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# Unoccupied surface states on Pd(111) observed in very-low-energy electron diffraction and inverse photoemission: Theoretical interpretation

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A three-dimensional calculation of projected electronic bulk and surface bands, spanning the energies studied by inverse photoemission and very-low-energy electron diffraction, reveals that the surface-electronic states observed by the two techniques are indeed two distinct states. We discuss their true character and the question of effective masses, and briefly comment on the validity of one-dimensional models.

## INTRODUCTION

Recent experimental developments in the so-called "empty-state spectroscopies"—in particular inverse photoemission (IPES) and two-photon photoemission (2PPE), as well as in very-low-energy electron diffraction (VLEED), have led to renewed interest in the study of electronic states in the local energy gaps in metals. In $\mathbf{k}_{\parallel}$-resolved inverse photoemission (KRIPES) the incoming electron with energy ($E$) above the vacuum level ($E_V$) emits a photon and drops into a lower unoccupied state, usually close to the Fermi level ($E_F$). $\mathbf{k}_{\parallel}$-resolved two-photon photoemission can be viewed as normal photoemission from a (previously unoccupied) electronic state which is populated by electronic excitation of an occupied state via the absorption of the first photon.

On the other hand, in VLEED the measured reflectivity as a function of the incoming electron energy and momentum contains information about the electronic structure of the diffracting or reflecting surface, through multiple scattering processes (formulated in the $T$-matrix series or via the wave-function matching), at this particular energy above $E_V$ (Ref. 1).

At present, IPES and 2PPE experiments usually scan the empty states between $E_F$ and $E_V$ in the vicinity of the $\Gamma$ point of the surface Brillouin zone (SBZ). These states are accessible to VLEED only indirectly, i.e., as intermediate states between two diffraction events on the surface lattice. Then, from kinematical considerations, VLEED states at energies several eV above $E_V$ could be extrapolated, say from the boundary of the SBZ to the $\Gamma$ point, assuming a parabolic dispersion, and thus connected with the states studied in IPES and 2PPE.

It is evident that a unified interpretation of the results of all these spectroscopies would give us a much richer understanding of the nature of empty surface-electronic structure, including a broader energy range and the $k$ dependence throughout the whole Brillouin zone.

In this paper we want to elucidate this connection, in particular between the IPES and VLEED measurements on the Pd(111) surface, the assumptions underlying the identification of surface states, and the conditions of applicability of the simplified one-dimensional models.[2,3]

An essential problem here is to define and unify the terminology. In the one-dimensional description we adopt the usual terminology introduced in Ref. 2. Surface states are the states with complex crystal momentum and real energy in the gaps of the bulk band structure below $E_V$. Surface resonances are of the same origin but because they are above $E_V$, they have complex energy, i.e., finite lifetime. In this sense IPES scans the surface states in the surface-electronic structure, and in VLEED we are dealing with the surface resonances.

In this paper we shall use the term surface resonance also for the surface states which are in the energy region of the bulk states, as is possible in the full three-dimensional band structure.

Several recent papers[3] have studied the dispersion of surface-state energies in the vicinity of the $\Gamma$ point. This dispersion parallel to the surface is usually described in terms of a free-electron-like parabola with some effective mass $m^*$. For image-potential states [say, of Pd(111)] the $m^*=m$ approximation is usually correct, since their wave functions extend far into the vacuum. However, the (crystal-induced) surface states and surface resonances have wave functions which penetrate into the bulk to varying degrees, so they are generally very sensitive to the details of the bulk- and surface-electronic structure.

At present, information about the dispersion of surface and image-potential states on Pd(111) is available from KRIPES,[4,5] PPE,[6] and VLEED,[7] but these experiments give seemingly different results for the surface state with respect to the effective mass and binding energy.

For Pd(111), the IPES measurements in the $\Gamma K$ direction[4] fit the effective mass $m^* = 0.3\ m$. To our knowledge the only experiment in the $\Gamma M$ direction[5] was performed with the photon energy $\hbar\omega = 9.5$ eV. Because of both the strong transition matrix element connecting the initial state with the unoccupied bulk *sp* and *d* states, and the crude angular scale in the experiment, the resulting set of angle-resolved intensity profiles show the bulk-state dispersion. The binding energy $E_B$ of the surface state at $\Gamma$ is in agreement with Ref. 5.

The intensity of the specularly reflected beam in VLEED shows three essential structures as can be seen in Fig. 1. First, the strong intensity cutoff at high $E_p$ due to the emergence of the (1,0) beam. Second, in the notation of Ref. 7, the minima *a* and *b* close to the threshold are due to the existence of the image-potential states. The third feature, the minimum *c* at lower energy, was interpreted as due to an empty surface state.

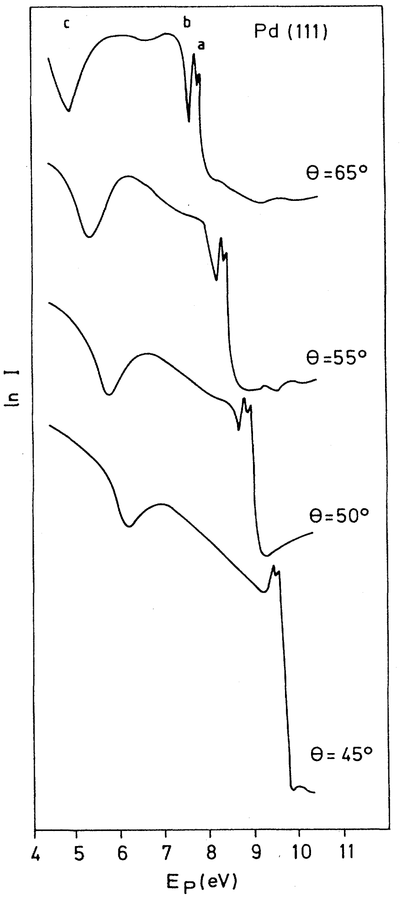

FIG. 1. Measured intensities of the specularly reflected beams at different angles as functions of primary energy (from Ref. 7).

We denote (crystal-induced) surface states as those electronic states that exist in the energy gaps forbidden to the electrons propagating in the bulk. The presence of the surface breaks the full three-dimensional translational symmetry and scattering on lattice potentials mixes the states with the same energy and parallel momentum $k_{\parallel}$ but with different perpendicular momenta $k_{\perp}$, which are no longer conserved. This means that the surface states will be found in the gaps in the projected bulk band structure, on the $k_{\parallel}$ plane given by the direction of the surface normal. Those gaps we can call intrinsic gaps, in contrast to the local gaps which will exist only for a particular region of $k_{\perp}$. Before proceeding with the discussion of the observed features in the VLEED spectra we have to locate the gaps in the projected bulk band structure.

As we shall argue later in the paper, we attribute this VLEED feature to a surface resonance. Namely, if we for the moment assume that we are dealing with the same surface state as observed in IPES, we have to extend (reflect) the observed data into the second SBZ and extrapolate the dispersion curve from the vicinity of $M$ to $\Gamma$. The experimental data fit the free-electron $(m^* = m)$ parabola, though in a rather limited region near the SBZ boundary. Extrapolating in this way to $\Gamma$ we obtain the energy 0.6 eV below $E_F$, a value which disagrees with the IPES result. On the other hand, connecting the IPES binding energy 4.15 eV below $E_V$ at $\Gamma$ with the VLEED results requires the effective mass $m^* \simeq 1.2\ m$, inconsistent with the IPES result that $m^* = m$.

This analysis raises not only the question of the applicability of the effective-mass approximation to the description of this state, but also the question of its physical origin. In other words, we have to determine whether the electronic structures observed in VLEED and IPES belong to the same surface state or resonance, or to two distinct states, and this problem cannot be addressed in the framework of a one-dimensional model.

The first "quasi-3D" calculations[3] which try to include the influence of the changes in the band gap with $k_{\parallel}$ by using $V_G(k_{\parallel})$ for an essentially 1D nearly free-electron (NFE) calculation gave reasonable results as long as the surface state stayed in the gap (e.g., for Cu). However, there are cases, such as Pd(111), where this method cannot be applied because in order to connect the experimentally observed states one has to go through a continuum of bulk states in the projected band structure [Fig. 2(a)].

## PROJECTED BAND-STRUCTURE CALCULATION

The basis of the approach is the layer–Korringa-Kohn-Rostoker (LKKR) method and the main features are as follows. In order to obtain a unified view and the same numerical approximation for the interpretation of IPES and VLEED in terms of projected bulk band structure and the density of states (DOS) we have used the modified computer code of the photoemission theory which was described in more detail in Ref. 8. The crystal is modeled by a stack of identical layers with two-dimensional periodicity and each atom is represented by a muffin-tin potential. The real part of the surface potential step corresponds to the difference between the

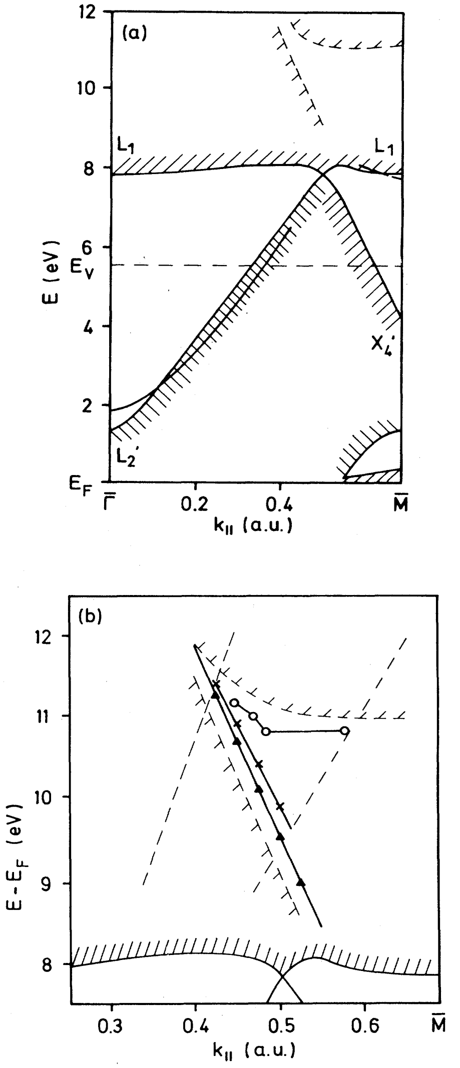

FIG. 2. Projected bulk band structure for Pd(111) surface in the $\Gamma M$ direction. (a) Solid line, surface state (resonance) in the main intrinsic gap, observed in IPES; dashed line, surface state (resonance) near $L_1$, not observed experimentally (surface-barrier displacement is 0.65*c*). (b) Dashed lines denote the range of VLEED measurements. Shown are the boundaries (⊥⊥⊥) of the local gap (also in Fig. 3), the experimental points for clean (×) and hydrogen-covered (○) surfaces of Pd(111), as well as the calculated position of the surface-resonance peak in the DOS (△).

muffin-tin zero and the vacuum level, and the imaginary part simulates the many-body effects, also providing the numerical convergence in the *z* direction. The calculation in the multiple-scattering scheme is performed in two steps: intralayer and interlayer. The surface is included through the matching of the wave function in terms of corresponding reflection and transmission matrices. The input geometry and atomic potential are taken from Ref. 9. The real and imaginary parts of the surface step were 12.4 and 0.1 eV, respectively.[10]

We shall assume a step potential, neglecting the long-range electrostatic tail which might induce image-potential states. This enables us to calculate the crystal-induced states which are not very sensitive to the image potential outside the solid (as can be verified by their proximity to the band-gap edges) since they penetrate appreciably into the solid.

In order to get correspondence with the experimental value of the binding energy and to see the effect of hybridization with the bulk bands on the energies and effective masses of the crystal-induced state, we also retain as a free parameter the surface-barrier displacement (SBD), i.e., the distance of the barrier potential step from the last atomic layer. By tuning the surface-barrier displacement, we change the matching condition at the surface, which modifies the relative position of the projected bulk band structure and the surface-state dispersion curve.

The barrier height in the layer KKR description has a direct physical interpretation: its energy value corresponds to the sum of Fermi level and the work function. The value used is justified by the interpretation of low-energy electron diffraction (LEED) intensity curves[11] and the experimentally determined work function. Changing the surface-barrier height would require further physical verification of the value used. In fact, the surface-barrier height was varied along with the barrier displacement in order to optimize the matching conditions, but no new physical results beyond those obtained by varying the surface-barrier displacement alone, were found.

## RESULTS AND DISCUSSION

The results of the projected bulk band structure calculation are shown in Fig. 2. For energies up to approximately 4.5 eV above $E_F$ they are in agreement with those of Louie,[12] but for higher energies they can only be compared to the bulk structure calculation of Christensen using the relativistic augmented-plane-wave (RAPW) method.[13] In particular, the projection of the high symmetry points (see, e.g., Fig. 3) to the SBZ gives practically identical results to those of Ref. 13. This remarkable agreement with the more elaborate self-consistent calculations is, of course, due to the quality of the atomic potential used.[9]

In comparison with the projected bulk band structure calculation for Cu(111),[3] the overall structure is more complicated. At the $\Gamma$ point there is a typical $L$ ($L_2'$-$L_1$) gap. The structure at the $M$ point is due to the intersection of the $L$ and $X$ ($X_4'$-$X_1$) gaps. The neck between $\Gamma$ and $M$ corresponds to the projection of the $K$ point of the bulk BZ. From the cut through BZ shown in Fig. 3, assuming for simplicity parabolic bands, one can conclude that this structure is formed by four parabolas starting at the reciprocal-lattice vectors $\mathbf{G}=(0,0,0)$, (1,1,1), (0,2,0), and $(1,\bar{1},1)$.

Near $\Gamma$ the gap is opened due to the hybridization of two bands with G vectors (0,0,0) and (1,1,1), and it contains an unoccupied surface state, in agreement with the calculation by Louie.[12] This state has been observed in IPES,[3] with the binding energy 1.45 eV (above $E_F$). The best agreement with this experimental value is obtained

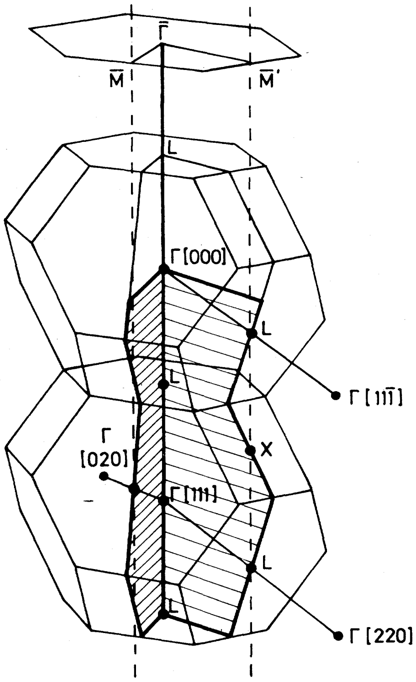

FIG. 3. The Brillouin zone of the fcc crystal with the projected surface Brillouin zone in the [111] direction.

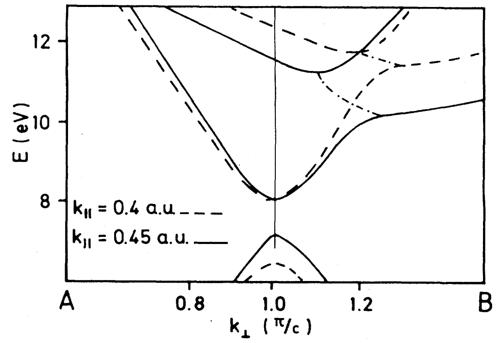

FIG. 4. Cuts through the Brillouin zone for $k_{\|}=0.4$ and 0.45 a.u. in the $\Gamma M$ direction. Dot-dashed line: surface-state branch.

with surface-barrier displacement equal to $0.65c$, where $c$ is the interlayer distance, but no specific conclusions should be drawn from this value, obtained in the non-self-consistent step model calculation. However, the existence of surface states and resonances and their dispersion are significant features of this model.

In the overall shape of the surface-state dispersion at the $\Gamma$ point one can recognize two different shapes, i.e., effective masses, corresponding to the change in their physical character. The surface state starts with $m^*/m \approx 0.3$ while the surface resonance disperses with $m^*/m \approx 0.6$ and gradually disappears. In view of the adopted model and type of calculation we may be satisfied with the obtained energies, and notice the agreement with the experimental data[4] for the surface state in the $\Gamma K$ direction.

The appearance of the gap at $M$ between the projections of the $X_4'$ and $L_1$ points of the bulk BZ complicates appreciably the analysis of the possible connection of the VLEED and IPES results. Moreover, there exists a surface state or resonance (depending on the value of surface-barrier displacement), which disperses in the opposite direction from the surface state at point $\Gamma$.[10] This state has not, to our knowledge, been experimentally observed, except possibly in the preliminary IPES measurement[14] scanning this region of the SBZ.

In the region where experimental structures are observed in VLEED, 6.5 eV above $E_V$, there are no inherent gaps in the projected bulk band structure, so we have to look for possible surface resonances. Figure 4 shows the cuts through the bulk band structure taken for $k_{\|}=0.4$ and 0.45 a.u., with the location in reciprocal space denoted in Fig. 5. The gap between 6.5 eV (7.2 eV) and 8.1 eV above $E_F$ for $k_{\|}=0.4$ a.u. (0.45 a.u.) is the main gap in Fig. 2, and one can easily identify the bands formed by the $\mathbf{G}=(0,0,0)$ and $(1,1,1)$ vectors. A new local gap appears between approximately 10 and 12 eV above $E_F$, due to the hybridization of the two bands with $\mathbf{G}=(0,0,0)$ and $(0,2,0)$, but it cannot be seen in projected bulk band structure because of the $\mathbf{G}=(1,1,1)$ band.

The boundaries of this local gap are shown in Fig. 2. One can see that the experimental data points for the clean (×) and for the hydrogen covered (○) surface,[7] which belong to the feature *c* in the reflectivity curve in Fig. 1, are located in this region of $(E,k_{\|})$ plane. The wave functions of the electronic states for these particular $E$ and $k_{\|}$ will be linear combinations of allowed states on the crystal side of the surface.

The matching with the wave function from the vacuum side will select the surface state from the surface-state branch (dotted line in Fig. 3) and will determine the proportion of the contribution from the bulk states from the

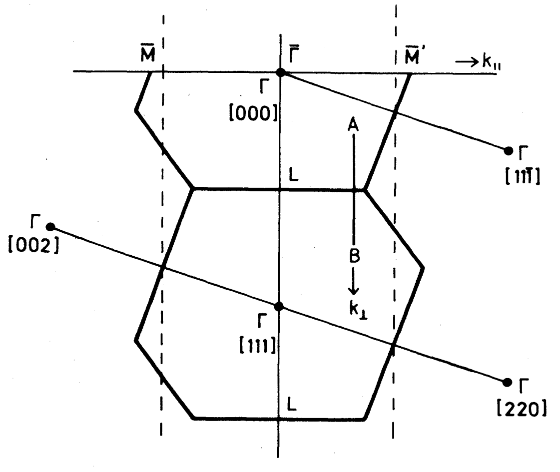

FIG. 5. Cut through the bulk Brillouin zone for $k_{\|}$ in the $M\Gamma M$ direction. The line $AB$ corresponds to the $k_\perp$'s in Fig. 4.

$G=(1,1,1)$ band of the bulk band structure and the surface state in the mentioned local gap.

Before discussing in detail the results, let us briefly mention that the usual criteria for identifying a surface state in the calculated DOS, or in the measured photoemission or inverse photoemission spectra, are (i) the energy $E$ and momentum $k_{\parallel}$ of the state should lie in the gap of the projected bulk band structure and (ii) the binding energy should be sensitive to the surface conditions (either theoretically, e.g., the matching conditions, or experimentally, e.g., the surface conditions).

Experimental results indeed fulfill the criterion (ii). Modification of the surface conditions by hydrogen adsorption caused a dramatic shift of the discussed feature in the VLEED intensity curve, as is shown in Fig. 2. From projected bulk band structure one can easily say that the criterion (i) cannot be fulfilled and we can talk only about a possible surface resonance. Theoretical calculations for clean Pd confirm the sensitivity of the corresponding peak in the DOS to the surface-barrier displacement, i.e., to the matching conditions. On the other hand, the empty surface state at the $\Gamma$ point is more sensitive to the same changes (Table I) but this is in accord with the interpretation that we are dealing with the surface resonance.

The dispersion of the surface resonance, like the one observed in VLEED, is determined by the position of the local gap for the particular momentum $k_{\parallel}$ and the matching conditions. The shape of the local gap in the SBZ and its dependence on $k_{\parallel}$ can be seen in Fig. 3. Assuming the free-electron parabolas starting from $\Gamma_{[020]}$ and $\Gamma_{[111]}$ points and moving along the $K$-$L$ line of the bulk BZ (Figs. 3 and 5; also center of Fig. 4), we see that the $\mathbf{G}=(0,2,0)$ branch moves with increasing $k_{\parallel}$ to slightly lower energies, while the $\mathbf{G}=(1,1,1)$ branch moves in the opposite direction. The resulting local gap is sketched in Fig. 2. The dispersion of the surface resonance follows the lower boundary of the local gap, where possible states are only weakly damped in space for a particular resonance energy. The resulting dispersion fits the experimental data surprisingly well, with the matching parameters taken to reproduce the experimental binding energy at the $\Gamma$ point (i.e., surface-barrier displacement is $0.65c$).

TABLE I. Surface-state resonance energies for different surface-barrier displacements (SBD).

| SBD | Surface state at $\Gamma$ $E_B-E_F$ (eV) | VLEED surface resonance, $k_{\parallel}=0.5$ a.u. $E_B-E_F$ (eV) |
|---|---|---|
| $0.6c$ | 1.71 | 9.65 |
| $0.65c$ | 1.45 | 9.47 |

The proposed interpretation of the surface resonance seen in VLEED as distinct from the surface state near $\Gamma$ seen in IPES is supported by the disappearance of the corresponding peak in the DOS in the vicinity of the main gap near $M$, and also by its behavior upon hydrogen adsorption. In this case the matching conditions are modified so that the surface resonance follows the upper boundary of the local gap, as was indeed seen in the VLEED experiment.[7]

The states at the inner boundaries of the gaps have the smallest imaginary momentum and therefore they have small damping.

We can therefore conclude that the structure observed in very-low-energy electron reflectivity spectra[7] is indeed a surface resonance which cannot be connected with the surface state at the $\Gamma$ point observed in IPES. The simplified one-dimensional approaches[15] are inapplicable in this situation, but even the standard LKKR method provides a satisfactory description of the electronic states and their role in the physical processes.

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