

ON THE GEOMETRY OF *d*-ORBITALS: W (001) SURFACE

Štěpán PICK

*The J. Heyrovský Institute of Physical Chemistry and Electrochemistry,  
Czechoslovak Academy of Sciences, 182 23 Prague 8*

Received July 9th, 1987

Low-order moment analysis of the W (001) surface reconstruction leads to the following conclusions: 1) The *d*-orbitals participate in the reconstruction-induced surface-surface coupling, the effect being most pronounced for the  $x^2 - y^2$  orbital. 2) A non-negligible surface-bulk coupling exists and it is due to the  $(x - y)z$  orbital. An additional mechanism favouring the zig-zag mode is suggested.

The W and Mo (001) surface reconstruction belongs to most studied effects observed on metallic surfaces. Despite of considerable effort, some aspects of this phenomenon are still not completely understood. There is a general consent that the zig-zag model of Debe and King<sup>1</sup> (the  $\bar{M}_5$  mode below) is the best candidate for the surface structure. Besides that, most authors agree that the very nature of the reconstruction is related to the surface state peak in the density of electronic states near the Fermi energy  $E_F$ . Recently, a simple model has been suggested describing a direct coupling between surface atoms, predominantly via  $x^2 - y^2$  orbitals<sup>2,3</sup>. This idea finds support in more elaborated theoretical studies. On the other hand, the influence of other *d*-orbitals and of the surface-bulk coupling was also stressed, see e.g. ref.<sup>4</sup>. (For newest results, we refer the reader to recent papers<sup>5,6</sup>.)

## THEORETICAL

It is the aim of the present paper to estimate the importance of various interactions in the reconstruction of W (001). Since it is now clear that the quantitative results are highly sensitive to details of computation both on the semiempirical<sup>7</sup> and *ab initio*<sup>8</sup> level, we try to formulate our conclusions in a rather qualitative way.

It is worthwhile to consider<sup>2,3</sup> the mode  $\bar{X}_3$  ( $L_2$  in ref.<sup>9</sup>,  $(2 \times 1)$  mode in ref.<sup>10</sup>) together with the  $\bar{M}_5$  one\* (Fig. 1). Though the modes have different quasiwave vectors  $\mathbf{Q}$  ( $\mathbf{Q}(\bar{M}) = \pi/a(1, 1)$ ,  $\mathbf{Q}(\bar{X}) = \pi/a(1, 0)$ ;  $a$  is the lattice constant), they resemble each other locally. For our purpose, it is more instructive to choose the orientation (polarization) of the  $\bar{M}_5$  mode along the  $[1, 0]$  direction rather than

\*  $\bar{M}$  and  $\bar{X}$  is a standard surface physics notation for high-symmetry quasiwave vectors  $\mathbf{Q}$ , whereas the indices "3", "5" refer to irreducible representations of the symmetry group  $C_{4v}$ .

along the  $[1, 1]$  one observed experimentally<sup>1</sup>. It is known<sup>2,3,9</sup> that the choice of polarization will influence the energy starting with terms which are of 4th order in deformation and are not taken into account below. (To study the  $[1, 1]$  orientation, one needs make the change  $\{xz, yz\} \rightarrow \{(x+y)z, (x-y)z\}$  in Table I.)

The possibility to express the electronic energy of a transition metal crystal as a function of the 2nd moment  $m_2$  of the electronic Hamiltonian  $\mathbf{h}$  has been discussed recently<sup>11,12</sup>. (The moment of  $k$ -th order is defined as  $m_k = \sum_j \langle \varphi_j | \mathbf{h}^k | \varphi_j \rangle$ , where the sum is taken over the five  $d$ -orbitals  $3z^2 - r^2$ ,  $x^2 - y^2$ ,  $xy$ ,  $xz$ ,  $yz$ . The zero of energy is chosen to give  $\langle \varphi_j | \mathbf{h} | \varphi_j \rangle = 0$ , i.e.  $m_1 = 0$ . The  $s$ ,  $p$  orbitals are ignored

TABLE I

Particular contribution to the change of the surface atom 2nd moment  $\Delta m_2$  (arbitrary units) for  $\bar{M}_5$  and  $\bar{X}_3$  modes; s-s and s-b denote surface-surface and surface-bulk contributions, respectively. See the text for details

Orbital	$\bar{M}_5$			$\bar{X}_3$		
	s-s	s-b	total	s-s	s-b	total
$3z^2 - r^2$	0.10	0.05	0.16	0.12	0.05	0.17
$x^2 - y^2$	0.28	0.05	0.33	0.36	0.05	0.40
$xy$	0.16	0.02	0.18	0.14	0.02	0.17
$xz$	0.15	0.03	0.18	0.14	0.03	0.17
$yz$	-0.02	0.18	0.16	0.00	0.18	0.18
all orbitals	0.67	0.33	1.00	0.76	0.33	1.10

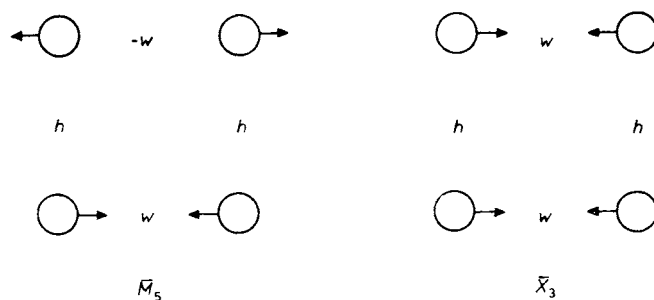


FIG. 1.

The geometry of  $\bar{M}_5$  and  $\bar{X}_3$  deformation modes, together with the matrix elements  $h$  and  $w$  (see the text). Open circles represent the surface atoms

supposing that they contribute implicitly to the energy stabilization via screening of any essential deviation from local charge neutrality.) There are many reasons to believe that such an approximation, although not highly accurate and not of quite general applicability, has a sound basis. As a consequence, the change of electronic energy for a small deformation should be proportional to the corresponding change  $\Delta m_2$  of  $m_2$ .

## RESULTS AND DISCUSSION

In Table I, we present the resulting  $\Delta m_2$  for  $\bar{M}_5$  and  $\bar{X}_3$  modes, and we show also the contribution from particular *d*-orbitals and decomposition into parts associated with surface-surface and surface-bulk interactions. Only the contribution quadratic in deformations has been included and the results are normalized to yield  $\Delta m_2(\bar{M}_5) = 1$ . To compute  $\Delta m_2$ , LCAO parameters of ref.<sup>7</sup> for tungsten were employed and a possible reconstruction in the subsurface layer or a surface layer relaxation was ignored. Also we did not include a small change in the surface potential which can hardly influence our rough estimates.

The results for  $\bar{M}_5$  and  $\bar{X}_3$  geometries are similar. The surface-surface interaction is responsible for about 2/3 of the electronic energy change. The  $x^2 - y^2$  orbital is the most active one, although other *d*-orbitals contribute as well. (Note that in ref.<sup>3</sup>, a possible generalization of the “ $x^2 - y^2$  model” to other orbitals is given.) The orbitals mediating interaction within the surface do not change their interaction with bulk atoms appreciably. The situation with the  $yz$  orbital ( $(x - y)z$  orbital for the [1, 1] polarization of the  $\bar{M}_5$  mode) which dominates in the surface-bulk coupling is exactly reversed.

Due to a lengthening of surface bonds in the [0, 1] direction,  $\Delta m_2$  is even slightly lower for the  $\bar{M}_5$  mode. In ref.<sup>10</sup>, the  $\bar{X}_3$  mode reconstruction was shown to be energetically unfavourable; this result calls for explanation. As a possible hint, analysis of an isolated “surface” layer is useful. A simple calculation (exploiting the high symmetry of the system) shows that the deformation described by the operator  $\mathbf{w} = (\boldsymbol{\eta}, \text{grad } \mathbf{h})$  couples the “bonding” states  $|i, \mathbf{k}\rangle$  ( $i = 1-5$ ) with energy  $E(\mathbf{k}) < 0$  to “antibonding” ones,  $|i, \mathbf{k} + \mathbf{Q}\rangle$ , having energy  $E(\mathbf{k} + \mathbf{Q}) = -E(\mathbf{k}) > 0$  in the  $\bar{M}_5$  case. (Above,  $\boldsymbol{\eta}$  is the deformation and  $\mathbf{h}$  is the unperturbed electronic Hamiltonian; the operator  $\mathbf{w}$  plays a central role<sup>2,3,13</sup> in the stability problem. Finally,  $|i, \mathbf{k}\rangle$  are the Bloch electronic states with quasiwave vector  $\mathbf{k}$ , based on the five *d*-orbitals.) For the  $\bar{X}_3$  mode, the resulting picture is complex, showing no clear “bonding-antibonding” coupling of states.

It is interesting, however, that also reasons based on local surface geometry analysis support the  $\bar{M}_5$  reconstruction. It has been found<sup>14</sup> that the (absolute value of) electronic energy is a decreasing function of the 4th moment  $m_4$ . This conclusion is a result of numerical tests performed for common transition metal

surface problems; nevertheless, a rigorous analysis is possible in the limiting cases  $m_4 \rightarrow \infty$  and  $m_4 \rightarrow m_2^2$  (supposing  $m_1 = m_3 = 0$ ) by using the continuous fraction technique<sup>14</sup>. A more careful examination of the change  $\Delta m_4$  of  $m_4$  reveals that an essential part of contributions to  $m_4$  change from positive to negative when going from  $\bar{X}_3$  to  $\bar{M}_5$ . Without going into details, let us consider an instructive example. As it is seen from Fig. 1, the typical surface contribution to  $\Delta m_4$  changes from  $h^2 w^2$  to  $(-h^2 w^2)$  ( $h = \langle \varphi(0, 0) | \mathbf{h} | \varphi(0, a) \rangle$ ,  $w = \langle \varphi(0, 0) | \mathbf{w} | \varphi(a, 0) \rangle$ , where  $\varphi(\mathbf{r})$  is an appropriate  $d$ -orbital (e.g.  $\varphi = x^2 - y^2$ ) centred at point  $\mathbf{r}$ ). As Pancíř<sup>15</sup> noticed, some formal analogies between the problem considered here and organic chemistry rules can be traced. For example, our “ $m_4$ -rule” has its counterpart in the fact that formation of four-membered conjugated rings is unfavourable. One can speculate that such an analogy reflects general properties of a larger class of systems for which the well known Hückel rules<sup>16</sup> on aromaticity of cyclic conjugated systems can be rederived due to a simple geometrical structure.

In conclusion, two mechanisms mediated by different  $d$ -orbitals can destabilize the ideal surface geometry: 1) interactions within the surface (probably more important), and 2) surface-bulk coupling. The special geometry of the zig-zag  $\bar{M}_5$  mode appears to be energetically more favourable due to more subtle effects.

*Note added in proof:* The  $m_4$ -rule is valid for systems with roughly half-filled electronic bands, cf. Pick Š.: Collect. Czech. Chem. Commun, in press.

#### REFERENCES

1. King D. A.: Phys. Scr. *T4*, 34 (1983).
2. Tomášek M., Pick Š.: Surf. Sci. *140*, L279 (1984); Czech. J. Phys., *B 35*, 768 (1985).
3. Tomášek M., Pick Š.: Physica (Utrecht), *B 132*, 79 (1985).
4. Fu C. L., Freeman A. J., Wimmer E., Weinert M.: Phys. Rev. Lett. *54*, 2261 (1985).
5. Wang X. W., Weber W.: Phys. Rev. Lett. *58*, 1952 (1987).
6. Joubert D. P.: J. Phys., *C 20*, 1899 (1987).
7. Legrand B., Tréglia G., Desjonquères M. C., Spanjaard D.: J. Phys., *C 19*, 4463 (1986).
8. Singh D., Su-Huai Wei, Krakauer H.: Phys. Rev. Lett. *57*, 3292 (1986).
9. Fasolino A., Santoro G., Tosatti E.: Phys. Rev. Lett. *44*, 1684 (1980).
10. Terakura I., Terakura K., Hamada N.: Surf. Sci. *111*, 479 (1981).
11. Spanjaard D., Desjonquères M. C.: Phys. Rev., *B 30*, 488 4822 (1984).
12. Broksch H. J., Bennemann K. H.: Surf. Sci. *161*, 321 (1985).
13. Pearson R. G.: *Symmetry Rules for Chemical Reactions: Orbital Topology and Elementary Processes*. J. Wiley, New York 1976.
14. Pick Š.: Czech. J. Phys., *B 37*, 777 (1987).
15. Pancíř J.: Private communication.
16. Murrell J. N., Kettle S. F. A., Tedder J. M.: *Valence Theory*. Wiley, London 1965.

Translated by the author.