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M.C. Desjonquères. Surface relaxation and electronic structure of Mo and W (100). Journal de Physique Lettres, 1979, 40 (12), pp.249-252. 10.1051/jphyslet:019790040012024900 . jpa-00231618

HAL Id: jpa-00231618

<https://hal.science/jpa-00231618>

Submitted on 1 Jan 1979

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Classification

Physics Abstracts

68.20 — 68.40 — 71.20 — 73.20

Surface relaxation and electronic structure of Mo and W (100)

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(Reçu le 19 mars 1979, accepté le 2 mai 1979)

Résumé. — L'influence de la contraction uniforme de surface, observée à température ambiante pour le Mo et le W (100), sur leur structure électronique est discutée dans un modèle de liaisons fortes. Le pic central d'états résonnants de la densité d'états à la surface n'est que très peu modifié et la contraction produit principalement un accroissement de la densité d'états près des bords de bande. En introduisant les répulsions de cœur à l'aide d'un potentiel phénoménologique, la minimisation de l'énergie conduit à une contraction de 6 ~ 8 % pour le Mo et 3,5 ~ 4 % pour le W, en bon accord avec l'expérience.

Abstract. — The influence of the uniform surface contraction, observed at room temperature for Mo and W (100), on their electronic structure, is investigated and discussed in a tight-binding framework. Unexpectedly, the central resonant peak of the surface density of states is only slightly modified and the contraction results mainly in an increase of the density of states near the band edges. Introducing the core-core repulsion with a phenomenological potential, the minimization of energy gives a 6 ~ 8 % and 3.5 ~ 4 % contraction for Mo and W respectively, in good agreement with experiment.

The (100) surface of bcc transition metals, especially of Mo and W, has been the subject of a large number of studies in recent years. Concerning the atomic geometry, LEED intensity analysis has shown that for a clean unreconstructed (100) Mo surface, at room temperature, the first underlayer spacing is reduced by about 12 % [1] while W (100) exhibits a smaller contraction ($\simeq 5\%$) [2]. Information about the electronic structure was obtained using various spectroscopic techniques (UPS, FES) [3]; they all confirmed the existence of resonant surface states just below the Fermi level. From a theoretical point of view, there were various lines of attack starting from the simpler tight-binding description of the d band [4] to more sophisticated models such as KKR [5], matching Green function [6] or pseudopotential [7] methods. They all provided a possible explanation for the experimental feature just below the Fermi level, but often neglecting the surface contraction. In fact, a complete study would require a self-consistent determination of the electronic structure and the equilibrium geometry. This involves considerable work and consequently can only be performed in the

tight-binding model, but up to now, only rough models for the density of states were used [8].

Here, using the method of ref. [4], we will first investigate the influence of the relaxation on the electronic structure and show that it does not affect the resonant state peak of Mo (100) but increases the density of states near the band edges. By minimizing the total energy (band energy plus a Born-Mayer core-core repulsive term) we do find a contraction larger for Mo (6 ~ 8 %) than for W (3.5 ~ 4 %) in good agreement with experiment.

We briefly recall the main features of the method used in our previous paper [4]. In a tight-binding approach for the d band, the wave function of the electron belonging to the eigenvalue E_n is written as a linear combination of atomic orbitals of symmetry $\lambda(xy, yz, zx, x^2 - y^2, 3z^2 - r^2)$ centred on each lattice site i :

$$|n\rangle = \sum_{i\lambda} a_{i\lambda}(E_n) |i\lambda\rangle. \quad (1)$$

The local density of states (LDS) on site i is then defined by

$$n_i(E) = \frac{1}{5} \sum_{i\lambda} |a_{i\lambda}(E_n)|^2 \delta(E - E_n). \quad (2)$$

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It can be obtained without computing the $a_{i\lambda}$'s, from its first moments, using a continued fraction expansion [9, 10]. The variation of the LDS from plane to plane gives a good description of the modification of the electronic structure due to the surface and has previously provided an interpretation of the experimental features just below the Fermi level [4]. Self-consistency is taken into account by assuming charge neutrality for each layer. This method gives similar corrections for the atomic levels at the surface as does the Friedel sum rule used in ref. [4].

The first purpose of this work is to analyse the influence of contraction on the surface LDS. Contraction produces an increase of the hopping integrals between the surface atoms and those of the first internal layers. The law of variation with distance is assumed to be

$$dd\beta = dd\beta_0 \left(\frac{R_0}{R} \right)^q \quad \beta = \sigma, \pi, \delta \quad (3)$$

where $dd\beta_0$ and R_0 are the bulk equilibrium values. The numerical value of q can be estimated from the ratio between first and second nearest neighbours hopping integrals if one assumes (3) is valid all over this domain of distances, this gives $q = 3.6$ for Mo. We will discuss this point later as the qualitative features we are concerned with now do not depend sensitively on it. Crystal field integrals are not explicitly introduced in our calculation as they are taken into account, in some manner, in the charge neutrality condition.

Taking the experimental value for the contraction (12 %) we have calculated the LDS of the contracted Mo (100) surface and plotted it with the unrelaxed one (Fig. 1). Unexpectedly the surface resonant peak is only slightly modified : it remains at the same energy and it has approximately the same width.

Let us first discuss the non-displacement of the peak which is different from Inglesfield's results [6]

showing a small shift to lower energies. This is obviously related to the assumption made for self-consistency as the position of the peak is very sensitive to the surface atomic level [10]. Here we have assumed that the number of d electrons in the surface orbitals remains the same as in the bulk i.e. there is no s-d transfer. This gives surface atomic levels which have practically the same value in the relaxed and unrelaxed cases. In contrast, Inglesfield uses a model where s electrons are included ; the lowering of the energy of the peak — which has a predominant d character — very likely corresponds to a $s \rightarrow d$ transfer [11] when contracting the first plane. In a tight-binding language this means that the surface s and d atomic levels should be shifted upwards [12]. From Herman and Skillman tables [12] one can infer that the d level is more shifted than the s level, giving a tendency towards a superposition of the two peaks. But this effect is not properly taken into account as Inglesfield achieves charge neutrality by a constant shift of the potential of the surface atomic cell. So the question is still open and we believe that only a completely self-consistent calculation could give an answer.

Friedel [13] has suggested that the resonant peak can be considered as a virtual bound d level interacting weakly with other surface atoms and with the substrate. By means of this picture one can qualitatively understand why the width of the peak does not vary upon contraction. In a simple model of an adatom — with a s orbital on a narrow s band substrate — in the weak coupling limit, the half-width Δ of the virtual bound state is given by [13] :

$$\Delta = \pi \mu_2 n(E_A) \quad (4)$$

where μ_2 is the second moment (proportional to the square of the hopping integrals) of the LDS on the adatoms and $n(E_A)$ is the surface LDS at the atomic level of the adsorbate. This is still qualitatively true in more realistic cases and, for a weakly bound

Fig. 1. — The local density of states on the surface of Mo (100) : unrelaxed surface (broken curve), 12 % contracted surface (full curve).

Fig. 2. — The local density of states on the first subsurface layer of Mo (100) : unrelaxed surface (broken curve), 12 % contracted surface (full curve).

surface atom, $n(E_A)$ must be taken as the LDS on the second layer. Upon contraction, due to (3), μ_2 increases and has a broadening effect, but subsequently the central minimum of the first sublayer LDS is lowered (Fig. 2) and this has a narrowing effect because the surface atomic level is located in it. Then both effects roughly compensate.

As a conclusion, contraction has no strong effect on the surface resonant states but it results in an increase of the densities of states near the band edges (Figs. 1, 2).

To study the stability of the displacement of the surface we will use the model developed by Ducastelle [14] in his study of elastic constants. The cohesive energy E_c of the bulk is

$$E_c = E_B + E_R \begin{cases} E_B = \int_{E_F}^{\infty} E n(E) dE \\ E_R = A \sum_{ij} e^{-pR_{ij}} \end{cases} \quad (5)$$

where E_B is the attractive d band term and E_R is a repulsive pair potential of the Born-Mayer form, accounting for the core-core repulsion between nearest and next nearest neighbour atoms (R_{ij} distance between atoms i and j). By using the bulk equilibrium condition and fitting the experimental cohesive energy E_c and bulk modulus K it is possible to derive values for q , A and pR_0 (R_0 : nearest neighbour distance at equilibrium). The resulting value of q for Mo is quite coherent with that previously quoted. In order to check the sensitivity of our results to parameters we have rather fixed q to that value and used various values of p , A being determined each time by the bulk equilibrium condition.

Assuming that only the first underlayer spacing is modified (by Δd), the equilibrium position of the surface is given by :

$$\frac{d(\Delta E)}{d(\Delta d)} = 0 = \frac{d(\Delta E_B)}{d(\Delta d)} + \frac{d(\Delta E_R)}{d(\Delta d)} \quad (6)$$

ΔE_B and ΔE_R are the variation of attraction and repulsion upon contraction. Because of the increase of the LDS in their wings, ΔE_B is attractive. It is evaluated from the LDS on successive layers and convergence is achieved on the fourth layer. Results for ΔE are given in figure 3 for various contractions. q was fixed to 3.6 and pR_0 has been varied between the

Fig. 3. — The variation ΔE of the total energy of Mo (100) with the contraction for various values of pR_0 (Δd surface displacement, d_0 bulk interlayer spacing).

limits that give the cohesive energy and bulk modulus within 10 % of the experimental value, the best fit being obtained with $pR_0 = 10.6$. We find that contraction stabilizes the system, the equilibrium value is 6 ~ 8 %. This is smaller than in experiment which in turn gives perhaps too large a value [7]. Let us also notice the weak magnitude of ΔE , which shows that the surface energy is not modified by the contraction.

The same model can be applied for W (100) under the assumption that spin-orbit coupling does not play the leading role in the surface equilibrium problem. This is highly probable as it is usually considered as contributing to the Hamiltonian only by one-centre terms which are not modified by contraction. Similar calculations as those for Mo (100) have been carried out for W. Stability is obtained for a 3.5 ~ 4 % surface contraction when q is varied between the values drawn from E_c and K ($q = 3$) or from the ratio between nearest and next nearest neighbour hopping integrals ($q = 3.6$). This is significantly less than for Mo, in agreement with experiment and this arises because the bulk ratio E_R/E_B , roughly equal to q/pR_0 , is smaller for W than for Mo

$$(q_W < q_{Mo}, (pR_0)_W > (pR_0)_{Mo}).$$

Acknowledgments. — It is a pleasure to thank Dr. F. Cyrot-Lackmann for stimulating discussions.

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