Electron–phonon coupling in the surface electronic states on Pd(111)

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\textbf{Abstract.} We present an \textit{ab initio} study of the electron–phonon interaction in the surface electronic states on Pd(111). The calculations based on density-functional theory were carried out using a linear response approach and a mixed-basis pseudopotential method. We find that the electron–phonon coupling on Pd(111) both in the surface electronic states and at the Fermi energy is largely determined by bulk electronic states and bulk phonon modes. It is shown that the strength of the electron–phonon interaction and its variation with electron energy and momentum depend first of all on the particular surface energy band. However, the directional anisotropy in the electron–phonon coupling is weak.

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The electron–phonon (e–ph) interaction is a many-body effect which has long been studied because of its role in many physical phenomena, from electrical conductivity and electronic heat capacity to BCS-type superconductivity [1, 2]. In particular, the electron–phonon coupling limits the lifetime of excited electrons (or holes) [3]–[5] which are essential in many processes such as photochemical and catalytical reactions [6, 7] or charge and spin transport in bulk materials, across interfaces and at surfaces [8]. Lately, the e–ph interaction has been of increasing interest due to both technological advances in experiment [9]–[13] and progress in theoretical methods [14, 15, 16]. While tunneling spectroscopy or heat capacity measurements have provided information on the electron–phonon coupling strength averaged over the bulk Fermi surface of metals [1], angle-resolved photoemission experiments give an opportunity for studies that are not confined to the Fermi surface averaged values but detailed information about the energy and momentum dependence of the interaction is achieved [10, 12], [17]–[20].

The theoretical evaluation of the e–ph coupling generally requires knowledge of the electronic and vibrational spectra and the self-consistent response of the electronic system to lattice vibrations. Formerly, that was usually done by assuming a constant e–ph coupling matrix element and using a Debye model for the phonon spectrum of a system [1]. In this model, the phonon density of states is taken as a smooth function which does not depend on the details of the phonon spectrum. As a result, the Eliashberg spectral function $\alpha^2 F(\omega)$ which is largely determined by the density of phonon states does not depend on a particular electronic state and the e–ph interaction is smoothed out both in energy and in momentum. The Debye model was used to fit the experimentally obtained real and imaginary parts of the electron–phonon self-energy. Such fittings give the e–ph coupling strength, $\lambda$, thus characterizing the measured surface state. Despite successful applications [9, 11, 21], the Debye model does not give detailed information about the e–ph interaction mechanism. Besides, ab initio calculations [5, 22, 23] as well as the experiments [24, 25] showed the strong dependence of the e–ph coupling on excited electron (hole) energy and momentum. Recently a more complex model for evaluating the e–ph interaction in surface electronic states has been proposed [17, 26] where the e–ph coupling matrix is calculated taking into account electronic wave functions and phonon modes. The model combines three independent approximations: (i) one-electron wave functions and energies are calculated with a one-dimensional model potential [27]; (ii) phonon frequencies and polarization vectors are obtained either from one-parameter force-constant model or from an embedded atom method [28]–[30]; (iii) the gradient of the one-electron potential is represented
by the Ashcroft pseudopotential [31] screened within Thomas–Fermi approximation. However, this model can only be applied to s, p, surface electronic states with a small binding energy on simple and noble metal surfaces. It turned out that this approach was less accurate for surface electronic states lying far (2–6 eV) below the Fermi energy ($E_F$).

All quantities that determine the e–ph interaction can also be obtained from ab initio calculations. An advantage of such an approach is that all the three ingredients of the e–ph coupling matrix are precisely evaluated on the same footing. To date, the most efficient method for calculating lattice dynamical properties of solids is the linear-response technique based on the solid-state Sternheimer theory [16, 32]. In this approach, atomic displacements are treated as perturbations and the electronic response is calculated self-consistently. This method has been implemented with different basis sets for representing electronic wave functions [14, 15]. So far, fully ab initio calculations of the e–ph coupling have been reported only for surface electronic states on simple metal surfaces like Be(0001) [33], Mg(0001) [23] and Al(001) [34].

Here we present an analysis of the electron–phonon interaction in surface electronic states on a transition metal surface, Pd(111), which is of particular interest because of its catalytic properties and practical importance [35, 36]. A great deal of experimental information is now available on both the clean and the chemisorbed Pd(111) surface. However, the complexity arising from the presence of both highly localized and delocalized electrons makes theoretical investigations of transition-metal surfaces rather difficult. There is only a couple of calculations [37, 38] where the details of the e–ph coupling at the Fermi level of the W(110) surface were revealed. An analysis of the momentum dependence of the mass enhancement parameter showed that at the Fermi energy, $\lambda$ varies between 0.64 and 0.81. We consider all surface electronic states on Pd(111) both occupied and unoccupied in the energy range from $-8$ eV up to 1.3 eV with respect to the Fermi level. The Eliashberg spectral function $\alpha^2 F(\omega)$ and the e–ph coupling parameter $\lambda$ are presented both energy and momentum resolved. We have also evaluated the contributions to the e–ph coupling from different phonon modes as well as the influence of the e–ph interactions on the lifetime of electronic excitations. It is shown that the strength of the e–ph coupling, being sensitive to the energy and momentum position of an electron state, ranges from 0.07 to 1.4.

The paper is organized as follows. A short outline of the calculation method is given in section 2. Section 3 contains the results for structural, electronic and dynamical properties of the surface and the electron–phonon coupling. Finally, in section 4 the conclusions are drawn.

2. Details of the calculation

The calculations were performed using the density-functional theory together with the local density approximation for the exchange–correlation functional in the parametrization given by Hedin and Lundqvist [39]. Phonon frequencies and polarization vectors were obtained within the mixed-basis density functional perturbation theory [40]. To calculate e–ph matrix elements, both phonon emission and absorption processes were taken into account without the usual quasielastic approximation. The interaction of valence electrons with core electrons and nuclei is described by a norm-conserving scalar-relativistic pseudopotential generated following the Vanderbilt scheme [41]. The surface is presented by repeated slabs consisting of nine Pd layers and separated by five layers of vacuum. This thickness is quite sufficient to avoid the interference between the two surfaces of a slab, especially for well localized d electronic states, because the surface perturbations do not penetrate deeply into the bulk [42]. Atomic
positions inside the Pd(111) planes maintain the symmetry of the bulk and are fixed at the theoretical lattice parameter, \(a = 7.34\) a.u., which nearly coincides with the experimental value, \(a = 7.35\) a.u. \[43\]. Forces between the atomic layers were minimized to obtain the relaxed positions.

In the mixed-basis scheme, a combination of local functions and plane waves for the representation of valence states is used \[44, 45\]. The plane-wave energy cutoff was 20 Ry and, additionally, one d-type localized function at each atomic site of Pd was employed. Integrations over the surface Brillouin zone (SBZ) were performed with a uniform mesh of 576 special points \[46\] and a Gaussian energy smearing scheme with a width of 0.2 eV \[47\]. All results have been checked for convergence with respect to both the number of special points and the plane-wave energy cutoff.

A central quantity of the e–ph interaction is the Eliashberg spectral function \(\alpha^2 F(\omega)\) which measures the contribution of phonons with energy \(\hbar \omega\) to the scattering of electrons. If an initial electron state with momentum \(\mathbf{k}\) and energy \(\epsilon_i\) is considered, the Eliashberg spectral function gives the e–ph coupling between this state and all other final states \((\epsilon_f)\) which differ in energy by \(\hbar \omega\) \[1\]. The electron state-dependent Eliashberg spectral function corresponding to phonon emission (E) and absorption (A) processes is defined as:

\[
\alpha^2 F^{(E)}(\epsilon_i, \mathbf{k}; \omega) = \sum_{\mathbf{q}, \nu, f} \delta(\epsilon_i - \epsilon_f \mp \omega_{\mathbf{q}, \nu}) \left| g^{i,f}(\mathbf{k}, \mathbf{q}, \nu) \right|^2 \delta(\omega - \omega_{\mathbf{q}, \nu}),
\]

where \(g^{i,f}(\mathbf{k}, \mathbf{q}, \nu)\) is the e–ph matrix element between the initial \((i)\) and final \((f)\) electron states. The ‘−’ and ‘+’ signs in the delta function with electron energies correspond to a phonon emission (E) and absorption (A), respectively. The sum is carried out over final electron states and phonon modes \((\mathbf{q}, \nu)\). The electron state dependent e–ph coupling parameter is just the first reciprocal moment of the Eliashberg function:

\[
\lambda(\epsilon_i, \mathbf{k}) = \frac{\int_0^{\omega_m} \alpha^2 F^{(E)}(\epsilon_i, \mathbf{k}; \omega) + \alpha^2 F^{(A)}(\epsilon_i, \mathbf{k}; \omega) \, d\omega}{\omega}. \tag{2}
\]

Here, \(\omega_m\) is the maximum phonon frequency. If \(\lambda(\epsilon_i, \mathbf{k})\) is averaged over all initial electron states on the Fermi surface, one obtains the usual isotropic e–ph coupling constant \(\lambda_{\text{EF}}\) \[48\].

The lifetime broadening of an electron state due to the e–ph interaction is defined as \[1\]:

\[
\Gamma_{\text{e–ph}}(\epsilon_i, \mathbf{k}, T) = 2\pi \int_0^{\omega_m} \left[ \frac{\alpha^2 F^{(E)}(\epsilon_i, \mathbf{k}; \omega)}{\omega} \right] \left[ 1 + n(\omega) - f(\epsilon_i - \omega) \right] \nonumber + \alpha^2 F^{(A)}(\epsilon_i, \mathbf{k}; \omega)[n(\omega) + f(\epsilon_i + \omega)] \, d\omega. \tag{3}
\]

Note that the temperature dependence of \(\Gamma_{\text{e–ph}}\) is introduced by the Fermi \((f)\) and Bose \((n)\) distribution functions. The term in the first square brackets represents phonon emission and the term in the second square brackets is associated with phonon absorption processes.

3. Calculation results and discussion

3.1. Structural, electronic and dynamical properties

The calculated relaxation of Pd(111) layers in the slab showed a very small contraction of the two outermost interlayer spacings relative to the bulk distance: \(\Delta d_{12} = -0.15\%\) and \(\Delta d_{23} = -0.6\%\). The negligible top layer relaxation is consistent with the experimental expansion of
Calculated surface electronic states (black lines) on Pd(111). The grey background gives the bulk Pd bands projected onto the two-dimensional Brillouin zone. The right panel shows the electronic density of states for a nine-layer Pd slab (solid line) and the local density of states for the surface Pd layer (dashed line) per atom.

0.9 ± 1.3% obtained by low-energy electron diffraction intensity analysis [49]. The calculated values are also in agreement with other \textit{ab initio} pseudopotential results, $\Delta d_{12} = +0.1\%$ [50] and $\Delta d_{12} \approx -0.1\%$ [51] as well as with the data from all-electron full-potential linearized augmented plane-wave calculations, $\Delta d_{12} \approx -0.22\%$ and $\Delta d_{23} \approx -0.53\%$ [52].

The calculated surface electronic bands are shown in figure 1 by black lines while the shaded background represents the bulk bands projected onto the (111) plane. Generally, as a consequence of the slab geometry, pairs of surface states, one from each side of the slab, are not degenerate. The splitting depends on the slab thickness and the surface state decay properties. The pair of electronic states associated with an unoccupied s–p surface state at the SBZ centre is split by 0.25 eV due to the overlap of wave functions. It is the only surface band in the figure that is represented as an average of a pair of states arising from two opposite surfaces of the slab. Since the other surface electronic states on Pd(111) are d-like, they are strongly localized and their splitting does not exceed 0.01 eV in spite of the finite slab size. We have summarized the surface electronic state energies both predicted theoretically and observed experimentally in table 1 for comparison.

The density of electronic states (DOS) calculated for the nine-layer Pd slab is nearly identical to the calculated bulk DOS. There is only a small increase (about 8%) of the peak near the Fermi energy. We do not show the local density of states (LDOS) with the exception of that for the surface layer shown in the right panel of the figure by a dashed line because layer-by-layer changes in LDOS are found to be identical to those reported earlier [42]. They indicate that perturbations caused by the surface do not penetrate far into the bulk. Only the LDOS for the surface atoms is enhanced within 0–2 eV below $E_F$ as compared to the others. This is largely a consequence of the numerous surface bands existing in this energy interval.
Table 1. Summary of surface electronic state energies in eV (relative to \(E_F\)) for Pd(111).

|   | Expt. [53] | Theory [53] | Theory [54] | Theory [55] | This work |
|---|------------|-------------|-------------|-------------|-----------|
| \(\bar{\Gamma}\) | 1.3\(^a\)  | \(\approx\) 1.2 | 0.9 | 1.21 |
| (1.26\(^b\), 1.35\(^c\)) | | | | |
| \(\bar{k}\) | \(-0.3\) | \(-0.2\) | \(-0.1\) | \(-0.2\) | \(-0.14\) |
| | \(-2.2\) | \(-2.0\) | \(-2.3\) | \(-2.45\) | \(-2.42\) |
| | | \(-4.9\) | \(\approx\) \(-5\) | | \(-5.1\) |
| \(\bar{k}\) | \(-0.3\) | | \(-0.2\) | | \(-0.25\) |
| | | \(-1.0\) | \(-1.2\) | \(-1.2\) | \(-1.2\) |
| | | \(-2.1\) | \(-1.9\) | \(-2.3\) | \(-2.25\) | \(-2.3\) |
| | | | \(-3.4\) | \(\approx\) \(-3\) | \(-3.4\) | \(-3.4\) |
| \(\bar{M}\) | | \(\approx\) 0.5 | 0.3 | | |
| | | \(-1.0\) | | | \(-0.92\) |
| | | | \(-3.8\) | \(-3.0\) | \(\approx\) \(-3\) | \(-3.0\) |
| | | | | \(-4.5\) | \(\approx\) \(-4.4\) | \(-4.5\) |

\(^a\) Reference [56].

\(^b\) Reference [57].

\(^c\) Reference [58].

Figure 2. Calculated phonon dispersion curves for a 50-layer Pd slab. The phonon spectrum contains surface modes related to both relaxed (black dots) and ideal bulk-truncated surfaces (grey dots, the lowest phonon mode).

The density of states at the Fermi energy changes slightly from 2.36 \(-\) 2.5 states/(eV atom) in bulk Pd [22, 59] to 2.18 states/(eV atom) for the nine-layer Pd(111) slab.

Although the phonon dispersion curves have already been reported [50, 60], they are also shown to facilitate the discussion because they are a necessary ingredient for the calculation of the e–ph coupling. The calculated phonon dispersion curves were obtained by interpolation of a (16 \(\times\) 16) \(q\) point mesh for the hexagonal surface BZ. The phonon spectrum in figure 2...
Table 2. Calculated electron–phonon coupling parameter, \( \lambda \), and linewidth, \( \Gamma_{\text{e-ph}} \) (in meV, at \( T = 0 \) K), for surface electronic states at the symmetry points.

| \( \Gamma_1 \) | \( \lambda \) | \( \Gamma_{\text{e-ph}} \) | \( \lambda \) | \( \Gamma_{\text{e-ph}} \) | \( \lambda \) | \( \Gamma_{\text{e-ph}} \) |
|---|---|---|---|---|---|---|
| 0.08 | 4 | 0.56 | 28 | 0.07 | 3 |
| 0.50 | 16 | 0.63 | 35 | 0.50 | 24 |
| 1.40 | 46 | 1.36 | 58 | 0.64 | 27 |
| 0.18 | 9 | 0.60 | 34 | 0.54 | 28 |

First, we have evaluated the strength of the e–ph coupling at the Fermi energy of the nine-layer film. To average \( \lambda(E_F, \mathbf{k}) \) over electron momentum, we used 256 special points in the SBZ. The calculated e–ph coupling parameter, \( \lambda_{E_F} = 0.4 \), coincides with the value obtained at the Fermi surface of bulk Pd [22, 59]. This is the expected result because (a) the e–ph interaction at \( E_F \) of the Pd(111) surface is largely determined by bulk electronic states; and (b) surface localized vibrations are less involved in the scattering processes with electrons compared to bulk phonon modes. An analysis of electronic states participating in the e–ph interaction revealed that
the predominant contribution comes from electronic states that are partly or entirely of $d_{x^2-y^2}$ symmetry, where $z$ is the surface normal.

Let us now see how the surface electronic states on Pd(111) couple to phonons and how this coupling varies with electron momentum and energy. A very weak e–ph coupling was obtained for unoccupied surface electronic states. One of them, $\Gamma_1$, is located very close to the bottom of the s,p energy gap at the L symmetry point of bulk Pd BZ [56]. This is the only surface electronic band on Pd(111) that is purely s–p in character. With increasing momentum it enters the bulk electronic bands and becomes a surface resonance. The other band, $M_1$, lies on the edge of the bulk band around the $\bar{M}$ point. The $M_1$ surface electronic states being of $d_{x^2-y^2}$ symmetry are well localized in the outermost surface layer. Note that a weak e–ph coupling was obtained only for the electronic states in the vicinity of the $\bar{M}$ symmetry point. The calculated $\lambda_{\bar{M}} = 0.08$ and $\lambda_{\bar{M}} = 0.07$ are very small and differ drastically from the e–ph coupling parameter averaged over electron momentum at the Fermi energy of both the nine-layer Pd(111) film and bulk Pd [22, 59]. Such a weak e–ph interaction in the unoccupied surface states is related to an abrupt decrease of the density of electronic states above $E_F$ and, correspondingly, to a decrease of the number of electronic states that can participate in the e–ph coupling (see figure 1) [62]. On going away from the $\bar{M}$ point, the e–ph coupling in the $M_1$ surface band becomes stronger and $\lambda$ comes up to 0.45. Figure 3(a) shows the e–ph coupling parameter for $M_1$ as a function of electron energy. One can see that $\lambda$ for the electronic states located inside the bulk d band (see figure 1) is not small and is close to the value averaged at the Fermi level. On the contrary, on approaching the bulk band edge, the strength of the e–ph interaction diminishes by a factor of six. Figure 4(a) shows $\alpha^2 F(\omega)$ for an unoccupied surface state near $\bar{M}$ at $\epsilon = 0.26$ eV and for a hole state in

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**Figure 3.** (a) Electron–phonon coupling parameter $\lambda$ as a function of binding energy for the surface electronic band $M_1$. (b) $\lambda$ as a function of binding energy for surface electronic band $\Gamma_4$ along two symmetry directions, $\bar{\Gamma}\bar{M}$ (solid line) and $\bar{\Gamma}\bar{K}$ (dashed line).
Figure 4. (a) Electron–phonon Eliashberg spectral function $\alpha^2 F(\omega)$ for an unoccupied state in the $M_1$ surface electronic band at $\epsilon = 0.26$ eV and for an electronic state in the same surface band at $\epsilon = -0.15$ eV. (b) $\alpha^2 F(\omega)$ for $K_4$ (solid line) and twofold $K_3$ (dotted line) surface electronic bands at the $\bar{K}$ symmetry point. The contribution from the Rayleigh surface mode for $K_3$ is indicated by the hatched area. (c) Calculated phonon density of states for a nine-layer Pd slab, $F(\omega)$, per atom: total (solid line) and for the topmost layer (dotted line).

Since the contributions from phonon emission and adsorption processes almost coincide, the averaged Eliashberg spectral functions are shown. The bottom panel of the figure gives the phonon density of states for the nine-layer Pd(111) slab. The spectral functions, $\alpha^2 F(\omega)$, with a similar shape were also obtained for $K_1$ and $\Gamma_2$ surface electronic bands located just below the Fermi level. A characteristic feature of the spectral functions is that the high-energy in-plane polarized vibrations participate weakly in the $e$–$ph$ coupling. Another feature, inherent to all the surface electronic states on Pd(111), is that the interaction of electrons with bulk phonons predominates.

The largest strength of the $e$–$ph$ coupling was obtained for surface states in the twofold electronic bands, $K_3$ and $\Gamma_1$, of $d_{x^2-y^2,xy}$ symmetry: $\lambda_\Gamma = 1.4$ and $\lambda_{\bar{K}} = 1.36$. Figure 4(b) shows the Eliashberg spectral function for a hole state at the $\bar{K}$ symmetry point (dotted line). The spectral function characterized by two main peaks is similar in shape to the phonon density of states for the topmost Pd layer (dotted line in figure 4(c)). The electronic states in this energy band are the only surface states on Pd(111) with an appreciable contribution of the Rayleigh phonon modes to the $e$–$ph$ coupling. It is indicated by a hatched area in the figure and is associated, to a large extent, with the coupling of electrons with the Rayleigh modes split off the
bulk phonon spectrum at the SBZ boundary (see figure 2). These surface phonons give about 15% of the total contribution to the spectral function for all electronic states in the \( \Gamma_3 \) band. Furthermore, the contribution coming from the high-energy surface phonons (at \( \approx 24 \) meV) is also large. These in-plane polarized phonon modes exist in the upper energy gap at the SBZ boundary. An analysis of the initial and final electronic states participating in the e–ph scattering showed that a substantial part of the phonon-mediated transitions is interband between \( \Gamma_3 \) and \( \Gamma_3 \). Such transitions between the surface electronic bands are another characteristic feature of the \( \Gamma_3 \) and \( \Gamma_3 \) electronic states. This interband (\( \Gamma_3 \leftrightarrow \Gamma_3 \)) interaction together with the intraband scattering gives about 30% of the contribution to the e–ph coupling. We note that within each band, \( \lambda(\epsilon, k) \) varies rather strongly with electron energy and momentum ranging between 0.8 and 1.5.

For most of the surface electronic bands on Pd(111), \( \lambda \) varies between 0.5 and 0.7. It is larger than the \( \lambda \) at the Fermi energy but does not exceed 0.74. Figure 4(b) shows \( \alpha^2 F(\omega) \) for a hole surface state in band \( \Gamma_4 \) (at \( \bar{K} \)) (solid line). One can see that the spectral function differs significantly from \( \alpha^2 F(\omega) \) for a hole state in \( \Gamma_3 \). First, the contribution of optical bulk phonon modes increases markedly and becomes predominant (a peak at 25–27 meV). These high-energy phonon modes are, to a considerable extent, associated with in-plane vibrations of the subsurface atoms. The electronic state \( \Gamma_4 \) being \( d_{x^2−y^2,xy} \) in character is also strongly localized in the subsurface Pd layer. Second, a substantial suppression of the lower-energy part of the phonon spectrum, from 10 to 18 meV, by e–ph matrix elements is observed. Similar Eliashberg functions were obtained for surface electronic states in the \( M_4 \) and \( K_2 \) energy bands. In the latter case, the surface states are localized in the two outermost Pd layers. Their symmetry in the first atomic layer, \( d_{x^2,zy} \), differs from the one in the subsurface layer, where they are \( d_{x^2,zy} \) and \( d_{y^2−x^2,xy} \) in character. \( K_2 \) is another surface band on Pd(111) along with \( K_4 \) and \( \Gamma_3 \) where a noticeable contribution to the e–ph coupling comes from the intraband scattering. Unlike the surface bands around the \( \bar{K} \) point, the electronic states in \( M_4 \) are mainly localized in the surface layer. As a result, the corresponding e–ph spectral function differs slightly in the high energy part where the contributions from the subsurface atoms dominate. Unlike the \( K_2 \) surface band, \( \lambda(\epsilon, k) \) in \( M_4 \) exhibits a noticeable dependence on hole energy and momentum increasing up to 0.74 on moving away from \( \bar{M} \).

A weaker e–ph coupling was obtained for the lowest occupied surface electronic state at the zone centre, \( \Gamma_4 \), where \( \lambda = 0.18 \). Being located at the lower edge of the energy gap, this surface state of \( d_{x^2−y^2} \) symmetry is well localized in the first two Pd layers. Figure 3(b) shows the e–ph coupling parameter for this surface band as a function of electron energy along two symmetry directions. As follows from the figure, the energy dependence of \( \lambda \) is strong. On moving away from the SBZ centre it increases from 0.18 at \( \bar{\Gamma} \) to 0.66. Such a behaviour is partly related to the energy position of the surface band at \( \bar{\Gamma} \) where many short-wave-length transitions are impossible due to the energy gap at the SBZ boundary. Besides, on moving along the \( \bar{\Gamma}K \) or \( \bar{\Gamma}M \) symmetry direction, the probability of intraband scattering increases. However, the directional anisotropy of \( \lambda \) is weak.

We have evaluated the lifetime broadening (linewidth) of excited holes (electrons) induced by the e–ph coupling. \( \Gamma_{e-ph} \) calculated at \( T = 0 \) K for the surface electronic states at the symmetry points are shown in table 2. For the unoccupied electronic states at \( \bar{\Gamma} \) and \( \bar{M} \) as well as for the lowest surface state in the SBZ centre, the linewidth is less than 10 meV. The largest \( \Gamma_{e-ph} \) is obtained for hole states in the twofold surface energy bands, \( K_3 \) and \( \Gamma_3 \). This is the expected result because the e–ph coupling in \( K_3 \) and \( \Gamma_3 \) is stronger than the e–ph interaction in

\[ \text{New Journal of Physics 11 (2009) 103038 (http://www.njp.org/)} \]
any other surface electronic band on Pd(111). On the one hand, it is explained by an appreciable participation of surface phonon modes in the e–ph coupling that is not the case for the other surface electronic states. On the other hand, it arises from numerous intraband as well as interband $K_3 \leftrightarrow \Gamma_3$ phonon-mediated transitions which, being a characteristic feature of the $K_3$ and $\Gamma_3$ electronic states, give a substantial contribution to the e–ph coupling. For the other occupied surface electronic states at $\bar{K}$ and $\bar{M}$, the phonon-induced linewidth varies between 28 and 35 meV. In contrast, $\Gamma_{e-ph}$ is quite small for the $\Gamma_1$ and $\Gamma_4$ surface states. However, the linewidth of the surface electronic states at the SBZ centre depends more on temperature compared with the surface states at $\bar{K}$ and $\bar{M}$. For instance, at room temperature $\Gamma_{e-ph}$ increases, on average, by a factor of 4, and even by a factor of 5 for $\Gamma_3$, while for the surface states at $\bar{K}$ and $\bar{M}$ the ratio of linewidths calculated at the two temperatures varies only between 3 and 3.5. Such temperature behaviour results from a particular feature of the Eliashberg spectral function. Unlike the surface electronic states at $\bar{K}$ and $\bar{M}$, $\alpha^2 F(\omega)$ for the $\bar{\Gamma}$ surface bands is characterized by a substantial contribution to the e–ph coupling from low-energy phonon modes (up to 10 meV). Since the temperature dependence of $\Gamma_{e-ph}$ in the calculation is introduced by the Fermi and Bose distribution functions which favour the low-energy part of the phonon spectrum, the linewidth of the $\bar{\Gamma}$ surface states increases more with temperature compared with $\Gamma_{e-ph}$ for other electronic bands.

We have also evaluated the e–ph influence on the surface vibrational modes. The obtained phonon linewidths are rather small and do not exceed 0.3 meV. They are close to those reported for bulk phonon modes except for an anomalously large broadening observed for some phonon modes in bulk Pd where the phonon linewidths comes up to 0.7 meV [22, 63].

4. Summary

We have presented an analysis of the electron–phonon interaction in the surface electronic states on a transition metal surface, Pd(111), using \textit{ab initio} calculations. The evaluated strength of the e–ph coupling at the Fermi energy, $\lambda_{E_F} = 0.4$, is close to the values obtained at the Fermi surface of bulk Pd [22, 59]. That is expected because the e–ph interaction on Pd(111), both in the surface electronic states and at $E_F$, is largely determined by bulk electronic states and bulk phonon modes. With regard to the surface localized phonon modes, their contribution to the scattering of electrons is not large except for the twofold surface electronic band $K_3$ where it amounts to 15%. The twofold surface bands at $\bar{\Gamma}$ and $\bar{K}$ are also distinguished by the strongest e–ph interaction, $\lambda > 1$, and, correspondingly, the largest phonon-mediated linewidth, $\Gamma_{e-ph}$, on the Pd(111) surface. It is largely determined by $K_3 \leftrightarrow \Gamma_3$ as well as intraband transitions which give about 30% of the total contribution to the e–ph coupling in these surface bands. The strength of the e–ph interaction in most of the surface electronic bands, except for the unoccupied surface states and the lowest one at $\bar{\Gamma}$, is noticeably higher than at the Fermi energy and varies in the range of 0.5–0.7. Very small values of the e–ph coupling were obtained for the unoccupied surface electronic states at $\bar{\Gamma}$ and $\bar{M}$. This is most likely due to the dominating effect of the electronic density of states. An analysis of the e–ph interaction showed that, like in the case of bulk Pd [22], its strength, although being sensitive to the energy and momentum position of an electron state, is determined first of all by the particular surface electronic band. However, the directional anisotropy of $\lambda$ is weak.
Acknowledgments

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