

Electronic States and Adsorbate-Induced Photoemission Structure on the Pd(111) Surface

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The electronic structure of the Pd(111) surface is calculated using a recently developed mixed-basis pseudopotential method. Fully self-consistent results, including surface states, work function, local densities of states, and electronic charge densities, are presented. The commonly observed adsorbate-induced changes in *d*-band structure in the photoemission spectra are interpreted in terms of the surface states. An *s-p*-like intrinsic surface-state band similar to the one observed on Cu(111) is also predicted.

The fcc group-VIII transition-metal surfaces (Ni, Pd, and Pt) have generated a great deal of interest in recent years because of their active catalytic properties. Experimentally, a wealth of spectroscopic data are now available for both the clean and the various chemisorbed surfaces. Theoretically, the complexity arising from the *d* electrons has made realistic calculations exceedingly difficult. Although several model calculations¹ have been performed on these surfaces, their surface electronic structure is still far from well understood. Thus far in the literature, the only fully self-consistent calculation even related to the group-VIII transition-metal surfaces is a three-layer slab calculation² on the (100) surface of Cu in which good agreement was obtained with experiment for the work function. The thinness of the slab, however, limits further information (e.g., on surface states) from being reliably obtained from such calculations.

In this Letter I present results of a realistic self-consistent theoretical study of the electronic structure of a member of this important class of surfaces. The (111) surface of Pd is chosen as a prototype. The calculation is carried out using a newly developed mixed-basis pseudopotential method³ and supercell technique with a seven-layer metal film. Achievement of electronic self-consistency for a seven-layer model allows a detailed study of the energy dispersion and spatial distribution of surface states as well as the layer-by-layer changes in both the electronic charge densities and the local density of states (LDOS) near the surface. The Pd(111) surface exhibits a rich electronic structure including eleven prominent surface-state bands. The energy spectrum of these surface states (resonances) provides a natural explanation for the origin of a frequently observed, but heretofore unexplained, adsorbate-induced feature in the photoemission spectra of the surface.^{4,5} Moreover, a surface-state band of *s-p* character existing near $\bar{\Gamma}$ [similar to that observed experimentally at the (111) surface of

Cu, Ag, Au, and Ni]^{6,7} is predicted.

A novel feature of the present approach over previous self-consistent methods is that a combined set of plane waves and localized functions (e.g., Gaussians) is employed as basis functions. This basis set leads to a very efficient representation of the wave functions of systems such as transition metals which contain both highly localized (atomiclike) and delocalized (plane-wave-like) electrons. Furthermore, since no shape approximations (e.g., muffin-tin potentials or exclusively atomic orbital wave functions) have been made, electrons in systems with open structure or those at surfaces and interfaces can be treated easily and accurately using this method.

In the present calculation, a seven-layer slab of Pd is placed in a periodic superlattice with the slabs separated by a distance equivalent to four atomic layers of Pd. The electron wave functions are expanded as

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\alpha} \alpha_{\alpha}(\mathbf{k}) \exp[i(\mathbf{k} + \bar{\mathbf{G}}) \cdot \mathbf{r}] + \sum_j \beta_j(\mathbf{k}) \varphi_j(\mathbf{k}, \mathbf{r}),$$

where the $\bar{\mathbf{G}}$'s are reciprocal lattice vectors and the φ_j 's are Bloch sums of localized orbitals. Each localized orbital is composed of a radial part $r^l e^{-\alpha r^2}$ and an angular part consisting of $l=2$ spherical harmonics around the Pd atom. Matrix elements involving the φ_j 's are accurately evaluated by performing three-dimensional numerical integrations using fast-Fourier-transform techniques. Electronic screening is achieved by use of a Hartree potential derived from the valence charge density⁸ via Poisson's equation and a local-density exchange-correlation potential.⁹ The input to the calculation therefore consists of the atomic positions [the ideal (111) surface] and a fixed ionic pseudopotential for the Pd⁺¹⁰ ion core. The Pd⁺¹⁰ ionic potential used is an *l*-dependent pseudopotential obtained by fitting to calculated (local-density) energies and wave functions of the neutral Pd atom in various atomic configurations. With this ionic potential and a basis set consisting of about ~ 30 plane waves plus five localized

functions per atom, a self-consistent bulk band structure is obtained which is in very good agreement with experiments and previous calculations.¹⁰ The same convergence criteria are used in the surface calculations, i.e., ~300 plane waves plus 35 φ_j 's in the basis set.

In the discussion of the surface-related results to follow, a layer is defined to be a slab, centered about an atomic plane, which is one interplanar distance thick. The surface layer, the first layer below the surface, the second layer below the surface, etc., are labeled as layer 1, layer 2, layer 3, and so on.

The calculated work function, φ , is 5.8 eV which agrees very well with the value of 5.6 eV obtained experimentally for Pd(111).⁵ An electronic charge distribution of 10.0, 10.1, 9.7, and 0.2 electrons per surface unit cell is found for layers 3, 2, 1, and the vacuum region extending beyond the surface layer, respectively. It is noted that, while the total charge is neutral near the surface, a nonnegligible charge redistribution is necessary to obtain the correct work function. For perspective, φ 's for the 3d transition metals calculated using a superposition of atomic charge densities are approximately twice the measured values¹¹ and the Thomas-Fermi approximation systematically gives $\varphi = 0$. Hence the requirement of rigid charge neutrality for each atom, as imposed in many non-self-consistent calculations,¹² appears to be too severe a restriction.

Eleven prominent surface-state bands (Fig. 1) are found to exist for the Pd(111) surface. Most of the surface states are predominantly d-like in character. An exception is the surface-state

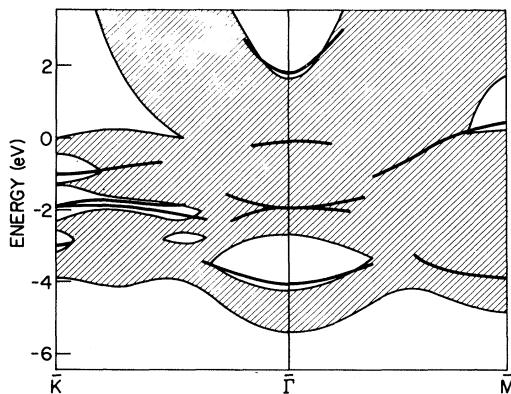


FIG. 1. Surface-state bands (solid curves) and the projected band structure (shaded areas) in the $\bar{K} = 2\pi/a(0, -\frac{2}{3}, \frac{2}{3})$ and $\bar{M} = 2\pi/a(-\frac{1}{3}, -\frac{1}{3}, \frac{2}{3})$ directions for the Pd(111) surface. (E_F is 0 eV.)

band ~2 eV above E_F which is purely s,p-like. A surface band of the same symmetry and at approximately the same energy relative to the bulk projected band gap has been observed experimentally for the (111) surfaces of Cu, Ag, and Au⁶ and recently for Ni(111).⁷ In Fig. 2(a) the charge density for a state at $\bar{\Gamma}$ of this s,p surface band is depicted. Because of its free-electron-like character, the wave function penetrates quite far both into the bulk and into the vacuum.¹³ For comparison, the charge distributions of a twofold degenerate surface state at -1.9 eV at $\bar{\Gamma}$ [Fig. 2(b)] and a surface state at -1.0 eV at \bar{K} [Fig. 2(c)] are presented in Fig. 2. As expected, the d-like surface states are much more localized on the surface atoms. The states at $\bar{\Gamma}$ [Fig. 2(b)] are mostly of $d_{x^2-y^2,xy}$ symmetry, where \hat{z} is the surface normal and \hat{x} is the direction of a primitive translation vector of the surface hexagonal unit cell. The state at \bar{K} [Fig. 2(c)] is primarily of $d_{zx,zy}$ symmetry. The remaining surface states correspond to states of various d-angular-momentum components localized in either the first

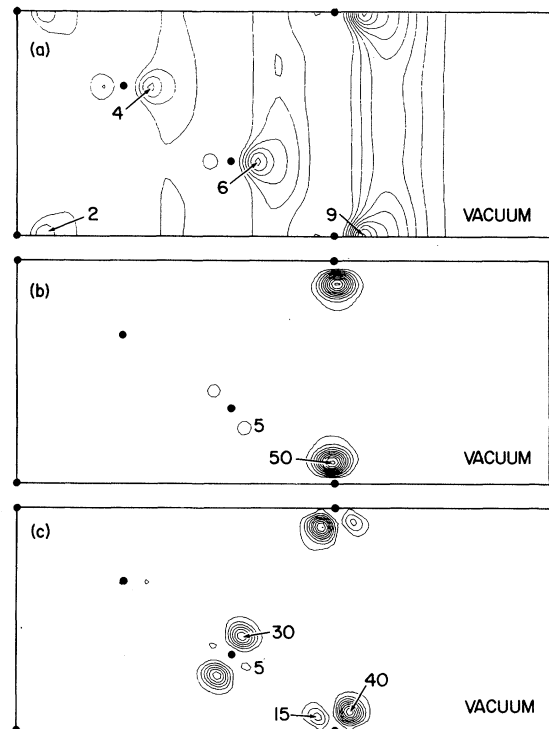


FIG. 2. Charge-density contour plots for surface states at (a) 1.9 eV at $\bar{\Gamma}$, (b) -1.9 eV at $\bar{\Gamma}$, and (c) -1.0 eV at \bar{K} . The charge densities are normalized to 1 electron per unit cell and plotted for a (110) plane cutting the Pd(111) surface.

or second atomic layers. A full discussion of the surface states will be given in a longer paper.

Figure 3(a) depicts the LDOS for layer 4 which is at the center of the slab. This spectrum is essentially identical to the calculated bulk density of states indicating that significant perturbations arising from the surface do not penetrate deeper than three layers into the bulk. Compared to the LDOS for the center layer (or the bulk), there are dramatic changes in the energy distribution of the electronic states at the surface layer [Fig. 3(c)]. Changes of a lesser extent are found for layer 2 [Fig. 3(b)]. For the surface layer, the LDOS is enhanced in the region from 0 to 2 eV below E_F at the expense of the state density near the bottom of the d bands. This is a direct consequence of the existence of numerous surface states near the Fermi energy. (See Fig. 1.) The calculated second moments for the d -band LDOS normalized to the value for the central layer are 1.01, 1.05, and 0.84 for layers 3, 2, and 1, respectively. (The value for layer 1 varies by $\sim 2\%$ depending on the choice of the d -band region.) The calculat-

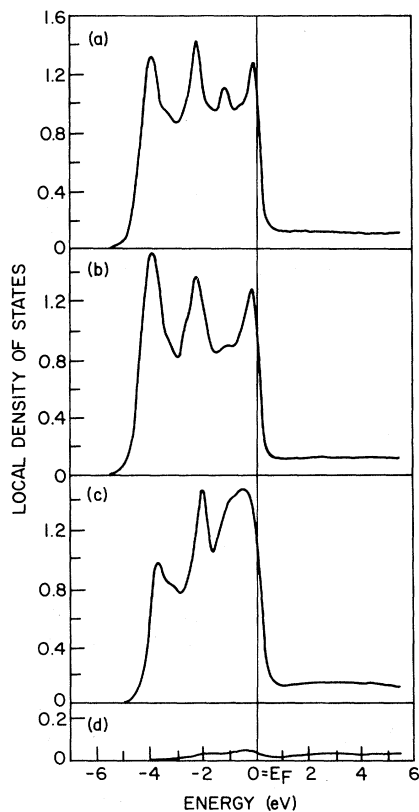


FIG. 3. Calculated local density of states for (a) layer 4, (b) layer 2, (c) layer 1 (the surface layer), and (d) a region one layer thick beyond the surface layer.

ed decrease of 16% in the second moment for the surface layer LDOS is smaller than the 25% predicted by nearest-neighbor tight-binding models.¹ The tight-binding result reflects only the reduced number of nearest neighbors in the surface layer (9 rather than 12) and ignores completely the effects of charge rearrangements. This incomplete narrowing of the surface d bands relative to that found in tight-binding models suggests that self-consistent screening enhances interactions among the surface atoms. Recent measurements by Mehta and Fadley¹⁴ on polycrystalline Cu appear to support this conclusion.

Finally, the present results provide a physical interpretation for a heretofore unexplained structure in the angle-integrated photoemission spectra of the Pd(111) surface. It is observed that, upon the introduction of the adsorbates, a very characteristic (approximately adsorbate-independent) reduction in the experimental photoemission intensity occurs in the energy range from 0 to 2 eV below E_F .^{4,5} (Similar effects are also observed in Ni and Pt.¹⁵) Since, roughly speaking, these experiments measure the LDOS near the surface, I interpret this reduction as largely due to the removal (bonding away to lower energies) of surface states and resonances by the adsorbates. Figure 4(a) shows the difference between the LDOS of layer 4 and that of the surface layer. Energy regions

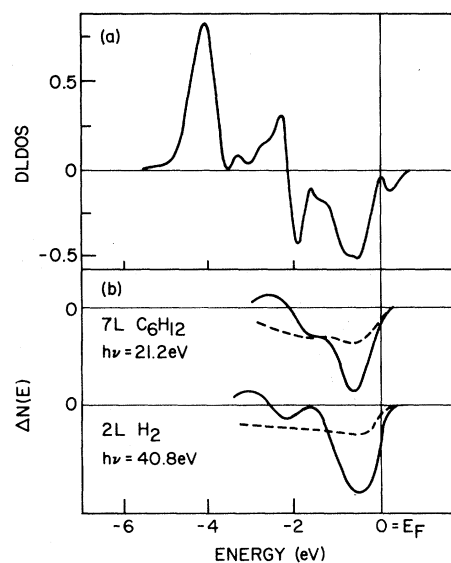


FIG. 4. (a) Calculated difference in LDOS between layer 4 and the surface layer. (b) Adsorbate-induced differences in photoemission intensities from Ref. 5. The dashed curves indicate the estimated attenuation if uniform attenuation of the d band were to occur.

where the curve is negative represent an excess in electronic states at the surface. This calculated state-density difference is seen to be quite similar to those shown in Fig. 4(b). The latter are the measured effect on the photoemission intensity of the chemisorption of two different adsorbates.⁵ The highly localized character of the wave functions of these surface states (Fig. 2) is consistent with the present interpretation of their high reactivity with adsorbates.

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Raman Spectroscopy of the Charge-Density-Wave State in TaS₃

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Raman spectroscopy has been used to study the quasi-one-dimensional charge-density-wave (CDW) compound, TaS₃. We determine for the first time both the temperature dependence of the CDW order parameter and the magnitude of the electronic gap $2\Delta(T)$ opened by the CDW at the Fermi surface. The transition to the CDW state appears to be continuous; our value of $2\Delta(0) \approx 530 \text{ cm}^{-1}$ is in agreement with both theory and transport measurements.

Sambongi *et al.*¹ have reported a charge-density-wave- (CDW-) induced semiconductor-to-metal transition and superlattice in the quasi-one-dimensional compound TaS₃ for $T < 220 \text{ K}$. Information concerning the phononlike excitations of the CDW states and the dynamics of the phase transitions from the CDW states has been obtained from Raman studies of layered-structure compounds.²⁻⁴ We report here the first study of the Raman spectrum of TaS₃. We observe temperature-depen-

dent shifts in the frequencies of the normal-state optic phonons which allow us to measure the temperature dependence of the CDW order parameter η since these shifts are proportional to η^2 .⁵ We have also been able to obtain, from the temperature dependence of the phonon linewidths, the magnitude of the electronic gap introduced at the Fermi surface by the CDW. While the existence of a gap at the Fermi energy E_F in the electronic structure of the CDW state is accepted, there has