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Brief Reports

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Calculation of electronic structure of Pd on Nb(110) interface

Vijay Kumar
Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-1000 Berlin 33, Germany

K. H. Bennemann*
Institut für Theoretische Physik, Eidgenossische Technische Hochschule, Zürich, Switzerland

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A theoretical study of the atomic and electronic structure of the Pd on Nb(110) interface is presented. In the commensurate (C) phase the interaction of Pd with Nb is strong and the Pd d band shows two resonant d states. The density of states at the Fermi energy is small but increases in the incommensurate (IC) structure. The C-IC transformation is predicted to occur when some Pd atoms occupy sites in the second layer.

Recent observations[1] of high hydrogen-uptake rate into Nb and Ta upon deposition of thin Pd layers aroused considerable interest in the detailed investigation of the atomic[2] and the electronic structure[3,4] of this interface. An interesting result of these experiments was the occurrence of structural transformation from commensurate (C) Pd*(110) to incommensurate (IC) Pd(111) overlayer for about a monolayer coverage and a simultaneous increase in the H-uptake rate. Low-energy electron diffraction[2] (LEED) and angle-resolved (AR) photoemission energy distribution[4] (PED) measurements revealed that at submonolayer coverages Pd occupies Nb sites. However, it was not clear how the Pd(111) structure was completed at about 1.3–1.4 monolayer coverage. Angle-integrated (AI) PED showed[3] two resonant d states at submonolayer coverages and for more than three Pd(111) overlayers the PED was similar to the one observed on a Pd(111) surface.[5] But it could not reveal any information about the structure of the interface. We present calculations of the electronic local density of states (LDOS) $\rho(E)$ of the Pd on Nb(110) interface and of the interface energies in the C and IC structures. It is shown that from the behavior of $\rho(E)$ in the two structures one can learn interesting facts about the C-IC transformation.

First, in the C structure one notes an increase of about 4% in the nearest-neighbor distance as compared to the bulk for Pd atoms deposited on Nb(110). The coordination is lower than in any low index plane of Pd. In the Pd(111) configuration the Pd overlayer can accomodate about 15% more atoms as compared to the Nb layer. Though the possibility of small contractions cannot be ruled out, we conclude in accordance with LEED[2] that the Pd*(110) structure transforms into Pd(111) structure in islands which grow with the addition of Pd. However, it seems likely that by the time the first Pd(111) layer is completed some Pd occupies sites in the second layer. Results of our LDOS calculations also support this possibility.

As the photoemission data[3,4] suggest, we consider for the determination of the electronic structure only the $4d$ electrons. These are treated in the tight-binding approximation. To calculate $\rho(E)$ the recursion method[6] is then best suited since the structural changes can be easily incorporated. The occupancy of the bulk d bands is taken to be 3.6 for Nb and 9.5 for Pd. The hopping integrals between Nb and Pd are taken equal to the mean of those of pure Nb and Pd and their distance dependence is assumed to follow R^{-5} law.[7] For Nb(110) and Pd(111) surfaces the center of gravity of the surface band is determined self-consistently from $\epsilon = \epsilon^0 + U(n - n^0)$. U is the intra-atomic Coulomb interaction taken to be 3.0 eV and $n(n^0)$ is the charge per atom per spin in the surface (bulk). In the occupied band the Nb LDOS shows (inset Fig. 1) a main peak at −0.037 Ry as also observed.[8] For Pd(111), $\rho(E)$ shows (inset Fig. 2) peaks just below the Fermi energy E_F and at energies −0.037, −0.074, −0.136, and −0.194 Ry. Photoemission results[9,10] also show peaks around −0.05 and −0.177 Ry.

In the C phase the work function ϕ of Nb is observed[3] to decrease linearly up to a Pd coverage $\Theta = 0.9$ by 0.2 eV and then it increases linearly with Θ

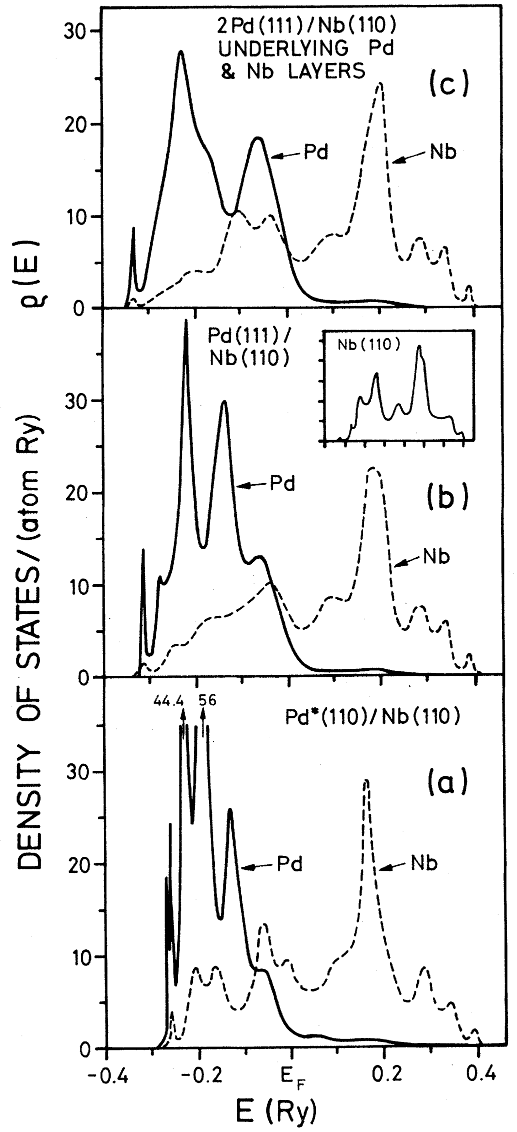

FIG. 1. LDOS for Pd and underlying Nb layers in (a) the C structure and (b) the IC structure on a Pd site having three equivalent Nb neighbors. (c) shows the same for two Pd(111) overlayers. The inset shows the clean Nb(110) surface LDOS.

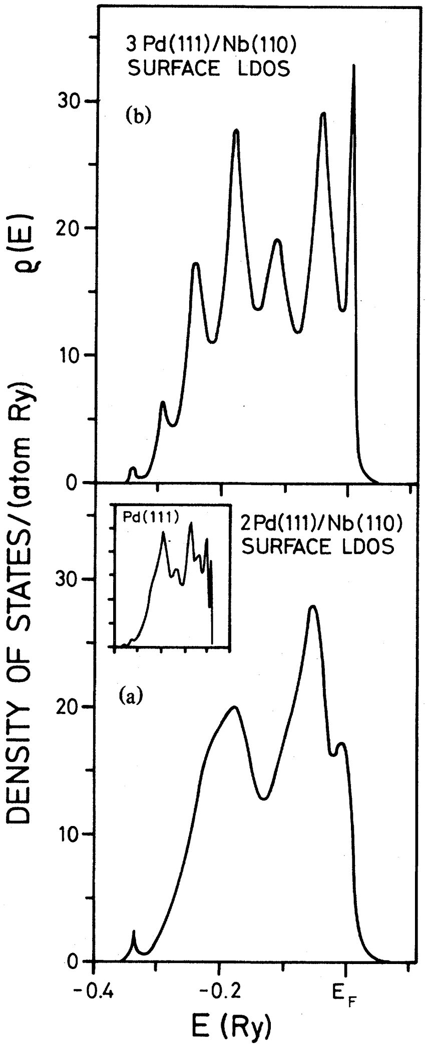

FIG. 2. Surface LDOS for (a) two and (b) three Pd(111) overlayers. The inset shows the Pd(111) surface LDOS.

to the value of Pd(111) surface. This suggests a very small charge transfer from Pd to Nb in the C structure and the reverse in the IC structure. Note, upon adsorption the *d* and *s*-*p* levels of Pd atoms will broaden and may lead to a *d*-charge transfer to Nb as well as a redistribution of the *s*-*p* and *d* charges. Further some *s*-*p* charge may flow from Nb to Pd similar to a situation encountered in alloys.[11] In the present work where only the *d* bands are considered, we assume the *d* charge on Pd atoms in the C phase to be 9.7*e* and no charge transfer at the interface. In the IC phase the Pd atoms are expected to behave more like those at the Pd(111) surface. A small charge transfer at the interface of order 0.026/atom to Pd is determined[12] from the dipole layer formed by matching the two Fermi energies.

For the C structure the LDOS are presented in Fig. 1(a). One obvious feature is that the Pd band is quite narrow as compared to the Pd(111) surface. It is because of the lower coordination and the increased nearest-neighbor distance which results in a decrease of the overlap integrals. The DOS at E_F is very small and the band is relatively filled. This also explains qualitatively why in this structure H_2 is not easily dissociated. A decrease in the *d* holes will decrease[13] the binding energy of atomic hydrogen and thus increase the barrier for H_2 dissociation. A small $\rho(E_F)$ implies a small charge transfer to the molecular antibonding state which would weaken the H_2 bond. Note that a large $\rho(E_F)$ for Pd also favors[14] hydride formation. Thus we expect a low H uptake for the Pd*(110) structure. This result is in complete agreement with the ARPED measurements.[4] Furthermore, there are three peaks[15] at energies −0.129, −0.181, and −0.224 Ry and a shoulder at −0.06 Ry. These are in close agreement with the AIPED data[3] which also show similar three peaks at −0.092, −0.176, and −0.228 Ry for $\Theta < 1$. Since these features exist even for low coverages we conclude that there should be a tendency of Pd*(110) island formation.[16] The peak around −0.092 Ry in the photoemission[3] should also have a contribution from the underlying Nb as a similar feature is observed even for a clean Nb surface. Further the main features of the Pd LDOS are similar to that of an unsupported Pd*(110) monolayer[17] except that the peaks around −0.181 and −0.224 Ry are more prominent. These have strong interactions with the states of the underlying Nb. It can be noted that the Nb LDOS has an appreciable number of states in this region whereas the clean Nb(110) has almost none. The shoulder at −0.06 Ry in the Pd LDOS is at an energy where the surface states (resonances) are expected to occur for the Pd(111) surface.

In Fig. 1(b) we present results for one Pd overlayer in the closed packed fcc (111) structure. In this case as the overlap with neighboring Nb layer changes, the LDOS also vary from one site to another. The band has broadened because the overlap and also the coordination has increased. However, the latter is still less than that for the Pd(111) surface and so the band is expected to become still broader as more Pd layers are added. An important feature of our Pd LDOS is that we now get only one peak at −0.218 Ry whereas in the C structure two distinct peaks were obtained around −0.2 Ry. This peak is due to the bulk Pd d bands but shifted slightly towards higher energy because of the interaction with Nb. The peak around −0.13 Ry and the shoulder at −0.06 Ry have grown further. Absence of strong Nb interaction peaks show that the interaction of Pd with Nb is weaker. It is because of more participation of the d electrons in the Pd-Pd binding. The Pd LDOS and the d holes at E_F have increased but are still small. This is again in agreement with the slight increase in the H-uptake rate[2] as the structural transformation takes place. ϵ of the Pd band is shifted to lower binding energy (−0.26 Ry). Quite similar features of the Pd LDOS are obtained for the Pd atoms asymmetrically placed (closer to the bridge site chemisorption) on three Nb atoms. Since in the AIPED results at $\Theta = 1.2$ peaks at −0.228 and −0.176 Ry and a shoulder at −0.092 Ry are distinctly observed, we interpret that around a monolayer coverage transformation from Pd*(110) to Pd(111) structure starts in the form of islands. Consequently, we expect a change in ϕ towards the pure Pd(111) value and furthermore around the transition coverage ϕ may be different for different observations.[3] At $\Theta = 1.4$ only a peak at −0.176 Ry is seen.[3] We believe that at this coverage some Pd has occupied sites in the second layer in the form of Pd(111) islands. It can be seen in Fig. 2(a) that for two Pd(111) overlayers $\rho(E)$ shows a broad peak at $E = -0.18$ Ry and a clear peak at −0.057 Ry. The latter peak is also observed in AIPED at $\Theta = 2.2$ and 2.8 and is interpreted to arise from surface states (resonances). It was seen,[3] also in our calculations, as a shoulder in the coverage range $1 < \Theta < 2$. The LDOS at E_F has sharply increased and the d band is less filled. ϵ of the Pd band has shifted further to lower binding energy (−0.23 Ry). One should therefore expect an increase in the H-binding energy and a sharp increase in the H-uptake rate as observed.[2] The bandwidth is now similar to the one of Pd(111) surface. Shifts of ϵ should also be reflected in the core levels which can be accurately measured by x-ray photoelectron spectroscopy.

$\rho(E)$ of the underlying Pd and Nb layers are shown in Fig. 1(c). The Pd LDOS shows peaks at −0.228 and −0.062 Ry and a shoulder at −0.18 Ry. The peak around −0.13 Ry observed for Pd*(110) and Pd(111) overlayers is not present. The interaction of Pd with Nb is further decreased and the Nb LDOS looks closer to the clean Nb(110) LDOS. Similar feature of the Nb LDOS is found when the first layer is in the Pd*(110) and the second layer is in the Pd(111) structure. However, we rule out this possibility as in the surface LDOS the peak around −0.13 Ry persists. We think that after about 0.9 coverage Pd occupies sites in the second layer and thus weakens the interaction of Pd with Nb significantly. The lateral interactions between Pd atoms then become more important and causes the structural transformation. This also explains completion of the first Pd(111) layer at $\Theta = 1.3 - 1.4$.

To confirm this we calculated the interface energies U_{int} using a bond model:

$$U_{\text{int}} = \sum_{i \neq j} \epsilon^{ij}_{\text{Pd-Pd}} + \epsilon^{ij}_{\text{Pd-Nd}} \quad .$$

$\epsilon^{ij}_{\text{Pd-Pd}}$ is taken from the heat of vaporization of pure Pd and $\epsilon^{ij}_{\text{Pd-Nb}} = (\epsilon^{ij}_{\text{Pd-Pd}} \epsilon^{ij}_{\text{Nb-Nb}})^{1/2}$. In the C phase, interaction up to second neighbors is considered with distance dependence as R^{-5}. In the IC phase $\epsilon_{\text{Pd-Nb}}$ is assumed to be 10% smaller as it is approximately the difference in binding energies on different sites. The number of Nb neighbors for each Pd is taken to be 2.5 on the average. For two overlayers $\epsilon^{ij}_{\text{Pd-Nb}}$ is expected to be smaller (15−25%) as the bonds get saturated. Our calculations show that two Pd(111) overlayers are energetically more favorable than two Pd*(110) overlayers whereas initially a Pd*(110) overlayer is more stable thus justifying our conclusions drawn from $\rho(E)$ results. More generally we expect IC as compared to C interfaces when the energy gain due to lateral interactions is more than the decrease in the heat of interface formation due to *AB* interactions.

In a further study we took three Pd(111) overlayers. The peaks at −0.046 and −0.181 Ry are fully developed [Fig. 2(b)]. The LDOS looks much closer to the Pd(111) surface, however, it still differs in details. For comparison note that for the Cu(100) surface three layers were not sufficient[18] to get correct surface LDOS.

Our calculations clearly illustrate that from such a relatively simple calculation it is possible to accurately reproduce details of the DOS and to learn about the frequently encountered structural transformations at metallic interfaces. These studies also show the importance of specific geometries which can poison or activate a particular reaction.

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[15] The sharp peaks at the bottom of the band are thought to be due to the truncation of the continued fraction.

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