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Electronic structure of a Pd monolayer on Nb(110)

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We present angle-resolved photoemission data and calculations for Pd monolayers adsorbed on Nb(110). We find good overall agreement between theory and experiment and demonstrate directly that the Pd states have a noble-metal configuration on the Nb surface but not as a free monolayer. We discuss the implications for hydrogen uptake in this system.

There has recently been considerable interest in thin layers of palladium on niobium,[1-3] particularly in connection with their influence on hydrogen absorption by the underlying metal. The experiments were performed on recrystallized foils of Nb which produced sharp low-energy-electron diffraction patterns indicating a (110) surface. At one monolayer coverage the Pd is commensurate with this structure. It is interesting that the near-neighbor distance for Nb(110) planes is 2.86 Å, only about 4% larger than that for Pd(111) planes which is 2.75 Å. So it is perhaps not so surprising that the Pd monolayer can distort and become commensurate with the underlying Nb. This structure also has an interesting interaction with hydrogen. At one monolayer Pd the system does not adsorb hydrogen, i.e., the sticking coefficient is zero.[3,4] This is unusual because the sticking coefficient for clean Nb and clean Pd are both large in the range of 0.2–0.6 as determined by photoemission and work-function change.[5]

In this paper we present angle-resolved photoemission data for the Nb + Pd system and electronic structure calculations for Pd monolayers and Nb films with adsorbed palladium. This represents the first detailed comparison of angle-resolved photoemission data and theory for a metal-on-metal system.

The two-dimensional Brillouin zone is shown in Fig. 1. The (110) face of a bcc crystal has C_{2v} symmetry so at the zone center (and at $\bar{N}$) the states can be classifed as Σ_i where $i = 1-4$. To fix ideas we note that s, d_{z^2}, and $d_{x^2-y^2}$ belong to Σ_1, d_{xy} belongs to Σ_2, $d_{yz,xz}$ belongs to $\Sigma_{3,4}$. Along $\bar{\Gamma}$-$\bar{N}$ the only symmetry is a vertical reflection plane, so Σ_1 and Σ_4 can mix, as can Σ_2 and Σ_3. Similarly, along $\bar{\Gamma}$-$\bar{H}$, Σ_1 and Σ_3 mix, as do Σ_2 and Σ_4. States along these lines can be classifed by even or odd symmetry under reflection. In the isolated monolayer there is an additional symmetry, reflection in the plane ($z \rightarrow -z$), which prevents these mixings. This fact goes a long way toward explaining the difference between the single layer and the multilayer systems.

The experiment was performed on 0.005-in. Nb single crystals. Pd films were evaporated onto the

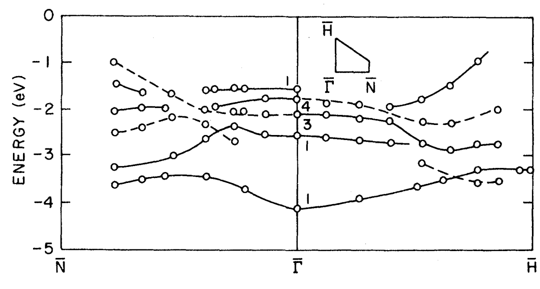

FIG. 1. Experimental dispersion of Pd-induced states on Nb(110). Also shown is the surface Brillouin zone. Solid lines are states which are even and dashed lines states which are odd under reflection. Symmetry labels are explained in the text.

(110) face and angle-resolved photoelectron spectra obtained with a Vacuum Generators analyzer and a discharge lamp. Both the emission angle and the angle of incidence of the light could be varied so that the dispersion of the Pd-like states could be studied and the symmetry identified by polarization selection rules. The results are shown in Fig. 1. The states are measured relative to the Fermi level of the Nb-Pd system. The symmetry labels, obtained from the selection rules, are given for the zone center. In addition, along the two symmetry lines, states which are even under reflection are solid while states odd under reflection are dashed. A more complete description of the experimental results is in preparation.[5]

In order to understand these results we have performed two calculations. The first is a self-consistent linear augmented plane-wave (LAPW) calculation on a five-layer film of Nb with a Pd monolayer on each side of the film. The lattice constant was taken to be 3.30 Å as in bulk Nb and the Pd atoms were placed at the in-plane sites which the next Nb atoms would occupy but with an interplanar distance of 2.27 Å based on a Nb-Pd bond length corresponding to the sum of the metallic radii. The LAPW method has been described in detail elsewhere.[6] Briefly, there are no shape approximations to the potential and the self-consistent spectrum was converged to 0.03 eV. Approximately 280 LAPW's were used. The exchange-correlation potential was given by the Wigner interpolation formula. The charge density was obtained by sampling the surface Brillouin zone at three special points. Palladiumlike features could be identified by the charge within the Pd muffin-tin spheres and also by the small splittings produced by the interaction between the two Pd layers on the front and back sides of the film. States with large Pd content are shown in Fig. 2. The symmetry labels at $\bar{\Gamma}$ and $\bar{N}$ are given as indicated. As in Fig. 1, states which are even under reflection along the two symmetry lines are solid while those which are odd are dashed. Most of the Pd features overlap Nb bands and are resonances rather than surface states. However, the Pd d-band manifold overlaps mainly s-like Nb bands and the coupling is not strong, which leads to sharp resonances. The dotted portions indicate that the states are not well localized on the Pd but have substantial Nb content as well. The Nb-like states form a dense background which is not shown.

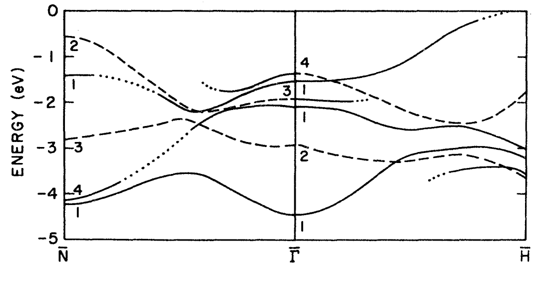

FIG. 2. Calculated states for a bcc(110) Nb film with adsorbed Pd monolayer. States which are dotted are strongly hybridized with Nb. Solid and dashed lines same as Fig. 1.

The second calculation was for a Pd monolayer with the geometry of the Nb(110) plane (see Fig. 3). As noted earlier this is similar but not the same as an fcc Pd(111) monolayer. A (non-self-consistent) film muffin-tin potenial was obtained using a planar generalization of the Mattheiss construction[7] and the Gunnarsson-Lundqvist exchange-correlation potential.[8] The states were calculated with the layer Korringa-Kohn-Rostoker method as presented by Kar and Soven.[9] The states are labeled as in previous figures. The energies are given relative to the muffin-tin zero (-9.6 eV). Since the calculation is not self-consistent, no attempt was made to find the work function. We also calculated the relative charge in the various angular momentum basis functions within the muffin-tin sphere for the states at $\bar{\Gamma}$. The dominant components are given in Table I.

In comparing these results we note first that there is good overall agreement between the two calculations and the experiment. We conclude that the interaction between the two metals is weak in the sense that the spectra are described reasonably well by those of an isolated monolayer. This is particularly interesting for the lowest state at Γ which one is tempted to think of as s-like in analogy with the lowest state at Γ in the bulk. Yet it is quite well defined on the surface, not part of a free-electron-like band extending into the Nb. We believe that one reason for this is that the state contains a significant admixture of d_z^2 and $d_{x^2-y^2}$ which would be forbidden at Γ in the bulk.

Another feature is that the Σ_2 state is not seen experimentally near Γ. This is simply a consequence of the dipole selection rule which forbids transitions between states of Σ_2 and Σ_1 and the fact that for nor-

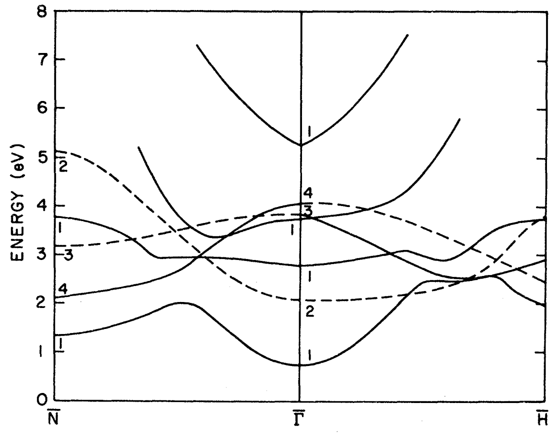

FIG. 3. Calculated states for a bcc(110) Pd monolayer. Solid and dashed lines same as Fig. 1.

TABLE I. Symmetry and orbital character of Pd states in Fig. 3. State 1 is the lowest, state 7 the highest.

States at $\bar{\Gamma}$	Symmetry	Dominant component
7	Σ_1	p_z
6	Σ_4	d_{xz}
5	Σ_3	d_{yz}
4	Σ_1	$d_{x^2-y^2}$
3	Σ_1	d_{z^2}
2	Σ_2	d_{xy}
1	Σ_1	s,d

mal emission only Σ_1 final states are detected.[10] This selection rule is not strictly obeyed off normal but the emission must still be suppressed until well out in the zone. There is also excellent agreement between the calculated and measured work functions. In a separate calculation the work function for a seven-layer Nb(110) film was found to be 4.84 eV and that of the Pd-Nb system 4.72 eV. Experimentally, the work function for Nb(110) is 4.87 eV and the change with one monolayer of Pd is roughly -0.1 eV.

There are, however, differences. Comparing first the two calculations, there are two principal effects. First, in the full calculation there are gaps due to avoided crossings of bands which cross in the monolayer. This can be traced to the fact that the monolayer has an extra symmetry, reflection in the plane of the film which prevents the states from mixing. Secondly, the ordering of the states is not the same. For example, at Γ the third state from the bottom with Σ_1 symmetry, which is predominantly $d_{x^2-y^2}$, lies lower than the $\Sigma_{3,4}$ states, while in the full calculation it lies between them. we believe this is due to level repulsion between the Nb and Pd Σ_3 and Σ_4 states in the full calculation. Similar reorderings occur near $\bar{H}$. Comparing the LAPW calculation with experiment we find that the principal discrepancy is the ordering of the levels at $\bar{\Gamma}$. Experimentally, the Σ_1 state near -1.5 eV lies above the $\Sigma_{3,4}$ states, while the theory has it in between. We speculate that this is due to the bond length chosen which was the sum of the Nb and Pd metallic radii. Had we assumed a constant volume per atom and recalculated the Pd metallic radius in the bcc structure it would have been less by about 0.04 Å. Now, the $\Sigma_{3,4}$ levels are being repelled by states of the same symmetry in Nb which lie higher. Therefore, pushing the Pd layer closer would be expected to cause a lowering of those states without much affecting the Σ_1 (which is predominantly $d_{x^2-y^2}$ and therefore lies in-plane). This is consistent with the fact that in the isolated layer the $\Sigma_{3,4}$ states lie above the Σ_1.

Our angle-resolved photoelectron spectroscopy and LAPW calculations both show directly that the Pd d-like states lie below the Fermi level. Therefore the Pd density of states resembles that of a noble metal. This point is consistent with the disappearance of the Fano-type profile for Pd 4p core level emission in this system.[3] Comparison with the monolayer calculation shows that the noble-metal configuration is a consequence of the interaction with Nb. The isolated layer clearly does not have a noble-metal configuration because the large s component on the lowest state at $\bar{\Gamma}$ implies that the Fermi level must fall below the top of the d complex. Also, for the starting iteration of the LAPW calculation, where the potential is based on overlapping atomic charges,[7] the Pd d states were still above the Fermi level. The center of gravity of these states subsequently drops by 2 eV as a reuslt of charge rearrangement. This picture is consistent with calculations on Nb-Pd alloys as well.[11]

As for the effect on the hydrogen uptake it is known that Cu and free-electron metals do not dissociate H_2, while Ni and Pd do.[12,13] It has been shown that dissociative chemisorption of H_2 on copper is an activated process with an activation barrier of 0.1 $-$ 0.2 eV on various surfaces.[13,14] Since our work shows that the electronic structure of the Pd-Nb system resembles Cu, it is likely that this system also has such a barrier and that this is the explanation for the observed zero sticking coefficient.[5] It has also been suggested that an energy accommodation effect rather than a barrier may be responsible.[15] This system is interesting because it shows that the electronic properties of a transition metal can be altered by interactions with its neighbors and rendered inert to hydrogen. Recently, a similar mechanism has been invoked by Tauster and co-workers[16] who have studied catalysts composed of group VIII metals dispersed on TiO_2. They have found the same effect; these catalysts do not chemisorb hydrogen but, in addition, found that these systems are excellent methanation catalysts. It would be very interesting to examine the catalytic properties of the Pd-Nb system.

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[10] For example, the matrix element

$$\int \psi_f^*(\vec{r})(\vec{\epsilon}\cdot\vec{r})\psi_{xy}(\vec{r})\,d^3r$$

vanishes unless ψ_f contains p_x, p_y, f_{xyz}, f_{xz^2}, or f_{yz^2}, but these functions have nodes normal to the surface.

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