Interference, resonances, and bound states at the Pd(001) and Rh(001) surfaces

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(Received 18 May 1994)

We have calculated the $\mathbf{k}_{||}$-, symmetry-, and layer-resolved density of states (DOS) at $\mathbf{k}_{||} = \mathbf{0}$ for Pd and Rh (001) surfaces. For the xy and x^2-y^2 subbands, which do not hybridize with any other low-lying orbitals, the resulting DOS closely resembles that of a one-dimensional semi-infinite chain of nondegenerate tight-binding atomic orbitals perturbed by a repulsive potential at the terminal site. It displays interference induced oscillations and bound states or resonances of particular simplicity.

Detailed knowledge of surface electronic structure is essential to a deep understanding of such surface phenomena as atomic and molecular mobility and the various aspects of surface chemistry — chemisorption, reactivity, and catalysis. We have shown, for example,[1,2] that the local density of states (DOS) at the surface of a metal plays a fundamental role in its chemical reactivity. It has long been known that the surface electronic structure differs from the bulk electronic structure. Tamm already recognized the possible existence of surface states, i.e., bound states, occurring within gaps in the bulk continuum and spatially localized near the surface.[3] These have been found experimentally, e.g., in studies of angular-resolved photoemission,[4] and theoretically in calculations of the electronic structures of slabs.[5]

However, more happens at the surface than simply the formation of bound states. To reveal these changes, it is necessary to disaggregate the total DOS into its component parts. In both Rh(001) and Pd(001), the energy dependence of the layer-resolved DOS for the surface layer is distinctly different from that of the bulk but rapidly relaxes back to the bulk dependence in successive atomic layers, becoming indistinguishable from that of the bulk in the third to fourth layer.[6,7] Decomposing the layer-resolved DOS into its components of various point symmetries reveals that d states of different symmetries are quite differently affected by the presence of the surface.[1] The rapid relaxation back to the bulk behavior persists in the symmetry- and layer-resolved DOS.

This rapid relaxation back to the bulk behavior even for the symmetry-resolved DOS is attributable to screening, i.e., the lowering of energy by the maintenance of almost perfect local charge neutrality and near sphericity of the electron distribution near the cores, except for the surface layer. However, it contrasts strongly with the behavior of simple one-dimensional (1D) models, which show strong interference effects in the local DOS.[8] These arise from reflection at the surface and persist deep within the material. In the present paper, we shall show that such persistent effects indeed occur in Pd(001) and Rh(001), but they are masked in the symmetry- and layer-resolved DOS both by the averaging over wave vectors parallel to the surface ($\mathbf{k}_{||}$) and by the mixing of states of different local angular momentum but equivalent symmetry.

To uncover the persistence of interference effects and to reveal clearly surface resonances and bound states, it is necessary to disaggregate the DOS further into the $\mathbf{k}_{||}$-, symmetry-, and layer-resolved DOS. One then finds that the resulting spectral density $A(\mathbf{k}_{||}, \alpha, p; E)$, with α the symmetry type and p the layer number, displays all of these features clearly at $\mathbf{k}_{||} = \mathbf{0}$ for certain symmetries. Such disaggregation is not merely an academic exercise; it is important for understanding chemical reactivity.[1,10] Moreover, the angular-resolved normal photoemission spectra are particularly suited for the investigation of electronic structure since they select transitions for which $\mathbf{k}_{||} \approx \mathbf{0}$, and the spectra are characterized by well-resolved peaks related to the one-dimensional density of states along the corresponding low-index symmetry line weighted by corresponding optical transition elements. It is particularly easy to see that along the $\Gamma X\langle 001\rangle$ symmetry line, the xy and $x^2 - y^2$ subbands do not mix with states of different angular momentum l but equivalent symmetry with $l < 3$. States of $l \geq 3$ are of too high an energy to be considered. Thus, we first consider the contributions from those d orbitals on the surface plane, namely xy and $x^2 - y^2$, to the spectral density of states $A(\mathbf{k}_{||}, \alpha, p; E)$ for $\mathbf{k}_{||} = \mathbf{0}$ and for a Pd(001) surface. The d orbitals here are referred to the coordinate system with the x and y axes along the edges of the bulk (cubic) unit cell. Figures 1 and 2 show these contributions as well as the total layer-resolved spectral density for the surface and first three interior planes for Pd(001) and the corresponding infinite crystal result. Corresponding results for Rh(001) are qualitatively very similar.

The DOS calculations were performed by means of an efficient scalar-relativistic self-consistent, surface Green's function technique based on the tight-binding linear muffin-tin orbital theory. The details of the method have been described elsewhere.[7,9] It is important to mention here that the potentials were calculated self-consistently in an intermediate region consisting of the surface layer, three substrate layers, and two layers of empty spheres

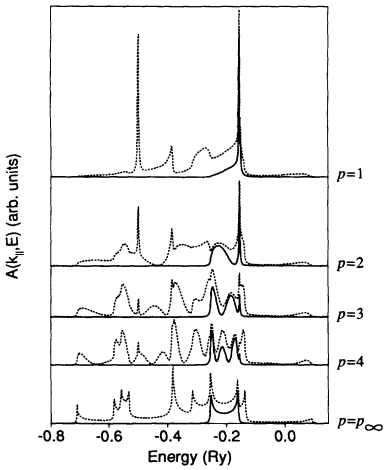

FIG. 1. $x^2 - y^2$ contribution (solid line) to the layer- and $\mathbf{k}_{||}$-resolved DOS at the $\bar{\Gamma}$ point for a Pd(001) surface. The top four sample layers are denoted by the layer number p, $p = 1, 2, 3, 4$, while $p = p_\infty$ refers to the bulk. The dotted lines are the total layer, and $\mathbf{k}_{||}$-resolved DOS. The position of the bulk substrate Fermi level is at -0.16 Ry.

simulating the vacuum-sample interface. This intermediate region is coupled to the semi-infinite vacuum on one side and to the semi-infinite crystal on the other, with frozen potentials. We note the overall good agreement of our calculated work functions, 5.82 eV for Pd(001) and 5.92 eV for Rh(001) with those obtained by other methods for the same systems.[11,12]

In general, there are two different types of stationary states that can exist in a cleaved crystal. There are bulk states, recognizable distortions of states existing in the infinite crystal, which occur over the energy interval of the full band width of the infinite crystal, and there are truly surface states at energies outside the allowed region for the particular $\mathbf{k}_{||}$.

Figures 1 and 2 show that $A(\mathbf{0}, \alpha, p; E)$, $\alpha = x^2 - y^2$, xy $p \to \infty$, i.e., for a perfect (infinite) crystal closely resembles the local density of states at any site in an infinite unperturbed 1D monatomic chain with nearest neighbor interactions t. The local DOS for that particular model, $1/\pi\ [(2t)^2 - E^2]^{-1/2}$, varies symmetrically from the minimum at the band center to the van Hove singularities at the band edges. For the surface layer and substrate layers underneath, on the other hand, $A(\mathbf{0}, \alpha, p; E)$, $\alpha = x^2 - y^2$, xy, resembles the local DOS at the mth atomic site ($p = m$) of the perturbed semi-infinite chain with a localized potential perturbation V_1 at the surface atom ($m = 1$).[8] Figures 1 and 2 illustrate how the local DOS asymptotically approaches the infinite crystal DOS as the layer index increases. It can be shown that the oscillatory behavior exhibited by these contributions inside the band is such that the number of minima equals $p - 1$.

An early surface state calculation using a Green's function formalism to investigate the density of states of both extended and surface states in semi-infinite crystals was performed by Kalkstein and Soven, who analyzed the case of a nondegenerate band in a simple cubic lattice.[13] In the present work, we deal with the analysis of a first-principles calculation of a realistic surface in an attempt to further our understanding of transition metal surface state properties. The similarity of these xy and $x^2 - y^2$ subband contributions to $A(\mathbf{k}_{||}, \alpha, p; E)$ at $\mathbf{k}_{||} = \mathbf{0}$ to the simple 1D-semi-infinite model enables us to analyze the existence condition for bound states of that particular symmetry at the (001) surface of Pd as an example. The possibility of such detailed analysis combined with angular-resolved photoemission measurements can be extremely helpful in determining the character of these states localized at the surface and, therefore, readily available for chemisorption.[1]

In Fig. 3, we show the d-subband contributions to the surface spectral DOS at the $\bar{\Gamma}$ point. An analysis of the surface state existence condition for those subbands other than xy and $x^2 - y^2$ in terms of the perturbed semi-infinite chain model, is not as straightforward due to the presence of hybridization of the orbitals of different angular momenta along the ΓX direction.

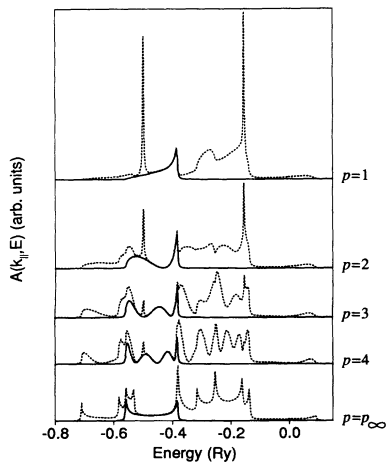

FIG. 2. The same as in Fig. 1 but for the xy subband.

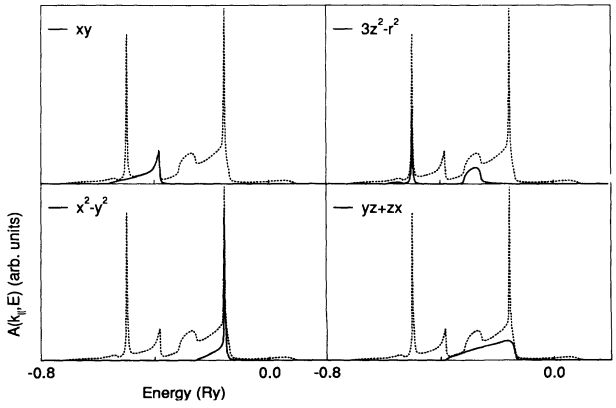

FIG. 3. d-subband contributions (solid line) to the layer- and $\mathbf{k}_{||}$-resolved DOS at the $\bar{\Gamma}$ point for a Pd(001) surface layer. The dotted line is the total layer- and $\mathbf{k}_{||}$-resolved DOS. The position of the bulk substrate Fermi level is at -0.16 Ry.

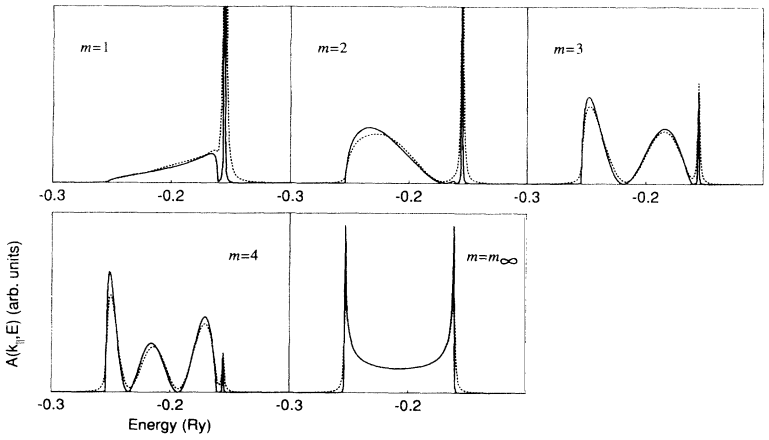

FIG. 4. The local density of states for the surface atom $m = 1$ and first three interior neighbors for the perturbed semi-infinite chain and the value $V_1/2t = 0.82$. $m = m_\infty$ refers to any site of the unperturbed infinite chain. The dotted lines are the $x^2 - y^2$ contributions to the layer- and $\mathbf{k}_{||}$-resolved DOS at the $\bar{\Gamma}$ point for the four top sample layers of a Pd(001) surface. The position of the bulk substrate Fermi level is at -0.16 Ry.

At a (001) surface the qualitative effects of a potential perturbation at the surface layer depend on whether it is strong enough to produce bound states.[13] In the perturbed 1D-semi-infinite chain, bound states can occur for $|V_1|/2t > 1/2$, where $4t$ is the subband width and V_1 the perturbation at the surface site.

In Fig. 4, the local DOS for the surface atom and the three interior atomic sites for the perturbed 1D-semi-infinite chain for the case $V_1/2t = 0.82$ are compared with the calculated $x^2 - y^2$ subband contributions to the spectral DOS at $\bar{\Gamma}$. The corresponding results are shown in Fig. 5 for the xy subband for $V_1/2t = 0.45$. It is very clear from this comparison that a surface bound state exists for $x^2 - y^2$ and that a resonance or virtual bound state exists for xy. The bound state is localized near the surface plane and decreases monotonically in probability as $(V_1/2t)^{2(m-1)}$ as one proceeds inwards. The resonance, of course, has a tail in the bulk.

The finite width of the bound state shown in Fig. 4 for the simple model arises from the fact that it not strictly $A(\mathbf{0}, \alpha, p; E)$ which we compute but $1/\pi$ times the imaginary part of the Green's function at $E - is$ with $s = 1 \times 10^{-3}$. The greater broadening of the peaks in $A(\mathbf{0}, \alpha, p; E)$ and the filling in of the minima apparent for the Pd(001) computations are artifacts which can be eliminated.

As one clearly sees from Figs. 4 and 5, the number of oscillations of $A(\mathbf{k}_{||}, \alpha, p; E)$ within the subband energy interval increases with the layer index p just as in the simple model. The oscillations in the DOS of the simple model arise from interference between the Bloch waves incident on and reflected from the surface both in the absence and presence of the surface-atom perturbation. For the (001) surfaces of Pd and Rh an entirely analogous process takes place at $\mathbf{k}_{||} = \mathbf{0}$ for $\alpha = xy$ and $x^2 - y^2$.

Thus, by comparing our calculated results for the surface electronic structures of fcc (001) surfaces of Pd and Rh with that of a 1D tight-binding semi-infinite chain of nondegenerate orbitals, we have clearly demonstrated the existence of interferences, surface states, and surface resonances of a particularly simple nature at $\mathbf{k}_{||} = \mathbf{0}$. This simplicity is lost away from $\mathbf{k}_{||} = \mathbf{0}$ because of hybridization and the breakdown of one dimensionality.

These results suggest that stronger perturbations of the surface by, for example, overlayers, segregation, or surface alloys can produce more strongly bound surface states which may retain their simple character and persist further away from $\mathbf{k}_{||} = \mathbf{0}$.

This work was part of the program of the Consor-

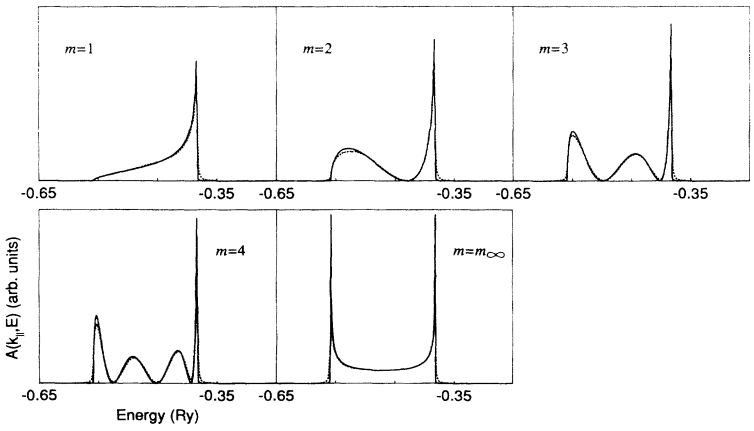

FIG. 5. The same as in Fig. 4 but for the xy subband and $V_1/2t = 0.45$.

tium on "The Physical Aspects of Surface Chemistry on Metals, Alloys, and Intermetallics." M. V. Ganduglia-Pirovano would like to thank Professor P. Fulde for his hospitality at the Max Planck Institute in Stuttgart, where part of this work was carried out. One of us (J.K.) acknowledges the financial support from the Academy of Sciences of the Czech Republic (Project No. 110437) and the Austrian Science Foundation (P8918).

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