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LETTER TO THE EDITOR

# The influence of d electrons on surface plasmon dispersion: Pd(110)

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**Abstract.** Surface plasmon dispersion on Pd(110) was investigated along the high-symmetry directions $\langle 1\bar{1}0\rangle$ and $\langle 001\rangle$ with angle-resolved electron-energy-loss spectroscopy. A large negative initial dispersion with transferred momentum is found in spite of the strong shift of plasmon and surface plasmon frequencies induced by the presence of the d bands. Their unfilled character in transition metals is thus demonstrated to affect the dispersion of the surface plasmon in a very different way than for noble metals, where the filled d bands are responsible for the positive initial dispersion.

Dynamical screening properties are central to many surface properties such as photoemission, second-harmonic generation and energy transfer between incident particles and substrate [1]. Such properties also affect the surface plasmon dispersion coefficient at small wavevector, whereby the linear dispersion term was demonstrated to provide information on the position of the centroid of induced charge at the surface plasma frequency, at least for simple metals [1, 2]. For alkali metals a negative initial dispersion was observed [3, 4], which corresponds accordingly to a centroid placed outside the geometric surface plane. This result can be understood in terms of the electron gas compressibility which is larger in the spill-out tail, where the electron density is lower. The situation is more complicated for noble metals. A positive linear dispersion was observed for all low-Miller-index surfaces of Ag [5, 6, 7, 8]. This was interpreted as evidence for a subsurface position of the centroid of the screening charge [5], which is evidently connected to the presence of the polarizable d electron shells. Recent theoretical models have confirmed that the origin of the positive dispersion is connected to the presence of d electrons, but have disagreed on the ultimate microscopic mechanism which causes the reversal of the sign of dispersion [9, 10].

Surface plasmons on d metals are usually strongly damped by the presence of interband transitions, so few other materials are suitable for investigations aiming to enlarge the experimental data base. Pd is a remarkable exception as a collective excitation appears in the electron energy-loss (EEL) spectra as a relatively well defined, albeit heavily damped, feature. It is, moreover, a very interesting case as no accurate angle resolved EELS data exist in literature so far for the surface plasmon dispersion on a transition metal. According to optical data [11, 12] the surface plasmon frequency (corresponding to the maximum of $\mathrm{Im}[-1/(\epsilon(\omega)+1)]$ in the neighbourhood of $\epsilon(\omega)=-1$, where $\epsilon(\omega)$ is the bulk dielectric function) is at $\hbar\omega_{sp}=7.3$ eV according to [11] and at $\hbar\omega_{sp}=6.9$ eV according to [12] and

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the peak has a full width at half maximum (FWHM) of about 2 eV. The bulk loss function ($\mathrm{Im}[-1/\epsilon(\omega)]$) has a maximum at $\hbar\omega_p = 7.6$ eV according to [11] and at $\hbar\omega_p = 7.8$ according to [12]. Thus the ratio of $\omega_{sp}$ to $\omega_p$ is 0.88 [12] or 0.96 [11], i.e. far away from the value of $1/\sqrt{2}$ expected for a free-electron gas. The situation is thus similar to the case of Ag where $\omega_{sp}/\omega_p = 0.98$. The s-electron density was estimated to be between 0.36 electrons/atom [13] and 0.59 electrons/atom [14]. Accordingly, $\hbar\omega_{sp}^{free}$ lies between 4.1 eV and 5.3 eV, i.e. lower than the optical value, in contrast to the case of Ag where $\hbar\omega_{sp}^{free}$ is larger than the optical value.

Pd(110) was investigated with angularly integrated EELS by Nishijima *et al* [15] who gave an exhaustive comparison with previous EELS work. The presence of a prominent peak in the loss spectra was reported in all studies (see references in the work by Nishijima *et al* [15]) and was mainly attributed to the excitation of the bulk plasmon. The reported energy-loss values range between 6.8 eV and 7.5 eV with no plausible explanation for the poor reproducibility. Nishijima *et al*, who worked at a primary energy, $E_i$, of 100 eV, found the loss to be at 7.5 eV, i.e. near to the value appropriate for the bulk plasmon. At this impact energy, however, the penetration depth of the electron beam into the crystal is minimal, so a stronger sensitivity of the experiment to the bulk rather than to the surface properties appears surprising. Moreover, they noticed that the peak is displaced to 6.5 eV without narrowing and without substantial reduction in intensity when the surface is exposed to oxygen. They did not comment further on this point, which is in evident contradiction with the assignment of the feature to a bulk excitation.

A major reason for the inconsistency of the data and of their spread in energy is probably that interband transitions are superimposed on the surface plasmon loss and that their relative contribution to the loss intensity depends on the conditions (impact energy, angle of incidence, etc) under which the EEL experiment is performed. Interband transitions on Pd have a d $\rightarrow$ d and d $\rightarrow$ sp character, as well as sp $\rightarrow$ sp and sp $\rightarrow$ d, as both d and sp bands are crossed by the Fermi level. An analysis of $\Im[\epsilon(\omega)] = \epsilon_2(\omega)$ [16] showed that interband transitions among d bands did indeed contribute to loss energies, $E_{Loss}$, of 5.8 eV, while interband transitions from d to sp peaked around $E_{Loss} = 4$ eV and 9 eV. At the surface further transitions are expected from bulk states which involve a Shockley state (6.6 eV above $E_F$) at $\bar{\mathrm{X}}$ and a Shockley state (3.4 eV above $E_F$) at $\bar{\mathrm{Y}}$ and an image state (6.6 eV above $E_F$) [17]. $\hbar\omega_{sp}$ hence lies in a region of low density of single-particle excitations. Further interband transitions were predicted by Lovrić and Gumhalter [18] at 16 eV and at 22 eV.

Most of the early EELS work was performed without angular resolution, so in the analysis the dispersion of the losses with momentum parallel to the surface was neglected. The assumption seemed to be justified by Netzer and El Gomati [19], who found no variation of the loss frequency on Pd(111) when moving the analyser of the EEL spectrometer off-specular. They devoted, however, little attention to effects connected to the finite angular resolution of the EEL spectrometer, which are now known to strongly affect the EELS measurement of surface plasmons [5].

In this letter we present a new set of EELS data which clearly demonstrate that the major feature observed in the loss spectra is due to excitation of the surface plasmon, which shows a strongly negative linear initial dispersion with transferred momentum $q_\parallel$. The dispersion is isotropic with respect to crystal azimuth within experimental accuracy. Pd therefore behaves like no other material investigated so far: not like a noble metal, in spite of the presence of d electrons and of the proximity of $\omega_{sp}$ to $\omega_p$, as in that case the dispersion should be positive; not like a simple metal with the appropriate s-electron density (which

Pd surely is not) as in that case a much smaller negative slope would be expected.

The experiment has been performed in an ultra-high-vacuum chamber (base pressure $\leqslant 1 \times 10^{-10}$ mbar) equipped with standard surface science facilities [20]. The EEL spectra were recorded on-specular at grazing incidence with a commercial VSW CLASS 150 hemispherical analyser equipped with multi-channel detection, variable entrance slit and variable magnification lens. Slit and lens settings were optimized to achieve 1.2° angular resolution. The electron source was a standard electron gun for the data with high ($\geqslant$100 eV) primary energy, with an energy resolution of 400 meV FWHM. In the low-primary-energy regime an electron monochromator was used which allows for an energy resolution of less than 0.2 eV. The sample preparation procedure is described in [21].

EEL spectra resolved with respect to $q_\parallel$ can be recorded in two ways: (a) one can tune the spectrometer at a low impact energy, $E_i$, so that the width of the dipole lobe (given roughly by $\hbar\omega_{sp}/2E_i$) is much larger than the angular acceptance of the spectrometer, and then perform an angular scan over the dipole lobe (the integration over $q_\parallel$ is then given by the angular acceptance of the spectrometer); (b) alternatively one can work at large $E_i$ where the dipole lobe is shrunken, and record the spectra on-specular by varying $E_i$. The integration over $q_\parallel$ is then given by the width of the dipole lobe. Method (a) was applied to investigate the surface plasmon dispersion on Ag [5, 6, 8] and on simple metals [3, 4]. However, it turned out that for Pd(110) in such conditions ($E_i$ between 15 eV and 30 eV) the contribution of interband transitions to the EEL spectra is important. These data will be presented elsewhere as they need a longer discussion than is possible in this letter [22]. Data collection at higher $E_i$, on the other hand, showed well defined and sharp peaks. We believe that the better quality of the data recorded at large $E_i$ is due to to the averaging out of the intensity associated to interband transitions in such conditions. Our conclusions are therefore based primarily on such data.

Typical energy-loss spectra recorded on-specular for Pd(110) at different $E_i$ are shown in figure 1 for conditions corresponding to the alignment of the scattering plane along $\langle 1\bar{1}0\rangle$ and in figure 2 along $\langle 001\rangle$. A major loss is present in all spectra and we assign it to the excitation of the surface plasmon. Its frequency was determined by fitting the maximum of the loss intensity after subtracting a suitable background. This procedure is to some degree arbitrary for the largest $q_\parallel$ where the loss peak intensity is smaller. A larger error bar was hence assumed for the determination of the loss energy under such conditions. In this procedure we assumed that the electron suffered a single energy-loss event during the interaction. This assumption proved to be adequate for EELS data on Ag [5, 6, 8] and for simple metals [3, 4]. The $q_\parallel$ value corresponding to the losses was computed following energy and momentum conservation for the scattered electron:

$$\hbar q_\parallel = \sqrt{2m}\ (\sqrt{E_i}\ \sin\theta_i - \sqrt{E_i - E_{Loss}}\ \sin\theta_s) \tag{1}$$

where $m$ is the mass of the electron, and $\theta_i$ and $\theta_s$ are the angle of impact and of scattering, respectively.

For the assignment of the loss to the surface plasmon we are also assuming that the contribution of the bulk plasmon and of the interband transitions to the inelastic intensity is negligible. Evidence in favour of this is given below.

(i) The loss peak looks like a sharp feature.

(ii) The weaker maxima at smaller loss values in figure 1 and 2, which are associated with interband transitions involving the d bands, are anisotropic with respect to the crystal azimuth. Such anisotropy is due to a non-dipolar contribution to the cross-section of interband transitions [25]. In contrast the dispersion of the main loss peak on Pd does not depend on the crystal azimuth.

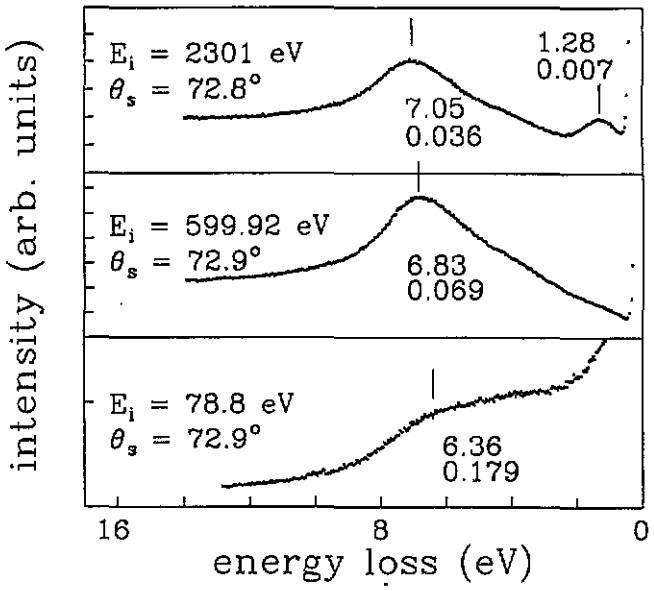


**Figure 1.** *Sample EEL spectra of the electronic excitations on Pd(110) recorded with the* scattering plane aligned along $\langle 1\bar{1}0 \rangle$. The major loss observed at larger $E_i$ is connected with the excitation of the surface plasmon of Pd and disperses with $q_\parallel$. The spectra do not represent constant-$q_\parallel$ scans. The value of energy loss (in eV) and of $q_\parallel$ (in Å$^{-1}$) corresponding to the maximum of the losses is given in the figure.

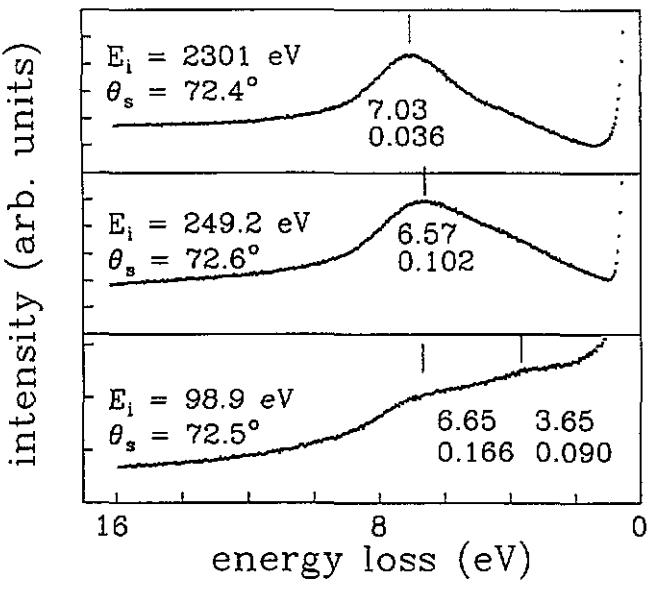


**Figure 2.** *The same as figure 1, but with the scattering plane aligned along* $\langle 001 \rangle$.

(iii) The loss frequency and FWHM of the major loss for the smallest investigated $q_\parallel$ (0.036 Å$^{-1}$) are close to those expected from optical data for the surface plasmon [11, 12]. In contrast, interband transitions are expected to be peaked around 4.5 eV and 9 eV [16],

while transitions among the d bands contribute to the loss spectra up to 5.8 eV. Transitions involving either image states or Shockley states are expected at 6.6 eV [17]. Such transitions were also expected for Ag, but were too weak to be detected with EELS [25].

(iv) The contribution of the bulk plasmon to the inelastic intensity for Ag was negligible [5, 25]. A peak at $\omega_p$ was observed for the simple metals [4] only when moving the monochromator towards normal incidence, thus increasing the penetration depth, $\lambda_\perp$, of the incident electrons. This effect is due to the efficient screening of external perturbations which means that the bulk plasmons are excited only while the electron is inside the solid whilst surface plasmons can also be excited while the electron approaches the surface and leaves it after the scattering event. This time is much longer than the time spent within the solid for grazing incidence. According to the universal curve of the electron mean free path [26] $\lambda_\perp \approx 3$ Å, at $E_i = 2000$ eV and $\theta_i = 73°$ and it is comparable to the value for $E_i = 15$ eV and $\theta_i = 60°$ (typical conditions reported in literature for surface plasmon dispersion studies). We expect, therefore, that the contribution of the bulk plasmon should also be negligible in this case. Moreover, the bulk plasmon of Pd was reported to be dispersionless with $q$ [23], while our data present a strong dispersion. Such dispersion could finally be mimicked by an $E_i$ dependence of the relative contribution of bulk and surface plasmon, even in the presence of a positive dispersion of the latter; if this were the case however, we would expect that the maximum of the loss feature could not be shifted below $\hbar\omega_{sp} \approx 7$ eV, contrary to the experimental evidence.

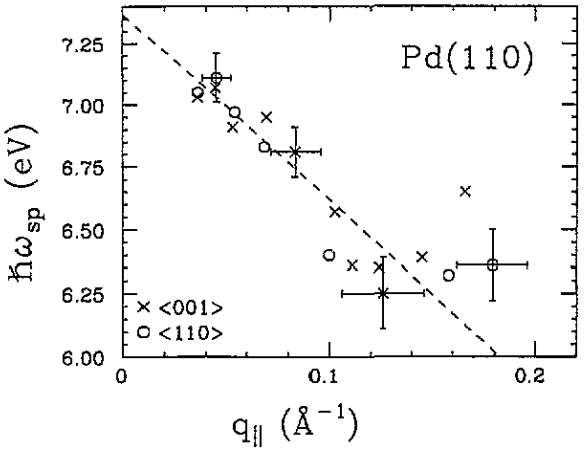


**Figure 3.** Dispersion of the surface plasmon as a function of transferred momentum $q_{\|}$.

The data are collected versus $q_\|$ in figure 3. As one can see, the initial dispersion is linear and negative. The upwards bending of the dispersion curve at larger $q_\|$ should be regarded with some caution as those data points might be affected more severely by the subtraction of the background and by the presence of interband transitions. The data were fitted with the linear form $\omega(q_\|) = \omega(0) + Aq_\|$ giving $\omega(0) = 7.37 \pm 0.10$ eV and $A = -7.4 \pm 1.2$ eV Å by minimizing the $\chi^2$ by using a MINUIT computing routine. $\omega(0)$ is thus close to the optical value of $\omega_{sp}$ in accordance with our assignment of the loss to a surface plasmon. The slope of the dispersion is, on the other hand, much larger than the values reported so far for surface plasmons, whose magnitude was typically of 1 eV Å. Below 6.6 eV, $\hbar\omega_{sp}(q_\|)$ matches the energy and wavevector of single-particle surface excitations. Such a situation occurred also for Ag(001) [5], but the surface plasmon dispersion was hardly affected.

A negative dispersion of the surface plasmon was so far assumed to be indicative of a free-electron gas behaviour of the electrons involved in the excitation. According to Feibelman [1] the negative dispersion is connected to the position of the centroid of the screening charge with respect to the geometrical surface by

$$\omega_{sp}(q_\parallel) = \omega_{sp}(0)(1 - \tfrac{1}{2}(d_\perp - d_\parallel)q_\parallel + O(q_\parallel^2)) \tag{2}$$

where $d_\perp$ is the centroid of the induced charge at $\omega_{sp}$, while $d_\parallel$ coincides with the geometrical surface plane for jellium. Equation (2) yields the unreasonably large value $d_\perp(\omega_{sp}) = 2$ Å for Pd(110). For comparison $d_\perp(\omega_{sp})$ values range from 0.5 Å to 0.88 Å for the alkali metals [4, 24]. Thus, as expected, equation (2) is not adequate for describing the dispersion of the surface plasmon for a transition metal.

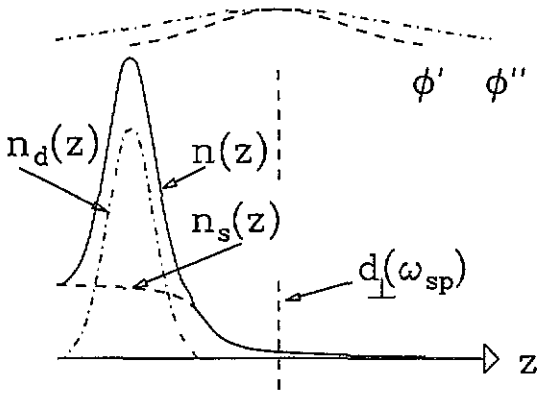


**Figure 4.** The charge density $n = n_s + n_d$ in the presence of s and d electrons seen by a surface plasmon excitation ($n_d(z)$ is depicted for the d electrons in the outermost crystal layer only). The relative height of $n_d$ with respect to $n_s$ depends on the fraction of d electrons which participate to the collective mode and is only indicative in the drawing. The potential $\phi$ associated with the surface plasmon is depicted for two $q_\parallel$ values, whereby $\phi''$ corresponds to a smaller $q_\parallel$ than does $\phi'$. The effective charge $n_{eff}$ seen by the surface plasmon thus decreases with $q_\parallel$ as long as the centroid of the total dynamical screening charge $d_\perp(\omega_{sp})$ lies outside the outermost crystal layer.

The strong and negative dispersion for Pd must therefore have a different origin than the location of $d_\perp$ with respect to $d_\parallel$. We suggest it to be connected to the particular electronic configuration of this material, i.e. to the unfilled character of its d bands. In the existing theories of surface plasmon dispersion [9, 10] the d electrons are described by polarizable shells located around the ions [9] or by a polarizable medium below the surface [10]. These pictures are not appropriate for Pd, as in this case the d electrons: (a) are mobile due to the unfilled character of the d bands and (b) can take part in the collective excitation as $\hbar\omega_{sp}$ is significantly larger than the energy of the d–s threshold. In this respect Pd is therefore similar to Si where the plasmon and the surface plasmon frequencies are determined by the electron density in the valence band. The strong negative dispersion could then be determined by the electron density close to the Fermi edge, which is particularly large in the case of a transition metal if both sp and d electrons are considered.

A hint for the solution of the puzzle may be found in a recent paper by Feibelman and Tsuei [27], who demonstrated that for jellium the surface plasmon dispersion can also be

described by

$$\omega_{sp}^2(q_\parallel) = \omega_p^2 \int \mathrm{d}z\; n(z)\; \phi(z, q_\parallel, \omega) \Big/ \int \mathrm{d}z\; \phi(z, q_\parallel, \omega) \tag{3}$$

with $n(z)$ the unperturbed charge density of the metal normalized to its value deep in the bulk and $\phi$ the fluctuating potential associated with the surface plasmon. Equation (3) shows that the value $\omega_{sp}(q_\parallel)$ is determined by the degree to which $\phi$ overlaps $n(z)$, thus feeling an effective charge $n_{eff}$. As $\phi$ becomes more and more localized at the surface with growing $q_\parallel$, $n_{eff}$ becomes $q_\parallel$ dependent. Assuming that the centroid of the induced charge is outside the crystal, as appropriate for a simple metal, $\omega_{sp}(n_{eff}(q_\parallel))$ decreases.

We suggest that this picture also holds qualitatively for Pd, the major difference being that now $n(z) = n_s(z) + n_d(z)$ and falls off much more rapidly towards the vacuum than for the case of a free-electron metal as $n_d$ is confined near to the ion cores as shown in figure 4. Hence $n_{eff}(q_\parallel)$ decreases more rapidly when the penetration of the surface plasmon field shrinks with $q_\parallel$ than for a simple metal, giving rise to a steeper dispersion. For small $q_\parallel$ the penetration of the surface plasmon field is probably large enough to allow one to neglect lattice effects. We note that this mechanism produces a negative slope as long as the centroid of the induced charge lies outside the outermost crystal layer and does not imply $d_\perp - d_\parallel > 0$. A subsurface position of $d_\perp$ is in fact likely for Pd in view of the proximity of $\omega_{sp}$ to $\omega_p$. Following Persson and Zaremba [28], in the presence of d electrons $d_\perp$ is in fact weighted with respect to the total charges of free (s) and bound (d) electrons in such a way that $d_{\perp d} < d_\perp < d_{\perp s}$. This mechanism would be inoperative for Ag as in this case the d shells are deep below the Fermi level, and so the d electrons are inhibited from contributing directly to the oscillating charge.

In conclusion, we have shown that the main energy-loss feature on Pd(110) is associated with the excitation of a surface plasmon and that it presents a negative dispersion in spite of the presence of d electrons and of the proximity of $\omega_{sp}$ to $\omega_p$. We demonstrate therefore for the first time that d shells affect the dispersion of the surface plasmon in a very different way depending on whether they are filled, as is the case for noble metals, or unfilled as for transition metals.

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