PHYSICAL REVIEW B VOLUME 28, NUMBER 6 15 SEPTEMBER 1983

Electronic structure of transition-metal—transition-metal interfaces: Pd on Nb(110)

Vijay Kumar and K. H. Bennemann
Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-1000 Berlin 33, Germany

(Received 7 March 1983)

With the use of a self-consistent tight-binding scheme, local electronic densities of states (LDOS) are calculated for commensurate (C) Pd*(110) and incommensurate (IC) Pd(111) layers on Nb(110). At low coverages ($\Theta < 1$) Pd induces a Pd-Nb resonance near the bottom of the Nb d band. In agreement with the experimental results this resonance shifts to lower binding energy as the coverage is increased. Comparing detailed features of the LDOS with the photoemission data we predict a C-IC structural transformation for approximately one monolayer of Pd. This we also conclude from a simple interface energy calculation. The d-electron charge transfer across the interface and the LDOS of Pd at the Fermi energy (E_F) are small. The latter, however, increases with the Pd coverage. The LDOS of the top Pd layer is nearly the same for Pd(111) on Pd*(110)-Nb(110) or Pd(111)-Nb(110) interfaces and in all cases there is a significant decrease of Nb d states near the E_F. This shows that the LDOS is mainly perturbed at the interface. Implications of these results for hydrogen uptake and work-function changes are discussed.

I. INTRODUCTION

There is growing interest in studying the microscopic structure of metallic interfaces[1] which exhibit technologically interesting catalytic,[2] magnetic,[3] and hydrogen uptake[4,5] properties. For example, a large increase in the reaction rate of cyclohexene dehydrogenation to benzene was recently reported[2] for Au on Pt(100) and a large increase in the H uptake was observed[4,5] for a few monolayers of Pd on Nb. To understand such properties it is necessary to study in detail the atomic and the electronic structure of metallic interfaces. Recently there have been a few such detailed experimental studies, in particular for Pd on Nb(110),[5–7] Ag(100), Ag(111),[8] and for Cu on Ni(111).[9] Theoretical studies of the electronic structure have been done only for ideal interfaces, such as Ni on Cu(100) (Refs. 10 and 11) and Pd on Ag(100) (Ref. 12). However, there may be structural transformations which are responsible for the interesting properties of the interfaces, such as the one observed[5] for Pd on Nb(110). In this case the overlayer is in an incommensurate (IC) structure with the substrate, and the usual band-structure approaches for understanding the electronic structure of such interfaces can no longer be applied. Therefore, in this paper we have used a tight-binding scheme and a real-space continued fraction method[13] for the Green's function to study the electronic structure of the Pd on Nb(110) interface. Thus extending our previous non-self-consistent calculations,[14] we present results of self-consistent calculations for Pd coverages ranging from submonolayers to two monolayers, and we identify the structure of the interface by comparing the results of our local density-of-states (LDOS) calculations for different interface structures with the photoemission data.[6,7] As we shall show, our results support all the main experimental findings which are summarized below and provide a physical understanding of the structural transformation. Furthermore, we give a detailed discussion of the charge transfer and the work-function behavior across the interface. Section II provides experimental background. In Sec. III details of our calculational procedure are described. In Sec. IV results of LDOS calculations are presented for various interface geometries, and in Sec. V results of LDOS calculations for unsupported layers are presented. A calculation of interface energies is given in Sec. VI. These results and their implications for other interfaces and for hydrogen uptake are discussed in Sec. VII.

II. EXPERIMENTAL BACKGROUND

Low-energy electron diffraction (LEED) measurements[5] show for $\Theta < 1$ a commensurate (C) structure [hereafter to be referred to as Pd*(110)] where Pd occupies the Nb lattice sites. However, no ordered patterns have been observed at low coverages. Further, in this structure no significant change is observed in the H uptake as compared to the clean Nb. Around $\Theta \approx 1$ there begins a structural transformation in the form of islands from Pd*(110) to the usual Pd(111) structure and it is reported to be completed around $\Theta \approx 1.3$–1.4. This is also accompanied by an increase in the H uptake. Further deposition of Pd leads to a clear Pd(111) structure pattern in LEED and a high increase in the H uptake.

Angle-resolved photoemission energy distribution (ARPED) shows[6] for $\Theta \ll 1$ a Pd-Nb resonance at about -0.22 Ry. This resonance shifts to lower binding energies as the coverage is increased reaching approximately -0.177 Ry at $\Theta \approx 1$. At this coverage the density of states at the Fermi energy (E_F) is very small, as in a noble metal. However, it increases as the structural transformation is completed, and for more than three overlayers, the ARPED looks similar to the one of a clean Pd(111) surface.[15]

In an angle-integrated photoemission energy distribution (AIPED) study[7] of this interface, two pronounced resonance states at approximately -0.228 and -0.176 Ry have been observed for submonolayer coverages. Emission at -0.228 Ry gets saturated at $\Theta \approx 1$ and was interpreted to be due to the resonance of Pd d levels with Nb bulk bands. Emission at -0.176 Ry continuously grows with the coverage and was interpreted to correspond to the formation of bulk Pd d bands. The work function decreases linearly up to about $\Theta = 0.9$ by 0.2 eV and then increases with Θ to the value of the clean Pd(111) surface. We shall illustrate that our calculations support the LEED and ARPED data and the LDOS agrees very closely with the AIPED results.

III. THEORY

We treat here[16] only the d electrons which are described in the tight-binding approximation by

$$H = \sum_{i,\alpha} |i\alpha\rangle \epsilon_{i\alpha} \langle i\alpha| + \sum_{\substack{i,j,\alpha,\beta \\ i \neq j}} |i\alpha\rangle t_{i\alpha,j\beta} \langle j\beta| \; . \quad (1)$$

$\epsilon_{i\alpha}$ is the center of gravity of the d band and $t_{i\alpha,j\beta}$ is the hopping integral. i refers to the atomic site and α to the electronic orbital. For clean surfaces $\epsilon_{i\alpha}$ is determined self-consistently from

$$\epsilon_{i\alpha} = \epsilon_{i\alpha}^{b} + U \sum_{\alpha'\,(\neq\alpha)} \Delta n_{i\alpha'} + V \sum_{\substack{j\,(\neq i), \\ \beta}} \Delta n_{j\beta} \; . \quad (2)$$

Here b refers to the bulk. U and V are, respectively, the intra-atomic and nearest-neighbor interatomic electronic interaction parameters. $\Delta n_{i\alpha}$ represents the difference between the electronic charge $n_{i\alpha}$ at the surface and the bulk. For the interface the center of gravities of the d bands of the adsorbate and the substrate layers are again calculated self-consistently from

$$\epsilon'_{i\alpha} = \epsilon_{i\alpha} + U \sum_{\alpha'\,(\neq\alpha)} \Delta n'_{i\alpha'} + V \sum_{\substack{j,\beta \\ j \neq i}} \Delta n'_{j\beta} \; , \quad (3)$$

where $\Delta n'_{i\alpha}$ is the difference in the d-electron charge on an atom i and orbital α in the adsorbate layer (substrate layer) and the unsupported adsorbate layer (clean surface). The hopping integrals at the clean surface are taken to be the same as in the bulk and at the interface a geometric mean of the corresponding two bulk values is taken. In another study[14] we considered a simple mean approximation. However, this does not change the LDOS results much. The distance dependence of the hopping integrals is taken according to the R^{-5} law.[17] The difference $\Delta\epsilon_d$ between the center of gravities of the substrate and the adlayer bands is chosen such that the Fermi energies of the two bulk materials coincide. Then the Pd d-band center of gravity lies[18] (see also Refs. 19–22) 0.248 Ry below the Nb d-band center of gravity. $\Delta\epsilon_d$ was kept the same for all the calculations.[23] The bulk charge configurations for Nb and Pd are chosen to be $4d^{3.6}$ and $4d^{9.5}$, respectively. U is taken[24] to be 0.172 and 0.261 Ry for Nb and Pd, respectively. V is kept equal to 0.035 Ry for both. For Nb and for C interface structure hopping integrals up to second nearest neighbors are considered. For Pd(111) only the nearest-neighbor interactions are taken into account. These are evaluated by using the three Slater-Koster parameters[25] $dd\sigma$, $dd\pi$, and $dd\delta$, which are taken by scaling Pettifor's parameters[26] to the proper bandwidth of Nb (0.69 Ry) and Pd (0.41 Ry). Since we consider only the d bands and upon interface formation there will in general be a redistribution of the s-p and d-electron charges, no attempt is made to keep strict charge neutrality. An excess or depletion of the d-electron charge at the interface (surface) is taken to be compensated by the s-p—electron charge.

The LDOS $\rho_i(E)$ at a site i is then calculated using a continued fraction expansion of the Green's function G:

$$\rho_i(E) = \sum_{\alpha} \rho_{i\alpha}(E) = -\frac{1}{\pi} \mathrm{Im} \sum_{\alpha} \langle i\alpha | G | i\alpha \rangle \; , \quad (4)$$

where

$$\langle i\alpha | G | i\alpha \rangle = \left[E - a_{1\alpha} - \frac{b_{1\alpha}^2}{E - a_{2\alpha} - b_{2\alpha}^2/E - \cdots} \right]^{-1} . \quad (5)$$

Here, $a_{i\alpha}$ and $b_{i\alpha}$ are the continued fraction coefficients. In our calculations we have used 20 levels. The charge in an orbital α is calculated with an accuracy of $0.001e$ from

$$n_{i\alpha} = \int_{-\infty}^{E_F} \rho_{i\alpha}(E)\,dE \; . \quad (6)$$

IV. RESULTS

In this section we present first results of the LDOS calculations for clean Nb(110) and ordered structures of Pd corresponding to $\Theta = 0.25$, 0.5, and 1.0. Then the results of an IC interface structure corresponding to one Pd(111) layer on Nb(110) are presented and are compared with the results obtained for $\Theta = 1$. In order to understand the structural transformation and the layer growth, results are then presented for two overlayers of Pd with various combinations of Pd*(110) and Pd(111) layers. These results are compared with those obtained for a clean Pd(111) surface.

The LDOS for clean Nb(110) and for submonolayer coverages of Pd are shown in Fig. 1. For clean Nb(110) the main feature of our LDOS is the presence of a peak at about -0.037 Ry, which is in close agreement with the photoemission results.[27] As compared to the bulk Nb there is a depletion of about 0.08 d-electron charge at the surface and the band is shifted to higher binding energy by a mean 0.025 Ry. The x^2-y^2 orbital has more charge and the smallest subband width because its lobes point away from the surface and the overlap is minimal. The yz and xz orbitals are degenerate.

In Fig. 1(b) we show results for a Pd and a nearest-neighbor Nb atom with the $p(2\times2)$Pd overlayer structure at $\Theta = 0.25$. In this structure there is no direct interaction between the Pd atoms and the Pd LDOS shows sharp peaks around -0.204 Ry. These are due to a broad resonance of the yz orbital and the splitting of the xy, x^2-y^2, and $3z^2-r^2$ orbital states as a result of interaction with the substrate. The interaction of the $3z^2-r^2$ orbital with the substrate is minimal. This is indicated from the smallest splitting and by the fact that Nb LDOS shows a bonding resonance near the bottom of the Pd band where the LDOS due to the $3z^2-r^2$ orbital is very small. Comparing these results with the clean Nb(110), it is apparent that the Nb states have been pulled toward higher binding energies and thus contribute to the heat of adsorption. Note, these results are in good agreement with the ARPED data[6] where at low coverages a Pd-Nb resonance is observed at $E \approx -0.22$ Ry. The center of gravity of the Pd

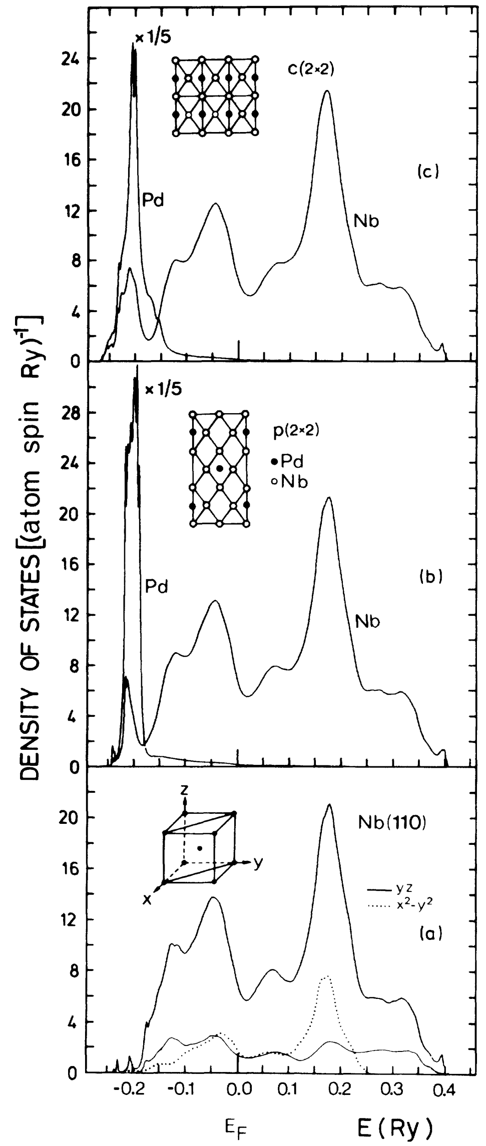

FIG. 1. LDOS for (a) clean bcc Nb(110) surface, (b) Pd on Nb(110) with $\Theta=0.25$, and (c) $\Theta=0.5$. The Pd atoms occupy the Nb lattice sites. Inset in (a) shows the choice of axes chosen for the Nb(110) and the interface calculations. xy and $3z^2-r^2$ orbitals have LDOS similar to yz and x^2-y^2 orbitals, respectively. In the following figures only significantly different partial LDOS are shown.

band lies at -0.189 Ry and the density of states at E_F is very small. As shown in Fig. 1(c) quite similar results are obtained for the $c(2\times2)$Pd overlayer structure corresponding to $\Theta=0.5$. In this structure Pd atoms form a chain structure and interact only via the second-nearest-neighbor interactions within a chain. This leads to a broadening of the band. The shoulder around -0.16 Ry in the Pd LDOS is due to the $3z^2-r^2$ orbital. The LDOS of the yz orbital shows a broad resonance and the splitting of the xy and x^2-y^2 orbitals is clearly reflected in the LDOS. In these calculations the initial charge configuration for Pd was taken to be the same as in the Pd atom. For a Pd coverage of $\Theta=0.25$ we obtain from our self-consistent calculations[28] for Pd and Nb atoms at the interface an electronic charge of 9.785e and 3.537e. This implies a reduction in the d-electron charge on Pd by 0.215e and an increase of 0.017e for Nb as compared to the situation when the two metals are separated. Similar charge configurations are obtained for $\Theta=0.5$. The overall charge transfer is small. A larger decrease of the Pd d-electron charge is to be compensated by a redistribution to the s-p electron charge.

In Fig. 2(a) results are shown for a monolayer of Pd on Nb(110) in the C structure. Note, the Pd LDOS shows two prominent peaks at energies -0.227 and -0.176 Ry and a shoulder around -0.12 Ry with a tail spreading up to the top of the Nb band. In the photoemission experiment[7] beyond a coverage $\Theta\approx0.5$ two similar peaks are obtained at about the same energies and a peak is observed at $E\approx-0.092$ Ry. The contribution to the latter comes from both the Pd and the Nb bands, as for clean Nb a similar peak is observed at the same energy. As the partial LDOS show, the dominant contribution to the peak at -0.227 Ry is due to the yz and xz orbitals. The peak at -0.176 Ry has dominant contributions from the xy and x^2-y^2 orbitals, whereas around the shoulder the states are dominantly of $3z^2-r^2$ character. In our previous non-self-consistent calculations[14] we obtained three prominent peaks for Pd in this structure. This is due to the fact that in those calculations the hopping integrals between Pd atoms were taken to be nonzero only between the nearest neighbors. In the present calculations second-nearest-neighbor interactions are also included. It will be shown later that this changes the density of states of an unsupported Pd*(110) layer significantly. Another important feature of the Pd LDOS is that the density of states at E_F is very small and the region of high density of states lies about 0.12 Ry below E_F. This is again in very good agreement with the photoemission experiments.[6] The charge on Pd and Nb atoms is 0.075e and 0.016e less as compared to the case when the two are separated. This shows a reversal of d-electron charge transfer for Nb as compared to the $p(2\times2)$ and $c(2\times2)$ overlayers. As the work-function change is small[7] we thus conclude that the s-p charge transfer should also be quite small. The Pd band is quite narrow (the d-band width up to the point of inflection of the tail is approximately 0.2 Ry) because of lower coordination and increased separation between the Pd atoms as compared to the Pd(111) surface. The states in the Nb band are distributed throughout the region of the Pd band. However, these are largely accumulated in the region where the Pd LDOS shows two peaks. In particular the Nb LDOS shows a peak around -0.179 Ry, an energy where the Pd LDOS also shows a peak. Interestingly, from ARPED results[6] emission around -0.177 Ry was concluded to have both the Pd and the Nb characters. Thus our calculations confirm that observation. This is, however, contrary to the interpretation given in Ref. 7, where the emission at $E\approx-0.228$ Ry was associated with the Pd-Nb resonance. Furthermore, in agreement with the ARPED results, this resonance is shifted to lower binding energy as compared to the $p(2\times2)$ structure. The center of gravity of the Pd band lies at -0.169 Ry.

For the IC Pd(111) layer on Nb(110), the LDOS

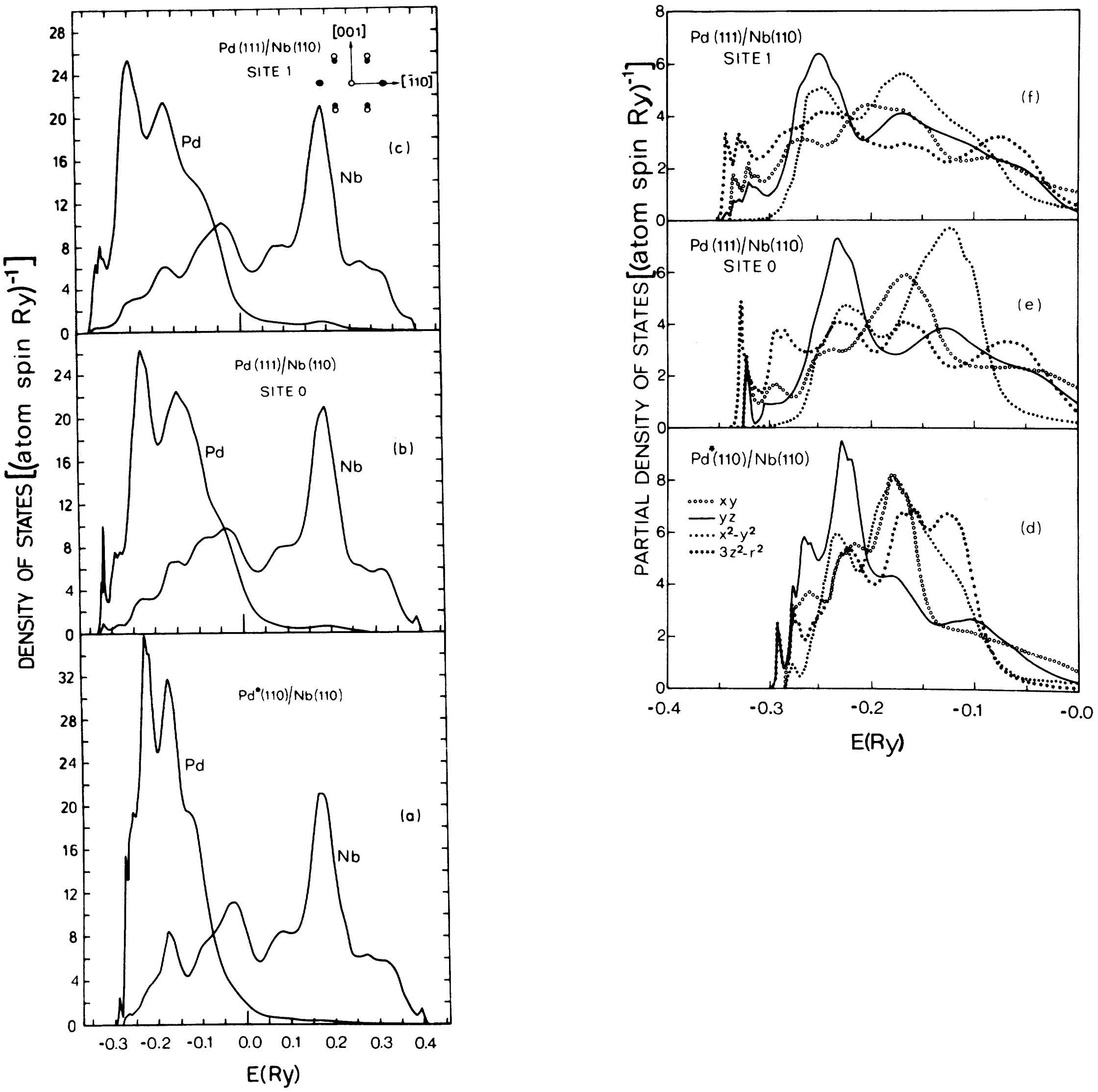

FIG. 2. (a) LDOS for the commensurate Pd*(110) interface structure ($\Theta = 1$). Note, in this structure the nearest-neighbor Pd distance is about 4% larger than in bulk Pd. The spacing between the Pd and Nb layers is chosen to be 2.3264 Å. (b) and (c) show the LDOS referring to Pd sites 0 and 1 (see Fig. 3) for one incommensurate Pd(111) layer on Nb(110). Inset of (c) shows the superposition of the corresponding reciprocal lattices for Pd(111) and Nb(110) layers. This is very similar to the pattern observed in LEED (Ref. 5). The partial LDOS shown in (d), (e), and (f) refer to Pd.

changes from one site to another. We have therefore calculated[28] the LDOS for the two sites shown in Fig. 3. Results for the LDOS are shown in Figs. 2(b) and 2(c). At site 0 the Pd LDOS shows a peak around -0.23 Ry, predominantly due to the yz and zx orbitals, a broad peak around -0.15 Ry with major contributions from the xy and x^2-y^2 orbitals, and a shoulder around -0.07 Ry. Comparing these results with the LDOS obtained for the C structure, we conclude that the peak around -0.23 Ry remains unchanged but the Pd-Nb resonance peak and the shoulder have now shifted to lower binding energies. The reason why the $(yz-zx)$-orbitals peak does not change much is that their two lobes lie away from the surface and thus the overlap is not changed much. Their occupancy is also almost the same. On the other hand, the overlap for the xy and $3z^2-r^2$ orbitals changes significantly as their two lobes lie in the plane, and thus because of more electron-electron repulsion these are less occupied and the subbands are broadened. The x^2-y^2 orbital subband width is smallest as in the case of the C structure. The mean width of the Pd band has increased because of the increased coordination and overlap of Pd atoms. The number of d holes is now larger, but the density of states at E_F is still small. The charge on Pd and Nb atoms is, respectively, $0.028e$ and $0.012e$ less as compared to the case when the two are separated. The mean center of gravity of the Pd band lies at -0.155 Ry. The overall Pd LDOS for the bridge site (site 1) is similar [Fig. 2(c)]. In this case the peaks lie at slightly higher binding energies (-0.248 and -0.170 Ry). This is due to the increased

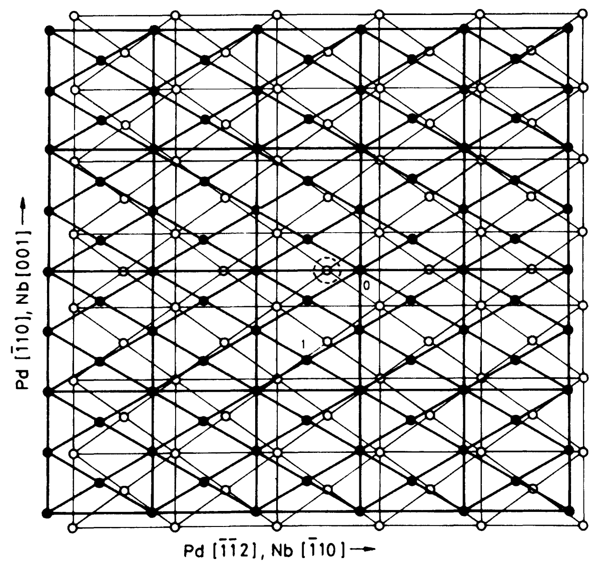

FIG. 3. Geometrical arrangement of atoms in the incommensurate Pd(111) on Nb(110). For our cluster calculations the central triangle of the Pd(111) structure (filled circles and thick lines) is placed on top of the central atom (encircled) of the Nb(110) surface (empty circles and thin lines) such that the $[\bar{1}\bar{1}2]$ direction of Pd(111) coincides with the $[\bar{1}10]$ direction of Nb(110). Note that the distance between two neighboring Pd atoms in the $[\bar{1}\bar{1}2]$ direction is only about 2% larger as compared to the one for Nb atoms in the $[\bar{1}10]$ direction. But in the $[\bar{1}10]$ direction of Pd(111) this distance is about 16.6% smaller as compared to the same for Nb in the [001] direction. Thus the Pd overlayer can accomodate about 15% more atoms as compared to the Nb layer. The interlayer separation is chosen to be equal to the mean of the interplanar distances for the Nb(110) surface (2.3264 Å) and for the Pd(111) surface (2.2402 Å).

overlap with Nb which shifts the band. In reality there may be some buckling in the overlayer which is not taken into account. The total overlayer density of states will be a combination of both types and will show a peak around −0.23 Ry and a broad feature around −0.15 Ry. The peaks in the Nb LDOS are less prominent and in particular the Pd-Nb resonance has moved to lower binding energy as compared to the *C* structure. On the basis of these results we rule out completely the possibility of having just one Pd(111) layer on Nb(110). This is because in the photoemission experiments[7] beyond $\Theta=1.0$, the peak around −0.228 Ry is getting weakened and at $\Theta=1.4$ it ultimately disappears, whereas the peak around −0.177 Ry persists and keeps on growing. Note, in going from the Pd*(110) to the Pd(111) structure, the number of states around both the peaks decreases and, moreover, we would expect in the photoemission the peak at −0.177 Ry to be shifted to lower binding energy. Incidently, we notice two closely lying peaks in the ARPED around the structural transition. One of these lies at the same energy as for the *C* structure whereas the other lies at about 0.036 Ry lower binding energy. Therefore, from our calculations we can associate these peaks with the coexistence of Pd(111) and Pd*(110) structures.

In order to get some understanding of the growth mode of the Pd layers, we calculated the LDOS for two Pd overlayers in different configurations. These results are presented in Fig. (4). For two Pd overlayers in the *C* structure ($\Theta=2.0$) the top Pd-layer LDOS shows a broad peak around −0.08 Ry and two other less prominent peaks around −0.17 and −0.22 Ry. As for one Pd*(110) overlayer the x^2-y^2 and $3z^2-r^2$ orbital subbands have the smallest bandwidths. The density of states at E_F is now significantly larger as compared to one overlayer, but the Pd bandwidth ($\sim$0.3 Ry) is smaller than in the case of a Pd(111) surface. At this coverage in the photoemission[7] two peaks are observed around −0.177 and −0.052 Ry. One expects that these will also have some contribution from the second layer. Now the LDOS of the underlying Pd layer shows a two-peaked structure around −0.23 Ry as also seen for a Pd*(110) overlayer and an almost flat region at lower binding energy. Therefore, a superposition of the LDOS of the two layers will reflect two peaks around −0.08 and −0.23 Ry. We therefore discard the possibility of the occurrence of two Pd*(110) layers on Nb(110). This is also consistent with the experiments which report a structural transformation around $\Theta=1$. Unlike for one overlayer, no Pd-Nb resonance is clearly evident and the states are distributed throughout the Pd band. The center of gravity of the top Pd layer has shifted to lower binding energy (−0.124 Ry). For the underlying Pd layer it lies around the same energy (−0.179 Ry) as for one Pd*(110) overlayer. The charges on the top and of the underlying Pd layers are, respectively, about 0.064*e* more and 0.1*e* less as compared to two unsupported layers, the charge on the Nb layer being very close (0.008*e* less) to the value of the clean Nb(110) surface. The x^2-y^2 orbital subband width for the underlying Pd layer has slightly increased because of the overlap with the top Pd layer. At the top of the band the LDOS of the top Pd layer decreases sharply to zero as compared to the underlayer indicating little involvement with the substrate.

Next we consider two Pd(111) layers on Nb(110). In this case the LDOS of the top Pd layer is quite similar to the results obtained from photoemission. In particular, there are two peaks at −0.2 and −0.06 Ry. The peak around −0.05 Ry was interpreted to be due to the surface states (resonances). In our calculations we cannot identify the surface states unless they lie completely outside the band. However, there may be surface states lying within the band. The LDOS resembles that of a clean Pd(111) surface (insert Fig. 4). However, it differs in details. It seems therefore that two layers supported on another metal are not sufficient to produce detailed features of the electronic structure of a metal surface. It is interesting to note that experimentally[7] it was also concluded that for more than three monolayers the surface behaves like a Pd(111) surface. A similar feature has been observed[8] for Pd on Ag(111). The density of states at E_F is quite large and also the number of *d* holes has increased. The band is broader than in any previous case and there is a small excess of charge of order 0.042*e* as compared to the two unsupported layers. The x^2-y^2 orbital is maximally occupied having 0.99*e* per spin. The mean center of gravity lies at −0.128 Ry. The LDOS of the underlying Pd layer shows two broad peaks around −0.228 and −0.072 Ry.

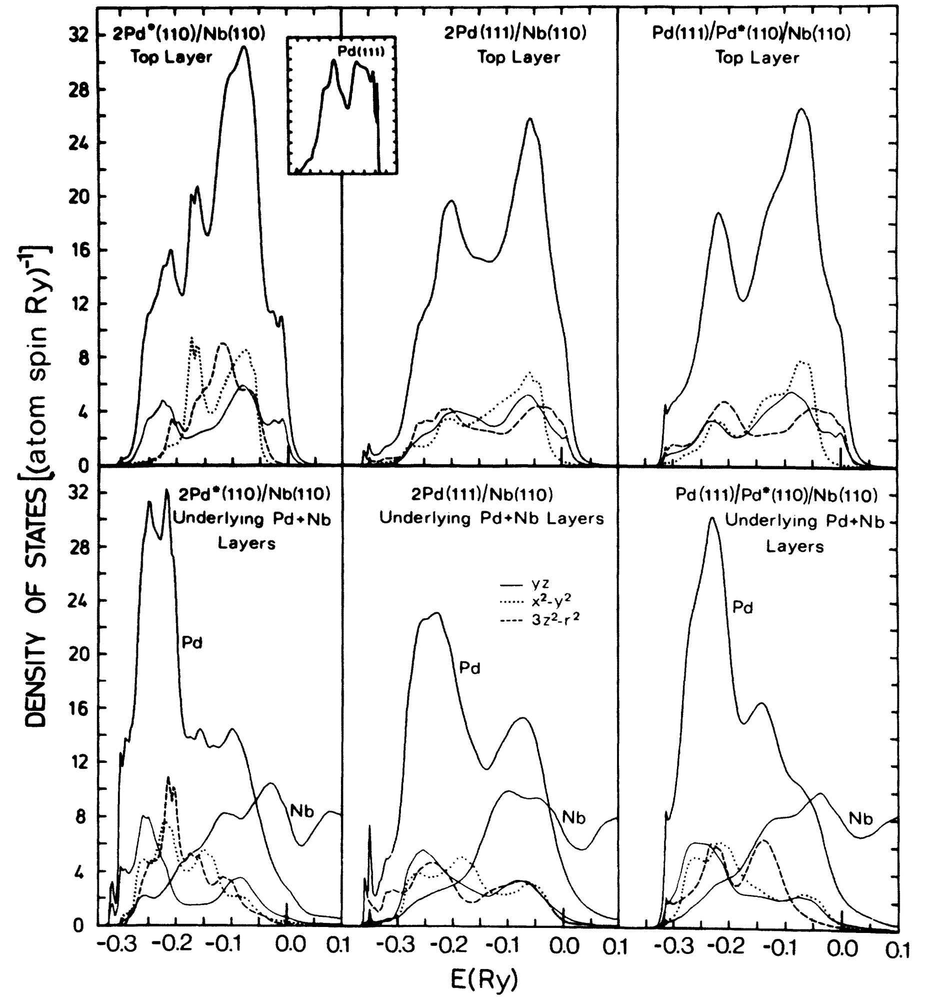

FIG. 4. LDOS for two Pd layers on Nb(110). Part of the LDOS not shown does not show significant changes. The inset shows the LDOS for a clean Pd(111) surface.

The peak around -0.228 Ry seems to remain unchanged as compared to the case of one Pd(111) overlayer except that it has broadened due to interactions with another Pd overlayer. The other peak lying at lower binding energy seems to disperse continuously with the coverage. The center of gravity of the d band is shifted to higher binding energy (mean -0.164 Ry) and the charge is about $0.065e$ less as compared to the case when the two Pd layers are unsupported. It seems that there is some d-electron charge transfer from the underlying Pd layer to the top Pd layer, the d-electron charge on Nb atoms being almost the same (0.01 less) as in the case of a clean Nb(110) surface. Note that after the Nb(110) is covered with another metal, the d-electron charge does not tend toward its bulk value. The center of gravity of the Nb band lies at slightly higher binding energy as compared to the clean surface. Note, the surface barrier (though not considered explicitly here) present at the clean metal surface is not there for the interface and so, independent of the net charge transfer at the interface, the effect should be that the Nb band is pulled toward higher binding energy. Though the total charge remains the same as on a clean surface, there is a redistribution of charge among the different orbitals, e.g., the occupancy of the x^2-y^2 orbital is significantly reduced in going from the clean surface to the interface because of electron-electron repulsion due to overlap with the Pd layer.

To check the possibility of the growth where the first Pd layer is in registry with the substrate [Pd*(110)] but the second layer grows in the Pd(111) structure, we performed self-consistent calculations of the LDOS and the results are presented in Fig. (4). The LDOS of the top Pd layer, which has the fcc(111) structure, is quite similar to the one obtained in the case of two Pd(111) overlayers. The partial density of states are also quite similar. The peak near the E_F lies at -0.071 Ry and the other peak lies at -0.218 Ry. The separation between the two peaks is almost the same as for two Pd(111) overlayers. But in the present case the peaks are shifted slightly to higher binding energies. The charge on the top Pd layer is about $0.1e$

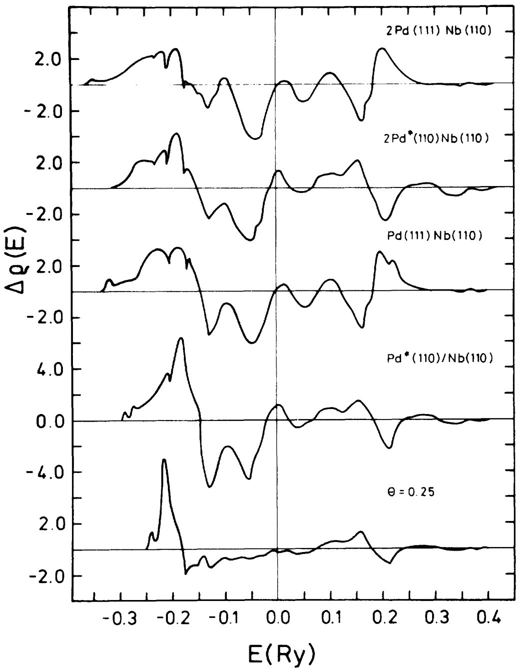

FIG. 5. Difference of the Nb LDOS after and before interface formation.

more than for the unsupported Pd(111) on Pd*(110) layers. The charges on the underlying Pd and Nb layers are, respectively, 0.064*e* and 0.02*e* less. The Pd *d*-band width is slightly less as compared to two Pd(111) on Nb. The LDOS of the underlying Pd layer shows a broad peak around −0.233 Ry as is also seen in the other case. But there are apparent differences as compared to the case of two Pd*(110) overlayers. This implies that though Nb has little influence on the LDOS of the top Pd layer, the LDOS of the underlying Pd layer has significant influence from both the top Pd layer and the substrate. As compared to two Pd(111) overlayers, a significant difference is that the peak around −0.143 Ry has the dominant character of the $3z^2-r^2$ orbital whereas for two Pd(111) layers all orbitals contribute almost equally to the peak at −0.06 Ry. Furthermore, the peak at −0.143 Ry also has some influence on the LDOS of the top Pd layer. The Nb LDOS also shows some changes but the LDOS is quite smooth. The centers of gravity of the top and the underlying Pd-layer *d* bands lie, respectively, at −0.13 and −0.179 Ry. From these results it will be hard to conclude whether two Pd(111) layers or the Pd(111)/Pd*(110) structure is more favorable. We can only say that in the case of two Pd(111) layers the emission around −0.06 Ry should be strong as both the top and the underlayer have states around the same energy, whereas for Pd(111)/Pd*(110) on Nb this should be weak and broad. However, our other calculations clearly indicate a structural transformation in the form of islands. The existence of the emission around −0.177 Ry beyond $\Theta=1$ is therefore either due to the coexistence of Pd*(110) and Pd(111) structures near the transition or due to two Pd(111) overlayers at higher coverages.

To learn how the structural transformation may happen, we plot in Fig. (5) the difference density of states of the Nb layer after and before chemisorption. We observe that states throughout the band are perturbed and there is a significant decrease of states just below the E_F and this is almost the same for all the cases except for $\Theta<1$. However, the reduction in the Nb states due to chemisorption around −0.13 Ry has been significantly reduced in going from one Pd*(110) overlayer to two Pd(111) overlayers. Consequently, the number of states pushed to higher binding energies due to chemisorption have also decreased. We can therefore conclude that the interaction of Pd with Nb should decrease as the second layer is deposited. On the other hand, because of the increased coordination and the bulklike interaction distances between the Pd atoms one should expect a gain in energy which may thus result in the structural transformation. We can imagine that after $\Theta\approx0.8$–0.9, there will be a significant probability that some Pd atoms start sitting in the second layer and thus weaken interactions of the underlying Pd atoms with Nb. The mutual interactions between Pd atoms then become more significant and cause structural transformation.[14] The observation of Pd(111) structural spots in LEED at $\Theta\approx1.4$ and the consequent interpretation of completion of structural transformation should mean that around this coverage the first layer is mostly a Pd(111) layer and, in addition, there should be[29] some Pd atoms sitting in the second layer in registry with Pd(111) structure.

V. UNSUPPORTED LAYERS

In order to show how the electronic structure changes upon interface formation we present in Figs. 6 and 7 results of the density-of-states calculations[30] (non-self-consistent) for an unsupported Pd*(110) and Pd(111) layer and for two Pd layers with different combinations. For a Pd*(110) layer calculations are performed by taking only the nearest-neighbor interactions [Fig. 6(a)] and also by including the second-nearest-neighbor interactions [Fig. 6(b)]. When only the nearest-neighbor interactions are taken into account, the Pd density of states shows a symmetric band with three prominent peaks. On the other hand, inclusion of second-nearest-neighbor interactions destroys this symmetry and there are only two prominent peaks. This explains the difference between the results presented here and our previous calculations.[14] The central peak in Fig. 6(a) is due to the $3z^2-r^2$ orbital. This is removed when the second-nearest-neighbor interaction is switched on. The other two peaks have dominant contributions due to the x^2-y^2 orbital and their position seems to remain almost unchanged upon inclusion of second-nearest-neighbor interactions. The x^2-y^2 orbital subband width is smallest because the overlap with neighbors is smallest. The x^2-y^2 and $3z^2-r^2$ orbitals are fully occupied.[31] It is interesting to note that except for a change in the bandwidth the density of states for Pd*(110) and Pd(111) layers look quite similar.[32] The bandwidth for the Pd*(110) layer is smaller because the nearest-neighbor distance is larger and the coordination is smaller. For the Pd(111) layer the $3z^2-r^2$ orbital subband has significantly broadened due to overlap and is less occupied. The

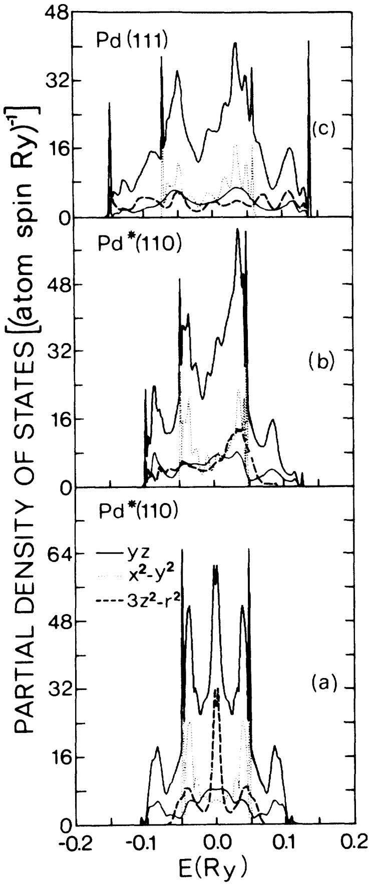

FIG. 6. Density of states of an unsupported Pd layer. In (a) and (c) we have taken into account only nearest-neighbor interactions and in (b) also second-nearest-neighbor interactions. Here, the center of gravity of the band is taken as the zero of energy.

separation between the two prominent peaks is about 0.075 and 0.1 Ry for Pd*(110) and Pd(111) layers, respectively. The occupancy of the yz orbital remains almost the same for the two layers[33] (also see Ref. 34). These trends were also found for the interface calculations. Thus comparing these results with those presented in Fig. (2) we can say that the LDOS features do not change much except that the Pd band is shifted to higher binding energy due to interaction with the substrate.

The density of states for two Pd*(110) and two Pd(111) layers is shown in Figs. 7(a) and 7(b), respectively. For the Pd*(110) case it shows again a two-peaked structure but the separation between the peaks has increased as compared to the unsupported Pd*(110) layer. The band has also broadened. In particular, the subband corresponding to the x^2-y^2 orbital has significantly broadened because of interactions between the two layers. Comparing these results with those presented in Fig. (4) we notice that after the interface formation states for the underlying Pd layer are pulled toward higher binding energy, as is also the case for one Pd*(110) on Nb, whereas for the top layer more states lie at lower binding energy. The overall LDOS is

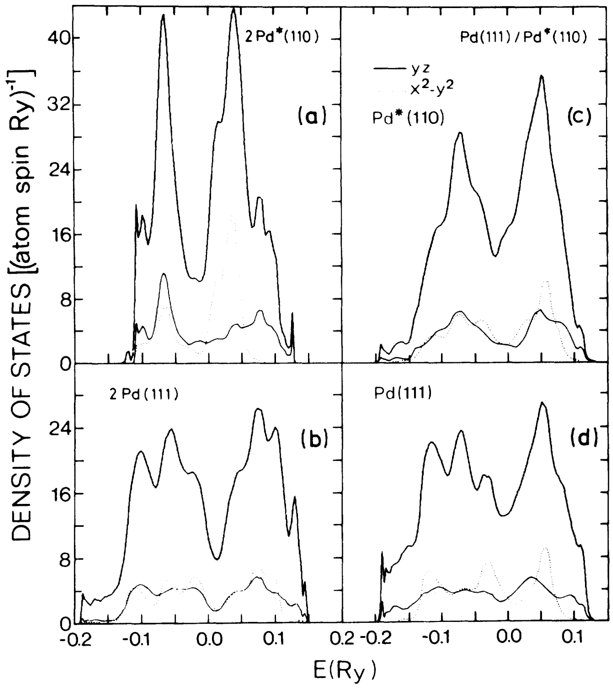

FIG. 7. Density of states for two unsupported Pd layers. The center of gravity of the band is taken as the zero of energy.

also significantly different. The LDOS for the Pd(111) layers differs appreciably from one Pd(111) layer or from two Pd*(110) layers or from a clean Pd(111) surface. The bandwidth is smaller as compared to the clean Pd(111) surface. For the case where one layer is in the Pd*(110) structure and the other layer has Pd(111) structure, the LDOS is calculated self-consistently and is shown in Figs. 7(c) and 7(d). The geometry was chosen in the same manner as for the IC interface. As the Fermi energies of the two layers are different, we again matched the two Fermi energies which gave the center of gravity of the Pd(111) layer to lie 0.021 Ry below the center of gravity of the Pd*(110) layer. Interestingly, the LDOS of the two layers are very similar as in the case of two Pd*(110) and two Pd(111) layers. However, the bandwidth for the Pd*(110) layer has increased. We conclude that the electronic structure of the Pd(111) layer is not very sensitive to whether one has a Pd*(110) or a Pd(111) layer beneath. The same was found to be true after the interface formation. The final charges on Pd*(110) and Pd(111) layers are, respectively, about 0.03e and 0.01e less as compared to one Pd*(110) and one Pd(111) layer. This shows that the change in the d-electron count in going from one structure to another is small for Pd. A similar behavior was obtained in a volume-dependent calculation for Pd by Pettifor.[21]

VI. INTERFACE ENERGIES

To understand the $C \rightarrow IC$ structural transformation from an energetical point of view we calculate, using a bond-energy picture,[14] the interface energies. Let $\epsilon_{\text{Pd-Pd}}(R_{ij})$ be the interaction energy between a pair of Pd atoms and $\epsilon_{\text{Pb-Nb}}(R_{ij})$ be the interaction energy between a pair of Pd and Nb atoms. Then one can calculate the total energy for one or two Pd overlayers from the relation

$$E_{\text{intf}} = \sum_{i \neq j} [\epsilon_{\text{Pd-Pd}}(R_{ij}) + \epsilon_{\text{Pd-Nb}}(R_{ij})] \ . \tag{7}$$

In order to calculate from Eq. (7) the energy difference between the *C* and *IC* structures, note that in the case of one Pd*(110) overlayer all the atoms lie on equivalent and more coordinated sites as compared to the Pd(111) overlayer. Therefore, in accordance with the LDOS calculations we expect the bonding of Pd with Nb to be stronger for one Pd*(110) overlayer. Furthermore, it is evident from Fig. (5) that for two Pd overlayers, the bonding of the underlying Pd layer with Nb is weaker as compared to when only one Pd overlayer is there. In studying the relative stability of the various combinations of the two Pd overlayers, the small changes in the contribution to E_{intf} of the Nb layer due to small changes in the LDOS will, however, be neglected. The bond enthalpies are estimated from the bulk thermodynamic data[35] and are modified at the surface (interface) to take into account surface relaxation as described by Kumar.[36] We write

$$\epsilon(R_{ij}) = \epsilon^{b}(R_{ij})(1+\delta) \ , \tag{8}$$

where δ is a surface relaxation parameter. This relaxation increases as one goes from a close-packed structure to an open structure. δ is estimated[36] to be 0.1 for a clean Pd(111) surface, 0.166 for one Pd layer in the *IC* structure, and 0.239 for the *C* structure. In the *IC* structure the effective coordination of each Pd atom is taken to be 8.5. $\epsilon_{\text{Pd-Nb}}$ is taken to be equal to the geometric mean of $\epsilon_{\text{Pd-Pd}}$ and $\epsilon_{\text{Nb-Nb}}$. The distance dependence of the bond enthalpies is taken as R^{-5}. E_{intf} can then be calculated in a straightforward manner. This comes out to be 111.2 and 104.4 kcal/mole for the *C* and *IC* structures, respectively. For the *IC* structure we take the Pd—Nb bond to be 10% weaker than for the *C* structure. If equal bonding is assumed then the *C* structure is favored by just 1.1 kcal/mole. For two overlayers the relaxations of the overlayer and the underlayer are different. Relaxation in the bond enthalpies of the underlayer is expected to be small and is therefore neglected. For the overlayer, δ is 0.239, 0.166, and 0.1 for two Pd*(110), Pd(111) on Pd*(110)/Nb(110), and two Pd(111) layers, respectively. The corresponding values for E_{intf} are $E_{\text{intf}}^{2C} = 165$ kcal/mole, $E_{\text{intf}}^{C\text{-}IC} = 177.1$ kcal/mole, and $E_{\text{intf}}^{2IC} = 186$ kcal/mole when $\epsilon_{\text{Pd-Nb}}$ is taken to be the same for all structures but 15% less as compared to the case of one Pd layer in the *C* structure. If no decrease in the $\epsilon_{\text{Pd-Nb}}$ bond enthalpy is assumed, then $E_{\text{intf}}^{2C} = 173.8$ kcal/mole, $E_{\text{intf}}^{C\text{-}IC} = 185.9$ kcal/mole, and $E_{\text{intf}}^{2IC} = 193.4$ kcal/mole. Therefore, from this calculation we find that for $\Theta \lesssim 1$ the Pd*(110) layer is energetically more favorable as compared to the Pd(111) overlayer. For $\Theta > 1$ two Pd(111) overlayers are most stable. This supports our conclusions from the LDOS calculations and the experimental evidence of a structural transformation. The *C-IC* structural transition is driven by the gain in energy due to the close-packed fcc(111) structure. In general one should observe *IC* as compared to *C* interfaces when the energy gain due to lateral interactions is larger than the decrease in the enthalpy of interface formation due to *AB* interactions.

VII. DISCUSSION

A. Interface structure

From a comparison of our self-consistent electronic structure calculations with the photoemission results,[6,7] we conclude unambiguously a structural transformation from a Pd*(110) to a Pd(111) configuration near $\Theta = 1$ as observed in LEED.[5] Since ordered structures at $\Theta = 0.25$ and 0.5 lead to features in the LDOS similar to a single-atom chemisorption, for $\Theta \ll 1$ there should be a random distribution of Pd atoms. This may also be due to low mobility of Pd atoms as no ordered structures of Pd have been observed at low coverages. Around a half-monolayer, islands of a Pd*(110) structure should be present and near the structural transition both the Pd*(110) and Pd(111) structures should coexist. As reported before[14] the structural transition begins when Pd atoms start occupying sites in the second layer. If the mobility of Pd atoms is low, this is very likely for $\Theta \approx 0.8$—0.9, the coverage at which the structural transition is observed to start. In addition, the structural transformation is reported[5] to be completed after $\Theta \approx 1.3$—1.4. For this coverage some Pd atoms should be in the second layer.[29] Furthermore, we cannot rule out the possibility of some contractions in the Pd layer. Note, a 2% contraction along the Pd[$\bar{1}\bar{1}2$] direction and a subsequent very small contraction along the Pd[$\bar{1}10$] direction will make the Pd(111) overlayer coincident with Nb(110) ($5a = 6b$ where a and b are vectors with nearest-neighbor distance along Nb[001] and Pd[$\bar{1}10$], respectively). This will result[37] in extra multiple-scattering spots in the LEED pattern with varying intensity. In Fig. 2 we showed the superposition of the reciprocal lattices for Nb(110) and Pd(111). Note that around the structural transformation up to five beats with the same spacing have been observed,[5] which were interpreted to be due to island formation. However, it seems more likely that they arise because of coincidence structure.

B. Electronic structure and the H uptake

At low coverages there is a Pd-Nb resonance at -0.204 Ry. If we consider a single Pd atom chemisorbed, then in the atomic form the 4*d* level of Pd is full and the 5*s* level is empty. Upon chemisorption these levels are broadened and shifted.[38] The shift will be proportional to the square of the hopping integrals between the Pd and Nb atoms. In our calculations we have taken the Pd—Nb bond length to be the same as for Nb—Nb (2.849 Å). However, if the covalent radii of Pd and Nb are taken, this bond length will be 2.7963 Å. Therefore, we would expect the Pd-Nb resonance to lie at a somewhat higher binding energy than -0.204 Ry. This is in very good agreement with the photoemission results where for very low coverages a peak around -0.22 Ry is observed. To check the consequences of a different bond length on the LDOS we performed a calculation for one Pd*(110) overlayer with the Pd—Nb bond length equal to the sum of the covalent radii. The results were in fact identical to those shown in Fig. 2, except for an almost rigid shift of the band. Furthermore, in complete agreement with the ARPED results the Pd-Nb resonance shifts toward lower binding energies as the coverage is increased. Also the center of gravity of the Pd band shifts to lower binding energy with the coverage. This should also be reflected in the core levels and can be measured by the x-ray photoelectron spectroscopy.

In general the LDOS curves become smoother and there is a redistribution of states as compared to when the adlayer is isolated. However, for one overlayer the LDOS of the adlayer preserves the characteristic features of the unsupported layer, which are largely determined from the structure of the adlayer. But the density of states at E_F may change significantly. This should, in particular, be true for the constituents whose bands do not overlap much. For an overlayer of Pd*(110) or Pd(111) the density of states at E_F is very small. This is again in agreement with the experiments on Pd on Nb(110) and on Pd on Ag(111).[8] It is due to the narrowing of the band because of fewer like neighbors and also because of the shift of the band due to the interaction with the substrate.

Another interesting result of the LDOS is that for two unsupported layers the LDOS of a Pd(111) layer does not depend very sensitively on whether the other layer has a Pd*(110) or a Pd(111) structure. This result can be understood presuming that the d electrons respond more sensitively to the distance changes than to the direction, the coordination being not very different. That this is true is also seen from the similarity of the LDOS of the unsupported Pd(111) and Pd*(110) monolayers. This trend is reflected again on interface formation where the LDOS of the top Pd(111) layer is very similar for Pd(111) or Pd*(110) underlayers.

Our results for a Pd(111) surface are in very close agreement with the self-consistent pseudopotential calculations of Louie[39] except that we do not get a peak near the bottom of the band because we have not considered the s-d hybridization. Similarly, the bulk density of states was in good agreement with the detailed band-structure calculations. In our calculations we did not consider the spin-orbit coupling. However, it has been shown[34] that for Pd, its effect on the LDOS is not significant.

Note that in the case of the Pd*(110) overlayer the H uptake is very small, as on a clean Nb(110) surface. For the latter this is because hydrogen prefers to sit at the surface due to its large chemisorption energy. For the interface we think two reasons are responsible for the small H uptake. (1) Initially H interacts with the free-electron-like s-p charge. For Pd*(110) we conclude that the density of this charge is smaller than it is in the case of the clean Pd(111) surface. It has been shown[40] from jellium-model calculations that the change in the binding energy of hydrogen is small as the jellium density is changed. In fact, for transition metals, over the whole series the jellium contribution to the chemisorption energy remains almost constant and the variation comes from the d-band contribution.[41] For Pd*(110) structures the d states are more filled as compared to the Pd(111) surface, and therefore a decrease in the binding energy of atomic hydrogen should be expected and this will inhibit hydrogen dissociation. In addition, if the binding energy of the molecular hydrogen remains the same as on Pd(111), there will also be an increase in the activation barrier for dissociation. (2) The density of states at E_F in the Pd*(110) structure is very small. This will again suggest little involvement of the d band in the hydrogen bonding and charge transfer as for noble metals. A small increase in the H uptake around structural transformation is due to a small increase in the density of states at E_F and the number of d holes. Notice that a large density of states at E_F for Pd is also responsible[42] for hydride formation. One can then further argue that if the hydrogen is dissociated at the Pd*(110) surface, the low density of states at E_F does not favor hydrogen to sit inside, and hence a low H uptake results. On the other hand, the diffusion barrier for hydrogen on Pd*(110) may be very small so that it can easily recombine, and therefore at room temperature no atomic hydrogen is observed[6] in the electron-stimulated desorption, and also no change is observed in the work function or photoemission.

We expect the H uptake to depend also on the interface binding energy. The stronger the interface binding, the smaller the probability to absorb hydrogen should be. For example, a significant increase in the H uptake is observed only after two or three layers of Pd are deposited. We interpret this to result partly also from the decrease in the interaction of Pd with Nb.

These remarks on the facts favoring H uptake may prove useful in designing materials which resist or favor absorption or chemisorption. In particular, it will be interesting to perform experiments for interfaces with a transition-metal-like Ni, Pd, or Pt on a simple metal such as Mg, which is a potential candidate for hydrides from a technological point of view, and on Ti, Zr, and V.

C. The work function and electron charge transfer

The work function ϕ of the Nb(110) surface decreases linearly up to Pd coverages of $\Theta \approx 0.8$ even though Pd is more electronegative. Also for Pd on Ag(100) (Ref. 8) and W(110) (Ref. 43) a decrease in ϕ is observed. Generally a decrease in the work function is explained by a charge transfer from adsorbate to the substrate. However, there are several factors which may be responsible for this different behavior of ϕ. First, at submonolayer coverages a decrease in the work function by a few tenths of an electron volt has been observed even in the case when a metal is depositied on its own substrate, e.g., W on W(110).[44] This is understood in terms of the smoothing effect discussed by Smoluchowski.[45] Note, rough surfaces have smaller work functions than smoother surfaces. Secondly, at interfaces the structure of the overlayer may be different from its bulk structure. This is generally expected and is also the case for Pd on Nb(110). With the use of these two arguments one may understand the behavior of ϕ observed for Pd on Nb. For example, for the C structure the number of d electrons on Pd is larger than in the bulk. Consequently, the free-electron charge density will be smaller. For simple metals it has been shown[46] that then ϕ decreases. Furthermore, note for the C interface that the electronic structure looks similar to that of Ag, which has a smaller work function[47] than clean Nb(110). Finally, the charge transfer between the adsorbate and the substrate will also change ϕ. (There can also be a contribution to ϕ due to the polarization of the core charge as discussed by Wimmer *et al.*[48]) Note, at low coverages there is a small d-charge transfer from Pd atoms to Nb. However, we expect a reverse transfer of s charge from Nb to Pd. If there is a net charge transfer to Nb then the smoothing effect and the dipole due to charge transfer will add to give a larger decrease in ϕ. Since the decrease in ϕ is small we conclude that the two effects may even be competing. Note that at low coverages both effects are linear in coverage and thus the resultant change in ϕ will also be linear. In any case we expect a very small net charge transfer. Now, according to the microscopic theories[49] for alloy heat of formation, the s-p charge transfer occurs in a direction such that the electron density mismatch at the boundary is eliminated. The d-charge transfer is a bit more complicated and depends[50] upon the difference in the number of d electrons of the two constituents, the relative position of the center of gravities of the d bands, and the alloy bandwidth, and not on the difference in the Fermi levels of the pure constituents. The intermediate charge density for Nb is more[51] than it is for Pd and so an s-p charge transfer from Nb to Pd should be expected.[52] In our calculations the d-charge transfer is always very small (less than $0.02e$). For $\Theta < 1$ the d-electron charge transfer is to Nb and for $\Theta \gtrsim 1$ the reverse occurs. Therefore, it seems that for low coverages where s- and d-electron charge transfers occur in opposite directions the smoothing effect and the changes in the electronic configurations are more responsible for the decrease in the work function. Also in analogy to expanded Pd on Ag(100) (Ref. 8) we expect for the expanded Pd layer on Nb(110) a smaller ϕ than the one for the equilibrium structure. For $\Theta \gtrsim 1$ the work function starts increasing, since both s- and d-electron charge transfer is from Nb to Pd and is also due to the structural transformation. Finally, the decrease of the work function upon hydrogen exposure in the *IC* structure may be due to the fact that hydrogen now lies below the surface.

D. General comments

Our results concerning the smaller density of states at E_F for an overlayer of Pd on Nb(110) should be true also for Ni and Pt irrespective of the substrate, at least within the same d series. Since for these elements ϵ_d lies below one of the other elements in the series (except noble metals), after chemisorption their band will be shifted to larger binding energy resulting in a smaller density of states at E_F. Note, this is important, e.g., for surface magnetism, superconductivity, and the properties of coherent modulated structures. Further the changes in the lattice structure induced by interface formation result in a s-d electronic configuration change. Since Ni, Pd, and Pt are next to the inactive noble metals, such changes are very important for their selectivity and catalytic properties. Among the transition metals, Ni has the smallest covalent radius and an overlayer of it will be in an expanded form. Contrary to Pd and Pt, the atomic configuration of Ni is $3d^8(3d^9)$. Thus the chemical activity of Ni-covered surfaces may help to clarify whether at the surface the charge configuration tends toward its atomic value. On the other hand, in the case of a noble-metal overlayer, lattice contractions and a likely d-electron charge transfer to the substrate will create d holes and can make them catalytically active as for Au on Pt(100).[2]

From a microscopic point of view metal-metal interfaces and an interface between atomic cells of the constituents in an alloy are similar. Therefore, the charge transfer and the heat of interface formation should behave similar to an alloy. Further, our conclusion that interface binding energy decreases when the second layer is deposited should be general. In case there is a large lattice mismatch, a structural transformation may occur around $\Theta = 1$. However, for systems where the lattice mismatch is small, strained structures may continue for several layers (particularly when both adsorbate and substrate have same lattice structure) as for Pd on Ag(100).[8]

While our calculation of interface energy is simple, it serves well for a qualitative understanding. Note, such a type of calculation has already proved very fruitful in the study of surface segregation.[36] A similar calculation could also be used for the study of interface mixing and segregation. For interfaces where the overlayer is contracted, repulsive (strain energy) contributions should also be taken into account.

In summary, we have illustrated that by comparing LDOS calculations with the photoemission data, it is possible to learn about interface structures and structural transformations which may occur as a function of coverage. Clearly, the electronic structure due to interface formation plays a very important role in surface reactions. Since a large variety of microscopically different interfaces can be fabricated, metal-metal interfaces form a unique class for catalysis and we expect more exciting results in this field in near future.

ACKNOWLEDGMENTS

We are thankful to M. Strongin, J. W. Davenport, A. R. Williams, and J. K. Nørskov for useful discussions. This work was partly supported by Deutsche Forschungsgemeinschaft.

---

[1] See for a review J. P. Bibérian and G. A. Somorjai, J. Vac. Sci. Technol. 16, 2073 (1979).

[2] J. W. A. Sachtler, J. P. Bibérian, and G. A. Somorjai, Surf. Sci. 110, 43 (1981).

[3] G. Bergmann, Phys. Rev. Lett. 41, 264 (1978); Phys. Today 32, (8) 25 (1979).

[4] M. A Pick, J. W. Davenport, M. Strongin, and G. J. Dienes, Phys. Rev. Lett. 43, 286 (1979).

[5] M. Strongin, M. El Batanouny, and M. Pick, Phys. Rev. B 23, 3126 (1980).

[6] M. El Batanouny, M. Strongin, G. P. Williams, and J. Colbert, Phys. Rev. Lett. 46, 269 (1981).

[7] Shang-Lin Weng and M. El Batanouny, Phys. Rev. Lett. 44, 612 (1980).

[8] G. C. Smith, C. Norris, C. Binns, and H. A. Padmore, J. Phys. C 15, 6481 (1982).

[9] I. Abbati, L. Braicovich, A. Fasana, C. M. Bertoni, F. Manghi, and C. Calandra, Phys. Rev. B 23, 6648 (1981).

[10] J. Tersoff and L. M. Falicov, Phys. Rev. B 26, 6186 (1982).

[11] Ding-sheng Wang, A. J. Freeman, and H. Krakauer, Phys.

Rev. B 24, 1126 (1981); 26, 1340 (1982).

[12] O. Bisi and C. Calandra, Surf. Sci. 67, 416 (1977).

[13] See articles by R. Haydock, V. Heine, and M. J. Kelly, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35.

[14] V. Kumar and K. H. Bennemann, Phys. Rev. B 26, 7004 (1982).

[15] J. E. Demuth, Surf. Sci. 65, 369 (1977).

[16] This has been done because (i) the most significant changes have been reported (Refs. 6 and 7) to occur in the *d*-band emission and (ii) in the incommensurate structure, the computer storage increases enormously with the inclusion of the *s*-*p* electrons.

[17] V. Heine, Phys. Rev. 153, 673 (1967).

[18] There are several band-structure calculations (Refs. 19—21) for the 4*d*-series metals which give different charge configurations and $\Delta\epsilon_d$ ranging between 0.3 and 0.4 Ry. Note that in the atomic case the *d* level of Pd ($4d^{10}5s^0$) lies (Ref. 22) 0.1383 Ry below that of Nb ($4d^4 5s^1$). We could have also chosen $\Delta\epsilon_d$ such that the difference in the Fermi energies become equal to the difference (0.055 Ry) in the work functions. In some calculations we tried different values of $\Delta\epsilon_d$. However, because of the self-consistency the final positions of the bands do not differ much except for the case of submonolayer coverages where $\rho(E_F)$ of Pd remains very small and the effect is almost a rigid shift of the Pd band.

[19] D. Glötzel and O. K. Anderson, Adv. Phys. (in press).

[20] L. Hodges, R. E. Watson, and H. Ehrenreich, Phys. Rev. B 5, 3953 (1972).

[21] D. G. Pettifor, J. Phys. F 7, 613 (1977).

[22] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, 1963).

[23] At very low coverages, the adsorption will be similar to the case of a single atom. For atomiclike adsorption the *d*-electron charge on a Pd atom will be more than in the bulk Pd and therefore the *d* level will be pushed to lower binding energy. However, the shift of the *d* level due to the compression of the *s*-*p* charge in the bulk will be much less at the surface and so the *d* level should drop to higher binding energy.

[24] S. Froyen, Phys. Rev. B 22, 3119 (1980).

[25] J. C. Slater and C. Koster, Phys. Rev. 94, 1498 (1954).

[26] R. Haydock and M. J. Kelly, Surf. Sci. 38, 139 (1973).

[27] R. J. Smith, Solid State Commun. 37, 725 (1981).

[28] At $\Theta=0.25$ and 0.5 and for the *IC* structure all the atoms in the Nb layer are treated equivalently for the purpose of self-consistency.

[29] In the case of Pd(111) overlayers, one layer will correspond to a coverage of about 1.15 monolayers.

[30] Our intention is to show the main features of the density of states, which do not change much by doing the calculations self-consistently.

[31] In a self-consistent calculation the excess charge on these orbitals will have an effect to shift their subband center of gravity to lower binding energy and, consequently, a shift in the peak positions of the total density of states.

[32] The sharp peaks at the two extremes of the band have very little weight and are due to some eigenvalue of the cluster.

[33] In our calculations we considered 9.8 and 9.6 electrons of *d* charge for Pd*(110) and Pd(111) layers. This should be a reasonable choice as we expect that in going from Pd(111) surface to a monolayer, the *d*-charge configuration should tend to go in the direction of atomic behavior. Note, in a recent self-consistent band calculation for unsupported (100) monolayers of Pd, Ni, and Fe, an increase of unsupported (100) monolayers an increase of about 0.2 *d*-electron charge as compared to bulk has been reported (Ref. 34).

[34] J. Noffke and L. Firtsche, J. Phys. C 14, 89 (1982).

[35] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley, and D. D. Wagman, *Selected Values of the Thermodynamic Properties of the Elements* (American Society for Metals, Metals Park, Ohio, 1973).

[36] V. Kumar, Phys. Rev. B 23, 3756 (1981).

[37] E. Bauer, Surf. Sci. 7, 351 (1967).

[38] J. P. Muscat and D. M. Newns, Prog. Surf. Sci. 9, 1 (1978).

[39] S. G. Louie, Phys. Rev. Lett. 40, 1525 (1978).

[40] H. Hjelmberg, Physica Scripta 18, 481 (1978).

[41] J. K. Nørskov, Phys. Rev. Lett. 48, 1620 (1982).

[42] A. R. Williams, J. Kübler, and C. D. Gelatt, Jr., Phys. Rev. B 19, 6094 (1979).

[43] W. Schlenk and E. Bauer, Surf. Sci. 93, 9 (1980).

[44] K. Besocke and H. Wagner, Phys. Rev. B 8, 4597 (1973).

[45] R. Smoluchowski, Phys. Rev. 60, 661 (1941).

[46] N. D. Lang, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1973), Vol. 28.

[47] *Handbook of Chemistry & Physics,* edited by R. C. Weast (CRC, Florida, 1981).

[48] E. Wimmer, A. J. Freeman, M. Weinert, H. Krakauer, J. R. Hiskes, and A. M. Karo, Phys. Rev. Lett. 48, 1128 (1982).

[49] A. R. Williams, C. D. Gelatt, Jr., and V. L. Moruzzi, Phys. Rev. Lett. 44, 429 (1980); 44, 764(E) (1980).

[50] D. G. Pettifor, Solid State Commun. 28, 621 (1978).

[51] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[52] Care should be taken as at the surface the Wigner-Seitz cell for the adsorbate layer may be different than in the bulk of that material and so there may be a different charge density at the boundary. However, the argument holds for Pd on Nb(110).