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INSTABILITY AND RECONSTRUCTION OF THE W (001) SURFACE

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Résumé - Nous introduisons une approche simple et qualitative du type Jahn-Teller pour décrire la reconstruction de la surface (001) du W et nous l'appliquons à l'étude des modes de déformation de haute symétrie. Ceux-ci sont séparés en deux groupes ("in-plane" et "buckled"), le mode du type $M_5$ étant le plus favorable.

Abstract. - A simple qualitative pseudo Jahn-Teller approach to the reconstruction of the W (001) surface is introduced and the results of its application to high-symmetry deformation modes are presented. They are split into in-plane and buckled modes, the $M_5$ zig-zag mode being most promising.

1. Introduction. - Interest in reconstruction of the W and Mo (001) surface and efforts invested led to the clarification of problems involved and crystallization of main ideas behind it /1-4/. Controversial points between experiment and theory still remain /5,6/ and it is not clear whether the phenomenon is the result of a general instability of the (001) surface or whether there exists a pronounced single deformation mode. However, local theory is getting more popularity now than in the past as it is not surprising with metals exhibiting a covalent component of bonding. Such a theory has to reflect correctly local features of the electronic structure and exhibit the inherent local symmetry. For the W and Mo (001) surface, these local features are ascribed to Shockley surface states (dangling bonds, SS) at $E_F$ /7-10/, also called the "central" peak /11/ in the local density of states. Local symmetry of the surface, of main importance here, is given by the symmetry of the orbitals forming these SS, and by the potential acting upon them. The above requirements are not met by earlier one-band (1 orbital) theories that can use selection rules based on translational symmetry only and are limited to the Peierls mechanism. The dielectric response calculations /2,12,13/ also do not offer full qualitative information on the reconstruction mechanism. Naturally, two-band (2 orbital) models /14,15/ grasp chemistry and local properties (symmetry) of the surface better and can lead to a richer scope of qualitative conclusions than one-band models /16/. Due to the important role of dangling bonds in surface electronic properties, the introduction of the concept of "broken covalency" /17-19/ appears to be natural here. As a rule, the latter is used when intrinsic lattice instability leads to the loosening of electrons from old bonds and so enables the electrons to couple in a new way. Here, the loosening is done by a mechanical process creating the surface.

2. Local model of the electron-phonon interaction. - In the present work, electron-phonon coupling is considered crucial for the reconstruction, SS are supposed to be the main electronic ingredient in this coupling. All the experimental and theoretical information presently available shows that there are two almost degenerated bands
of SS at $E_p$ on the W and Mo (001) surface stemming from the hybridization of the $x^2-y^2$ and $xy$ orbitals with the appropriate linear combinations of $xz$ and $yz$ orbitals. Resulting surface hybrids are non-bonding with respect to the bulk, since in each hybridizing pair, the functions have opposite parity with respect to reflection in the surface plane /20/. According to /10,11/, the $x^2-y^2$ orbital is well localized in the surface layer while the $xy$ orbital shows /11/ some interaction with the subsurface layer and can be sensitive to interplanar deformations (see the $\Gamma_8$ mode below). Following Friedel /11/, atoms in a two-dimensional layer provide a sharp "central" peak only if their interactions with the neighbours superpose coherently, which is possible for a layer with highly symmetrical geometry. The latter imposes severe restrictions on the values of orbital-based matrix elements. If one atom in the surface is displaced perpendicularly, the symmetry of its neighbourhood is preserved and no drastic change in the "central" peak occurs. However, if the latter geometry is locally destroyed by one atom displacement parallel to the crystal surface, the coherence effect disappears and the "central" peak is split. This leads to the decrease $\delta E$ of the electronic energy

$$\delta E = - \sum_{\alpha,\beta} \eta^2 |<a|w|b>|^2/(E_b-E_\alpha)$$

(1)

in the pseudo Jahn-Teller (vibronic) theory /21,22/, according to which the most perspective deformation modes $\mathcal{Q}$ are estimated here. The latter will give the largest change in the form of the "central" peak. $|a\rangle$, $|b\rangle$, $E_a$ and $E_b$ are the wave functions and energies of occupied (a) and empty (b) SS of the original (unreconstructed) system, and $w$ is the first derivative of the electronic energy (potential function) with respect to $\mathcal{Q}$. As seen from (1), "broken covalency" yielding a global band of dangling bond states around $E_p$ ideally fits the general instability condition saying that there should exist "soft" excited states with symmetry lower than that of the ground state. Vis-a-vis the electron-phonon matrix element $w_{ab} = <a|w|b>$, (1) exploits the symmetry fully since $w_{ab}$ represents a selection rule. Namely, for some deformations $\mathcal{Q}$, $w_{ab}$ contains a much larger amount of new non-zero orbital-based matrix elements than for other $\mathcal{Q}$. This simple behaviour prompts one to introduce /22/ a purely local molecular field model which considers only one single atom carrying the mentioned four d-orbitals from $E_p$ giving rise to the "central" peak.

For in-plane deformations ($\overrightarrow{\mu_1}$, $\overrightarrow{\mu_2}$, $\overrightarrow{\mu_3}$, $\overrightarrow{\mu_4}$) to be considered below /22/, the change of the molecular field potential $\delta V$ behaves like x or xy and hence leads to the repulsion in the pairs of orbitals forming the SS. This is a sort of "rehybridization" that can be looked upon as a result of the new bonding mechanism of the reconstructed surface in which ("saturated") dangling bonds are now engaged.

On the other hand, for buckled modes, $\delta V$ is either fully symmetric ($\overrightarrow{\mu_1}$) or behaves like $x^2-y^2$ ($\overrightarrow{\mu_3}$), therefore, no repulsion ($\overrightarrow{\mu_4}$) or only a slight splitting ($\overrightarrow{\mu_3}$) of $xz$, $yz$ orbitals is to be expected /22/.

3. Considerations of the k-space symmetry. - There exists a relationship /22/ between Peierls' mechanism and the pseudo Jahn-Teller effect in the delocalized Bloch function (BF) picture. Consider the (12x12)R45° reconstruction which occurs both for buckled $\overrightarrow{\mu_1}$ and zig-zag $\overrightarrow{\mu_5}$ modes. Of special importance here are directions $\overrightarrow{\Sigma}_1'' \parallel [1,1]$ and $\overrightarrow{\Sigma}_2'' \parallel [1,-1]$, the centres $\overrightarrow{X}_1^4$ and $\overrightarrow{X}_2^4$ of which fall on the boundary of the new surface Brillouin zone. Due to purely translational symmetry, for $\overrightarrow{\mu_1}$ each SS branch is split in $\overrightarrow{X}_1^4$ points. Hence, one could assume that buckled deformations would be well described by the BF picture. If $\overrightarrow{\Sigma}_1'' [1,1]$ holds, the same is true for $\overrightarrow{\mu_5}$ in $\overrightarrow{X}_1^4$. In $\overrightarrow{X}_2^4$, however, no splitting occurs for $\overrightarrow{\mu_5}$ and a single $\overrightarrow{X}_2^4$ band. Owing to the presence of a glide plane, the folded SS branches are pinned /10/ in the 2-dim. projective irreducible representation $P'$.
of the group C\textsubscript{2v}. Nevertheless, when considering both the two SS bands of the original (lxl) surface, repulsions invoked by symmetry also appear. From this one infer, that it is important to include a larger number of orbitals on the atom than one.

4. Enumeration of reconstruction-active surface modes /22/. Let us enumerate all the transitions (deformation modes) which, due to the change of scalar parameters, the (lxl) surface can undergo continuously according to the Landau theory /23/. Only deformations in the surface layer will be considered and the surface relaxation (\text{P1}) will be omitted. The latter theory singles out the points \(k = (0,0)\), \(\bar{\Gamma} = (\frac{\pi}{a} (1,0), \frac{\pi}{a} (0,1))\) and \(\bar{\Pi} = (\frac{\pi}{a} (1,1))\) from the surface Brillouin zone and considers the following irreducible representations (IR) as the only candidates for the transition (\(\varphi_k = \cos \theta k\)).

<table>
<thead>
<tr>
<th>IR</th>
<th>Basis of IR</th>
<th>Sign (\lambda)</th>
<th>Structure</th>
<th>Atoms with different environments:</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\bar{\Gamma}_5)</td>
<td>(\tilde{x} \varphi_k), (\tilde{y} \varphi_k)</td>
<td>+</td>
<td>(\text{lx}1)</td>
<td>no no</td>
</tr>
<tr>
<td></td>
<td>(\tilde{y} \varphi_k)</td>
<td>-</td>
<td>(\text{lx}1)</td>
<td>no no</td>
</tr>
<tr>
<td>(\bar{\Gamma}_1)</td>
<td>(\tilde{x} \varphi_k), (\tilde{y} \varphi_k)</td>
<td>+</td>
<td>(\text{lx}1)</td>
<td>no no</td>
</tr>
<tr>
<td></td>
<td>(\tilde{y} \varphi_k)</td>
<td>-</td>
<td>(\text{lx}1)</td>
<td>yes no</td>
</tr>
<tr>
<td>(\bar{\Gamma}_3)</td>
<td>(\tilde{x} \varphi_k), (\tilde{y} \varphi_k)</td>
<td>+</td>
<td>(\text{lx}1)</td>
<td>no yes</td>
</tr>
<tr>
<td></td>
<td>(\tilde{y} \varphi_k)</td>
<td>-</td>
<td>(\text{lx}1)</td>
<td>no yes</td>
</tr>
<tr>
<td>(\bar{\Gamma}_4)</td>
<td>(\tilde{x} \varphi_k), (\tilde{y} \varphi_k)</td>
<td>+</td>
<td>(\text{lx}1)</td>
<td>no yes</td>
</tr>
<tr>
<td></td>
<td>(\tilde{y} \varphi_k)</td>
<td>-</td>
<td>(\text{lx}1)</td>
<td>no no</td>
</tr>
<tr>
<td>(\bar{\Pi}_1)</td>
<td>(\tilde{x} \varphi_k)</td>
<td>+</td>
<td>((\sqrt{2} \times \sqrt{2}) \times R45^\circ)</td>
<td>yes no</td>
</tr>
<tr>
<td></td>
<td>(\tilde{y} \varphi_k)</td>
<td>-</td>
<td>((\sqrt{2} \times \sqrt{2}) \times R45^\circ)</td>
<td>no no</td>
</tr>
</tbody>
</table>

Note that for 2-dim. IR, it is necessary to add the sign of the cubic anisotropy term \(\lambda(\gamma_1^4 + \gamma_2^4)\) in the thermodynamical potential expansion to fully specify the deformation mode.

One remarks, that for some \(\bar{\Pi}_5\), atoms in the surface and subsurface layer exist which differ by the geometry of their environment, so favouring a partial charge transfer. For such situations, one can suspect that ionic superlattices can emerge /16/ which are generally not advantageous on energetical grounds for metals (naturally in the absence of adsorbates or external electric fields). Hence, the \(\bar{\Gamma}_5\) and \(\bar{\Pi}_5\) deformations should be more advantageous. They exhibit an interesting extremal property, namely, that \(\bar{\Gamma}_5\) (rigid shift) maximizes the interplanar deformation as compared with the surface one, the opposite being true for \(\bar{\Pi}_5\). In particular, for a coordinate system connected with a surface atom and for a suitable normalization, the equation \(\mathbf{R}(\bar{\Pi}_5) = \mathbf{R}(\bar{\Gamma}_3) + \mathbf{R}(\bar{\Gamma}_4)\) holds for the displacements of the first surface neighbours of this atom and similarly, \(\mathbf{R}(\bar{\Pi}_5) = \mathbf{R}(\bar{\Gamma}_3) = \mathbf{R}(\bar{\Gamma}_4)\) is true for displacements of its subsurface neighbours.
5. Phenomenological phonon model. - As has been found /24,25/, the ideally terminated (001) surface of W exhibits a rich scope of surface phonons which lower their frequencies simultaneously /25,26/ and thus can be considered as candidates for reconstruction. The $M_1$ and $X_3$ modes are the most promising /25,27/ of them (the $F_5$ mode does not appear in this particular model). They are expected to soften earlier than the remaining $X_1,4$ ones. Results obtained for W and Fe show that there are no marked qualitative differences between these two systems /24,25/. One concludes, that to discover such differences, the surface electronic factor has to be included explicitly.

6. Discussion. - The present simple and heuristic approach leads to the following conclusions:

Local features of SS cause a genuine splitting of deformations on the W (001) surface into buckled and in-plane ones. For the latter, local electronic properties appear to be decisive whereas for the former, the BF picture seems suitable. Most promising is the $M_5$ (and perhaps the $F_5$) mode, although a global lowering of stability of the (001) surface is to be expected. The $F_5$ mode can intervene in the optimization of surface-subsurface interactions if relaxation is not sufficient /28/. Under special experimental conditions, also the $M_1$ and $X_3$ modes could be important. For $M_1$, this can happen in field-emission where this mode can be energetically stabilized by the external electric field, especially due to the presence of the Tamm surface state at EF /16,29/. However, this state is insensitive to the reconstruction (according to photoemission results /30/), which shows a preference of the $M_5$ mode under normal conditions (absence of electric field). The $X_3$ reconstruction, in its turn, can be according to Willis /1/ induced by the adsorption. The importance of the $M_5$ mode is supported also by the results on hydrogen chemisorption. Naturally, the sign of the cubic anisotropy constant $A$ changes as a result of chemisorption /3,4/.

As far as the weakly incommensurate Mo (001) reconstruction is concerned /31/, symmetry reasons prevent a strict separation of in-plane and buckled modes in this case. However, the situation will not lie far from the commensurate one of W (001).

Recent calculation, similar in spirit to /14/, was performed for the W and Ta (001) surface /32/. It includes explicitly correlation effects and leads to conclusions in some controversy to the commonly accepted point of view. Naturally, correlation in surfaces is a difficult problem which is still at the very beginning.

References

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/26/ PICK Š. and TOMASEK M., Surface Sci., in press.