Prediction of a Ag multipole surface plasmon

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It is argued that Ag should exhibit a multipole surface plasmon near $\omega_m \approx 0.8\omega_p \approx 7$ eV ($\omega_p \approx 9$ eV is the s-electron bulk plasma frequency) since the density profile at the surface has predominantly s-electron character and since the multipole mode is much less affected by s-d screening than the monopole surface plasmon. Calculations of nonlocal optical spectra based on the s-d polarization model and the time-dependent density-functional approach support this picture. [S0163-1829(98)01407-6]

The collective surface excitations of non-nearly-free-electron metals exhibit substantial deviations from the behavior observed on simple metals such as Na, K, and Mg, whose dynamical surface response properties can be well understood in terms of the semi-infinite jellium model.[1–4] The most dramatic case is Ag, since the presence of the filled d bands leads to a strong lowering of the surface plasma frequency and to a positive dispersion with parallel wave vector.[5] Other examples are Hg (Ref. 6) and Li,[2] whose surface-plasmon dispersion is appreciably influenced by shallow core levels and strong ionic pseudopotentials, respectively. Curiously, electron-energy-loss spectra of Ag, Hg, and Li revealed no clear evidence of the multipole surface plasmon, which is by now well established on all metals exhibiting weak lattice effects.[1,2,7] Recent high-resolution loss spectra on Ag (Ref. 8) show slight variations of the shape of the main loss feature near 3.72 eV as a function of incident energy, but no separate loss peaks. As discussed below, it is doubtful whether this behavior can be associated with a multipole surface plasmon. A crucial test would be p-polarized photoyield data from (cesiated) Ag, but so far there is no evidence of a multipole excitation below the interband onset.[9] The conclusion from these studies seems to be that the multipole surface plasmon is a fragile surface excitation that is easily suppressed by interference with lattice-induced single-particle transitions.

The aim of this paper is to argue that the Ag multipole surface plasmon should exist despite strong lattice effects. However, in contrast to the simple metals, its frequency should be *above* rather than *below* the bulk plasma frequency. More specifically, we expect the multipole mode to lie in the 6–8 eV range, and we would like to encourage surface photoyield (or other nonlocal optical) measurements at these frequencies.

A hint for the possible existence of the Ag multipole surface plasmon comes from recent photoyield measurements and calculations on thin Li overlayers.[10] These spectra show a pronounced multipole mode but only a weak, highly damped bulklike overlayer plasmon. The explanation of this surprising behavior is that the fluctuating multipole charge is concentrated at the Li-vacuum interface. It is therefore much less exposed to the lattice potential than the bulklike mode which corresponds to a standing wave extending across the entire overlayer. Thus, the multipole mode is a genuine dynamical property of the surface density profile and to a great extent is decoupled from interband transitions within the metal.

Applying this picture to the case of Ag, we recognize first that the spill-out density has predominantly s-electron character, since the d electrons are more tightly bound. The multipole mode therefore arises mainly from s states. In addition, as shown below, the multipole frequency is much less affected by the s-d screening polarization which is crucial for the true bulk plasmon and monopole surface plasmon of Ag. The frequencies of the latter modes are given by $\omega_p^* \approx \omega_p/\sqrt{\varepsilon_d} \approx 3.8$ eV and $\omega_s^* \approx \omega_p/\sqrt{1+\varepsilon_d} \approx 3.7$ eV, where $\omega_p \approx 9$ eV is the bulk plasma frequency of the s-electron density, and $\varepsilon_d \approx 5$ is the d-electron contribution to the bulk dielectric function $\varepsilon(\omega)$. Thus, we suggest that the Ag multipole frequency follows the approximate rule $\omega_m \approx 0.8\omega_p$ that is obeyed by all simple metals.[11–13]

Why is the Ag multipole mode less affected by s-d screening than the monopole mode? At $q_\parallel = 0$, the latter excitation is determined by the condition $\varepsilon(\omega)+1=0$. Because of the infinite range of the plasmon field, this mode is fully exposed to the s-d polarization. ω_s^* is therefore a bulk property. At finite $q=|q_\parallel|$, however, the plasmon field decays exponentially like $e^{-q|z|}$, and the s-d screening is gradually switched off.[14] The fluctuating plasmon charge then becomes more s-like, and the frequency is shifted upwards in the direction of the unscreened surface plasma frequency $\omega_s = \omega_p/\sqrt{2} \approx 6.5$ eV. Now the electric field of the multipole mode is short ranged even in the $q_\parallel = 0$ limit, since its density exhibits an extra node compared to that of the monopole mode. Thus the influence of the s-d polarization is much weaker, and the multipole frequency must be significantly higher than ω_s^*. A zero-order estimate is $0.8\omega_p$, with minor shifts due to residual s-d screening. Of course, there is no reason to expect a multipole surface plasmon at $0.8\omega_p^* \approx 3$ eV. But the physical arguments presented above also indicate that a multipole mode between ω_s^* and ω_p^*, as claimed by Moresco *et al.*,[8] seems implausible: Because of its dipolar charge profile, the multipole mode is much less subject to s-d screening than the monopole mode.

To make these ideas more concrete, we performed calculations using the s-d polarization model,[14] which provides a qualitative understanding of the positive dispersion of the Ag monopole surface plasmon. In this model, the nonlocal dy-

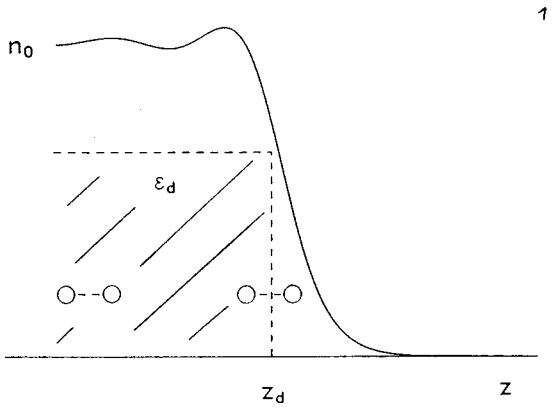

FIG. 1. Schematic representation of s-d polarization model. The solid curve denotes the ground-state s-electron distribution. The shaded area indicates the polarizable medium representing the occupied d bands. Because of the s-electron spill-out, electrons near the surface are less exposed to the s-d screening polarization than electrons inside the metal.

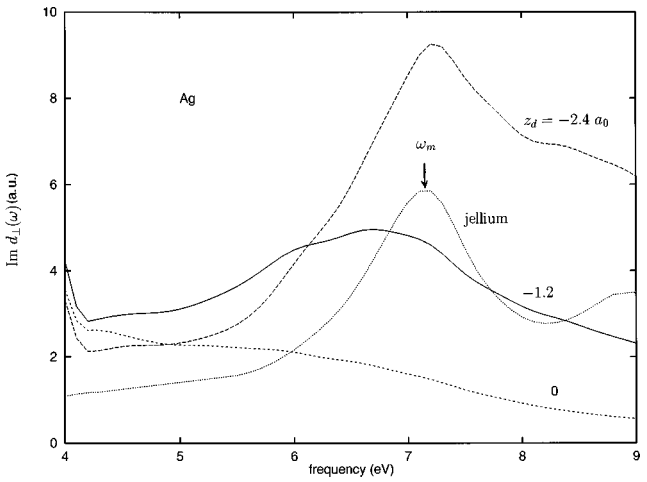

FIG. 2. Spectral distribution of Im $d_\perp(\omega)$ above the interband onset for several values of z_d. The results are based on the s-d polarization model and the TDLDA. The dotted curve denotes the spectrum for standard jellium ($r_s=3$) in the absence of the d bands. The multipole frequency in this case is $\omega_m \approx 0.8\omega_p \approx 7.2$ eV.

namical response of the $5s$ electrons is represented by that of a semi-infinite homogeneous electron gas ($r_s=3$) while the occupied d bands are replaced by a dielectric medium with dielectric function $\varepsilon_d(\omega)$. This function is obtained by writing the measured bulk dielectric function[15] as $\varepsilon(\omega)=\varepsilon_s(\omega)+\varepsilon_d(\omega)-1$, where $\varepsilon_s(\omega)=1-\omega_p^2/(\omega^2+i\gamma\omega)$ is the Drude function characterizing the s-electron density. The only parameter in this problem is the boundary z_d of the d electron medium (see Fig. 1). Response calculations using the time-dependent local density approximation (TDLDA) (Ref. 16) show that, for reasonable choices of z_d ($\approx -1.0\cdots -1.5a_0$), the dispersion of the monopole surface plasmon is indeed positive in agreement with experiment.[5] As z_d is shifted further inside the metal, the blueshift of the plasma frequency at finite $q_\parallel$ is enhanced, since the finite range of the plasmon field diminishes the s-d polarization. The surface plasmon then becomes even more s like.

The s-d polarization model outlined above is applicable mainly below the onset of interband transitions (~ 3.9 eV), i.e., as long as these transitions contribute virtually to the surface collective modes and $\varepsilon_d(\omega)$ is real. Above this onset, Im $\varepsilon_d(\omega)>0$, so that s and d electrons presumably should be treated on an equal footing. We recall, however, that as a result of the s-electron spill-out, the fluctuating multipole density is spatially separated from the ion cores where the d-electron transitions take place. Moreover, the frequency dependence of Im $\varepsilon(\omega)$ shows that the d-electron transitions are peaked near 4 eV. Toward higher frequencies, their spectral weight decreases. This effect further enhances the s-electron character of the Ag multipole mode. For the qualitative discussion of this paper, we therefore extend the s-d polarization model beyond the interband onset. A full microscopic description of the joined s- and d-electron response would be computationally extremely demanding and is not yet feasible.

To illustrate the Ag surface excitations, in Fig. 2 we show the frequency dependence of Im $d_\perp(\omega)$ for several values of z_d. $d_\perp(\omega)$ is the centroid of the charge density induced by an electric field normal to the surface or, more generally, the integrated weight of the normal component of the surface polarization. (The latter definition holds also above the bulk plasma frequency.) The evaluation of this quantity is carried out using the scheme by Liebsch and Schaich,[17] who focused on the nonlocal optical response of Ag below the interband onset. Without the d bands, Im $d_\perp(\omega)$ exhibits the familiar local field enhancement or multipole peak near $\omega_m \approx 0.8\omega_p \approx 7.2$ eV.[11–13] In the presence of the d bands, $d_\perp$ includes contributions from both s- and d-electron screening charges.

The calculations show that, for $z_d=-1.2a_0$, Im $d_\perp(\omega)$ exhibits a peak near 6.7 eV$\approx 0.74\omega_p$, i.e., slightly below the jellium value because of weak s-d screening. For $z_d=0$, the screening increases strongly so that only a weak, rather broad feature in the range from 5 to 8 eV remains. On the other hand, as z_d is shifted to $-2.4a_0$, the s-d polarization is rather small and the fluctuating multipole charge is more purely s like. The multipole peak then becomes sharper, and its frequency approaches the jellium value $0.8\omega_p$. The spectral weight and shape differ from the jellium case because of the different bulk dielectric functions.

As mentioned above, the positive surface-plasmon dispersion seen in inelastic electron scattering experiments can be reasonably reproduced using $z_d \approx -1.2a_0$. Accordingly, the spectrum shown in Fig. 2 for this value serves as the most appropriate guideline in the long-wavelength limit. Since the physical origin of the excitation near 6.7 eV is the s-electron character of the surface density profile and the short range of the multipole field, we believe that such a mode should also follow from more complete microscopic response calculations for Ag. Qualitatively similar results are also obtained in a hydrodynamical model,[18] if the s-electron density is replaced by an appropriate two-step distribution and the d electrons are described by a polarizable medium as discussed above.

The $q_\parallel=0$ excitations shown in Fig. 2 correspond approximately to those observable in surface photoyield spectra. In principle, the latter includes the contribution Im $d_\parallel(\omega)$ arising from tangential surface currents. In the present model, $d_\parallel=z_d(\varepsilon_d-1)/(\varepsilon-1)$, which gives a weak and fea-

tureless background. Also, $d_\perp$ involves not only the emitted photocurrent but also the internal absorption. However, these two channels differ mainly in their spectral shapes, not with regard to the mode frequencies.[19] Since we predict the Ag multipole frequency to lie above the bulk plasmon, the multipole mode can in principle decay by coupling to propagating bulk modes. This effect should be rather weak since the modes are energetically well separated: The bulk plasmon exists mainly in the range from 3.8 to 4.3 eV.[20] Beyond this interval, it becomes rather broad due to Landau damping and interband transitions. Moreover, as we argued above, the multipole mode has predominantly s electron character and couples inefficiently to bulk excitations exhibiting strong d character.

In Ref. 17, we used the s-d polarization model to study the frequency dependence of $d_\perp(\omega)$ below the interband onset. While the real part of $d_\perp(\omega_s^*)$ for $z_d \approx -1.2a_0$ is consistent with the experimentally observed positive surface-plasmon dispersion, the imaginary part shows no evidence of a multipole surface plasmon below the bulk plasmon. The interval between ω_s^* and ω_p^* is too small compared to that in the simple metals for an additional surface excitation to exist in this frequency range. We are also not aware of any photoyield measurements on Ag that reveal a multipole excitation below 4 eV. The p-polarized yield spectra of cesiated Ag observed by López-Ríos and Hincelin[9] show spectral features near 3.7 and 3.85 eV, that were associated with the usual Ag surface plasmon (induced by surface roughness) and with a spurious signal from the back of the sample, respectively.

We point out that, in principle, it might also be possible to observe the Ag multipole surface plasmon near 7 eV using inelastic electron scattering. Unfortunately, however, loss spectra are more difficult to analyze than photoyield spectra because of the remnant of the s-electron monopole surface plasmon: The distribution $\mathrm{Im}\,(\varepsilon-1)/(\varepsilon+1)$ has a broad maximum near 7.2 eV, i.e., near the multipole peak. Since Ag has a fairly high bulk density, the multipole mode is in any case not expected to be very strong. Thus its separation from the s-like monopole mode and the interband transitions in the same energy range is problematic. We have carried out TDLDA calculations at finite $q_\parallel$ using the s-d polarization model in order to locate the multipole mode in electron-energy-loss spectra.

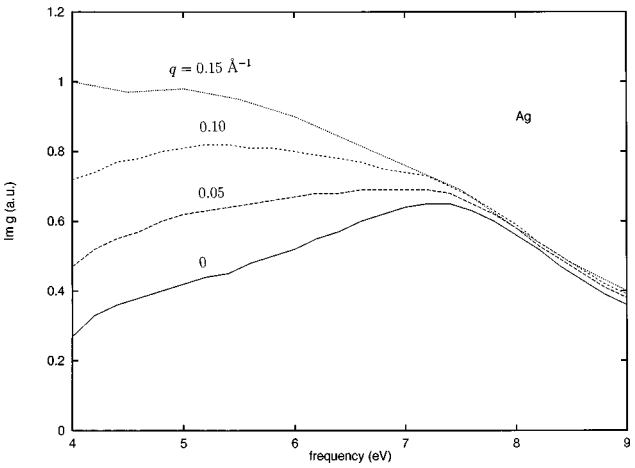

FIG. 3. Surface loss function $\mathrm{Im}\, g(q,\omega)$ above the interband onset for several values of q ($z_d = -1.2a_0$). The results are based on the s-d polarization model and the TDLDA. The $q=0$ spectrum corresponds to $\mathrm{Im}\,(\varepsilon-1)/(\varepsilon+1)$, where $\varepsilon(\omega)$ is the measured bulk dielectric function of Ag. The maximum near 7.2 eV represents the remnant of the s-like monopole surface plasmon.

As shown in Fig. 3, the surface loss function reveals a broad spectral feature between 5 and 8 eV, and does not allow a separation of s-like monopole and multipole features. At $q=0$, $g=(\varepsilon-1)/(\varepsilon+1)$, i.e., the peak corresponds to the s-like monopole surface plasmon of Ag. At finite q, this feature exhibits a negative dispersion just as in the case of the simple metals. The linear coefficient is, however, much larger. It is not clear whether this behavior is related to the large negative dispersion of the main feature observed in loss spectra on Pd.[21] We emphasize that the spectra shown in Fig. 3 convey an approximate picture since above the d-band onset, s and d electrons ought to be treated on the same basis.

In conclusion, we have provided qualitative arguments for the existence of an Ag multipole surface plasmon. In contrast to all simple metals, this mode should appear above rather than below the bulk plasma frequency. The physical reason for this behavior is that the multipole is an intrinsic property of the s-electron density profile and is much less subject to the s-d polarization than the Ag monopole surface plasmon. Surface photoyield measurements in the range from 4 to 9 eV should provide an excellent test of this picture.

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