# *L*-gap surface resonance at Pt(111): Influence of atomic structure, *d* bands, and spin-orbit interaction

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Pt(111) hosts a surface resonance with peculiar properties concerning energy vs momentum dispersion and spin texture. At variance with the free-electron-like behavior of the *L*-gap Shockley-type surface states on the fcc(111) surfaces of Au, Ag, and Cu, it splits into several branches with distinct spin polarization around the center of the surface Brillouin zone  $\overline{\Gamma}$ . Theoretical predictions based on density-functional theory vary depending on the particular functionals used. To clarify this issue, we investigate the atomic structure of Pt(111) by low-energy electron diffraction and the unoccupied electronic structure by spin- and angle-resolved inverse photoemission. The experimental results are backed by theoretical studies using different functionals, which show that the characteristics of the surface band depend critically on the lattice constant. From the analysis of the energy-dependent low-energy electron diffraction intensities, we derive structural parameters of the Pt(111) surface relaxation with high accuracy. In addition, we give an unambiguous definition of the nonequivalent mirror-plane directions  $\overline{\Gamma M}$  and  $\overline{\Gamma M}$  at fcc(111) surfaces, which is consistent with band-structure calculations and inverse-photoemission data. Concerning the surface resonance at the bottom of the *L* gap, we identified a delicate interplay of several contributions. Lattice constant, hybridization with *d* bands, and the influence of spin-orbit interaction are critical ingredients for understanding the peculiar energy dispersion and spin character of the unoccupied surface resonance.

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# I. INTRODUCTION

Already in the very first paper by Shockley on the occurrence of surface states associated with a periodic potential [1], it became clear that the energetic position of such states depends on the interatomic distance, i.e., on the lattice constant *a*. The paradigmatic *sp*-derived surface states around the center of the Brillouin zone at many fcc(111) metal surfaces [2,3] are known as Shockley or *L*-gap surface states. They have been thoroughly investigated with respect to their energy vs momentum dispersion but also in view of their spin texture caused by the Rashba effect [4–7]. These states are energetically positioned within Shockley-inverted band gaps and are often partly occupied. Slight deviations in energy positions for different materials do not result in significant differences in their free-electron-like dispersion behavior.

The situation is different for Pt(111). The *L* gap appears completely above the Fermi level. Only few early inversephotoemission (IPE) studies are available, which show high Brillouin zone [8–10]. Scanning tunneling spectroscopy experiments [11] and band-structure calculations [12] indicate that the L-gap surface state appears at the lower gap boundary and is completely unoccupied. No spin splitting was observed [11]. On the basis of calculations, this state was reinterpreted as topologically derived surface state including a Dirac point [13]. However, no experimental evidence for the existence of a Dirac point or any spin texture was provided so far. The state seems to exhibit some peculiarities, which are discussed and summarized by Dal Corso based on density-functional theory (DFT) calculations [14]: Within the generalized gradient approximation (GGA) employing the PW91 functional [15], one expects a free-electron-like surface state with Rashba splitting. By using the local-density approximation (LDA), however, the calculation yields a more complex behavior of the surface state: it vanishes at  $\overline{\Gamma}$  and a split-off structure diving into the bulk bands appears. The experimental results available so far [8-11] are not able to distinguish between the different scenarios obtained theoretically.

intensity just above the Fermi level at the center of the

For a thorough analysis of the unclear situation, it is indispensable to ensure that the crystallographic structure is correctly captured and any layer relaxations are properly taken into account. Therefore, in Sec. II, we determine the atomic structure of Pt(111) with picometer accuracy by a low-energy electron diffraction intensity vs voltage [LEED-I(V)] study. The nonequivalence of the mirror-plane directions  $\overline{\Gamma M}$  and  $\overline{\Gamma M}'$  at fcc(111) surfaces shows up in both LEED and IPE

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data as well as in the theoretical calculations. We use the LEED data to give a clear definition of these directions. This approach is also transferable to other fcc(111) surfaces. The unoccupied electronic structure of Pt(111) is the subject of Sec. III. Experimental data obtained with angle-resolved IPE are displayed and compared with DFT calculations along the distinct high-symmetry directions of the Pt(111) surface in Sec. III C 1. The results reflect the nonequivalence of the high-symmetry directions in agreement with the conclusions of Sec. II. Section III C 2 is dedicated to the image-potentialinduced surface state. An in-depth analysis of the L-gap surface feature and its spin texture by theory and spin- and angle-resolved IPE is given in Sec. III C 3. The combination of the applied experimental and theoretical approaches provides a consistent description of the L-gap surface resonance at Pt(111).

## **II. ATOMIC STRUCTURE**

#### A. LEED-*I*(*V*) analysis

The LEED-I(V) experiments were performed in Erlangen using a Pt(111) crystal from the same provider and with a very similar preparation recipe as described in Sec. III A. The sample holder allowed for rapid cooling down to below 100 K within minutes after preparation as well as alignment of normal incidence of the LEED beam with an accuracy of  $\approx 0.2^{\circ}$ . For more experimental details see Ref. [16].

LEED-I(V) data were taken via recording the full LEED pattern by a cooled 12-bit CCD camera within the energy range 50 eV-600 eV in steps of 0.5 eV and stored for off-line evaluation. From this stack of frames we extracted background-corrected integral spot intensities as function of energy [I(V)] spectral for all accessible diffraction beams using the semiautomated acquisition system EE2010 [17]. Subsequently, I(V) spectra of symmetrically equivalent beams were averaged, moderately smoothed where necessary, and normalized by the primary beam current. The resulting experimental data set consisted of ten nonequivalent beams with a cumulated energy range of  $\Delta E \approx 3500$  eV and is supplied in the Supplemental Material (SM) [18]. In the optimization process we neglected energies below 100 eV [only available for the (0|1) and (1|0) beams, in total 100 eV data width] as suggested by Materer et al. [19] because of the known improper treatment of spin-orbit coupling for heavy elements such as Pt relevant at lower energies.

The calculation of I(V) spectra and parameter fitting were performed using the VIPERLEED program package [20], which manages a modified and parallelized TENSERLEED code [21]. Atomic scattering was modeled by phase shifts up to  $\ell = 14$  derived from Rundgren's program EEASiSSS [22], which also provides a related energy-dependent inner potential  $V_{0r}(E) = (-0.06 - 85.88/\sqrt{E/eV} + 17.53)$  eV for the energy range of the LEED-I(V) calculations. The lateral lattice parameter for Pt at 90 K was set to 2.770 Å [23] and the bulk vibrational amplitude to  $u_b = 0.065$ Å, according to a Debye temperature of  $\Theta_D = 240$  K [24]. In an advanced state of the analysis also the optical potential  $V_{0i}$ , the surface layer vibrational amplitude  $u_s$ as well as the effective half-angle  $\theta$  of the slightly con-



FIG. 1. (a) Ball model of the Pt(111) surface in side view (z scale exaggerated) with relaxation of layer spacings (in percent of the bulk layer distance) derived from the LEED-I(V) analysis (red) compared with the predictions of DFT (LDA: green; PW91-GGA: blue). (b) Selection of experimental I(V) spectra for various beams with their counterparts calculated for the best fit structural model. The R factor values denote the quality of the single beam correspondence. (c) Error curves displaying the R factor increase with a vertical shift of single layers from their best fit position. The range below the R + var(R) line is an estimate for the statistical error of the determined vertical positions of layers.

vergent incident beam were optimized to  $V_{0i} = 4.85$  eV,  $u_s = 0.080$  Å, and  $\theta = 0.44^{\circ}$ .

Since the Pt(111) surface is unreconstructed, we started just from a bulk truncated  $1 \times 1$  model. Only the correct assignment of beams in relation to the stacking direction chosen in the model had to be determined, which, however, was evident already from the calculation for the unrelaxed surface model. We then optimized the vertical position of the outermost six Pt layers with a final precision of 0.002 Å via minimization of the Pendry *R* factor [25]. With a total number of P = 9 fitted parameters (three nonstructural ones, see above) we have a very high redundancy  $\rho = \Delta E / (4V_{0i} \cdot P) \approx$ 19 [16], i.e., we have a nineteenfold overdetermination in the fit and thus a high degree of trustworthiness within the results.

The best fit configuration schematically displayed in Fig. 1(a) achieved an overall *R* factor value as low as R = 0.060, which is among the best values ever reached in a LEED analysis. The excellent spectral correspondence is directly visualized in the selection of experimental and best fit I(V) curves compiled in Fig. 1(b). The full set of spectra is given in the SM [18]. The statistical accuracy of the determined parameter values can be estimated via the so-called variance of the Pendry *R* factor var(R) =  $R \cdot \sqrt{8V_{0i}/\Delta E}$  [25], whereby the range of uncertainty of a parameter is given by the span where the corresponding *R* factor value lies below R + var(R) level (here: 0.066). Figure 1(c) displays such error curves for

the vertical position of single atomic layers, whereas all other parameters were held at their best fit value. As can be seen, the error margins for the outermost four layers are well below a single picometer, those for the fifth and sixth layer slightly above (for numerical values of the errors see the SM [18]).

Regarding the result of the LEED-I(V) analysis [Fig. 1(a)], we can state with high confidence that the detected surface relaxation is quite small as already reported before. The outermost layer is found to be relaxed outwards by 2.7 pm (1.2 %) in quantitative agreement with the previous result of Materer *et al.* [19] ( $\Delta d_{12} = 2.5$  pm, determined at an *R* factor level of R = 0.15) and with predictions by DFT (LDA: 2.3 pm; GGA: 3.6 pm). While the next two layer distances turn out to be practically unrelaxed within the limits of error, we surprisingly find an expanded fourth layer distance  $[\Delta d_{45} = +1.4 \text{ pm } (0.6 \%)]$ , which appears statistically significant on the basis of the extremely small error margins achieved for the atomic positions, for details see the SM [18]. The corresponding DFT calculations (described in Sec. III B), however, predict this (and deeper) layer spacings as quasibulklike, independent of the applied approximation LDA or PW91-GGA. In order to check for possible parameter couplings in the LEED fit we performed a series of allparameter fits for different scenarios. We found the expansion of the forth layer spacing (with only small numerical scatter) independent of the number of fitted layer positions below and also for various subsets of the data base. Fixing this spacing to the bulk value led to an expansion of adjacent layer distances also at variance to the DFT results (and an increased R-factor value of R = 0.064). And fixing all layer spacings below the second/third one to the bulk value led to further increased *R*-factor values of R = 0.073 and R = 0.070, respectively, clearly beyond the variance level of the best fit. It is also worth to note that for all these attempts the first two layer distances always stayed at their best fit values within 0.2 pm (0.1%), which thus can be taken as definite. On the other hand, using the predicted relaxation values from DFT much higher *R*-factor values resulted (LDA: R = 0.084; GGA: R = 0.095). At the moment, we have no explanation for this admittedly quite small discrepancy between experimental and theoretical results, which, as we want to emphasize, has no relevance to the further interpretation of the electronic structure.

# B. Distinguishing $\overline{\Gamma} \overline{M}$ and $\overline{\Gamma} \overline{M}'$ directions at fcc(111) surfaces

The outermost atomic layer of an fcc(111) singlecrystal surface is hexagonally close packed with sixfold rotational symmetry C<sub>6</sub>. The layers of the crystal show an ABCABC...-type stacking sequence with all atoms in threefold-coordinated hollow sites. Already the second layer reduces the single-layer C<sub>6</sub> symmetry to a threefold symmetry C<sub>3</sub>. This is illustrated in Fig. 2(a), where the topmost atomic layer is shown in yellow and the second layer in red. While the topmost layer contains six mirror planes perpendicular to the surface, the double layer contains only three. For example, the plane containing the  $[\overline{1}\ \overline{1}\ 2]$  direction is a mirror plane for both topmost and double layer, while the plane containing the  $[\overline{1}\ 1\ 0]$  direction is only a mirror plane of the topmost layer. Interestingly, the two opposite directions  $[\overline{1}\ \overline{1}\ 2]$  and  $[1\ 1\ \overline{2}]$ within the mirror plane are not equivalent because there is a



FIG. 2. (a) Real-space sketch of the fcc(111) surface with first (yellow) and second (red) layer, and crystallographic directions. (b) The fcc reciprocal structure (purple truncated octahedron) with projection to the (111) surface Brillouin zone (yellow). (c) LEED pattern of Pt(111) with (1|0) and (0|1) diffraction spots and overlayed surface Brillouin zone. (d) Measured LEED-I(V) spectra of the (1|0) and (0|1) diffraction spots [see Fig. 1(c)]. The dashed red line marks the energy of the LEED pattern in (c), indicating the observed intensity difference.

next-nearest-neighbor atom in the second layer along  $[\overline{1}\ \overline{1}\ 2]$ , while there is none along  $[1\ 1\ \overline{2}]$ . In contrast, the two opposite directions  $[\overline{1}\ 1\ 0]$  and  $[1\ \overline{1}\ 0]$  are equivalent.

In reciprocal space, the high-symmetry points of the surface Brillouin zone are denoted as  $\overline{M}$  and  $\overline{K}$ . This is illustrated in Fig. 2(b), where the surface Brillouin zone is shown in yellow in relation to the bulk Brillouin zone in red. The highsymmetry points of the Brillouin zone are labeled according to the point symmetry of the atomic structure. While in the twodimensional single-layer case all six  $\overline{M}$  points are equivalent, the consideration of the bulk symmetry divides them into two differing groups, i.e., three  $\overline{M}$  and three  $\overline{M}'$  points. At the  $\overline{M}$  The nonequivalence of  $\overline{\Gamma} \overline{M}$  and  $\overline{\Gamma} \overline{M}'$  due to the influence of the second and further layers has important consequences for experimental studies of, e.g., the crystal structure via low-energy electron diffraction or the electronic structure via photoemission techniques. However, an unambiguous distinction between  $\overline{M}$  and  $\overline{M}'$  is often missing. In the literature, there seems to be consensus about the labeling of the two points  $\overline{M}$ and  $\overline{M}'$  [26–28]. We have adapted this notation in Fig. 2(b).

A direct experimental approach to correlate  $\overline{\Gamma M}$  and  $\overline{\Gamma M'}$ with the atomic structure is provided by a LEED study of the fcc(111) surface via intensity vs. voltage [I(V)] curves. A LEED pattern of Pt(111) obtained at an electron energy of 65.8 eV is shown in Fig. 2(c). The (1|0) and (0|1) diffraction spots are highlighted. The surface Brillouin zone is superimposed. Figure 2(d) shows the experimental intensities of the (1|0) (green) and (0|1) (black) spots as a function of the electron energy. The I(V) curves differ significantly for the two diffraction spots. This allows us to identify unambiguously the  $\overline{\Gamma M}$  and  $\overline{\Gamma M'}$  directions, see labeling in Fig. 2(c).

### **III. ELECTRONIC STRUCTURE**

#### A. Experimental method: Inverse photoemission

All IPE experiments were performed in Münster under ultrahigh-vacuum (UHV) conditions at a base pressure of  $<5 \times 10^{-11}$  mbar. The unoccupied electronic structure was investigated by spin and angle-resolved IPE [29]. Spinpolarized electrons (P = 29%) used for excitation were extracted from a GaAs photocathode [30]. The transversal spin polarization of the electron beam was oriented within the sample surface plane and perpendicular to  $\mathbf{k}_{\parallel}$ , i.e., sensitive to the Rashba component. The incomplete spin polarization of the electron beam was taken care of by normalizing the data to 100% electron spin polarization [29,31]. The electron beam impinged on the sample with variable energy at a defined angle  $\theta$  relative to the surface normal with a divergence  $\Delta \theta_{\rm FWHM} < 3^{\circ}$  [30,32]. The emitted photons were detected with a bandpass detector, which was positioned at 65° relative to the electron beam within the measuring plane and at  $32^{\circ}$  out of it. The detection energy was  $\hbar \omega = 9.9 \text{ eV}$  with a bandpass width of 330 meV [33–35]. The overall energy resolution of the IPE experiment amounts to  $\Delta E_{\rm FWHM} \approx 400 \text{ meV}$  [36]. All IPE measurements were carried out at 291 K.

A single crystal of Pt with (111) surface was obtained from MaTecK GmbH (Germany) and mounted on a molybdenum sample holder. The sample was cleaned as discussed in the literature [37] by first sputtering (Ar<sup>+</sup> ions, 600 eV, 2  $\mu$ A sample current, 10 min) to break carbon structures and then flashing to 1300 K in oxygen atmosphere of  $\approx 1 \times 10^{-7}$  mbar to remove residual carbon. The sample was prepared in a separate chamber connected with the analysis chamber for IPE by a UHV sample-transfer system. The surface quality of the sample and the reproducibility of the preparation procedure were monitored by LEED for the crystallographic order and Auger electron spectroscopy (AES) for contaminants on the surface. For a freshly prepared sample, no oxygen or carbon contamination was detected in AES. LEED experiments verified the single-crystalline structure of the surface: sharp spots and a low background signal were observed. The work function was determined from target-current spectroscopy measurements to  $\Phi = 5.86 \pm 0.06$  eV and agrees with values found in the literature, e.g.,  $\Phi = 5.84 \pm 0.05$  eV [38].

#### **B.** Theoretical methods

Our calculations for bulk Pt are carried out in the framework of DFT [39] employing a code [40-42] based on pseudopotentials and a basis of atom-centered Gaussian orbitals of *s*, *p* and *d* symmetry [43]. We use the local-density approximation [44] as well as the generalized gradient approximation with the so-called PW91 exchange-correlation functional according to Perdew and Wang [15]. The respective norm-conserving pseudopotentials that include scalar relativistic corrections as well as spin-orbit interaction [45] are generated following the prescription of Hamann [46] and transformed into the separable Kleinman-Bylander form [47]. For details of the method, see Ref. [42].

For platinum, the bulk lattice constant resulting from LDA  $a_{\text{LDA}} = 3.905 \text{ Å}$  is closer to the experimental values  $a_{\text{exp, 0 K}} = 3.916 \text{ Å}$  and  $a_{\text{exp, 291 K}} = 3.924 \text{ Å}$  [23] than the value derived from PW91-GGA  $a_{\text{GGA}} = 3.981 \text{ Å}$ . This observation is in line with reports in the literature [14,48]. To study the influence of the lattice constant (which is distinctly overestimated in PW91-GGA) on the *L*-gap surface state, we have carried out further GGA calculations employing the second-order GGA (SOGGA) functional proposed by Zhao and Truhlar [49]. This approach leads to a lattice constant  $a_{\text{SOGGA}} = 3.918 \text{ Å}$ .

The Pt(111) surface is described by periodically repeated slabs of 41 Pt layers with 20 Å of vacuum between the slabs. In structure optimization, relaxations of the topmost six layers were taken into account. Brillouin zone integrations are carried out using a  $16 \times 16 \times 1$  Monkhorst-Pack mesh for the slab calculations [50].

For a direct comparison between band-structure calculations and IPE data, we search for direct transitions between unoccupied Pt bulk bands, which differ in energy by 9.9 eV, i.e., the photon energy used in our experiment. To estimate spectral intensities, we took matrix elements of the transitions into account. As only  $\mathbf{k}_{\parallel}$  is conserved when the electron passes the vacuum-crystal interface, additional effort is needed to estimate  $k_{\perp}$  within the crystal from the known  $k_{\perp,vac}$  in vacuum. Approximating the initial states as parabolic free-electron-like bands in a constant inner potential  $V_0 = 5.4$  eV [51] relative to the Fermi level  $E_{\rm F}$  [52],  $k_{\perp}$  in the crystal is given by

$$k_{\perp} = \sqrt{\frac{2\,m_{\rm e}}{\hbar^2} \cdot \left(E - E_{\rm F} + \hbar\omega + V_0 - \frac{\hbar^2}{2\,m_{\rm e}}k_{\parallel}^2\right)},$$

This estimate for  $k_{\perp}$  is essential to predict the experimental transitions for the nonequivalent directions  $\overline{\Gamma} \overline{M}$  and  $\overline{\Gamma} \overline{M}'$ . Without restricting the possible  $k_{\perp}$  values, the surfaceprojected  $E(\mathbf{k}_{\parallel})$  calculation would contain all transitions independent of  $k_{\perp}$ . In view of the simplifications of this



FIG. 3. Angle-resolved IPE spectra of Pt(111) along the highsymmetry directions (a)  $\overline{\Gamma} \overline{M}$ , (b)  $\overline{\Gamma} \overline{M}'$ , and (c)  $\overline{\Gamma} \overline{K}$ . The blue and purple lines connect spectral features attributed to transitions into the surface resonance SR and image-potential state IS, respectively. The black lines indicate features from transitions into bulk states B1–B8. The wide gray lines indicate non-**k**-conserving transitions to *d* bands.

model, we allowed a  $k_{\perp}$  window of  $\pm 0.2$  Å<sup>-1</sup> in our calculations.

#### C. Results and discussion

# 1. Unoccupied electronic states along $\overline{\Gamma} \overline{M}$ , $\overline{\Gamma} \overline{M}'$ , and $\overline{\Gamma} \overline{K}$

Figure 3 presents angle-resolved IPE spectra series of Pt(111) along (a)  $\overline{\Gamma} \overline{M}$ , (b)  $\overline{\Gamma} \overline{M}'$ , and (c)  $\overline{\Gamma} \overline{K}$ , which are the nonequivalent high-symmetry directions for an fcc(111)surface. The dispersions of peak positions in the spectra as a function of the electron incidence angle  $\theta$  are indicated by thin lines. The peak positions observed along  $\overline{\Gamma} \overline{M}$  and  $\overline{\Gamma} \overline{M}'$ , which mark the final-state energies of optical transitions, are transferred as solid squares into the  $E(\mathbf{k}_{\parallel})$  diagram shown in Fig. 4. The golden-shaded areas in Fig. 4 represent the calculated surface-projected bulk band structure, the white areas are gaps with no states allowed in the bulk. The colored dots are calculated final-state energies of direct transitions between bulk states taking into account the  $k_{\perp}$  restriction as described above. The colors of the dots indicate the components of the vector potential **A** for the transition [53]: brown for  $A_{[111]}$ , yellow for  $A_{1\overline{2}11}$ , and green for  $A_{10\overline{1}1}$ . The size of the dots is proportional to the expected intensity based on the transition matrix elements.

A comparison between the experimental and theoretical results in Fig. 4 allows us to interpret the spectral features:

IS (purple color) shows a free-electron-like parabolic dispersion within an energy gap with a vertex at  $\overline{\Gamma}$  at  $E - E_{\rm F} \approx 5$  eV, which corresponds to approximately 0.5 eV below the vacuum level. It behaves in the same way along all



FIG. 4. Energy vs  $\mathbf{k}_{\parallel}$  dispersion of electronic states at Pt(111) along  $\overline{\Gamma} \overline{\mathbf{M}}'$  (left) and  $\overline{\Gamma} \overline{\mathbf{M}}$  (right). Squares represent peak positions of experimental spectra from Figs. 3(a), 3(b). The golden-shaded areas display the calculated surface-projected bulk band structure. The brown dots represent calculated and  $k_{\perp}$ -selected transitions to bulk states with vector potential along  $A_{[111]}$  (see text for details). Yellow dots represent transitions with  $A_{[\bar{2}11]}$  and green dots transitions with  $A_{[0\bar{1}1]}$ . The size of the dots is proportional to the transition probability.

high-symmetry directions. Therefore, we interpret IS as the n = 1 image-potential-induced surface state. It will be discussed in more detail in Sec. III C 2.

The spectral feature SR (light blue) appears in all three spectra series. It shows a paraboliclike dispersion around  $\overline{\Gamma}$ starting from  $E - E_{\rm F} \approx 0.5$  eV and following closely the gap boundary. It has no counterpart in the bulk calculation. Therefore, we interpret SR as surface-induced state at the *L*-gap boundary, whose existence was already concluded from scanning tunneling spectroscopy (STS) experiments [11]. Due to the overlap with bulk states, we classify the state as surface resonance and label it as SR. This state will be further discussed in Sec. IIIC 3. We note in passing that both IS and SR are sensitive to surface contamination, which supports our interpretation as surface-related states.

The remaining spectral features B1–B4 for  $\overline{\Gamma} \overline{M}$ , B5 and B6 for  $\overline{\Gamma} \overline{M}'$ , and B7 and B8 for  $\overline{\Gamma} \overline{K}$  (all indicated in black) appear within  $E(\mathbf{k}_{\parallel})$  areas, where bulk bands exist, see also Ref. [14]. In addition, as shown for  $\overline{\Gamma} \overline{M}$  and  $\overline{\Gamma} \overline{M}'$  in Fig. 4, they coincide convincingly with calculated transitions of  $\hbar \omega = 9.9$  eV (colored dots) in the respective  $k_{\perp}$  range. We want to emphasize that the dispersions along  $\overline{\Gamma} \overline{M}$  and  $\overline{\Gamma} \overline{M}'$  differ significantly both in experiment and theory. This behavior underlines the bulklike behavior of the states due to the threefold symmetry and the nonequivalence of  $\overline{\Gamma} \overline{M}$  and  $\overline{\Gamma} \overline{M}'$ . We find excellent agreement between experiment and theory for all spectral features B1–B6.

In addition to these direct transitions for certain energy and  $\mathbf{k}_{\parallel}$  values, we observe small spectral intensity where no direct transitions are predicted. Spectral intensity appears just above the Fermi level independent of  $\theta$ , e.g., along  $\overline{\Gamma} \overline{\mathbf{M}}'$ . At the very surface,  $k_{\perp}$  is not a good quantum number, which is strictly conserved. As a consequence, in cases of high density of states, non-k-conserving or density-of-states transitions, as they are called in the literature [54], may give rise to intensity in IPE spectra. In our case, they are caused by the high density of unoccupied *d* states in Pt just above  $E_F$ . Along  $\overline{\Gamma} \overline{M}$ , the spectral intensity just above  $E_F$  is caused by both direct and density-of-states transitions. The small spectral intensity along  $\overline{\Gamma} \overline{M}'$  is attributed to density-of-states transitions only.

One additional interesting detail should be mentioned here. In the experimental data (Fig. 3), the intensity of B1 for  $40^{\circ} \leq \theta \leq 70^{\circ}$  along  $\overline{\Gamma} \overline{M}$  stands out in comparison with the other spectral features. In the calculations, it is remarkable that almost all bulk transitions are dominated by the  $A_{[111]}$  component, except for B1, which gains contributions from the other two components upon increasing  $\mathbf{k}_{\parallel}$  (Fig. 4). Given the position of the photon detector, with increasing  $\theta$ , it becomes less sensitive to the  $A_{[111]}$  component and more sensitive to the other two components. As a consequence, B1 should gain intensity with increasing  $\theta$ , while B2–B4 become less prominent as it is observed in experiment.

In summary, the unoccupied electronic structure of Pt(111) comprises bulk-derived states with nonequivalent dispersions along  $\overline{\Gamma} \overline{M}$  and  $\overline{\Gamma} \overline{M}'$  and surface-derived states with parabolic dispersions independent of the particular direction. This observation underlines the threefold symmetry of the Pt(111) surface for states where more than the top layer is involved. Since the atomic configuration enters the calculations, the different dispersions of the states are a second approach to unambiguously identify the  $\overline{\Gamma} \overline{M}$  and  $\overline{\Gamma} \overline{M}'$  directions. We emphasize that both calibrations via LEED-I(V) curves and  $E(\mathbf{k}_{\parallel})$  dispersions came to the same result.

#### 2. Image-potential state

Electrons approaching a conductive surface may be trapped in front of the surface between the Coulomb-like barrier potential and the crystal barrier in case of high surface reflectivity, caused by, e.g., an energy gap in the surface-projected bulk band structure. These states, which exist far in front of the surface layer, are called image-potential states and form a Rydberg-like series of states within less than 1 eV below the vacuum level. Image-potential states, in particular the n = 1 members of the series (IS), have been observed via IPE and two-photon photoemission on many surfaces, in particular also on Pt(111) [9,10,55,56]. We have identified IS in our angle-resolved IPE data as shown in Fig. 3. In order to study IS in more detail, we measured IPE spectra in a restricted energy interval around IS with a reduced angular step width of two degrees along  $\overline{M} \cap \overline{\Gamma} \overline{M}$ , as presented in Fig. 5(a). The n = 1 image-potential state IS is clearly resolved with a pronounced peak-to-background ratio from  $\theta = -10^{\circ}$  to  $\theta = 20^{\circ}$ . To deduce the energy positions, we fitted the data as described in the literature [57]. The black solid lines show the results of a fitting procedure. The fit function consists of a linear background with a steplike increase at the position of the vacuum level, one Lorentzian function to describe the n = 1 image-potential state, and a second Lorentzian peak pinned 200 meV below the vacuum energy to approximate the higher members  $(n = 2, ..., \infty)$  of the Rydberg series. The fit functions consisting of background and Lorentzian



FIG. 5. (a) IPE spectra of the image-potential state IS at Pt(111) for various angles of electron incidence  $\theta$  along  $\overline{M}'\overline{\Gamma}\,\overline{M}$ . Black lines are fits to the data (see text for details.) (b)  $E(\mathbf{k}_{\parallel})$  dispersion of IS with a parabolic fit to the data resulting in an effective mass of  $m^*/m_e = 1.21 \pm 0.05$  and a binding energy  $E_{\rm B} = E_{\rm V} - E = 0.55 \pm 0.07$  eV. For comparison, the dashed gray line shows the free-electron parabola  $(m^*/m_e = 1)$ .

functions were then convoluted with the apparatus function, approximated by a Gaussian function.

Figure 5(b) presents the angle-dependent peak positions of the n = 1 state as open circles in an  $E(\mathbf{k}_{\parallel})$  diagram. The uncertainty bars relate to the varying peak-to-background ratios and the different number of counts accumulated for each spectrum, as visible in Fig. 5(a). The purple parabola is a fit to the peak positions including these uncertainties. The uncertainties of the parameters from the fit result in an overall uncertainty of the parabola, which is well within the width of the purple line. The minimum of the parabola is determined to  $E - E_{\rm F} =$  $5.31 \pm 0.02$  eV (or  $E_{\rm B} = E_{\rm V} - E = 0.55 \pm 0.07$  eV). This value is slightly lower but compatible with values from a DFT calculation ( $E_B = 0.65$  eV [56]), or two-photon photo emission experiments ( $E_{\rm B} = 0.65 \pm 0.05$  eV [56],  $E_{\rm B} =$  $0.78 \pm 0.05$  eV [55]). The effective mass is determined to  $m^*/m_e = 1.21 \pm 0.02$ , which is higher than theoretically predicted  $(m^*/m_e = 1.05 [58])$ . Note that the shape of the surface barrier used in the calculation influences the resulting effective mass. For comparison, we included a free-electron parabola  $(m^*/m_e = 1)$  as dashed gray line in Fig. 5(b).

Image-potential states at elements with high atomic number Z are predicted to exhibit a Rashba-type spin splitting due to spin-orbit interaction [58]. The strength of this effect is often characterized by the Rashba parameter  $\alpha_R$ :

$$E_{\pm}(\mathbf{k}_{\parallel}) = \hbar^2 \mathbf{k}_{\parallel}^2 / 2m^* \pm \alpha_{\mathrm{R}} |\mathbf{k}_{\parallel}|$$

With spin-resolved IPE, this effect was experimentally detected for the Re(0001) surface with  $\alpha_R = 105 \pm 33 \text{ meV Å}$  [59]. Calculations for Pt(111) predict significantly lower values of  $\alpha_R = 25 \text{ meV Å}$  [58] and  $\alpha_R = 23 \text{ meV Å}$  [60]. Nevertheless, we searched for a spin splitting for Pt(111) by spin-resolved IPE measurements. This is a challenging task due to the low count rates and the low peak-to-background ratio, especially at higher  $\theta$ . We were not able to detect a significant spin splitting but were able to detect a upper limit of  $\alpha_R \leq 25 \text{ meV Å}$ , which is compatible with the predictions.

#### 3. L-gap surface resonance

The fcc(111) surfaces of the noble metals Cu, Ag, and Au exhibit a characteristic L-gap surface state around  $\Gamma$ , whose spin-orbit-induced Rashba-type spin splitting has been thoroughly investigated [5-7,61,62]. The lower boundary of the Shockley-inverted gap defined by the  $L_{2'}$  point is well separated from the lower-lying d bands. This changes for Ni, Pd, Ir, and Pt, where d bands affect the lower band-gap boundary and dominate the density of states at the Fermi level. In addition, the surface state becomes unoccupied and, therefore, inaccessible to photoemission. The transition from a surface state to a surface resonance and the hybridization with d bands was discussed in the literature for ferromagnetic Ni(111), where, in addition, the state becomes exchange split [63,64]. At Pt(111), the situation is similar to Ni(111) with regard to the influence of d states but very different in view of the electron spin. While the low-Z Ni is a ferromagnet, the high-Z Pt is not ferromagnetic. Instead of an exchange splitting, a Rashba-type spin splitting can be expected. Our angle-resolved IPE data of Figs. 3 and 4 indicated already the existence of a surface resonance SR at Pt(111).

We start the analysis of the surface resonance SR with a presentation of the different expectations from widely used theoretical approaches. In Fig. 6 the results of our DFT slab calculation within Fig. 6(a) PW91-GGA and Fig. 6(b) LDA are shown as gray lines. The golden-shaded areas represent the surface-projected bulk band structure. In case of spin polarization for the bands, red and blue dots on top of the gray lines indicate spin-up and spin-down character, respectively. The spin directions are oriented within the surface plane and perpendicular to  $\mathbf{k}_{\parallel}$ , i.e., along the Rashba component, as illustrated in the inset of Fig. 6(b). The dot size is proportional to the expectation value of the spin polarization. The cuts for IPE measurements at  $\theta = -2^{\circ}$  and  $\theta = +2^{\circ}$  are shown as thin black lines.

The two calculations provide qualitatively different predictions concerning SR: In PW91-GGA, it shows up as a Rashba-split surface state pair around  $\overline{\Gamma}$  separated from the bulk bands and develops into a surface resonance with increasing  $\mathbf{k}_{\parallel}$ . In LDA, the surface resonance appears at lower energy and both Rashba branches hybridize with bulk bands around  $\overline{\Gamma}$ , while an additional surface resonance within the bulk-band region splits off to lower energies [65]. The energetic position of SR seems to be critical whether the split-off state around  $\overline{\Gamma}$ exists or not.

To understand the different energetic positions we take a closer look into the calculations: The lattice constant a



FIG. 6. Theoretical data from DFT calculations in (a) PW91-GGA and (b) LDA. Gray lines represent results from the slab calculation and golden-shaded areas the surface projected bulk band structure. The *L*-gap surface feature is shown with its up and down spin polarization as red and blue dots. The symbol size is proportional to the expectation value of the Rashba spin-polarization direction as defined in the inset of (b). The paths for IPE measurements at  $\theta = \pm 2^{\circ}$  are shown as thin black lines.

of the optimized spatial structure differs significantly within PW91-GGA ( $a_{GGA} = 3.981$  Å) and LDA ( $a_{LDA} = 3.905$  Å). Experimentally, the lattice constant was determined by x-ray diffraction experiments to 3.924 Å at 291 K [23]. The experimental value is much closer to the value obtained in LDA, while  $a_{GGA}$  deviates significantly from the experiment. Good agreement for *a* between experiment and LDA calculation was already reported by Dal Corso [14] and Haas *et al.* [66]. From these findings, one might suspect that the different energy positions of SR in the calculations are mainly influenced by the lattice constant. For a given structural configuration, the influence of the different functionals LDA or GGA on the electronic structure is not so strong.

Figure 7 displays the energetic positions of SR for different *a* at a  $k_{\parallel}$  value that corresponds to  $\theta = 2^{\circ}$  in Fig. 6. Here we distinguish the energies of the Rashba branches inside the *L* gap, the split-off branch, and the *d* bands. The spin polarization at the surface is again proportional to the dot size, but increased for better visibility. These calculations were done in Fig. 7(a) PW91-GGA and Fig. 7(b) LDA, and the range of the examined *a* was chosen to include the experimental and both theoretically calculated lattice constants. Both theoretical approximations yield qualitatively identical results: with decreasing *a* all branches shift to lower energy while the *d* bands are at constant position. Also, the split-off branch



FIG. 7. Theoretical data from DFT calculations in (a) PW91-GGA and (b) LDA as a function of the lattice constant *a*. Displayed are the energetic positions of the SR branches (with their spin polarization) and of the *d* bands at a  $k_{\parallel}$  value that corresponds to  $\theta = 2^{\circ}$  along  $\overline{\Gamma} \overline{M}$ . Symbols and colors have the same meaning as in Fig. 6.

gains spin polarization in contrast to the branches within the L gap [67].

Among the many GGA functionals which are used nowadays in calculations, the SOGGA functional is known to yield very accurate lattice constants of solids [48]. Interestingly, the resulting band structure for Pt(111) at  $a_{SOGGA} = 3.918$  Å [18] is very close to the LDA result shown in Fig. 6.

We further tested the influence of relaxation. From the calculations in LDA as well as PW91-GGA, the relaxation between first and second layers amounts to 1%-2% only. For further layers up to layer seven, the relaxation values are well below 1%. These results fit the relaxation values from our LEED measurements in Sec. II. Taking these small relaxation values into account in the calculations of the electronic structure does only cause negligible changes, even when we used the relaxation values of LDA in PW91-GGA and vice versa. We therefore conclude that the relevant parameter for the energetic position of SR is the lattice constant *a* rather than the type of functional used in the calculation of the electronic bands for a given lattice configuration.

Based on our theoretical studies in LDA, instead of a pure L-gap surface-state parabola as observed on Cu, Ag, and Au, we expect SR to touch the bulk bands at the bottom of the L gap in the vicinity of  $\overline{\Gamma}$  and to hybridize with d bands. A similar scenario was reported for Ni(111), yet with the additional influence of exchange interaction [64]. In the case of Pt(111), a surface-derived branch splits off with negative dispersion within the bulk bands, while the lowerlying Rashba branch almost vanishes [see LDA calculations in Fig. 6(b)]. The two remaining branches on each side of  $\overline{\Gamma}$  show a distinct spin-orbit-induced spin texture with predominantly one spin character, spin-down (spin-up) for the up-dispersing, spin-up (spin-down) for the down-dispersing branch for positive (negative)  $\mathbf{k}_{\parallel}$ . Figures 8(a)-8(c) show simplified sketches of the various scenarios for the L-gap surface states (lines) in relation to the d bands (gray or hatched



FIG. 8. (a)–(c) Simplified sketches of the *L*-gap surface states and *d* bands at (a) Au(111) [5,7], (b) Ni(111) [64], and (c) Pt(111) [data from Fig. 6(b)]. Red and blue lines in (a) and (c) denote the Rashba-type spin polarization as defined in Fig. 6(b). Red and green colors in (b) indicate minority and majority spin directions, respectively. (d) Spin- and angle-resolved IPE spectra of Pt(111) along  $\overline{\Gamma} \overline{M}$ . Red (blue) triangles indicate spin up (down). The spectra for  $\theta = +2^{\circ} [\theta = -2^{\circ}]$  are enlarged in (e) [(f)] and presented with the corresponding spin asymmetry.

areas) for Au(111) [5,7], Ni(111) [64], and Pt(111) [data from Fig. 6(b)].

In the following, we put the theoretical predictions to an experimental test. The largest differences between the predictions from LDA and PW91-GGA appear within a few degrees around  $\overline{\Gamma}$ . While in PW91-GGA the surface-derived state shows a typical Rashba-type behavior with small differences between the two spin components, the situation is very different in LDA, where the spin splitting for, e.g.,  $\theta = \pm 2^{\circ}$  should appear much larger in the experimental data. The upper and lower branches are expected to show only one spin component yet with reversed sign. Unfortunately, the states appear within about 0.5 eV above the Fermi level and the energy resolution in IPE is limited to about 400 meV. Nevertheless, we performed spin-resolved IPE measurements in small angular steps around  $\overline{\Gamma}$  to shine more light on this issue.

Figure 8(d) displays a series of spin- and angle-resolved IPE spectra of Pt(111) close to the Fermi energy around  $\overline{\Gamma}$ . The red (blue) triangles represent the up (down) spin direction as defined in the inset of Fig. 6(b). This series in small angular steps shows two features, whose dispersions are indicated by thin lines: The bulk band B2 at almost constant energy close to the Fermi level and the upward dispersing feature SR. SR shows a spin asymmetry at the high-energy side, which changes sign upon sign reversal of  $\theta$ . This is indicative of a spin-dependent energy splitting of Rashba type: SR consists of two branches with opposite spin polarization that partially overlap in the IPE spectra. This observation is still compatible with both PW91-GGA and LDA predictions.

To distinguish between the varying PW91-GGA and LDA predictions, we need a further criterion. We decided for IPE spectra taken at  $\theta = -2^{\circ}$  and  $\theta = +2^{\circ}$  to test the band structure along the thin black lines in Fig. 6. According to PW91-GGA, the two spin components of SR appear very close to each other and above the d bands. In the LDA calculation, the lower branch of SR splits off from the upper branch by some 100 meV down to the Fermi level with a clear spin polarization. A closeup of the spectra at  $\theta = +2^{\circ}$ is shown in the top part of Fig. 8(e). This enlargement displays not only the spin asymmetry at the high-energy side of SR, but also opposite spin asymmetry at the low-energy side close to  $E_{\rm F}$ . Spectra for the complementary angle  $\theta = -2^{\circ}$ shown in the top part of Fig. 8(f) give equivalent results but with reversed spin asymmetry. The findings are underlined by spin-asymmetry curves in the lower part of Figs. 8(e), 8(f). This behavior is not expected from the PW91-GGA calculations. Instead, close to  $E_{\rm F}$ , where only unpolarized non-k-conserving transitions into empty d states might interfere, no spin asymmetry should appear. In contrast, the experimental findings are in good agreement with the LDA calculations.

The well-known *sp*-derived *L*-gap surface state characteristic of fcc(111) surfaces appears at Pt(111) as a surface resonance at the bottom of the gap, which splits into two branches via hybridization with *d* states. On the one hand, this behavior is reminiscent of the surface resonance at Ni(111). On the other hand, and in contrast to the ferromagnetic low-*Z* Ni, it shows a unique spin texture caused by spin-orbit interaction. The degree of hybridization and, as a consequence, the formation of a split-off state depends critically on the lattice constant. Our experimental findings on SR are in agreement with the LDA prediction but at variance with the GGA prediction. Our analysis shows that this follows from the difference in the lattice constants resulting from these approximations. Both calculations predict the experimentally

observed behavior of SR provided a lattice constant similar to the experimental value is used.

#### **IV. CONCLUSION**

We presented a comprehensive experimental and theoretical study of the clean Pt(111) surface. A detailed LEED-I(V)study revealed that the atomic structure of the Pt(111) surface is very close to a truncated bulk crystal with only minor relaxation effects for the outermost layers. In addition, we used the LEED study to unambiguously define the nonequivalent  $\overline{\Gamma} \overline{M}$  and  $\overline{\Gamma} \overline{M}'$  high-symmetry directions within the mirror planes of the surface. An in-depth study of the unoccupied electronic structure by spin- and angle-resolved IPE and DFT calculations using different functionals revealed bulk as well as surface electronic states. The bulk states reflect the nonequivalence of the mirror-plane directions  $\Gamma M$  and  $\Gamma M'$ , while the surface states follow symmetric paraboliclike energy vs momentum dispersions. For the image-potential state, we determined an upper limit for the Rashba parameter  $\alpha_R$  of 25 meV Å.

For the L-gap surface resonance, theoretical predictions based on different functionals within DFT differ concerning energy vs momentum dispersion and spin texture. Spinresolved IPE results enabled us to distinguish between the predictions by unambiguously detecting the split-off hybridized band. Our analysis shows that the lattice constant is a decisive parameter in the calculations, which lead to either a Rashba-type parabolic band or to an additional downward dispersing band of one spin direction only that splits off the parabolic band. Provided a lattice constant similar to the experimental value is used, DFT calculations with different functionals confirm the experimentally observed behavior. We compared the surface resonance of Pt(111) with the corresponding states at Au(111) and Ni(111) by evaluating the influences of *d*-band hybridization, spin-orbit interaction, and exchange interaction. We find for Pt(111) that the position of the surface resonance at the very bottom of the L gap in combination with the d bands at and above the Fermi level lead to hybridization between surface resonance and d bands and, hence, the unusual spin-polarized split-off branches not observed before. In summary, we found that the surface resonance at Pt(111) is a showcase for a delicate interplay of atomic structure, hybridization with d bands, and the influence of spin-orbit interaction.

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