Surface Plasmon Dispersion of Ag

A. Liebsch

Institut für Festkörperforschung, Forschungszentrum, 517 Jülich, Germany

The time-dependent density functional approach is used to calculate the wave-vector dispersion of the surface plasmon of Ag. The $5s$ conduction electrons are treated as a semi-infinite homogeneous electron gas and the influence of the $4d$ electrons is described in terms of a polarizable medium. It is shown that the reduction of the s-d screening interaction in the surface region leads to a positive dispersion of the surface plasmon in agreement with recent electron energy loss measurements.

Considerable progress has recently been made in the understanding of the electronic excitations at simple metal surfaces. The dispersion of the ordinary monopole surface plasmon and of the so-called multipole surface plasmon with parallel wave vectors has been calculated for various metals with widely different bulk densities (Al, Na, K, Cs) and found to be in excellent overall agreement with the dispersion obtained from experimental electron energy loss data [1]. In all of these cases, the monopole surface plasmon first shifts linearly to lower frequencies at small $q = |q_{||}|$. It then disperses upwards as q increases. This initial negative slope is directly related to the fact that, in the long wavelength limit, the centroid of the induced charge associated with the surface plasmon is located outside the nominal metal surface [2,3]. In contrast to these observations, the surface plasmon of Ag exhibits a remarkably different behavior: In a recent series of papers [4–7] reporting electron energy loss spectra on all single crystal faces of Ag it was shown that the surface plasmon disperses towards higher frequencies even in the limit of small q. The mechanism that determines the dispersion is therefore fundamentally altered due to the presence of the Ag $4d$ electrons.

The fully occupied $4d$ band of Ag can influence the dynamical surface response in two distinct ways: First, the s-d hybridization modifies the single-particle energies and wave functions. As a result, the nonlocal density-density response function exhibits band structure effects. Second, the effective time-varying fields are modified due to the mutual polarization of the s and d electron densities. Here we focus on the second mechanism for the following reason: At the parallel wave vectors of interest, the frequency of the Ag surface plasmon lies below the region of interband transitions. Thus, the relevant single-particle transitions all occur within the s-p band close to the Fermi energy where it displays excellent nearly-free-electron character. Transitions involving the filled $4d$ bands or higher-lying unoccupied s-p bands enter therefore only as virtual transitions and should not be the primary factor that governs the surface plasmon dispersion. These virtual transitions depend on the crystal face and are presumably responsible for the different slopes observed on the three low index faces of Ag [4–7].

The common positive dispersion on all of these faces, on the other hand, i.e., the fundamental sign reversal compared to the dispersion found for the simple metals, clearly seems to be caused by one common mechanism that modifies the intraband transitions within the s-p band.

The aim of this paper is to demonstrate that the mutual s-d polarization does indeed provide such a mechanism which explains the observed positive dispersion of the Ag surface plasmon. The essential feature of our model is that the $5s$ and $4d$ electrons are treated as a two-component system whose electrostatic interaction extends only up to a certain distance from the surface. In particular, this interaction is absent in the region where the $5s$ electron density spills out into the vacuum. Since the electrons oscillate in this region with the unscreened plasma frequency, this mechanism leads to a blueshift of the surface plasmon. This effect becomes more important with increasing q because of the shorter penetration depth of the induced electrostatic fields. As a result, the surface plasma frequency is found to exhibit a positive dispersion with q in agreement with the data.

In a recent paper, Tarriba and Mochán [8] presented a model for the dynamical response of Ag surfaces which is based on a lattice of polarizable dipoles embedded in a homogeneous electron gas with cavities at the sites of the lattice. This model can be viewed as complementary to ours in the sense that it includes the crystalline structure while it neglects the detailed nonlocal response properties of the s electron distribution near the surface. In an alternative approach Feibelman [9] suggested that the centroid of the induced surface charge at $q=0$ might be shifted inwards due to band structure effects in the surface region. The importance of the polarizable background for the surface plasmon dispersion of Ag was emphasized by Lipparini and Pederiva [10] who used sum rule arguments to estimate the linear coefficient. Several years ago, in their work on the surface corrections to the van der Waals reference plane of the noble metals, Zaremba and co-workers [11] represented the centroid of the induced density by a superposition of s and d contributions which were taken from independent calculations for the jellium model and dielectric solid, respectively. For the optical case, Apell and Holmberg [12] modified

this approach by taking into account the actual macroscopic fields in the bulk. However, in none of these models was a sufficiently detailed evaluation of the s electron response carried out, with an electrostatic interaction that is screened due to the presence of the $4d$ electrons. As the results discussed below demonstrate, such a self-consistent treatment is crucial for an adequate description of the surface plasmon dispersion of Ag.

In the bulk, the mutual polarization of the Ag $5s$ and $4d$ electrons is known to cause a large renormalization of the plasma frequency from its unscreened value, $\omega_p = 9.2$ eV, to the observed value which is approximately given by $\omega_p^* \approx \omega_p/\sqrt{\mathrm{Re}\epsilon_d} \approx 3.76$ eV. Here, $\epsilon_d(\omega)$ represents the "bound" contribution to the total dielectric function which can be decomposed as $\epsilon(\omega) = \epsilon_s(\omega) + \epsilon_d(\omega) - 1$ [13]. $\epsilon_s(\omega)$ represents the Drude term appropriate for the $5s$ electrons. Correspondingly, the frequency of the surface plasmon in the long wavelength limit is given by $\omega_s^* \approx \omega_p/\sqrt{1 + \mathrm{Re}\epsilon_d} \approx 3.64$ eV whereas the unscreened value is $\omega_s = 6.5$ eV. At finite parallel wave vectors our calculations show that this renormalization is less effective which amounts to an upward distortion of the dispersion relation.

The s-d surface response calculations are based on the time-dependent local density approximation (TDLDA) [14]. Since we are mainly concerned with excitations within the s-p band, we do not explicitly include transitions from the $4d$ states or to higher-lying s-p states. Instead we assume that the $5s$ electrons can be characterized by the nonlocal surface response function $\chi(z,z',q,\omega)$ of a semi-infinite jellium system. Here, z is the coordinate normal to the surface and the neutralizing positive background is located in the half space $z \leq 0$. The influence of the $4d$ electrons is represented via the same local dielectric function $\epsilon_d(\omega)$ as in the bulk; the position of the boundary up to which this polarizable medium is assumed to extend is denoted by z_d. This distance, which is the only free parameter in our model, should be located somewhere between the edge of the positive background and the first plane of nuclei. Figure 1(a) shows in a schematic way the model on which our calculations are based. The frequency dependence of the real and imaginary parts of $\epsilon_d(\omega)$ [13] and of the real part of the measured dielectric function $\epsilon(\omega)$ [15] are shown in Fig. 1(b).

The electronic surface excitations can be calculated from the imaginary part of the surface response function which may be expressed as (atomic units)

$$g(q,\omega) = \int dz \, e^{qz} \delta n(z,q,\omega) \,, \qquad (1)$$

where $\delta n(z,q,\omega)$ is the surface charge density induced by an external potential of the form $\phi_{\mathrm{ext}}(\mathbf{r},t) = -(2\pi/q) \times \exp(qz + i[\mathbf{q}_\parallel \cdot \mathbf{r}_\parallel - \omega t])$. Within the time-dependent density functional approach [14], the induced density is given by
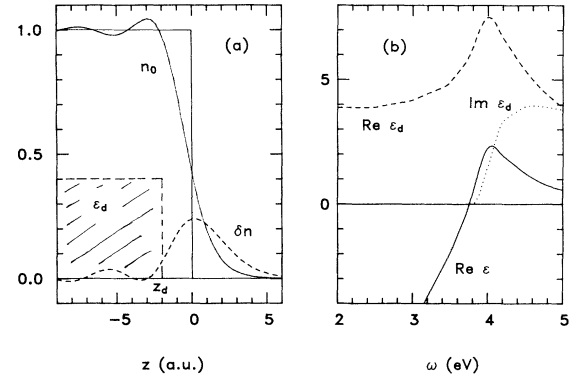

FIG. 1. (a) Schematic model for dynamical response of two-component $5s$-$4d$ electron system. Solid curve: ground state density profile of $5s$ electrons; dashed curve: induced density. The positive background is located in the half space $z \leq 0$; the polarizable medium representing the $4d$ states extends up to $z \leq z_d$. (b) Frequency dependence of the real and imaginary parts of "bound" dielectric function $\epsilon_d(\omega)$ (dashed and dotted curves, respectively). Solid curve: real part of measured dielectric function of bulk Ag [15].

$$\delta n(z,q,\omega) = \int dz' \chi(z,z',q,\omega) \phi_{\mathrm{scf}}(z',q,\omega) \,, \qquad (2)$$

with $\phi_{\mathrm{scf}} = \phi_{\mathrm{ext}} + \delta\phi + \delta V_{\mathrm{xc}}$ and $\phi_{\mathrm{ext}}(z) = -(2\pi/q) \times \exp(qz)$. The independent-particle response function χ is calculated within the LDA for a semi-infinite electron gas with a volume density given by $\bar{n} = 3/4\pi r_s^3$ and $r_s = 3$ a.u. The Poisson equation for the induced potential reads

$$\delta\phi''(z,q,\omega) - q^2\delta\phi(z,q,\omega) = -4\pi\delta n(z,q,\omega)/\epsilon_d(z,\omega) \,, \qquad (3)$$

where $\epsilon_d(z,\omega) = \epsilon_d(\omega)\Theta(z_d - z)$. At the boundary of the polarizable medium representing the d states, the total electrostatic potential $\phi = \phi_{\mathrm{ext}} + \delta\phi$ satisfies the boundary condition

$$\epsilon_d(\omega)\phi'(z_d^-) = \phi'(z_d^+) \,. \qquad (4)$$

Finally, the exchange-correlation term is given by

$$\delta V_{\mathrm{xc}}(z,q,\omega) = [\partial V_{\mathrm{xc}}(n)/\partial n]|_{n=n_0(z)} \delta n(z,q,\omega) \,, \qquad (5)$$

where V_{xc} is the local ground state exchange-correlation potential. In a random phase approximation (RPA) treatment of the dynamical response this term is omitted from the self-consistent potential ϕ_{scf}.

We have solved the above set of response equations self-consistently without any further approximations. The details of these calculations will be published elsewhere [16]. The important feature of the above scheme is that the $5s$ and $4d$ electrons are not assumed to respond independently to the incident field; instead they are treated as a single two-component system subject to the time-dependent perturbation. Since we are here concerned

only with the surface plasmon dispersion, propagating bulk plasmon modes do not need to be taken into account. Figure 2 shows several calculated surface excitation spectra at different values of q. The boundary of the polarizable medium is in this case located at $z_d = 0$. The main peak in these spectra corresponds to the surface plasmon which is seen to shift to higher frequencies with increasing q. The spectral weight above 3.8 eV corresponds to transitions from the d band as illustrated in Fig. 1(b). We have found no evidence for the existence of a multipole surface plasmon mode.

The dispersion of the Ag surface plasmon for $z_d = 0$ is compared in Fig. 3(a) with the corresponding dispersion in the absence of the s-d interaction, i.e., for a semi-infinite electron gas with $r_s = 3$. In the latter case, the surface plasmon exhibits a behavior that is typical for all simple metals [1], with a negative initial slope given by $d(\omega)$, the centroid of the screening charge in the $q = 0$ limit [2,3]. The LDA response leads to slightly lower frequencies than the RPA because the more attractive induced potential in the surface region pulls the surface charge somewhat farther into the vacuum. The s-d interaction is seen to cause not only an overall lowering of the plasma frequency by about 3 eV but also a strong upward distortion of the dispersion with q: In the RPA, the negative slope at small q has disappeared so that the plasma frequency now rises monotonically with q. Only in the LDA treatment is there a remnant of an extremely weak minimum at very small q.

The variation of the surface plasmon dispersion with the parameter z_d is shown in Fig. 3(b). For the sake of clarity, only the RPA curves are plotted; the LDA results lie slightly lower. In the limit of small q, these curves converge, as they should, to the frequency ω_s^*, which is determined solely by the bulk dielectric function and therefore must be independent of z_d. At finite q, the dispersion is seen to be positive for $z_d \leq 0$. Thus, the absence of the s-d interaction in the vacuum region causes a
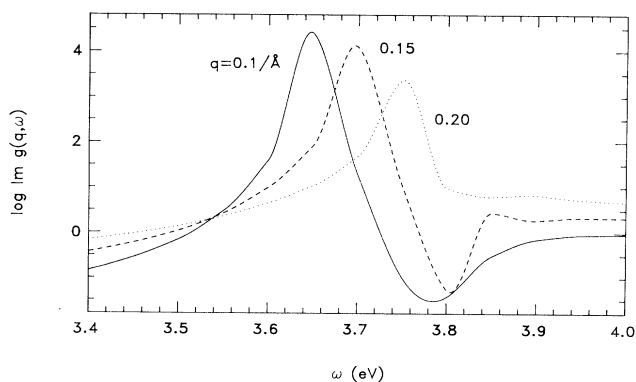
blueshift of the surface plasma frequency with increasing q. This effect becomes more pronounced as z_d is shifted deeper inside since the unscreened portion of the plasma oscillation is enhanced. Conversely, if the boundary z_d is located outside the surface, the induced surface density is more fully screened at all q, so that the dispersion shows an initial negative slope just as on the simple metal surfaces.

Another way of interpreting these results is the following: The large redshift from the bare plasmon frequency $\omega_s(q)$ to the screened one $\omega_s^*(q)$, due to the mutual polarization of s and d states, depends strongly on q: It is largest in the limit of small q because the induced field decays very slowly into the solid. With increasing q, this field decays more rapidly and the s-d interaction is gradually "switched off." This q-dependent reduction of the mutual s-d polarization leads to an upward skewing of the surface plasmon dispersion.

In the jellium model, the edge of the positive background is located half a lattice spacing above the first plane of nuclei. In the case of the Ag (111), (001), and (110) faces, this distance d_0 amounts to 1.18, 1.02, and 0.72 Å, respectively. The theoretical results in Fig. 3(b) show that, for z_d in the range $-d_0 \leq z_d \leq 0$, the surface plasmon dispersion within our model is positive and that the overall slope agrees qualitatively with the data. For the Ag (001) and (111) crystal faces these are indicated by the dotted and dashed lines, respectively [4,6]. These curves have been rigidly shifted downwards by 0.06 eV in order to make them coincide with $\omega_s^*(q=0)$ obtained from the measured bulk dielectric function [15]. For the (110) face the dispersion along the rows is similar to that
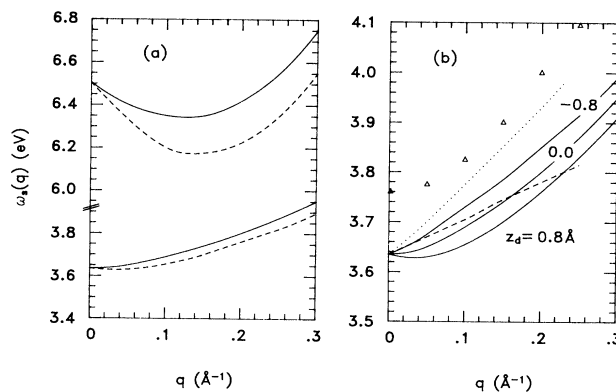

FIG. 2. Frequency dependence of the logarithm of surface loss function Im$g(q,\omega)$ at several wave vectors q for $z_d = 0$ (TDLDA).

FIG. 3. (a) Dispersion of surface plasmon of Ag for $z_d = 0$ (lower curves) and of semi-infinite electron gas with $r_s = 3$ (upper curves). Solid lines: RPA response treatment; dashed lines: TDLDA. (b) Dispersion of surface plasmon of Ag for $z_d = 0$ and $z_d = \pm 0.8$ Å calculated within RPA (solid curves). The dotted and dashed lines denote the measured dispersions for the (001) and (111) faces of Ag, respectively (see text) [4,6]. The triangles indicate the measured dispersion of the volume plasmon [17].

on Ag(111), whereas across the rows the dispersion is nearly the same as on Ag(001) [7]. For completeness, the measured dispersion of the Ag bulk plasmon is also shown [17]. Obviously, the dependency of the dispersion on the crystal face and the anisotropy on the (110) face are beyond the scope of the present model since it is based on a homogeneous polarizable medium that is abruptly terminated at a fixed distance from the surface. Crystallinity could be approximately incorporated for example, by treating the 4d states as polarizable shells located at the sites of an fcc lattice. It is possible, however, that band structure effects must also be taken into account in order to understand the more detailed aspects of the observed dispersions.

There is a remarkable analogy between the surface plasmon dispersion on Ag and the size dependence of the Mie resonance of small Ag particles: With decreasing radius R, the Mie plasmon also shifts to higher frequencies [18-22] in contrast to the redshift observed for alkali metal particles [23]. It is plausible that the blueshift of the Ag Mie resonance can be understood within the same model as the one proposed above [21]: In the outer regions of a silver particle where the 5s electrons spill out into the vacuum, the s-d screening interaction is absent. This leads to a blueshift since part of the fluctuating charge density oscillates with the unscreened plasma frequency. This effect becomes more pronounced with decreasing particle radius because of the larger surface to volume ratio.

In conclusion, we have presented a model which explains the main difference between the surface plasmon dispersion relations for Ag and the simple metals. The model includes the nonlocal response of the 5s electrons at the surface but neglects higher-lying interband transitions. Instead, the influence of the filled 4d band is described in terms of a polarizable medium that extends up to some distance from the surface. The key feature of this model is that the combined s-d dynamical response is treated self-consistently and not approximated by a superposition of separate quantities taken from independent calculations for the s and d densities alone. The absence of the s-d electrostatic interaction in the outer surface region leads to a blueshift of the surface plasmon frequency. This effect increases with parallel wave vectors because of the more rapid decay of the induced field towards the interior. Thus, the polarization of the filled d states causes not only a large reduction of the surface plasmon frequency but also a significant distortion of the dispersion relation.

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