for an f initial state :

— a, b, c : — 10 % relaxation ; 5 % relaxation, --- unrelaxed surface
— α , β , γ : — reconstructed surface ; ---- unreconstructed surface.

On the contrary, the bulk azimuthal pattern of Ta(100) is significantly modified by relaxation effects. This could be confirmed by comparing experimental results for Ta and W(100), for these conditions.

On the right hand side of the same figure, we have illustrated the influence of the « zig-zag » reconstruction on the azimuthal patterns of W(100) assuming a single domain of reconstruction. Herealso, the main difference can be seen on the bulk pattern in the four $\langle 11 \rangle$ directions which all exhibit an enhanced lobe. Much less pronounced is the slight departure from fourfold symmetry which anyway cannot be observed experimentally due to the existence of several domains of reconstruction with perpendicular displacements. Contrary to the case of the relaxation, it is possible to measure the variation of the azimuthal patterns when the surface reconstructs by performing the experiment at room and nitrogen temperatures. The results will be presented and discussed in the next section.

Finally, we have considered also the influence of the possible reconstruction of the (110) face of W. The results are shown in figure 4 for the two sets of experimental conditions mentioned in section 3. The overall effect of the reconstruction is to smooth the structures of the azimuthal patterns. According to the most recent experiments, it appears that this reconstruction does not occur on a clean surface, but is triggered by a small amount of hydrogen [29]. The presence of these hydrogen atoms should not modify the calculated azimuthal patterns of the reconstructed face since hydrogen is a very weak scatterer. Therefore, it should be of greatest interest to perform the corresponding experiments.

5. Experiments on W(100).

Angle resolved core level spectra are obtained using radiation from the 540 MeV ACO storage ring at L.U.R.E. in Orsay. The chosen excitation energy ($h\nu = 65$ eV) is obtained from a high flux toroidal grating monochromator. Emission at 30° from the normal of W(100) is collected to perform azimuthal photodiffraction scans. The energy resolution for the combined monochromator/analyser system is about 190 meV whereas the angular resolution of the spherical analyser is better than 1° . The chamber and experimental equipment have been described elsewhere [11-13]. Here, two-axis rotations of the sample *in situ* are possible (polar angle θ and azimuthal angle ϕ , see Fig. 1a) with ϕ rotations up to 220° . The angle α between the polarization vector $\hat{\epsilon}$ and the surface normal is fixed at : $\alpha = 22.5^\circ$ (p-like polarization). W(100) $4f_{7/2}$ level intensities are measured from a highly polished W surface, oriented to within $\pm 0.5^\circ$ of the (001) plane. The surface is prepared by argon ion sputtering, cycles of oxidation at 1 500 K, annealing at 2 100 K and finally flashing up to 2 400 K. A high degree of surface order is verified by LEED : $p(1 \times 1)$ for the unreconstructed surface, $c(2 \times 2)$ when the surface is reconstructed at low temperature (~ 90 K). No impurity peaks were detected by Auger spectroscopy.

Let us recall that after subtracting a linear background each $4f_{7/2}$ spectrum is decomposed into three peaks with Doniach-Sunjic lineshapes corresponding to the bulk (B), surface (S_1) and first underlayer (S_2) emissions. These peaks are then convoluted with the 190 meV-instrumental Gaussian function. The scattered intensities correspond to the areas of each component, normalized to the value of the secondary electron background taken at an energy sufficiently far from the 4f region to have a negligible azimuthal anisotropy. The corresponding results for the reconstructed and unreconstructed surfaces are shown in figure 6. The raw data have been symmetrised with respect to $\langle 11 \rangle$, then to $\langle 10 \rangle$ axis, in

Fig. 6. — Polar plots of the experimental azimuthal dependence of W(100) $4f_{7/2}$ core photoelectron intensities for the total (a, α), bulk (b, β) and surface (c, γ) emissions for the following conditions: $\theta = 30^\circ$, $\alpha = 22^\circ 5'$, $h\nu = 65$ eV

— a, b, c : unreconstructed surface
— α , β , γ : thermally reconstructed surface.

accordance with the fourfold symmetry of both systems. For the unreconstructed surface, the agreement between experiments (Figs. 6a, b, c) and theory (Figs. 2a', b', c' and Figs. 3a', b', c') is excellent even when using an s-initial state. On the other hand, the influence of the reconstruction on the azimuthal patterns (Figs. 6 α , β , γ), which is particularly significant for bulk emission, distorts the four $\langle 11 \rangle$ lobes in the same way as in the calculations (Figs. 5 α , β , γ). Finally, let us emphasize that the experiments have been performed twice with an excellent reproducibility.

6. Discussion and conclusion.

Our calculations have demonstrated that the use of an s initial state instead of the exact wave function in the case of a filled inner shell (with $\ell_i > 0$), is quite hazardous even though good results can be obtained in some cases. However, the existence of two allowed transitions when $\ell_i \neq 0$ sets some problems since rigorously, the knowledge of the corresponding radial matrix elements is needed. This simplifies in the limits of low and high energies in which case the transitions towards $\ell_i - 1$ and $\ell_i + 1$ are respectively predominant. Unfortunately, the intermediate energy range in which both transitions are important is not very precisely delimited (see Appendix) and not very far from the energy used in the present

study. Actually for $h\nu = 65$ eV we have estimated $\tilde{\rho}_k(4, 3)/\tilde{\rho}_k(2, 3) \approx 10^{-1}$ whereas Goldberg *et al.* [31] predict 0.5. It is thus interesting to investigate what would be obtained if we neglect d wave and instead include g wave final states. The results obtained using equation (20) with obvious changes are shown in figure 7 for the three low index faces of W. The patterns are quite different from those of figure 2, although their intensities are quite alike, which justifies that the relative importance of the two transitions is indeed governed by $\tilde{\rho}_k(\ell, \ell_i)$. The comparison with experimental data in the case of W(100) (see Figs. 6a, b, c) clearly confirms that the transition $f \rightarrow d$ is predominant at this energy. Thus it would be of great interest to perform experiments with increasing photon energies from $h\nu = 65$ eV. The comparison with the calculated patterns should give a means to precise the energy dependence of $\tilde{\rho}_k(4, 3)/\tilde{\rho}_k(2, 3)$.

As a conclusion, we have shown (at least for W(100)) that a single scattering treatment of photoelectron diffraction is sufficient to account for the observed azimuthal patterns, even in the kinetic energy range ($E_c \sim 30$ eV) for which bulk and surface emissions are well separated. Moreover, in view of our results on the reconstruction of W(100), we can be optimistic in the use of photoelectron diffraction to study clean surface atom rearrangements.

Fig. 7. — Polar plots of the theoretical azimuthal dependence of W(110) : a, b, c, W(100) : a', b', c' and W(111) : a'', b'', c'' $4f_{7/2}$ core photoelectron intensities for the total (a, a', a''), bulk (b, b', b'') and surface (c, c', c'') emissions, calculated from Fujikawa formula (neglecting the $f \rightarrow d$ transition) for the following conditions: $\theta = 30^\circ$, $\alpha = 22^\circ 5'$, $h\nu = 65$ eV.

Finally, it would be highly desirable to perform experiments on other faces of W and other metals in order to precise to what extent our findings are general. On the other hand, it should be useful to check the validity of the plane wave approximation by performing a calculation with spherical waves (Eq. (13)). Some work is currently done in these directions.

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Appendix.

CALCULATION OF RADIAL MATRIX ELEMENTS. — The radial matrix elements are given by :

$$\tilde{\rho}_k(\ell, \ell_i) = \int \mathcal{R}_\ell(kr) R_{\ell_i}(r) r^3 dr \quad \text{with} \quad \ell = \ell_i \pm 1.$$

For the core wave functions we have taken a Slater orbital [32] :

$$R_{\ell_i}(r) = \frac{(2\alpha)^{\frac{2n^*+1}{2}}}{\sqrt{\Gamma(2n^*+1)}} r^{n^*-1} e^{-\alpha r}$$

where Γ is the gamma function.

For a W 4f level : $\ell_i = 3$, $n^* = 3.7$, $\alpha = 6.34$. The final wave function is approximated by a plane wave so that :

$$\begin{aligned} \mathcal{R}_\ell(kr) &= \sqrt{\frac{k}{\pi}} j_\ell(kr) \\ &= \frac{1}{\sqrt{2}r} J_{\ell+\frac{1}{2}}(kr) \end{aligned}$$

where the normalization of continuum wave functions per unit energy range is used [33]. Using [34] :

$$\begin{aligned} \int_0^\infty e^{-\alpha x} J_\nu(\beta x) x^{\mu-1} dx &= \\ &= \frac{\left(\frac{\beta}{2\alpha}\right)^\nu \Gamma(\nu + \mu)}{\alpha^\mu \Gamma(\nu + 1)} \times \\ &\times F\left(\frac{\mu + \nu}{2}, \frac{\mu + \nu + 1}{2}, \nu + 1, -\frac{\beta^2}{\alpha^2}\right) \end{aligned}$$

where F is the hypergeometric function, one finds :

$$\begin{aligned} \tilde{\rho}_k(\ell, 3) &= \frac{2^{n^*-\ell-\frac{1}{2}}}{\alpha^{\ell+\frac{5}{2}}} k^{\left(\ell+\frac{1}{2}\right)} \frac{\Gamma(\ell+3+n^*)}{\Gamma\left(\ell+\frac{3}{2}\right)} \times \\ &\times \frac{F\left(\frac{\ell+3+n^*}{2}, \frac{\ell+4+n^*}{2}, \ell+\frac{3}{2}, -\frac{k^2}{\alpha^2}\right)}{\sqrt{\Gamma(2n^*+1)}} \end{aligned}$$

$\tilde{\rho}_k(2, 3)$ and $\tilde{\rho}_k(4, 3)$ are plotted in figure A(a) as a function of the photon energy. At the energy used in the present study ($h\nu = 65$ eV) $\tilde{\rho}_k(4, 3)/\tilde{\rho}_k(2, 3) \approx 10^{-1}$. For comparison we have also plotted in figure A(b), the same radial matrix elements calculated by Goldberg *et al.* [31] using a central field potential and the discrete orbitals $\psi_{n\ell m}$ calculated by Hermann and Skillmann. The maxima of both curves are displaced towards lower photon energies. Nevertheless $\tilde{\rho}_k(2, 3)/\tilde{\rho}_k(4, 3)$ remains smaller than one for $h\nu = 65$ eV (≈ 0.5). Note that fitting a Slater type orbital to the corresponding Hermann-Skillmann wave function does not change our results significantly. Therefore, the difference with the calculations of Goldberg *et al.* comes from the final wave function which, in both cases, is rather approximated.

Fig. A. — Radial dipole matrix elements for the transition $f \rightarrow d$ ($\tilde{\rho}_k(2, 3)$) : ... and $f \rightarrow g$ ($\tilde{\rho}_k(4, 3)$) : — in the case of W as a function of the photon energy : (a) using a plane wave approximation, (b) from Goldberg *et al.* [31].

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