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Angle-resolved photoemission study of the clean and hydrogen-covered Pt(111) surface

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We report the results of a high-resolution angle-resolved photoemission study of the surface electronic structure of clean and hydrogen-covered Pt(111). Several surface-resonance bands and one surface state are observed on the clean surface. These exhibit qualitative similarities to, as well as some differences from, previous studies and calculations for Pd(111). Unlike the results for Pd(111), essentially all surface bands are quenched upon hydrogen exposure, even at room temperature. There is no clear support in our data for a structural model placing the hydrogen atoms in an underlayer adsorption site, as had been suggested from a previous photoemission study. The significance of our results to a recently proposed correlated-quantum-liquid model is investigated. We also discuss the relevance of our bands near E_F to a recent controversy about the possible existence of phonon anomalies on this surface.

I. INTRODUCTION

In the past several decades, many investigations have been undertaken to elucidate the interesting and diverse properties of the (111) surface of elemental platinum.[1] However, a complete and detailed description of the Pt(111) surface electronic structure, which plays a key role in determining these surface properties, is still unavailable. In this paper, we report an accurate study of the clean and hydrogen-covered Pt(111) surface at room temperature using high-resolution angle-resolved photoemission spectroscopy (ARP). Our results indicate a rich surface electronic band structure along the symmetry lines of the surface Brillioun zone (SBZ) of the clean Pt(111) surface. We find that all of the surface bands are removed from the spectra upon hydrogen adsorption.

In addition to its importance as a model catalytic system, Pt(111) has also been the subject of some controversy in the area of its elementary excitations. In the past few years, three groups have reported measurements of the surface-phonon dispersion relations for this system using inelastic helium scattering.[2–5] Two of these reported what they believed to be two surface-phonon anomalies (or Kohn anomalies) along the $(1\bar{1}0)$ or $\bar{T}$ direction of the SBZ.[2,3] The third group failed to observe evidence for any anomalies.[4] More recently, corresponding theoretical calculations concluded that the initial assignments were probably mistaken.[5] Part of our motivation for the present experiment was to try to obtain relevant information on the surface electronic structure of the Pt(111) surface in order to elucidate this issue more completely. Specifically, in our ARP study we have determined a complete set of two-dimensional (2D) Fermi contours for this surface. The results basically rule out the existence of the proposed surface-phonon anomalies and provide a guide for future phonon measurements searching for such anomalies.[6]

The chemisorption of hydrogen on the fcc group-VIIIB transition-metal surfaces (Pd, Pt, Ni) has also been the subject of debate.[7–19] Some agreement has been reached on relevant issues for the (111) surfaces at low temperature. That is, the hydrogen atoms occupy the threefold hollow sites forming an ordered (1×1) overlayer at saturation, and the chemisorption bonding interaction is predominantly between hydrogen 1*s* and metal *d* bands. The situation at room temperature is still controversial. Eberhardt, Greuter, and Plummer performed angle-resolved photoemission experiments in which the intrinsic surface spectral features undergo no changes at all upon H adsorption for Ni(111), Pd(111), and Pt(111) at room temperature.[7] To explain this they proposed a subsurface adsorption site for hydrogen atoms which could be occupied only by overcoming an energy barrier after the initial adsorption event.[9] This suggestion is contradicted by a recent study of the hydrogen vibrational modes with eigenvectors oriented parallel to the surface plane.[13] These modes were found to be significantly softer than predicted by the nearest-neighbor central force constant model, in excellent agreement with theoretical predictions.[14] This suggests that the hydrogen binding mechanism is largely nondirectional and can be adequately described by effective medium theory.[16] In the mean time, a totally different model was postulated in which the hydrogen atoms are described by wave functions localized normal to the surface but delocalized along the surface.[15–19] Motion parallel to the surface is that of a correlated quantum liquid. Recent evidence from elastic He scattering for H/Pd(111) was presented to support this model.[18,19]

We find that the ARP spectra from clean Pt(111) are very sensitive to hydrogen adsorption at room temperature, in contradiction to the previous study.[7] We observe that the surface resonances or states are largely quenched by hydrogen adsorption at room temperature. Unlike observations and calculations for Pd(111),[7–9] no well-defined resonances or states induced by hydrogen can be observed within the platinum *d* bands.

The structure of this paper is as follows: the next section describes our experimental procedures. Section III presents our experimental ARP results and the resulting band dispersions in the symmetry planes of the SBZ, and discusses these in terms of the Fermi contours for this surface. Section IV discusses our results in relation to previous investigations, and the final section is a summary of our results.

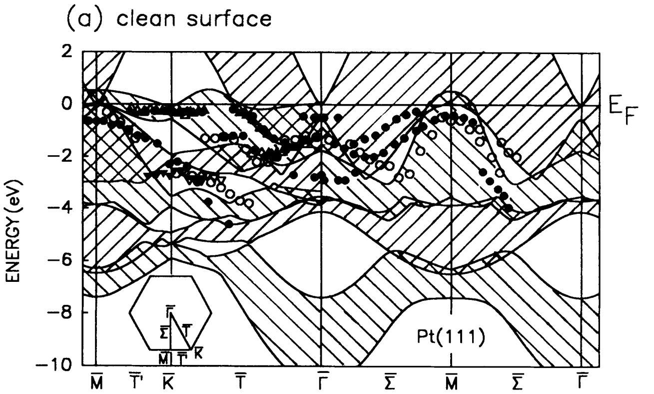
II. EXPERIMENTAL PROCEDURES

Our ARP system, located at the National Synchrotron Light Source at Brookhaven National Laboratory, has been described in detail previously.[20,21] The total instrumental energy and angular resolutions are typically less than 120 meV and 1°, respectively, at full width at half maximum. A 99.999% purity Pt(111) crystal[22] 1 cm in diameter and 0.5 mm thick was oriented to within 0.5° of the (111) bulk crystalline axis by Laue x-ray back reflection. The surface was first prepared by mechanical polishing and chemical etching in hot aqua regia, and then inserted into our vacuum system. After many cycles of heating to 1000 K in oxygen, or occasionally neon-ion sputtering at 700 K, followed by annealing at 1200 K,[23] an extremely clean and well-ordered surface was prepared as determined by low-energy electron diffraction and Auger electron spectroscopy. The surface remained clean for typically 30–45 min at an operating pressure of $(0.8-1.2)\times 10^{-10}$ torr, as evidenced by the gradual disappearance of some of the more contamination-sensitive features in the photoemission spectrum. The residual surface contaminants (CO and H) were easily thermally desorbed by flashing the crystal to 800–1200 K every 15–20 min. Hydrogen was dosed as H_2 at room temperature. The saturated surface typically was prepared by exposure to 15 L (1L = 1 langmuir = 1×10^{-6} torr sec) of H_2.

III. EXPERIMENTAL RESULTS

The procedures for the identification of the surface states or resonances used here are the same as used previously.[24,25] Firstly, the surface features in the spectra must be sensitive to the adsorption of impurities (hydrogen, in this case). This so-called "crud" test might be manifested by reduced spectral intensity and/or shifted binding energy of a particular ARP feature. Secondly, due to the two-dimensional characteristics of the surface states or resonances, the surface features should have little dispersion with perpendicular component of the wave vector $k_\perp$, the variation of which is accomplished by changing the photon energy while keeping the momentum parallel to the surface ($k_\parallel$) fixed. Theoretically, no dispersion at all would be observed for a true, intrinsic surface state. Some small dispersion can be expected for a surface resonance, since these may be understood to be hybrids between a true surface state and a bulk state. We return to this matter below. If a feature in the spectrum passes the above tests, we assign it as a surface state or resonance. To make a further distinction, the 3D bulk band structure is projected along lines of constant $k_\perp$ onto the relevant (111) surface Brillouin zone. If the surface band, plotted on this projection, falls in a gap or in a projected continuum which has a different symmetry from the surface feature itself, it is determined to be a true surface state. Otherwise, it is assigned as a surface resonance. We acknowledge some ambiguity in comparing calculated[26] projected bulk bands to experimental surface band dispersion relations. However, the calculated bands provide a fairly good representation of the experimentally determined bulk dispersion relations.[27,28] Thus, except for bands near a projected band edge, our procedure is valid. The same criteria can be applied to distinguish hydrogen-induced states or resonances except that what we are looking for are the new features observed upon hydrogen adsorption instead of those changed by it.

The combination of the above principles with more than 1500 ARP spectra enables us to obtain the surface band dispersion relations along the symmetry lines of the SBZ of the clean and hydrogen-covered Pt(111) surface at room temperature. Our results are summarized in Fig. 1. The shaded region is the projection of the platinum bulk band structure calculated using a Slater-Koster three-center nonorthogonal tight-binding interpolation scheme fitted to an augmented plane-wave band structure.[26] As



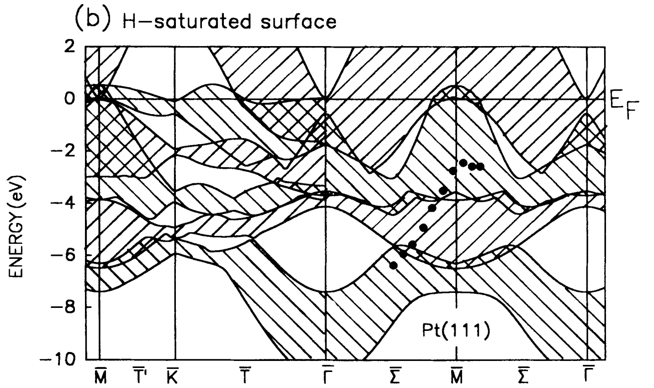


FIG. 1. Representative sampling of our experimentally determined surface band dispersion relations of clean and hydrogen-covered Pt(111), plotted on a projection of the calculated bulk band structure onto the (111) surface Brillouin zone (shaded). Along $\bar{\Sigma}$, only bands of even symmetry are projected. (a) presents the rich variety of bands observed on the clean surface, while (b) demonstrates the relative absence of surface bands on the hydrogen-covered surface. The experimental points were collected with the sample normal, the emission direction, and the photon polarization vector in a plane. The different symbols correspond to different photon energies and sweeping either away from (solid symbols) or toward the photon polarization vector (open symbols): 0, 40 eV; Δ, 24 eV; ∇, 26 eV.

shown in the figure, there is a rich intrinsic surface band structure on the clean Pt(111) surface. However, very few states are observed on the hydrogen-covered surface. All the intrinsic surface features are resonances except those inside the gap about 3 eV below the Fermi level (E_F) around the $\bar{K}$ point of the SZB. In the following, we give a detailed description of our data and results.

A. Clean Pt(111) surface bands

1. *Surface resonances and states along $\bar{T}$*

Figure 2 shows several ARP spectra collected from the clean surface near normal emission at a series of photon energies. $k_{\parallel}$ is very nearly zero in all these spectra, so we sample the center of the SBZ, $\bar{\Gamma}$. In the spectra collected at $h\nu=24$ and 40 eV, we include for comparison spectra collected from the hydrogen-covered surface. At $h\nu=40$ eV, the three peaks located 0.5, 1.3, and 2.8 eV below E_F are effectively quenched upon hydrogen adsorption. These features are visible at some but not all photon energies. At $h\nu=24$ eV, there is evidence of contamination sensitivity only for the most tightly bound feature, while emission closer to E_F is dominated by a large feature which exhibits less sensitivity to contamination. This behavior is often associated with surface resonances.[29] Bulk features will dominate the spectra at the expense of the resonance emission when the photon energy corresponds to a value of $k_{\perp}$ which samples the bulk band near the energy of the resonance. At $h\nu=24$ eV, we sample bulk states near zone center (Γ),[27,28] where band 6 dips below E_F to dominate the spectra. Conversely, at $h\nu=40$ eV we sample bulk states near the zone boundary L point where band 6 lies above E_F so that the resonant levels are easily observed. Note that all three features fall in the bulk projected continuum shown in Fig. 1(a), providing confirmation for the assignment as resonances. The middle feature exhibits a small dispersion ($<0.2-0.3$ eV) as a function of photon energy, again reflecting its resonance nature. This minimal dispersion with $k_{\perp}$ provides a final confirmation that these features are indeed surface resonances, since none of the bulk bands along the Λ line of the bulk Brillouin zone has such a narrow bandwidth.[27,28] The lowest peak in the spectra, located at a binding energy of about 4 eV, exhibits ambiguous behavior. Although reduced in intensity, the feature remains in the hydrogen-contaminated spectra with the same shape and energy. It is a semantic issue whether one calls this bulk band number 2 which is slightly resonantly enhanced at the surface or a surface resonance which is very strongly coupled to bulk band number 2. We choose not to include such features in our surface band structure.

Figure 3 shows a set of spectra collected as a function of emission angle in the $\bar{T}$ azimuth at $h\nu=24$ eV; Fig. 4 shows similar data collected at $h\nu=40$ eV. The solid and dashed curves correspond to spectra collected from the clean and hydrogen-covered surfaces, respectively. The resonances at 0.5 and 2.8 eV disappear rapidly away from normal emission; this can be seen more clearly in the data set collected at $h\nu=40$ eV. The middle resonance disperses downwards slightly at first and then splits in two. At $h\nu=24$ eV, the lower of these two features disappears just after the splitting, while at $h\nu=40$ eV it continues out to $k_{\parallel}=1.20$ Å^{-1}. The upper feature

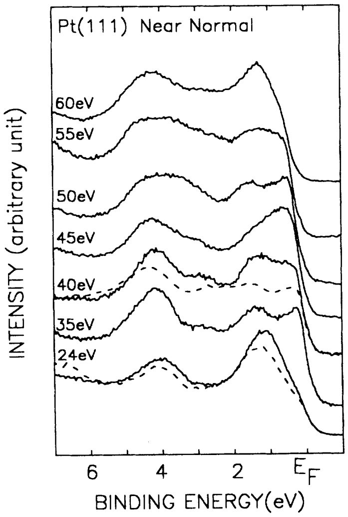


FIG. 2. Spectra of clean (solid curves) and hydrogen-covered (dashed curves) Pt(111) collected near normal emission. Note the relative ease with which the surface resonances are distinguished near E_F at $h\nu=40$ eV, where bulk states near the zone boundary are being sampled.

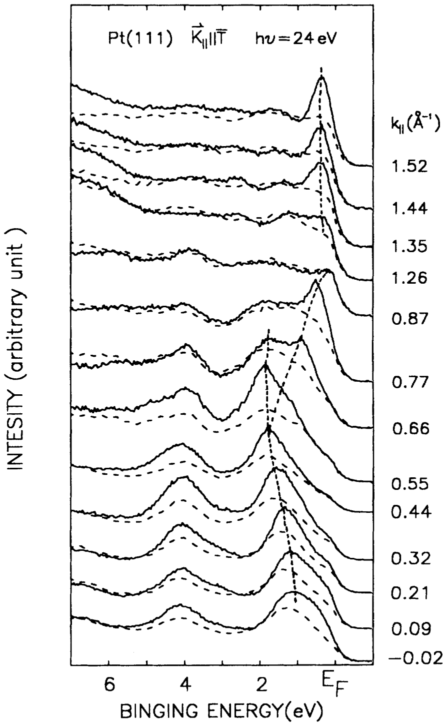


FIG. 3. ARP spectra of clean (solid curves) and hydrogen-covered (dashed curves) Pt(111) collected as a function of emission angle in the $\bar{T}$ azimuthal direction at $h\nu=24$ eV. Spectra are labeled by the parallel momentum at a kinetic energy corresponding to E_F.

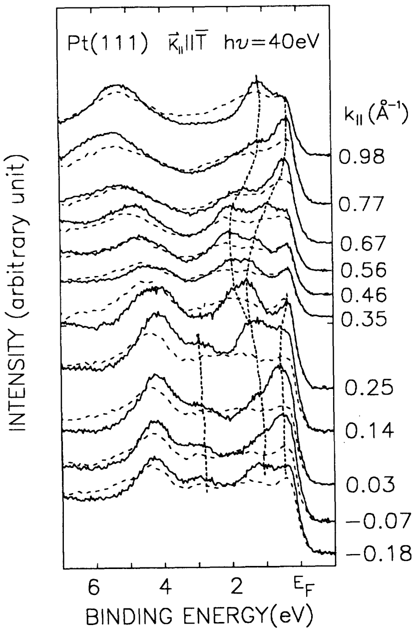


FIG. 4. ARP spectra of clean (solid curves) and hydrogen-covered (dashed curves) Pt(111) collected as a function of emission angle in the $\bar{T}$ azimuthal direction at $h\nu=40$ eV. Spectra are labeled by the parallel momentum at a kinetic energy corresponding to E_F.

disperses rapidly toward E_F and crosses it at about $k_\parallel=0.85$ Å^{-1} with a Fermi velocity of ~ 3 eV/Å^{-1}, as seen in Figs. 3 and 4. The Fermi wave vector was checked at different photon energy values and found to be essentially independent of $k_\perp$.[6]

Figure 5 shows spectra collected with $k_\parallel$ fixed at 1.37 Å^{-1} along $\bar{T}$ as a function of photon energy. This momentum is close to the $\bar{K}$ point of the SBZ, which lies at $k_\parallel=1.51$ Å^{-1}. Two surface features are identified. One is the sharp peak just below E_F and the other one is the broader peak about 2.8 eV below E_F. Comparison with the bulk band projection in Fig. 1(a) indicates that the first feature is also a resonance. As shown in Fig. 3, this resonance barely disperses with $k_\parallel$ and disappears, presumably through crossing E_F, at $k_\parallel=1.20$ and 1.93 Å^{-1} at $h\nu=24$ eV (the latter crossing is not shown here). Unlike the first Fermi level crossing at $k_\parallel=0.85$ Å^{-1}, the location of these two crossings depends significantly upon $k_\perp$, indicating a stronger coupling between this surface resonance and the bulk electronic continuum.

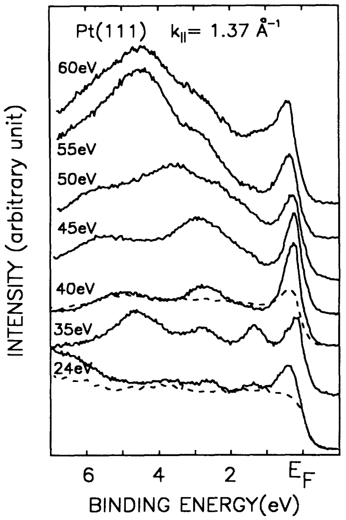


FIG. 5. ARP spectra of clean (solid curves) and hydrogen-covered (dashed curves) Pt(111) at fixed $k_\parallel$ as a function of photon energy. The dispersionless features just below E_F and at a binding energy of ~ 3 eV are assigned as a surface resonance and a surface state, respectively.

The lower surface feature near $\bar{K}$ lies in the middle of the gap in the bulk band projection about 3 eV below E_F around the K point, and is therefore probably a true surface state. Figure 6 shows spectra which indicate its dispersion with $k_\parallel$. It attains a maximum intensity in the middle of its dispersion through the gap, and actually becomes invisible outside the gap.[30] The spectra in Fig. 6 were collected for emission in a particular $\bar{T}$ azimuth. The same measurement along the opposite azimuthal direction also reveals a surface feature inside the gap. However, this feature shows more dispersion with $k_\parallel$, as shown in Fig. 1(a), and is not symmetric with the feature shown in Fig. 6. These $\bar{T}$ azimuths are symmetry inequivalent for bulk states and possibly for surface resonances, but should be symmetry equivalent for true surface bands. The surface state dispersion relation should be the same in the two azimuths, although the photoemission intensities may differ. We conclude that there exists at least one true surface state inside the gap, and possibly two.

Moving further along the same $\bar{T}$ azimuthal direction into the second SBZ (often labeled $\bar{T}'$), we detected another intense surface resonance close to E_F near the $\bar{M}$ point, as shown in Fig. 7. The same resonance is also found at the $\bar{M}$ point located along $\bar{\Sigma}$, which will be described in the next section.

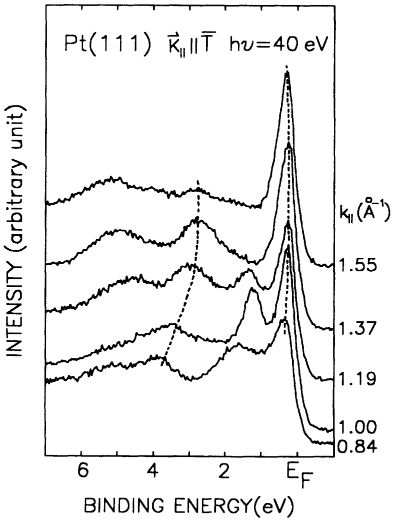


FIG. 6. ARP spectra of clean Pt(111) collected along $\bar{T}$ as a function of $k_\parallel$ near the $\bar{K}$ point of the surface Brillouin zone. Spectra are labeled by the parallel momentum at a kinetic energy corresponding to E_F, with $\bar{K}$ at 1.51 Å^{-1}.

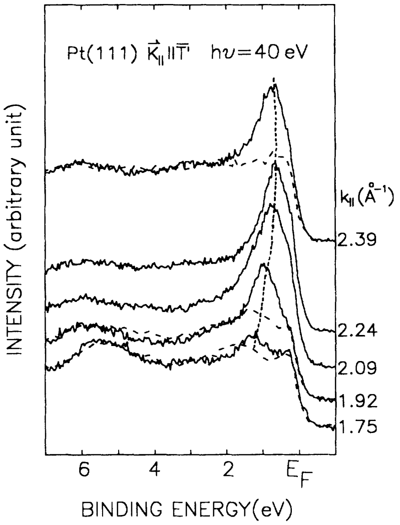


FIG. 7. ARP spectra of clean (solid curves) and hydrogen-covered (dashed curves) Pt(111) collected along $\bar{T}'$ as a function of $k_{\|}$ near the $\bar{M}$ point of the surface Brillouin zone. Spectra are labeled by the parallel momentum at a kinetic energy corresponding to E_F, with $\bar{M}$ at 2.26 Å^{-1}.

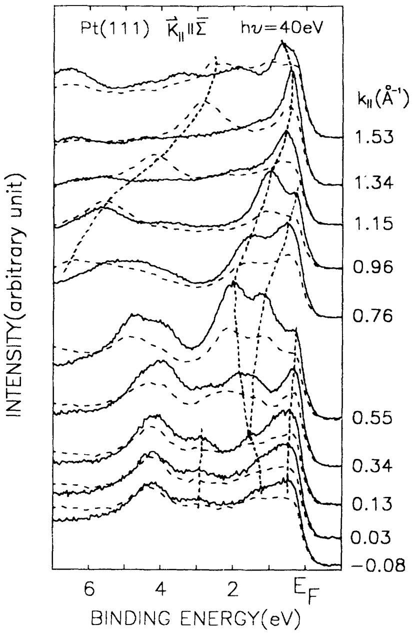


FIG. 8. ARP spectra of clean (solid curves) and hydrogen-covered (dashed curves) Pt(111) collected along $\bar{\Sigma}$ as a function of $k_{\|}$. The $\bar{M}$ point of the surface Brillouin zone occurs at 1.31 Å.$^{-1}$ Spectra are labeled by the parallel momentum at a kinetic energy corresponding to E_F.

2. *Surface resonances along* $\bar{\Sigma}$

As shown in Fig. 1(a), we found along $\bar{\Sigma}$ the counterpart of the surface resonance which forms the Fermi level crossing along $\bar{T}$ closest to $\bar{\Gamma}$. In this azimuth, however, the crossing occurs at about $k_{\|}=1.00$ Å^{-1} instead of 0.85 Å^{-1}. Spectra indicating this crossing are shown in Fig. 8. As long $\bar{T}$, this Fermi crossing point proved to be independent of $k_{\perp}$. A surface band is also observed in Fig. 8 just below E_F near the $\bar{M}$ point ($k_{\|}=1.34$ Å^{-1}) along this azimuth. This corresponds nicely to the surface resonance forming a similar surface band along $\bar{T}$ near $\bar{M}$ mentioned above. As shown in Fig. 1(a), this band extends all the way from $\bar{M}$ to $\bar{\Gamma}$. The energies of this surface band near these two symmetry points measured along opposing $\bar{\Sigma}$ directions are in very close accord. However, near the middle of the $\bar{\Sigma}$ axis we again find that the dispersion relations are not symmetrical with each other. A similar ambiguity exists beyond the $\bar{M}$ point, where the band seems to be split in two. We conjecture that there might be two different surface bands present along $\bar{\Sigma}$ which are degenerate (or nearly so) at $\bar{\Gamma}$ and $\bar{M}$.

All the surface resonances that we presented above along $\bar{\Sigma}$ were measured with the polarization vector of the incident light oriented in the mirror plane defined by the electron emission direction and the $\bar{\Sigma}$ line. Therefore, ignoring the spin-orbit interaction, these spectra all sample states of even mirror plane symmetry. We have also made the same measurements with the light of mixed polarization so that we can detect the contribution from both even and odd states. Spectra obtained in this way contain no new surface features. Therefore, we conclude either that there are no surface resonances or states of predominantly odd symmetry in this azimuth, or that the spin-orbit interaction sufficiently mixes even and odd states that the designation is meaningless. The $\bar{T}$ azimuth has no mirror plane symmetry if one includes the first few layers, so that distinguishing odd and even symmetry has no relevance along that line.

B. Hydrogen-saturated Pt(111) surface bands

The only clearly observable hydrogen-induced feature on the saturated Pt(111) surface is observed along the $\bar{\Sigma}$ line at $h\nu=40$ eV, as indicated by the spectra in Fig. 8. Its dispersion, as shown in Fig. 1(b), deviates slightly (about 0.3 Å^{-1}) from symmetry about the $\bar{M}$ point. This intense feature only appears in one azimuthal direction of $\bar{\Sigma}$ at 40 eV. We also fail to detect it at $h\nu=24$ eV. We assign it tentatively as a hydrogen-induced surface resonance. We do not find any hydrogen-induced features along the $\bar{T}$ line. There are other regions where hydrogen adsorption seems to lead to increased intensity within the platinum d band (see, for example, the top two spectra in Fig. 5), but in these cases we do not observe a well-defined peak.

IV. DISCUSSION

A. Comparison to previous studies

A previous angle-integrated photoemission study on a stepped Pt(111) surface at 200 K found that hydrogen adsorption results in a preferential decrease in emission just below E_F and fails to produce any prominent resonances within the d band.[31] This is in broad agreement with our ARP data. According to our data, a number of surface-resonance bands exist within 1 eV of E_F. The destruction of these surface features upon hydrogen adsorption would lead to a drop in the angle-integrated photoemission signal close to E_F as observed. Also our data do not give solid proof for the existence of any extrinsic states or resonances induced by hydrogen within the Pt *d* band, in accord with the angle-integrated result.

A theoretical surface band calculation for a clean and hydrogen-covered Pt(111) surface is not available. It makes sense to compare our data qualitatively with calculated results for the Pd(111) surface, which has the same lattice and similar valence electronic structure as Pt(111). The theoretical surface bands for clean and hydrogen-covered Pd(111) surface, with hydrogen occupying each threefold hollow site, have been calculated by Louie using a self-consistent pseudopotential mixed-basis method.[8] Not surprisingly, his projected continuum bears striking similarity to that shown in Fig. 1 for Pt(111), although Louie does not separate even and odd symmetries along the $\overline{\Sigma}$ line. Many of our clean surface bands are qualitatively matched by Louie's calculation. Around the $\overline{K}$ point, Louie predicts two surface bands inside the gap about 2 eV below E_F. We found at least one and perhaps two surface bands inside the corresponding gap on the Pt(111) surface. Our data also show a band which is loosely associated with the next higher gap near $\overline{K}$. This was also found in the calculation for Pd(111), although the calculated dispersion is centered in the gap while ours is not. Both distinguish a surface-resonance band close to E_F localized around the $\overline{\Gamma}$ point. Both also find a band at higher binding energy at $\overline{\Gamma}$ which splits into two resonances away from the symmetry point. The connectivity of the higher of these two bands to the Fermi level crossings along the two symmetry azimuths is less clear in the calculation than in our experiment. This might result from a varying degree of surface localization of the band which could cause the calculation to "lose" it in the middle of the zone. Qualitatively, the Fermi crossings along $\overline{\Sigma}$ and $\overline{T}$ are quite similar.

There are also some qualitative differences between the palladium calculation and our results on platinum. We predict two bands at $\overline{M}$, one above E_F and one below, while the calculation predicts just the one above. Our lower band at $\overline{M}$ connects smoothly to one of the doublet bands at zone center; this is not reproduced by the calculation. Also the lowest resonant band we observe at $\overline{\Gamma}$ cannot be easily related to any band in the calculation. There is a calculated band near the bottom of the gap at zone center between bulk bands 1 and 2 which may be related to the slight surface sensitivity of the feature at 4–5-eV binding energy in Fig. 2.

For the hydrogen-saturated surface, there is generally very poor agreement with calculation, except that our tentative assignment of an extrinsic surface band near $\overline{M}$ bears qualitative similarity to one calculated for H/Pd(111).[7–9] The calculation predicts that several of the clean surface resonances shift downward in energy upon hydrogen adsorption. Our results indicate that this does not appear to be the case for Pt(111), at least at room temperature. The calculation distinguishes the hydrogen 1*s*-related state splitoff below the projected bulk bands. This commonly exists on the hydrogen-chemisorbed (111) surfaces of transition metals.[32] We have not investigated this band on Pt(111). A detailed theoretical calculation for the Pt(111) surface similar to that for Pd(111) is needed in order to have a more significant comparison with our data, and to understand some of these differences and similarities.

Our results indicate some significant differences from the few results available from the previous ARP study of the Pt(111) surface at room temperature.[7] Our data exhibit a large perturbation of the *d*-like intrinsic surface states or resonances on the clean Pt(111) surface upon hydrogen adsorption. The previous study observed this at low temperature, but found only small changes upon adsorption at room temperature. We thus cannot support, at least for Pt(111), the subsurface chemisorption site for H at room temperature, proposed based upon the former ARP experiment.[7]

Perhaps the most surprising result in our measurement is the absence of any surface resonances which simply shift upon hydrogen adsorption. These were both predicted and observed on Pd(111).[7,8] It is possible that there is a large temperature dependence in the ARP spectra of this system, and that these shifted resonances would be observed if we were able to cool the surface to lower temperature. Our data suggest that adsorbed hydrogen is delocalized or disordered at room temperature, thereby disrupting the translational symmetry of the surface so that well-defined bands do not exist.

B. Surface bands and Fermi contours

In a previous paper,[6] we reported the experimental 2D Fermi surface of the clean Pt(111) surface at room temperature. The hexagonlike pocket around Γ shown in Fig. 2 of Ref. 6 is formed by the surface band which crosses E_F at $k_{\parallel}=0.85$ Å^{-1} along $\overline{T}$ and 1.00 Å^{-1} along $\overline{\Sigma}$ [see Fig. 1(a)]. This band is made of surface resonances which behave very much like true surface states, as evidenced by the sixfold symmetry of the Fermi contour and lack of dispersion with $k_{\perp}$ mentioned previously. Along $\overline{T}$ at least, the band which forms the Fermi contour follows closely the upper edge of the sixth bulk band projection. One can think of this band as a resonant enhancement of the sixth bulk band edge near the surface plane for the following reason. Simple tight-binding models predict that a true surface band will split from the bulk band if the shift in self-energy of an orbital at the surface relative to the bulk is comparable to the bulk bandwidth.[33] The sixth band is fairly wide, so this condition is not easily met. However, one might expect (and we observe) that a smaller self-energy shift might lead to a resonant level at the energy of the band edge. Indeed, the surface Fermi contour very nearly inscribes the projection of bulk Fermi surface formed by the sixth bulk band. If the surface perturbation were larger, a true state would presumably form, with a Fermi contour having an area larger than the projection.

The smaller, triangular-shaped pocket at each $\overline{K}$ point reported previously is formed by the very flat surface-resonance band just below E_F around $\overline{K}$. This band is sufficiently close to E_F that we have trouble assigning a true binding energy. Indeed, given the apparent resonant broadening of this level, we can actually treat the whole pocket as bracketing the Fermi level. As emphasized previously, this will have the effect of delocalizing (in momentum space) any potential screening anomalies. The exact shape of this pocket should not be taken as distinct as Fig. 2 in Ref. 6 indicates. The dependence of the surface band which forms this pocket upon $k_\perp$ implies that the surface Fermi wave vectors have a similar large dependence. We have tried unsuccessfully to characterize this dependence. The morphology of the 2D Fermi contours and the nature of the surface bands which form them make us conclude that the proposed existence of surface-phonon anomalies on Pt(111) caused by surface bands is dubious, and suggest a direction for future phonon measurements searching for such anomalies.[6]

V. SUMMARY AND CONCLUSIONS

We have characterized several surface-resonance bands and one surface state for the clean Pt(111) surface. While these exhibit some similarities to previous studies and calculations for Pd(111), essentially all surface bands are quenched upon hydrogen exposure, even at room temperature. We thus do not support a structural model placing the hydrogen atoms in an underlayer adsorption site. The differences between Pt(111) and Pd(111) might be explained by the existence of a correlated quantum liquid on the former. Further calculations will address this issue. Our bands near E_F produce Fermi contours which do not support the existence of recently proposed surface-phonon anomalies.

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